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**Interconnecting Controlled Synthesis, Plasmonic, and
Catalysis: From Education to the Next Generation of
Nanomaterials for Triggering Green Transformations**

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*Dissertation Presented in the Chemistry Institute at
University of São Paulo in order to obtain the Ph.D.
degree in Chemistry*

Advisor: Prof. Dr. Pedro Henrique Cury Camargo

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Dedication

To people that make my life happen.

*“Success is going from failure to
failure without losing enthusiasm”*

Winston Churchill

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Abstract

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This dissertation is directed towards the fundamental understanding of the controlled synthesis of noble-metal (silver, gold, and palladium) and metal oxide (manganese and copper oxide) nanostructures as well as their applications in heterogeneous and plasmonic catalysis. In the first part of this work (Section 1), we provided a general background concerning the science of controlled nanomaterials, their syntheses, properties, and applications in catalysis and plasmonic catalysis. Then, we describe and developed a series of protocols for the synthesis of these nanomaterials with controlled sizes and structures (spheres, cubes, rods, shells, flowers, dendrites, and tadpoles), mainly focusing on the mechanistic understanding of their formation and how physical and chemical parameters (size, shape, composition, surface morphology) may influence/modify their catalytic properties (Sections 2 and 3). In Section 4, we turned our attention for the design of simple protocols for the synthesis of advanced nanomaterials that are interesting for green catalytic transformations applications. In this case, we envisioned the use of MnO₂-Au nanomaterials (nanowires and nanoflowers) displaying several properties (unique pore structure, high surface area, ultrasmall Au NPs at the surface, high concentration of oxygen vacancies and Au^{δ+} species, strong metal-support interactions, and uniform shapes and sizes) that are desirable for catalyzing a series of green oxidation reactions in mild conditions (low temperatures and molecular oxygen or atmospheric air as the oxidants). In Section 5, we have demonstrated that catalysis and optical properties can be merged together to improve catalytic processes, the so called-plasmonic catalysis. This allowed us the use of visible light as the energy input to drive chemical transformations in mild conditions and then provide new insights regarding the various factors that affect SPR-mediated catalytic activities in plasmonic nanostructures. Finally, in Section 6, we focused our attention on how important is to introduce both nanoscience and the synthesis/characterization of nanomaterials having controlled physicochemical features to undergraduate students. Specifically, we have described simple laboratory experiments for the synthesis of nanomaterials (gold nanospheres and Cu(OH)₂/CuO nanowires) displaying uniform sizes and shapes in order to investigate and explain their optical properties, catalytic activities and formation mechanisms.

Keywords: Controlled nanomaterials, Catalysis, Plasmonic, Noble-metals, Metal Oxides.

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Section 1.

Background

Chapter 1. Science of Controlled Metal Nanomaterials: Synthesis, Properties, and Applications

1.1. Introduction

Metal nanomaterials differ from the corresponding bulk analogues in many ways, and this difference is the reason for the establishment of a field that describes their properties and performances.^{1,2} In the last decades, nanomaterials have revolutionized applications in nanotechnology that includes plasmonics, catalysis, sensing, electronics, photonics, information storage, medicine, energy conversion, cosmetic, among others as shown in Figure 1.1.³⁻⁹

Figure 1.1. Applications of nanomaterials in different fields.

The term nanotechnology has been used to describe the design, characterization, production, and application of materials displaying at least one dimension in the nanometer range (usually between 1-100 nm). In this nanometric range,¹⁰ materials exhibit many remarkable

chemical and physical properties that are different from both individual metal atoms and bulk counterparts.¹⁰ Therefore, the emergence of these novel properties is the driving force for a rapid development of research in nanomaterials, which has been on the forefront of scientific disciplines including chemistry, physics, materials science, medicine, and biology.³⁻⁹

However, an important question must be clarified. Why are materials on this 1-100 nm range distinguished relative to those bulk counterparts? When multiple atoms are put together, this group of atoms have properties that significantly differ relative those single atoms for obvious reasons. Firstly, by increasing the number of atoms in the particle, it includes a perturbation of the atomic energy levels, leading to the formation of energy bands, in which the energy difference between neighboring states is $E/2N$ (E is the width of the energy band and N is the number of atoms).^{1,10,11} Also, smaller sizes lead to higher surface area to volume ratios. For example, Table 1.1 shows the relationships between particle size versus the percentage of surface atoms for Pt nanoparticles with cuboctahedral shapes.¹²

Table 1.1. Calculated sizes of cuboctahedral Pt nanoparticles and their corresponding surface atom percentages.¹²

Number of shells	Number of surface atoms	Number of total atoms	Percentage of surface atoms (%)	Size of Pt nanoparticles (nm)
1	12	13	92	0.8
2	42	55	76	1.4
3	92	147	63	1.9
4	162	309	52	2.4
5	252	561	45	3.0
6	362	923	39	3.5
7	492	1415	35	4.1
8	642	2057	31	4.6
9	812	2869	28	5.1

Besides their sizes, it has been well-established that the properties of metal nanoparticles (NPs) are dependent on a set of physicochemical parameters, including composition (mono- versus bi- or multimetallic, and the spatial distributions of different elements), size (the effect of quantum confinement, as well as the proportions of atoms at corners, edges, and faces), geometric shape (faceting or arrangement of atoms on the surface), and structure (convex, concave, solid, hollow, or porous).^{13–17} Thus, a precise control only over the shape of a metal nanoparticle can be employed as a simple and versatile strategy for tailoring particle performance for a targeted application. For example, it has been demonstrated that Pd nanocubes bound by {100} facets are significantly more active relative to the other shapes toward the formic acid oxidation reaction as shown in Figure 1.2.¹⁸

Figure 1.2. Maximum current densities for formic acid oxidation employing Pd nanocrystals displaying controlled shapes as electrocatalysts.¹⁸

As {100} surface facets are more active relative to {111} for the electro-oxidation of formic acid, a gradual increase in the current densities was observed as the shape was changed

from cubes to truncated cubes, cuboctahedrons, truncated octahedrons, and finally octahedrons, as these shapes gradually enable an increased exposure of $\{111\}$ relative to $\{100\}$ surface facets.¹⁸ It can be as explained by the differences in the surface energy of each facet. Nanocrystals displaying $\{100\}$ surface facets can interact more efficient with formic acid molecules, leading a higher catalytic activity.¹⁸

Surface energy (γ) can be defined as the energy required for creating a unit area of “new” surface, or as the excess free energy per unit area for a particular crystallographic face,¹ according to Equation 1.1:

$$\gamma = (1/2)N_b\epsilon\rho \quad (1.1)$$

where N_b is the number of bonds that need to be broken to produce the new surface, ϵ is the bond strength, and ρ is the density of surface atoms. For an *fcc* structure (metal such as Ag, Au, Pd, Pt, Cu) with a lattice constant of a , the surface energies of the low-index crystallographic facets that typically encase noble metal-nanocrystals can be estimated as: $\gamma_{100} = 4(\epsilon/a^2)$, $\gamma_{110} = 4.24(\epsilon/a^2)$, and $\gamma_{111} = 3.36(\epsilon/a^2)$, resulting in the energetic sequence of $\gamma_{111} < \gamma_{100} < \gamma_{110}$ as shown in Figure 1.3.

Figure 1.3. Atomic arrangements and surface energy values for $\{100\}$, $\{110\}$, and $\{111\}$ surface facets (from left to right, respectively).

It is noteworthy that, to reach its full potential, the controlled synthesis of metallic nanomaterials must meet several requirements that include monodispersity in terms of size, shape, structure, and composition. Therefore, understanding the growth mechanisms of metal nanoparticles (NPs) is imperative to enable synthetic strategies that can be used to rationally design nanostructures with performances optimized for target applications.

1.2. Strategies for the Synthesis of Nanomaterials

Formation of metal nanomaterials can be basically achieved by two basic approaches,^{10,19,20} so-called top-down and bottom-up methods as shown in Figure 1.4.

Figure 1.4. Top-down and bottom-up approaches for producing controlled nanomaterials

In the top-down strategy, macroscopic materials are used to fabricate nanomaterials using typically sophisticated and expensive methods that includes molecular beam epitaxy, dip pen lithography, nanoimprint lithography, e-beam lithography, and roll-to-roll processing.^{10,19,20} This

method typically provides better control, but is limited to "countable" number of structures.^{10,19,20}

On the other hand, a bottom up synthesis method implies that the nanomaterials are synthesized from their ultimate building blocks – atoms and molecules – via self-assembly. In this case, it includes methods such as chemical solution-phase approaches, vapor deposition (CVD), plasma or flame spraying synthesis, laser pyrolysis, among others.^{10,19,20} The most advantage of bottom-up approach is the cost and scalability, even though the uniformity of the produced nanomaterials has demonstrated to be a challenge.^{10,19,20}

Among different methods for the controlled synthesis of metallic nanomaterials, solution-phase approaches offer many advantages that include the facile stabilization by the addition of proper capping and stabilizing agents, easy extraction/separation from the reaction mixture (by centrifugation, for example), straightforward surface modification/functionalization, potential for large-scale production, and versatility regarding the several experimental parameters that can be controlled during the synthesis (temperature, nature of precursors, stabilizers, solvent, reducing agents, their molar ratios, concentrations, etc).^{1,21} Surprisingly, substantial developments on the solution-phase-controlled synthesis of metallic nanomaterials with a variety of shapes and sizes were achieved only recently. Figure 1.5 illustrates a variety of shapes that have been described by the controlled synthesis of metal nanostructures.^{1,21,22}

Cube and truncanded cube

Pd, Ag, Au, Pt, Cu, Rh, Bi, Fe

Octahedron and truncanded octahedron

Pd, Ag, Au, Pt

Tetrahedron and truncanded tetrahedron

Ag, Au, Pt, Rh

Retangular bar

Pd, Ag, Pt

Octagonal rod

Pd, Au, Fe, Co, Ni

Retangular wire

Pb, In, Sn, Sb, Fe, Co

Bipyramid

Pd, Ag

Decahedron

Pd, Ag, Au

Icosahedron

Pd, Au

Pentagonal rod

Pd, Ag, Au, Cu

Pentagonal wire

Ag, Au, Cu

Triangular or pentagonal plate

Pd, Ag, Au, Cu, Pd, Bi, Co, Ni

■ {100} ■ {111} ■ {110}

Figure 1.5. Different shapes that have been enabled for a range of metals nanocrystals by solution-phase synthesis.^{1,21,22}

Despite this progress, a detailed atomic understanding of the mechanisms of nucleation and growth stages during nanoparticle formation is still not completely understood, and most fundamentals are currently borrowed from classical colloidal theories.²³

1.3. Formation of a Metal Nanoparticle: The Mechanism

In the context of colloidal synthesis, nucleation represents the very first step that atomic or molecular species must undertake before emerging as noble-metal nanocrystals. In a one-pot synthesis of metal nanocrystals, a precursor is reduced or decomposed to generate atoms—the building blocks (also referred to as monomers) of a nanocrystal.²⁴ In general, the atoms can take two distinct routes: homogeneous nucleation (or self-nucleation) to generate nuclei/seeds and heterogeneous nucleation—a process involving the deposition of atoms onto the surface of existing seeds.²²

In the case of homogeneous nucleation, much of the understanding is based on the assertions first put forward by LaMer and Dinegar.²³ These studies date back from the 1950s and are still the basis of our understanding on the synthesis of uniform nanomaterials (including metallic, polymeric, semiconducting, and oxide systems). In this case, the control of the morphology of colloidal metal nanocrystals has been mainly understood by adopting atom-mediated nucleation and growth theory,^{1,23,25} in which atoms are the basic building blocks for the nucleation and growth. Nucleation can be defined as the process by which building blocks (metal atoms in the synthesis of metal nanomaterials) arrange themselves according to their crystalline structure to form a site upon which additional building blocks can deposit over and undergo subsequent growth. In this context, nuclei correspond to infinitesimal clusters consisting of very

few atoms of the growth species. Such nucleation and growth processes can therefore be described by referring to the evolution of the atomic concentration over time, as illustrated by the so called LaMer curve in Figure 1.6.^{1,23,25} The nucleation and growth process of colloidal metal nanocrystals described by the LaMer curve can be divided into three stages: (i) atom production, (ii) nucleation from atoms aggregation, and (iii) nanocrystal growth from atoms addition.

Figure 1.6. Variations in the atomic concentration of growth species in solution as a function of time during the generation of atoms, nucleation, and growth stages.

From these studies, the concept of “burst nucleation” has been established to be crucial for the synthesis of monodispersed particles.²⁶ Burst nucleation refers to the formation of a large number of nuclei in a short period of time, followed by growth without additional nucleation.²⁶ This allows nuclei to have similar growth histories and, therefore, yield nanoparticles with same

sizes. This concept is normally referred to as the separation of nucleation and growth stages during the synthesis.²¹ For instance, if nucleation and growth could occur simultaneously, the nuclei growth histories would be significantly different and heterogeneous size distributions would be obtained.

Figure 1.6 depicts the Lamer plot, which shows the change in the atomic concentration of the solute (growth species) during the nucleation and growth processes as a function of time. This plot is also very useful for illustrating the concept of burst nucleation. In the first stage of the Lamer curve, metallic atoms are produced either through a reduction of metallic ions with reducing reagents or the thermal decomposition of organometallic compounds. Once the atomic concentration exceeds the point of supersaturation ($C_{\text{nu min}}$), in the second stage, the atoms start to aggregate to form stable small clusters (i.e., nuclei) via self- (or homogeneous) nucleation. Afterwards, the concentration of atoms quickly drops below the minimum supersaturation level ($C_{\text{nu min}}$) and no additional nucleation events will occur. Then, in the third stage, the size of the nuclei gradually increases due to the continuous addition of metal atoms. In this stage, once a cluster has grown past a certain critical size, the activation energy for structural fluctuation will become so high that the cluster eventually becomes locked into a well-defined structure. This critical point marks the birth of a seed. This seed further grows to form the final nanocrystal through the addition of metal atoms until the concentration decreases to C_s (solubility concentration of nanocrystals).

However, from the viewpoint of the control over the shape of noble-metal nanoparticles, the classical theory does not explain the various crystallization pathways and outcomes that emanate from the same experiment.^{22,27,28} The lacks of the classical nucleation theory include a set of oversimplified assumptions, including: 1) the nucleus is modeled as a perfect sphere, 2) the

density and surface energy of the nucleus are size-invariant, and 3) the nucleus grows by taking one monomer at a time.^{22,27,28} Since nucleation is a highly dynamic process that involves irregularly shaped nuclei that grow with size-dependent surface energies, internal defects, impurities, and nucleus–nucleus collisions, a more comprehensive theory is necessary to properly model the nucleation process.²² Over the last decade, a series of theories have been developed to describe the nucleation and growth of colloidal noble-metal nanocrystals displaying controlled sizes and shapes.^{1,22,29–31}

We have mentioned that the solution-phase synthesis of metal nanomaterials is comprised of nucleation and growth. In the shape-controlled synthesis of metal nanomaterials, these stages can be further subdivided into (i) nucleation; (ii) growth of nuclei into seeds; (iii) and growth and evolution of the seeds into the final nanocrystal. Notable examples have been demonstrated for structures composed of Ag, Au, Pd, Pt, and Cu covered by low-index facets such as cubes, octahedra, cuboctahedra, bipyramid, rectangular bars, and pentagonal rods or wires.^{1,22,29,32–35} Additionally, nanocrystals covered by high-index facets, including concave cubes or octahedra, octapods, decahedron, icosahedron, and triangular/pentagonal plates, have also been prepared with great uniformity. Figure 1.7 shows TEM and SEM of a variety of shapes that have been successfully reported by employing the seeded growth method. As nuclei correspond to infinitesimal clusters consisting of very few atoms formed as the new solid phase in solution, structure fluctuations may occur in the nuclei with the incorporation of defects to minimize surface energy until they evolve into seeds. The seeds can then be defined as species that are larger than the nuclei that are locked into a specific structure, in which structure fluctuation does not occur as they become energetically costlier as the size increases. Interestingly, for noble-metals (Ag, Au, Pd, and Pt), it has been established that the final shape assumed by the nanocrystal is determined

by both the structure of its corresponding seed and the relative binding affinities of capping agents to its distinct surface facets.

Figure 1.7. TEM and SEM images for a variety of shapes that have been successfully reported by employing the seeded growth method.^{1,22,29,32–34}

Figure 1.8 illustrates the typical seeds available to an fcc metal (Ag, Au, Pd, and Pt) and how the structure of the seeds play an important role in determining the final shape of a metal nanocrystal in solution-phase synthesis.¹

Figure 1.8. Main stages of controlled synthesis of metal nanomaterials (with face-centered cubic (fcc) structure): (i) nucleation; (ii) growth of nuclei into seeds; (iii) and evolution of the seeds into the final nanocrystal. The shape assumed by the nanocrystal depends on the structure of its corresponding seed and the relative binding affinities of capping agents to its distinct surface facets. R, for example, refers to the ratio between the growth rates along the $\{100\}$ and $\{111\}$ directions.

Considering their *fcc* structure, seeds can assume single-crystalline, single-twinned, multiple-twinned and/or stacking faults structures as shown in Figure 1.9.^{22,36}

Figure 1.9. HAADF-STEM and HTEM images of typical single-crystalline, single-twinned, multiple-twinned and/or stacking faults seeds for metals displaying fcc structures.^{22,37–39}

Thus, the key for the synthesis of metal nanocrystals with controlled shapes relies on maneuvering nucleation and growth processes so that only one kind of seed, with the proper structure, is present in the reaction mixture. The structure of seeds during solution-phase synthesis (single crystalline, single-twinned, or multiple-twinned) are dependent upon many parameters that include thermodynamic and kinetic considerations, while the relative population distribution of seeds can be further influenced by oxidative etching processes.^{22,37–39}

When the synthesis is under thermodynamic control, the population of seeds displaying different structures will be determined by the statistical thermodynamics of their free energies.⁴⁰

The most stable (lowest energy) seeds will be favored, and surface energy considerations are crucial in understanding and predicting the structure of the produced seeds.⁴⁰ For example, Figure 1.10 A shows a typical phase diagram for Au seeds as functions of particle size and temperature, indicating that multiply twinned and single-crystal seeds are favored at relatively small and large sizes. Therefore, by varying the temperature and fixing a specific particle size, it is possible control colloidal noble-metal nanocrystals displaying controlled sizes and shapes.

Figure 1.10. Thermodynamic and kinetic approaches to controlling the internal structure of seeds. (a) Phase diagram of Au seeds as a function of temperature and nanoparticle size (b) Population of Pd nanocrystals as a function of the initial reduction rate, displaying plates with stacking faults (orange), multiply twinned icosahedra (purple), and single-crystal cuboctahedra (blue).^{22,38,40}

Kinetic control relies on the manipulation over the structure/population of seeds containing different numbers of twin defects by decreasing the reduction or decomposition rate of a precursor that is responsible for providing metal atoms (growth species).³⁸ It has recently discovered that the initial reduction rate of a precursor is crucial to the formation of seeds with a particular internal structure in high purity.³⁸ Specifically, the initial reduction rates necessary for generating different types of seeds tend to decrease in the order of single-crystal, singly twinned, multiply twinned, and stacking-fault-lined seeds.³⁸ Figure 1.10B shows the percentages of Pd seeds with different internal structures as a function of the initial rate for the reduction of PdCl_4^{2-} . Of interest is the existence of different ranges of reduction rates, within which the purity of seeds could approach 100%. The reduction rate could be experimentally adjusted by temperature, as well as the type and concentration of reducing agent and precursor involved in the synthesis.

1.4. Stabilization in Solution-Phase Synthesis

The main feature that sets nanomaterials apart from their micro- and macro-counterparts is their large surface to volume ratios, which is responsible for many unique or improved properties that nanomaterials possess.⁴¹ A large surface to volume ratio implies that nanomaterials display high-surface energies (as surface energy increases with surface area), which makes them thermodynamically unstable or metastable.^{21,42} Consequently, the synthesis of nanomaterials in solution requires one to overcome their large surface energies and prevent them from agglomerating. Agglomeration is thermodynamically driven by the reduction in surface area and thus surface energy.²¹ In fact, the reduction of surface energy is also the driving force for other processes in solution-phase syntheses such as surface restructuring, formation of facets, and

Ostwald ripening.²¹ Therefore, it is important to discuss about two main approaches that are commonly employed to stabilize metallic nanomaterials against agglomeration: the electrostatic and steric (or polymeric) stabilization.

The concept behind the electrostatic stabilization is illustrated in Figure 1.11, which is based on the repulsion of electrical charges having the same sign present in the electrical double layers between neighboring particles.^{21,43}

Figure 1.11. Electrostatic stabilization between two approaching particles: the electrostatic repulsion of like-charges drive particles apart as their double layers overlap

The DLVO theory,²⁷ which was named after Derjaguin, Landau, Verwey and Overbeek, successfully describes how the electrostatic stabilization between neighboring nanoparticles in suspension works. The DLVO theory states that the distance-dependent potential energy (VT) between colloidal particles is simply defined a short range attractive van der Waals potential (VA) and a long range repulsive electrostatic potential (VR), as according the following equations:^{27,44}

$$V_{total} = V_A + V_R \quad (1.2)$$

where:

$$V_R = -\frac{AR}{12D} + 2\pi\epsilon\epsilon_o R \psi^2 e^{-kD} \quad (1.3)$$

and where:

$$k = \left[\sum_i \frac{z_i^2 q^2 c_i}{k_B T} \right]^2 \quad (1.4)$$

In the above formulations, A is the Hamaker constant, R is the radius of the particles, ϵ_o is the permittivity of vacuum, ϵ is the dielectric constant of the solvent, ψ is the Stern potential, k is the Debye constant, z_i is the charge number of the ionic species, i is the elementary charge, c_i is the concentration of ion i (co- or counter-ions) at $x = \infty$ (in the bulk solution), k_B is the Boltzmann constant, D is the distance between the outermost surface of two colliding particles, and T is the temperature of the system. When the two particles are far away from each other (distance is large), both V_A and V_R tend to zero. As the particles start to approach each other, the electrostatic repulsion is stronger than the Van der Waals attraction ($V_R > V_A$), leading to an increase in the overall potential (V) with the decrease in distance until a maximum is reached at V_{MAX} , which corresponds to the repulsive energy barrier. As the distance is further decreased, the Van der Waals attraction surpasses the electrostatic repulsion ($V_A > V_R$), and the overall potential becomes strongly dominated by V_A , which leads to the agglomeration of the particles.

On the other hand, the steric (also called polymeric) stabilization consists in preventing neighboring particles of getting close to each other in the range of attractive forces where Van der Waals attraction would lead to agglomeration by the presence of polymers at the particles surface.^{43,45–47} In general, a polymer can interact with a solid surface by one-end binding (anchored polymer) or via weak interactions from random points along its backbone (adsorbing polymer). When two particles covered with polymer approach each other, the polymer layers from each particle will interact only when the distance between particles become lower than the sum of the

thicknesses of the neighboring polymer layers. Figure 1.12 depicts two approaching nanoparticles presenting an anchored polymer at their surface. As the distance between the particles becomes lower than the sum of the thicknesses of the neighboring polymer layers, they can overlap or become compressed resulting in strong repulsion between the neighboring nanoparticles.

Figure 1.12. Steric stabilization between two approaching particles containing anchored polymers at their surface. Under both low- and high- surface coverage conditions, the polymer layers repel one another as they approach and/or interact.

It is important to mention that the steric stabilization is not so well understood in comparison to the electrostatic stabilization.²¹ Nevertheless, it is widely employed in the solution-phase synthesis of nanomaterials, offering many advantages when compared with electrostatic stabilization. For instance, steric stabilization is thermodynamic (agglomerated particles can be redispersed), it is not restricted to dilute systems, and is not sensitive to the presence of electrolytes, which is highly desirable for several applications. Moreover, it contributes to the production of monodisperse nanoparticles as the polymer layer adsorbed at the nanoparticle surface can also work as a diffusion barrier to the addition of growth species. Polymers employed for steric stabilization can also play other roles in solution-phase syntheses such as serving as reducing

agents, helping in manipulating precursor reduction rates, and interacting with distinct nanocrystals surface facets with different binding affinities, which is central in the context of shape-controlled synthesis.

1.5. Synthesis of Hollow Nanomaterials: The Galvanic Replacement Reaction

Nanostructures with hollow interiors have been extensively studied for their applications in microencapsulation - a process that is useful in many areas including catalysis, drug delivery, and protection of environmentally sensitive biological species.^{48–53} When used as fillers in preparing composites, hollow structures also offer some advantages over their solid counterparts in terms of their hollow interiors provide higher surface-to-volume ratios, lighter weight, saving of material, and reduction of cost.^{3,52,54} Hollow nanostructures made of metals are intriguing to synthesize and study because they exhibit surface plasmonic properties and catalytic activities different from their solid counterparts. For example, Prevo and co-workers have demonstrated that the surface plasmon resonance (SPR) band of gold nanoshells could be smoothly tuned over the spectral regime from 600 to 900 nm by varying their diameter and shell thickness.⁵⁵ In comparison, the SPR band of solid, spherical colloids of gold can only be tuned around 520 nm by as much as ~50 nm.⁵⁶

Among several approaches that have been reported, methods based on the Ostwald ripening, Kirkendall effect, galvanic replacement, and oxidative etching have been successfully employed for fabricating hollow nanomaterials.^{48,52,57–60} The galvanic replacement reaction is especially interesting as it allows us to easily control the sizes, shapes, compositions and internal structures, leading to the formation of nanomaterials displaying a high surface to volume ratio and

large pore volume.⁵² More specifically, this strategy is promising due several factors: (i) galvanic replacement process between a metallic nanoparticle (sacrificial template) and another metal precursor (having a higher standard reduction potential) often occurs spontaneously; (ii) this procedure is quite versatile and can be adapted for almost all metal nanoparticles templates and salt precursors; and (iii) it represents a simple route to the synthesis controlled nanostructures with ultrathin walls, in only one step, in which the atomic composition can be easily controlled by the metallic precursor solutions employed and their concentrations.^{52,61,62}

A galvanic replacement reaction, extensively employed for the synthesis of hollow metal nanomaterials, can be described as an oxidation-reduction (redox) process.^{52,61,62} In this case, a redox reaction occurs when electrons are transferred from a metal nanoparticle (a reducing agent or sacrificial template) to ions in solution of a second metal (an oxidizing agent). The difference in the reduction potentials of both metals employed in the galvanic replacement reaction acts as the driving force in this process, being the reduction potential of the metal precursor necessarily higher than metal sacrificial template at the reaction conditions. Taking the galvanic replacement reaction between Ag nanoparticles and HAuCl₄ precursor as an example, the galvanic process can be understood as a sum of the two following half equations as shown bellow:

And the final balanced equation:

The composition and structure of hollow nanomaterials obtained by the galvanic replacement reaction can be easily controlled by adjusting the molar ratio between Ag and $\text{AuCl}_4^- (\text{aq})$ precursor added into the reaction mixture. In this case, when a Ag nanosphere is kept in contact with small amounts of an aqueous $\text{AuCl}_4^- (\text{aq})$ solution, the Ag atoms from the sphere surface with high surface energy (defects, stacking faults, among others) can quickly be oxidized and dissolved by $\text{AuCl}_4^- (\text{aq})$ ions, producing Ag^+ ions into the suspension reaction, leading to the formation of small cavities at the nanoparticle surface as shown in Figure 1.13.¹⁴

Control over the composition by increasing the molar ratio between $\text{AuCl}_4^- (\text{aq})$ and Ag seeds

Figure 1.13. TEM (A-D) and STEM EDX mapping images and of the AgAu nanoshells displaying showing the inversion of surface segregation behavior as the Au content is increased during the galvanic replacement reaction: (A and E) $\text{Ag}_{91}\text{Au}_9$, (B and F) $\text{Ag}_{68}\text{Au}_{32}$, (C and G) $\text{Ag}_{60}\text{Au}_{40}$, and (D and H) $\text{Ag}_{43}\text{Au}_{57}$.¹⁴

At the same time, Au atoms are deposited at the nanoparticle surface because of the reduction of the $\text{AuCl}_4^- (\text{aq})$ ions precursor. As Au and Ag have a great miscibility at nanoscale due

to their same face-centered cubic (fcc) crystal structure and similar lattices constants ($a_{\text{gold}} = 4.079$ Å; $a_{\text{silver}} = 4.086$ Å), the initial Au atoms tend to deposit as a uniform thin Au layer at the Ag nanoparticle surface (Figure 1.13 A and E).¹⁴ As can be observed, the first step led to the formation of an incomplete Au layer, which cannot prevent that intern layers from reacting with AuCl_4^- (aq) precursor. Subsequently, small cavities at the nanoparticle surface serves as the main sites for continuous galvanic replacement between Ag and AuCl_4^- (aq) precursor. As more Ag is replaced by Au by the increasing the amount of metal precursor into the reaction suspension, it is expected the formation of AgAu nanoshells displaying larger holes together with Ag-Au alloying process leading to the formation of a homogenous distribution of Ag and Au at the nanoparticle surface (Figure 1.13 B, C, F, and G).¹⁴ It can be explained due to the generation of an increased driving force to minimize the particle's intermetallic bond energy and surface energy, leading to the homogeneous Ag-Au alloying to be thermodynamically more stable relative to the segregated forms of Au and Ag for Au atomic percentages up to 50 %.¹⁴ If more metal precursor is added into the reaction suspension, the additional AuCl_4^- (aq) surprisingly promotes a dealloying process of the AgAu nanoshells by selectively movement of Ag layers to the nanoparticle surface (Figure 1.13D and H).¹⁴ Previous theoretical and experimental studies have demonstrated that nanoparticles having Ag segregated to the surface are formed as a result of this element's lower surface energy relative to Au, which tends to decrease their total surface energy.^{14,16,63} And finally, if this reaction is continued even further, the observed holes inside the nanostructure became so large, leading to the rupture of the nanoshell morphology and resulting in the formation of several polydisperse Au nanoparticles. This simple approach can be extended for a variety of metal nanoparticles templates and salt precursors, representing a simple route to the synthesis controlled nanostructures with ultrathin walls, in one step, in which the atomic composition can be easily controlled by the

metallic precursor solutions employed and their concentrations.^{52,61,62}

1.6. Optical properties of Metal Nanomaterials

The beautiful and brilliant colors of Au and Ag and their nanostructures have fascinated people for thousands of years.^{2,64–66} For example, everyone knows that bulk gold displays a vivid yellow color as shown in Figure 1.14 A.

(A) Bulk gold

(B) Nanoshells

(C) Nanocages

Figure 1.14. (A) Bulk gold and (B-C) metallic nanostructures with tunable localized surface plasmon resonance (LSPR): (B) Au nanoshells with different shell thickness, and (C) AgAu nanocages with different composition and shell thickness.⁶⁶

However, an aqueous suspension of nanoparticles can exhibit different colorations. For example, Figure 1.14 B-C shows two types of metallic nanostructures with tunable LSPR

properties: nanoshells, and nanocages. Their optical properties can be controlled by shell thickness, and composition of Au and Ag.⁶⁶

These phenomena arise from surface plasmon resonance (SPR).^{67–70} SPR is the resonant collective oscillation of free electrons of metallic nanostructures under light irradiation.^{67–70} The excitation of SPR occurs when the incident electromagnetic radiation induces collective oscillation of conducting electrons in the metallic nanostructure, which can result in strong light absorption, scattering, and enhanced local electromagnetic field as shown in Figure 1.15.^{67–70}

Figure 1.15. Excitation of localized surface plasmon resonance in metallic nanostructures.^{67–70}

One remarkable feature of SPR is that its frequency and intensity are strongly dependent on the size, shape, and composition of the plasmonic metallic nanostructures.^{71–74} This provides an important method to tailor the SPR of metallic nanostructures by synthetically tuning their structural parameters. Another feature of SPR is that some metallic nanostructures (based on gold, silver, and copper) display SPR in the visible wavelength range.^{1,71–74} This allows a direct application of SPR in the visible wavelength range for enhancing the Raman scattering cross-sections of molecules adsorbed on a nanoparticle surface, providing a “fingerprint” spectrum rich with chemical information.^{68,75} Also, the development of a library of plasmonic nanoparticles with

distinct shapes, sizes, and thus SPR spectra could be particularly useful for a wide range of applications, including biological labeling, photothermal therapy, catalysis, and others.^{3,4,68,76,77}

1.7. Metal Nanomaterials in Heterogeneous Catalysis

Catalysis represents a crucial discipline when it comes to providing the scientific and technological foundation for making cleaner, more efficient, and economically viable chemical production processes, which represent essential requisites towards enabling a sustainable future.^{78–}

⁸⁰ Catalysis is one of the most relevant topics in the industrial industry, leading advances sustainability by improving the exploitation of raw materials, enabling the transition from fossil to renewable feedstocks, reducing energy consumption, and minimizing the environmental footprint.

^{78–80} Catalysis also plays a central role in the fields of transportation and health, encompassing the development of new fuels and devices (such as fuel cells), synthetic biology, and the synthesis of bioactive molecules such as antibiotics.^{5,81,82} As a matter of fact, because catalysis is involved in the synthesis of over 85% of all chemical products produced today, new developments in catalysis will have a huge impact addressing the several challenges currently faced by humankind.^{78–81}

Heterogeneous catalysts are normally comprised by active sites (usually transition metals) deposited at the surface of a solid support that will change/increase the rate of a target chemical reaction.^{78,79,83} They usually display high surface areas ($200\text{--}1600\text{ m}^2\text{g}^{-1}$) and are desirable to maximize the number of active sites per unit of volume.^{80,84} However, it is well-established that there is a lack of methods/protocols that are efficient for producing highly active, stable, and recyclable catalysts as well as still economically viable^{78,83,85}.

Even though the research and implementation of catalysis in industry requires a clear understanding on several chemical and physical phenomena that take place at a variety of dimensions, the study, understanding, and optimization of the catalysts represents one of the most fascinating and important aspects. As a matter of fact, in the last decades, the interest in the use of metal nanoparticles in catalysis has increased extremely.^{86–88} Due to their large surface area to volume ratios, they favor the interaction between reactants and the catalyst surface, leading to higher activities even at mild reaction conditions, which has been traditionally associated with homogenous catalytic systems. As they are insoluble in the reaction mixture (allowing recovery and re-use), they enable one to combine the advantages and bridge the gap between homogeneous and heterogeneous catalysis, opening a huge potential for catalyzing green transformations.⁸⁹

Green transformations have emerged as a new frontier in heterogeneous catalysis as it represents an eco-friendly approach based on the use non-toxic solvents such as water, low catalyst loadings, and mild temperature and pressure conditions.^{87,90} Despite these very attractive features, green transformations remain very challenging owing to the low conversion percentages, selectivity, and substrate versatility under these conditions.⁹¹

Among metal nanoparticles, those based on noble metals, such as silver (Ag), gold (Au), palladium (Pd), platinum (Pt), ruthenium (Ru), rhodium (Rh), and iridium (Ir) have been widely employed as catalysts for a myriad of transformations that are relevant to the chemical and pharmaceutical industries.^{92–95} Examples include hydrogenation, oxidation, dehydrogenation, carbon-carbon coupling, reforming of fuels, and electrocatalytic reduction and oxidation.^{92–96} In this context, nanomaterials that display both high catalytic activities and selectivity are of tremendous importance in the field of catalysis, as they enable one to potentially reduce the metal loading (several catalysts are based on expensive noble metals), employ milder or more

environmentally friendly conditions, and minimize the formation of side products (and thus the need for several purification steps).

While it has been shown that catalytic properties can be optimized by careful control over particle size, shape, surface composition, and structure (e.g., solid vs hollow interiors),^{1,15,97,98} the facile and versatile synthesis of nanocatalysts in which these parameters can be tightly controlled remains limited in terms of large-scale production and manufacturing robustness.^{99,100} Another current challenge in catalysis by noble metals comprises the generation of supported materials in which the metal component presents a uniform dispersion over the entire surface of the support (without agglomeration).^{99,100} In this regard, the synthesis of supported state-of-the-art catalysts is often characterized by poor control over size, shape, composition, and distribution of the noble metal component over the support as illustrated in Figure 1.16.⁹⁵

Figure 1.16. STEM HAADF image for a conventional Au/TiO₂ catalyst prepared by co-precipitation.⁹⁵

Due to these drawbacks, progress in the field of catalysis, in general, has mainly occurred *via* an observation driven approach consisting of collected knowledge, trial and error, and interpretation of results.⁸³ In this context, a transition from observation-driven to an design-driven

approach may represent the next chapter in the field of catalysis, in which the development of controlled nanocatalysts is a must.

1.8. Plasmon-mediated or Plasmon-enhanced Catalytic Processes.

In addition to optimizing and controlling catalytic properties by manipulating the various physical and chemical parameters that define a nanocatalyst, plasmonically-enhanced or plasmonically-mediated transformations (SPR-enhanced or SPR-mediated catalysis) represent a new frontier in heterogeneous catalysis,^{4,101–105} in which visible light is employed as a sustainable energy input to drive and control chemical reactions. Plasmonic nanostructures, such as silver (Ag) and gold (Au) NPs, can strongly interact with visible light as a result the SPR excitation. In the context of catalysis, the SPR excitation can be put to work for enhancing or mediating chemical transformations by several mechanisms as expressed in Figure 1.17.

Figure 1.17. Main mechanisms involved in plasmonic catalysis: (A) photo-induced temperature increase provides heat to an adjacent reactant; (B) the enhancement of the optical near field at the vicinity of the NP increases the photon rate seen by an adjacent reactant; (C) a photo-induced hot electron is transferred to a nearby reactant; (D) the electron–hole (e^-h^+) generation rate in a photocatalyst is enhanced by heat generated by the NP; (E) the electron–hole generation rate in a photocatalyst is enhanced by the strong optical near-field of the plasmonic NP; and (F) the photocatalyst adjacent to the NP is activated by hot electron transfer from the plasmonic NP.^{4,101–105}

These include: i) by increasing the local electric field close to the nanostructure surface

that enhances absorption at the metal-molecule interface; ii) by generating electron-hole pairs that enable the occurrence of a charge-transfer process at the metal-molecule interface; and iii) by generating local heating at the metal surface that provide energy input for some conversions. Thus, in addition to the “classical” heterogeneous catalysis, plasmonic catalysis has emerged as a relatively new frontier in the field of catalysis which enables the utilization of visible light an eco-friendly energy input to drive and control chemical reactions.^{4,101–105} It is noteworthy that, while heat is a major parameter in any chemical reaction, light can be used to achieve high selectivity in chemical mechanisms thanks to quantum selection rules and adjustable photon energies. Moreover, electron transfer is the basis of redox reactions. Hence, the idea to use metal NPs as efficient sources of heat, light and electrons appears to be an appealing and intuitive concept to both improve yields and control of chemical reactions.

1.9. Specific Aims

To address the above-mentioned challenges, this thesis is focused on the synthesis of truly controlled nanomaterials for generating fundamental knowledge on the understanding of the controlled synthesis of noble-metal (silver, gold, and palladium) and metal oxide (manganese and copper oxide) nanostructures as well as their applications in heterogeneous, plasmonic catalysis, and education in chemistry. This includes a systematic investigation towards the influence of: *i*) physical/chemical parameters that define a nanomaterial (size, shape, composition, and surface morphology); *ii*) their influences into the catalytic applications and metal-support interactions between both active phase and support; and *iii*) use of an external input by visible light to enhance chemical transformations (plasmonic catalysis). It is anticipated that this knowledge, in turn, enabled us the development of next generation nanocatalysts by design displaying tailored activity,

selectivity, recyclability, and distribution of active sites towards different classes of transformations. This ambitious goal is not only strategically important for Brazil, but also may represents a milestone the field of catalysis and nanotechnology.

1.10. References

- (1) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem. Int. Ed. Engl.* **2009**, *48* (1), 60–103.
- (2) Eustis, S.; El-Sayed, M. A. Why Gold Nanoparticles Are More Precious than Pretty Gold: Noble Metal Surface Plasmon Resonance and Its Enhancement of the Radiative and Nonradiative Properties of Nanocrystals of Different Shapes. *Chem. Soc. Rev.* **2006**, *35* (3), 209–217.
- (3) Pang, B.; Yang, X.; Xia, Y. Putting Gold Nanocages to Work for Optical Imaging, Controlled Release and Cancer Theranostics. *Nanomedicine* **2016**, *11* (13), 1715–1728.
- (4) Baffou, G.; Quidant, R. Nanoplasmonics for Chemistry. *Chem. Soc. Rev.* **2014**, *43* (11), 3898–3907.
- (5) Polshettiwar, V.; Varma, R. S. Green Chemistry by Nano-Catalysis. *Green Chem.* **2010**, *12* (5), 743–754.
- (6) Kogure, K.; Hama, S. Nanomaterials for Cosmetics. In *Encyclopedia of Polymeric Nanomaterials*; Kobayashi, S., Müllen, K., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, **2015**; 1349–1352.
- (7) Arico, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J.-M.; van Schalkwijk, W. Nanostructured Materials for Advanced Energy Conversion and Storage Devices. *Nat Mater* **2005**, *4* (5), 366–377.
- (8) Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C. Carbon Nanomaterials for Electronics, Optoelectronics, Photovoltaics, and Sensing. *Chem. Soc. Rev.* **2013**, *42* (7), 2824–2860.
- (9) Lee, K.-S.; El-Sayed, M. A. Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition. *J. Phys. Chem. B* **2006**, *110* (39), 19220–19225.
- (10) Vajtai, R. Science and Engineering of Nanomaterials. In *Springer Handbook of Nanomaterials*; Vajtai, R., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, **2013**; 1–36.
- (11) Niu, W.; Lu, X. Metallic Nanostructures: Fundamentals. In *Metallic Nanostructures: From Controlled Synthesis to Applications*; Xiong, Y., Lu, X., Eds.; Springer International

- Publishing: Cham, **2015**; 1–47.
- (12) An, K.; Somorjai, G. A. Size and Shape Control of Metal Nanoparticles for Reaction Selectivity in Catalysis. *ChemCatChem* **2012**, *4* (10), 1512–1524.
 - (13) Watanabe, Y.; Wu, X.; Hirata, H.; Isomura, N. Size-Dependent Catalytic Activity and Geometries of Size-Selected Pt Clusters on TiO₂(110) Surfaces. *Catal. Sci. Technol.* **2011**, *1* (8), 1490–1495.
 - (14) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O'Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, *14* (4), 1921–1926.
 - (15) Mostafa, S.; Behafarid, F.; Croy, J. R.; Ono, L. K.; Li, L.; Yang, J. C.; Frenkel, A. I.; Cuenya, B. R. Shape-Dependent Catalytic Properties of Pt Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132* (44), 15714–15719.
 - (16) da Silva, A. G. M.; Rodrigues, T. S.; Slater, T. J. A.; Lewis, E. A.; Alves, R. S.; Fajardo, H. V.; Balzer, R.; da Silva, A. H. M.; de Freitas, I.; Oliveira, D. C. de; et al. Controlling Size, Morphology, and Surface Composition of AgAu Nanodendrites in 15 S for Improved Environmental Catalysis under Low Metal Loadings. *ACS Appl. Mater. Interfaces* **2015**, *7*, 25624–25632.
 - (17) da Silva, A. M.; Rodrigues, T.; Taguchi, L. K.; Fajardo, H.; Balzer, R.; Probst, L. D.; Camargo, P. C. Pd-Based Nanoflowers Catalysts: Controlling Size, Composition, and Structures for the 4-Nitrophenol Reduction and BTX Oxidation Reactions. *J. Mater. Sci.* **2015**, 1–12.
 - (18) Jin, M.; Zhang, H.; Xie, Z.; Xia, Y. Palladium Nanocrystals Enclosed by {100} and {111} Facets in Controlled Proportions and Their Catalytic Activities for Formic Acid Oxidation. *Energy Environ. Sci.* **2012**, *5* (4), 6352–6357.
 - (19) Mijatovic, D.; Eijkel, J. C. T.; van den Berg, A. Technologies for Nanofluidic Systems: Top-down vs. Bottom-up-a Review. *Lab Chip* **2005**, *5* (5), 492–500.
 - (20) Hobbs, R. G.; Petkov, N.; Holmes, J. D. Semiconductor Nanowire Fabrication by Bottom-Up and Top-Down Paradigms. *Chem. Mater.* **2012**, *24* (11), 1975–1991.
 - (21) Camargo, P. H. C.; Rodrigues, T. S.; da Silva, A. G. M.; Wang, J. Controlled Synthesis: Nucleation and Growth in Solution. In *Metallic Nanostructures: From Controlled Synthesis to Applications*; Xiong, Y., Lu, X., Eds.; Springer International Publishing: Cham, **2015**; pp 49–74.
 - (22) Xia, Y.; Gilroy, K. D.; Peng, H.-C.; Xia, X. Seed-Mediated Growth of Colloidal Metal Nanocrystals. *Angew. Chemie Int. Ed.* **2017**, *56* (1), 60–95.
 - (23) LaMer, V. K.; Dinegar, R. H. Theory, Production and Mechanism of Formation of Monodispersed Hydrosols. *J. Am. Chem. Soc.* **1950**, *72* (11), 4847–4854.
 - (24) Sear, R. P. Nucleation: Theory and Applications to Protein Solutions and Colloidal Suspensions. *J. Phys. Condens. Matter* **2007**, *19* (3), 33101.
 - (25) You, H.; Fang, J. Particle-Mediated Nucleation and Growth of Solution-Synthesized Metal Nanocrystals: A New Story beyond the LaMer Curve. *Nano Today* **2016**, *11* (2), 145–167.

- (26) Park, J.; Joo, J.; Kwon, S. G.; Jang, Y.; Hyeon, T. Synthesis of Monodisperse Spherical Nanocrystals. *Angew. Chemie Int. Ed.* **2007**, *46* (25), 4630–4660.
- (27) Polte, J. Fundamental Growth Principles of Colloidal Metal Nanoparticles - a New Perspective. *CrystEngComm* **2015**, *17* (36), 6809–6830.
- (28) Erdemir, D.; Lee, A. Y.; Myerson, A. S. Nucleation of Crystals from Solution: Classical and Two-Step Models. *Acc. Chem. Res.* **2009**, *42* (5), 621–629.
- (29) Xiong, Y.; Xia, Y. Shape-Controlled Synthesis of Metal Nanostructures: The Case of Palladium. *Adv. Mater.* **2007**, *19* (20), 3385–3391.
- (30) Wiley, B.; Sun, Y.; Xia, Y. Synthesis of Silver Nanostructures with Controlled Shapes and Properties. *Acc. Chem. Res.* **2007**, *40* (10), 1067–1076.
- (31) Niu, W.; Zhang, L.; Xu, G. Seed-Mediated Growth of Noble Metal Nanocrystals: Crystal Growth and Shape Control. *Nanoscale* **2013**, *5* (8), 3172–3181.
- (32) Tao, A. R.; Habas, S.; Yang, P. Shape Control of Colloidal Metal Nanocrystals. *Small* **2008**, *4* (3), 310–325.
- (33) Lim, B.; Jiang, M.; Tao, J.; Camargo, P. H. C.; Zhu, Y.; Xia, Y. Shape-Controlled Synthesis of Pd Nanocrystals in Aqueous Solutions. *Adv. Funct. Mater.* **2009**, *19* (2), 189–200.
- (34) Liao, H.-G.; Jiang, Y.-X.; Zhou, Z.-Y.; Chen, S.-P.; Sun, S.-G. Shape-Controlled Synthesis of Gold Nanoparticles in Deep Eutectic Solvents for Studies of Structure–Functionality Relationships in Electrocatalysis. *Angew. Chemie* **2008**, *120* (47), 9240–9243.
- (35) Watt, J.; Cheong, S.; Tilley, R. D. How to Control the Shape of Metal Nanostructures in Organic Solution Phase Synthesis for Plasmonics and Catalysis. *Nano Today* **2013**, *8* (2), 198–215.
- (36) Niu, W.; Xu, G. Crystallographic Control of Noble Metal Nanocrystals. *Nano Today* **2011**, *6* (3), 265–285.
- (37) Casillas, G.; Velázquez-Salazar, J. J.; Jose-Yacaman, M. A New Mechanism of Stabilization of Large Decahedral Nanoparticles. *J. Phys. Chem. C* **2012**, *116* (15), 8844–8848.
- (38) Wang, Y.; Peng, H.-C.; Liu, J.; Huang, C. Z.; Xia, Y. Use of Reduction Rate as a Quantitative Knob for Controlling the Twin Structure and Shape of Palladium Nanocrystals. *Nano Lett.* **2015**, *15* (2), 1445–1450.
- (39) Xia, X.; Choi, S.-I.; Herron, J. A.; Lu, N.; Scaranto, J.; Peng, H.-C.; Wang, J.; Mavrikakis, M.; Kim, M. J.; Xia, Y. Facile Synthesis of Palladium Right Bipyramids and Their Use as Seeds for Overgrowth and as Catalysts for Formic Acid Oxidation. *J. Am. Chem. Soc.* **2013**, *135* (42), 15706–15709.
- (40) Barnard, A. S.; Young, N. P.; Kirkland, A. I.; van Huis, M. A.; Xu, H. Nanogold: A Quantitative Phase Map. *ACS Nano* **2009**, *3* (6), 1431–1436.
- (41) Roduner, E. Size Matters: Why Nanomaterials Are Different. *Chem. Soc. Rev.* **2006**, *35* (7), 583–592.
- (42) Vitos, L.; Ruban, A. V.; Skriver, H. L.; Kolla, J. The Surface Energy of Metals. **1998**, *411*, 186–202.

- (43) Tadros, T. Electrostatic and Steric Stabilization of Colloidal Dispersions. In *Electrical Phenomena at Interfaces and Biointerfaces*; John Wiley & Sons, Inc., **2012**; 153–172.
- (44) Marshall, C. E. “Theory of the Stability of Lyophobic Colloids. The Interaction of Particles Having an Electric Double Layer.” E. J. W. Verwey and J. T. G. Overbeek, Elsevier, New York-Amsterdam, **1948**, 413–414.
- (45) Orleans, N. Steric Stabilization Dispersions in Liquids : Suspensions , Emulsions , and Foams Rates of Flocculation – Strength of Interparticle Forces. **2008**, 335-346.
- (46) Zhulina, E. B.; Borisov, O. V; Priamitsyn, V. a. Theory of Steric Stabilization of Colloid Dispersions by Grafted Polymers. *J. Colloid Interface Sci.* **1990**, *137* (2), 495–511.
- (47) Chemistry, P. Steric Stabilization. **2006**, 2-10.
- (48) An, K.; Hyeon, T. Synthesis and Biomedical Applications of Hollow Nanostructures. *Nano Today* **2009**, *4* (4), 359–373.
- (49) Sun, Y.; Mayers, B.; Xia, Y. Metal Nanostructures with Hollow Interiors. *Adv. Mater.* **2003**, *15* (7–8), 641–646.
- (50) Lou, X. W. (David); Archer, L. A.; Yang, Z. Hollow Micro-/Nanostructures: Synthesis and Applications. *Adv. Mater.* **2008**, *20* (21), 3987–4019.
- (51) Cobley, C. M.; Xia, Y. Engineering the Properties of Metal Nanostructures via Galvanic Replacement Reactions. *Mater. Sci. Eng. R Reports* **2010**, *70* (3–6), 44–62.
- (52) Xia, X.; Wang, Y.; Ruditskiy, A.; Xia, Y. 25th Anniversary Article: Galvanic Replacement: A Simple and Versatile Route to Hollow Nanostructures with Tunable and Well-Controlled Properties. *Adv. Mater.* **2013**, *25* (44), 6313–6333.
- (53) Gilroy, K. D.; Ruditskiy, A.; Peng, H.-C.; Qin, D.; Xia, Y. Bimetallic Nanocrystals: Syntheses, Properties, and Applications. *Chem. Rev.* **2017**, *56*, 60–95.
- (54) Skrabalak, S. E.; Chen, J.; Sun, Y.; Lu, X.; Au, L.; Cobley, C. M.; Xia, Y. Gold Nanocages: Synthesis, Properties, and Applications. *Acc. Chem. Res.* **2008**, *41* (12), 1587–1595.
- (55) Prevo, B. G.; Esakoff, S. A.; Mikhailovsky, A.; Zasadzinski, J. A. Scalable Routes to Gold Nanoshells with Tunable Sizes and Response to Near-Infrared Pulsed-Laser Irradiation. *Small* **2008**, *4* (8), 1183–1195.
- (56) Bastús, N. G.; Comenge, J.; Puentes, V. Kinetically Controlled Seeded Growth Synthesis of Citrate-Stabilized Gold Nanoparticles of up to 200 nm: Size Focusing versus Ostwald Ripening. *Langmuir* **2011**, *27* (17), 11098–11105.
- (57) Ruditskiy, A.; Xia, Y. The Science and Art of Carving Metal Nanocrystals. *ACS Nano* **2017**, *11* (1), 23–27.
- (58) Wang, L.; Yamauchi, Y. Metallic Nanocages: Synthesis of Bimetallic Pt–Pd Hollow Nanoparticles with Dendritic Shells by Selective Chemical Etching. *J. Am. Chem. Soc.* **2013**, *135* (45), 16762–16765.
- (59) Yin, Y.; Rioux, R. M.; Erdonmez, C. K.; Hughes, S.; Somorjai, G. A.; Alivisatos, A. P. Formation of Hollow Nanocrystals Through the Nanoscale Kirkendall Effect. *Science* **2004**, *304* (5671), 711-714.
- (60) Yuan, S.; Zhang, Q.; Xu, B.; Jin, Z.; Zhang, Y.; Yang, Y.; Zhang, M.; Ohno, T. Porous

- Cerium Dioxide Hollow Spheres and Their Photocatalytic Performance. *RSC Adv.* **2014**, *4* (107), 62255–62261.
- (61) Rodrigues, T.; da Silva, A. M.; Macedo, A.; Farini, B.; Alves, R.; Camargo, P. C. Probing the Catalytic Activity of Bimetallic versus Trimetallic Nanoshells. *J. Mater. Sci.* **2015**, *50* (16), 5620–5629.
- (62) Lu, X.; Chen, J.; Skrabalak, S. E.; Xia, Y. Galvanic Replacement Reaction: A Simple and Powerful Route to Hollow and Porous Metal Nanostructures. *Proc. Inst. Mech. Eng. Part N J. Nanomater. Nanoeng. Nanosyst.* **2007**, *221* (1), 1–16.
- (63) da Silva, A. G. M.; Lewis, E. A.; Rodrigues, T. S.; Slater, T. J. A.; Alves, R. S.; Haigh, S. J.; Camargo, P. H. C. Surface Segregated AgAu Tadpole-Shaped Nanoparticles Synthesized Via a Single Step Combined Galvanic and Citrate Reduction Reaction. *Chem. – A Eur. J.* **2015**, *21* (35), 12314–12320.
- (64) Huang, X.; El-Sayed, M. A. Gold Nanoparticles: Optical Properties and Implementations in Cancer Diagnosis and Photothermal Therapy. *J. Adv. Res.* **2010**, *1* (1), 13–28.
- (65) McFarland, A. D.; Haynes, C. L.; Mirkin, C. A.; Van Duyne, R. P.; Godwin, H. A. Color My Nanoworld. *J. Chem. Educ.* **2004**, *81* (4), 544A.
- (66) Dreaden, E. C.; Alkilany, A. M.; Huang, X.; Murphy, C. J.; El-Sayed, M. A. The Golden Age: Gold Nanoparticles for Biomedicine. *Chem. Soc. Rev.* **2012**, *41* (7), 2740–2779.
- (67) Klar, T.; Perner, M.; Grosse, S.; von Plessen, G.; Spirk, W.; Feldmann, J. Surface-Plasmon Resonances in Single Metallic Nanoparticles. *Phys. Rev. Lett.* **1998**, *80* (19), 4249–4252.
- (68) Jain, P. K.; Huang, X.; El-Sayed, I. H.; El-Sayed, M. A. Review of Some Interesting Surface Plasmon Resonance-Enhanced Properties of Noble Metal Nanoparticles and Their Applications to Biosystems. *Plasmonics* **2007**, *2* (3), 107–118.
- (69) Willets, K. A.; Van Duyne, R. P. Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annu. Rev. Phys. Chem.* **2007**, *58* (1), 267–297.
- (70) Haes, A. J.; Haynes, C. L.; McFarland, A. D.; Schatz, G. C.; Van Duyne, R. P.; Zou, S. Plasmonic Materials for Surface-Enhanced Sensing and Spectroscopy. *MRS Bull.* **2005**, *30* (5), 368–375.
- (71) Xiong, Y.; Chen, J.; Wiley, B.; Xia, Y.; Yin, Y.; Li, Z.-Y. Size-Dependence of Surface Plasmon Resonance and Oxidation for Pd Nanocubes Synthesized via a Seed Etching Process. *Nano Lett.* **2005**, *5* (7), 1237–1242.
- (72) Xia, Y.; Halas, N. J.; Editors, G. Shape-Controlled Surface Plasmonic Nanostructures. **2005**, *30* (5), 338–348.
- (73) Wiley, B. J.; Im, S. H.; Li, Z.-Y.; McLellan, J.; Siekkinen, A.; Xia, Y. Maneuvering the Surface Plasmon Resonance of Silver Nanostructures through Shape-Controlled Synthesis. *J. Phys. Chem. B* **2006**, *110* (32), 15666–15675.
- (74) Liu, K.-K.; Tadeballi, S.; Tian, L.; Singamaneni, S. Size-Dependent Surface Enhanced Raman Scattering Activity of Plasmonic Nanorattles. *Chem. Mater.* **2015**, *27* (15), 5261–5270.
- (75) Schatz, G. C.; Young, M. A.; Van Duyne, R. P. *Surface-Enhanced Raman Scattering:*

- Physics and Applications*; **2006**, 1-45.
- (76) H. A. Atwater; A. Polman. Plasmonics for Improved Photovoltaic Devices. *Nature* **2010**, *9*, 205–213.
 - (77) Xu, P.; Kang, L.; Mack, N. H.; Schanze, K. S.; Han, X.; Wang, H.-L. Mechanistic Understanding of Surface Plasmon Assisted Catalysis on a Single Particle: Cyclic Redox of 4-Aminothiophenol. *Sci. Rep.* **2013**, *3*, 2997.
 - (78) Norskov, J. K.; Bligaard, T.; Hvolbaek, B.; Abild-Pedersen, F.; Chorkendorff, I.; Christensen, C. H. The Nature of the Active Site in Heterogeneous Metal Catalysis. *Chem. Soc. Rev.* **2008**, *37* (10), 2163–2171.
 - (79) Schlögl, R. Heterogeneous Catalysis. *Angew. Chemie Int. Ed.* **2015**, *54* (11), 3465–3520.
 - (80) Mizuno, N.; Misono, M. Heterogeneous Catalysis. *Chem. Rev.* **1998**, *98* (1), 199–218.
 - (81) Wells, A.; Meyer, H.-P. Biocatalysis as a Strategic Green Technology for the Chemical Industry. *ChemCatChem* **2014**, *6* (4), 918–920.
 - (82) Dincer, I. Environmental and Sustainability Aspects of Hydrogen and Fuel Cell Systems. *Int. J. Energy Res.* **2007**, *31* (1), 29–55.
 - (83) Corma, A. Heterogeneous Catalysis: Understanding for Designing, and Designing for Applications. *Angew. Chemie Int. Ed.* **2016**, *55* (21), 6112–6113.
 - (84) LePage, J. F.; Schlögl, R.; Wainwright, M. S.; Schü, F.; Unger, K.; Ko, E. I.; Jacobsen, H.; Kleinschmit, P.; Menon, R. G.; Delmon, B.; et al. Preparation of Solid Catalysts: Sections 2.0 and 2.1. In *Handbook of Heterogeneous Catalysis*; Wiley-VCH Verlag GmbH, 1997; pp 49–138.
 - (85) Astruc, D.; Lu, F.; Aranzaes, J. R. Nanoparticles as Recyclable Catalysts: The Frontier between Homogeneous and Heterogeneous Catalysis. *Angew. Chemie Int. Ed.* **2005**, *44* (48), 7852–7872.
 - (86) Zaera, F. Nanostructured Materials for Applications in Heterogeneous Catalysis. *Chem. Soc. Rev.* **2013**, *42* (7), 2746–2762.
 - (87) Duan, H.; Wang, D.; Li, Y. Green Chemistry for Nanoparticle Synthesis. *Chem. Soc. Rev.* **2015**, *44* (16), 5778–5792.
 - (88) Bell, A. T. The Impact of Nanoscience on Heterogeneous Catalysis. *Sci.* **2003**, *299* (5613), 1688–1691.
 - (89) Zhang, Y.; Cui, X.; Shi, F.; Deng, Y. Nano-Gold Catalysis in Fine Chemical Synthesis. *Chem. Rev.* **2012**, *112* (4), 2467–2505.
 - (90) Sheldon, R. A. Fundamentals of Green Chemistry: Efficiency in Reaction Design. *Chem. Soc. Rev.* **2012**, *41* (4), 1437–1451.
 - (91) Gilbertson, L. M.; Zimmerman, J. B.; Plata, D. L.; Hutchison, J. E.; Anastas, P. T. Designing Nanomaterials to Maximize Performance and Minimize Undesirable Implications Guided by the Principles of Green Chemistry. *Chem. Soc. Rev.* **2015**, *44*, 5758–5777.
 - (92) Xie, S.; Choi, S.-I.; Xia, X.; Xia, Y. Catalysis on Faceted Noble-Metal Nanocrystals: Both Shape and Size Matter. *Curr. Opin. Chem. Eng.* **2013**, *2* (2), 142–150.
 - (93) Pakhare, D.; Spivey, J. A Review of Dry (CO₂) Reforming of Methane over Noble Metal

- Catalysts. *Chem. Soc. Rev.* **2014**, *43* (22), 7813–7837.
- (94) Cheong, S.; Watt, J. D.; Tilley, R. D. Shape Control of Platinum and Palladium Nanoparticles for Catalysis. *Nanoscale* **2010**, *2* (10), 2045–2053.
 - (95) Freakley, S. J.; He, Q.; Kiely, C. J.; Hutchings, G. J. Gold Catalysis: A Reflection on Where We Are Now. *Catal. Letters* **2015**, *145* (1), 71–79.
 - (96) Fihri, A.; Bouhrara, M.; Nekoueishahraki, B.; Basset, J.-M.; Polshettiwar, V. Nanocatalysts for Suzuki Cross-Coupling Reactions. *Chem. Soc. Rev.* **2011**, *40* (10), 5181–5203.
 - (97) Wang, Q.; Cui, X.; Guan, W.; Zhang, L.; Fan, X.; Shi, Z.; Zheng, W. Shape-Dependent Catalytic Activity of Oxygen Reduction Reaction (ORR) on Silver Nanodecahedra and Nanocubes. *J. Power Sources* **2014**, *269*, 152–157.
 - (98) Petri, M. V.; Ando, R. A.; Camargo, P. H. C. Tailoring the Structure, Composition, Optical Properties and Catalytic Activity of Ag–Au Nanoparticles by the Galvanic Replacement Reaction. *Chem. Phys. Lett.* **2012**, *531* (0), 188–192.
 - (99) Rodrigues, T. S.; da Silva, A. G. M.; Gonçalves, M. C.; Fajardo, H. V.; Balzer, R.; Probst, L. F. D.; Camargo, P. H. C. AgPt Hollow Nanodendrites: Synthesis and Uniform Dispersion over SiO₂ Support for Catalytic Applications. *ChemNanoMat* **2015**, *1*(1), 46–51.
 - (100) Rodrigues, T. S.; da Silva, A. H. M.; da Silva, A. G. M.; Ceara, D. G.; Gomes, J. F.; Assaf, J. M.; Camargo, P. H. C. Hollow AgPt/SiO₂ Nanomaterials with Controlled Surface Morphologies: Is the Number of Pt Surface Atoms Imperative to Optimize Catalytic Performances? *Catal. Sci. Technol.* **2016**, *6* (7), 2162–2170.
 - (101) Christopher, P.; Xin, H.; Linic, S. Visible-Light-Enhanced Catalytic Oxidation Reactions on Plasmonic Silver Nanostructures. *Nat Chem* **2011**, *3* (6), 467–472.
 - (102) Sun, M.; Xu, H. A Novel Application of Plasmonics: Plasmon-Driven Surface-Catalyzed Reactions. *Small* **2012**, *8* (18), 2777–2786.
 - (103) Catchpole, K. R.; Polman, A. Plasmonic Solar Cells. *Opt. Express* **2008**, *16* (26), 21793–21800.
 - (104) Kang, L.; Han, X.; Chu, J.; Xiong, J.; He, X.; Wang, H.-L.; Xu, P. In Situ Surface-Enhanced Raman Spectroscopy Study of Plasmon-Driven Catalytic Reactions of 4-Nitrothiophenol under a Controlled Atmosphere. *ChemCatChem* **2015**, *7* (6), 1004–1010.
 - (105) Wang, J. L.; Ando, R. A.; Camargo, P. H. C. Investigating the Plasmon-Mediated Catalytic Activity of AgAu Nanoparticles as a Function of Composition: Are Two Metals Better than One? *ACS Catal.* **2014**, *4* (11), 3815–3819.

Section 2.

Synthesis of Palladium Nanomaterials by Non-classical Growth Mechanisms

Chapter 2. One-pot Synthesis of Size-controlled Porous Pd Nanospheres by a Non-classical Growth Mechanism Combining the LaMer and DLVO Theories

2.1. Introduction

Palladium (Pd) nanomaterials have been intensely investigated over the last decades as a result of their applications in heterogeneous catalysis and electrocatalysis.^{1–4} In these applications, it has been demonstrated that the control over the Pd size and shape (*e.g.*, cubes, spheres, rods, and octahedra) strongly affects their properties, endowing nanoparticle shape-control as an efficient strategy for maximizing performance.^{5–8}

Among several Pd nanoparticle varieties, porous nanostructures (*e.g.*, dendrites, flowers, spheres) are attractive for catalytic and electrochemical applications due to their relatively high surface-to-volume ratios and potential exposure of more active surface facets as compared to their counterparts displaying smooth surfaces.^{9–13} Although several studies have previously described the synthesis of Pd-based porous nanoparticles by reducing PdCl_4^- (aq) in the presence of a reducing agent (*e.g.*, ascorbic acid, sodium borohydride, etc.),^{9,14–17} the exact nucleation and growth mechanisms remain unexplained. Therefore, a deeper understanding on their formation is imperative to the development of a mechanistic framework to enable the rational design of Pd nanoparticles with well-controlled properties and desired performances for target applications.

Most reported mechanistic investigations regarding the synthesis of metal nanoparticles have been explained by adopting classical nucleation and growth theory, which is based on the three-stage LaMer curve: (i) production of atoms from the reduction of a metal precursor; (ii) nanoparticle nucleation; and finally (iii) nanoparticle growth.^{18,19} However, it has been

demonstrated that, in some scenarios, non-classical growth involving inter-particle attachment (*i.e.*, oriented attachment) can also affect the shape and morphology of the final nanocrystal,¹⁹ opening up new possibilities for the synthesis of nanostructures with unique architectures.

Here, we demonstrate that the reduction of $\text{PdCl}_4^{2-}(\text{aq})$ by hydroquinone (HQ) induces the formation of uniform porous Pd nanospheres with controlled sizes in a single synthesis step by a non-classical growth mechanism based on LaMer and DLVO theories. Our approach also employed water as the solvent and polyvinylpyrrolidone (PVP) as the stabilizing agent. Based on the product morphology, crystallinity, and several control experiments, we propose a novel mechanism for the formation of porous Pd nanospheres, where the temperature and ionic strength modulation permits tight control over the resultant diameter and morphology of the obtained nanoparticles.

2.2. Experimental Section

2.2.1. Materials and Instrumentation

Analytical grade chemicals potassium tetrachloropalladate trihydrate ($\text{K}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$, 98%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$, 99%, Sigma-Aldrich), and potassium chloride (KCl, 99%, Sigma-Aldrich) were used as received. All solutions were prepared using deionized water (18.2 M Ω cm). Transmission electron microscope (TEM) images were obtained with a Hitachi HT7700 microscope operating at 120 kV. High resolution secondary electron (HR-SE), high resolution transmission electron microscope (HRTEM), and high-angle annular dark-field scanning TEM (HAADF-STEM) images were obtained with a HD2700 Hitachi microscope with STEM aberration corrector operated at 200 kV.

Samples for TEM analysis were prepared by drop-casting aqueous suspensions of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. The Pd atomic percentages were measured by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer, NexION 300Q).

2.2.2. Synthesis of size-controlled Pd Porous Nanospheres

In a typical procedure, 9.4 mL of a PVP aqueous solution (1 mg/mL) was transferred to a 20 mL round-bottom flask and stirred for 10 min, followed by the addition of 170 μL of a 12 mM $\text{PdCl}_4^{2-}(\text{aq})$ solution. After 2 min, 100 μL of a 30 mM aqueous hydroquinone solution was added to this mixture. The control over the nanoparticle size was easily obtained by changing the reaction temperature. In this case, different reactions were performed at 20, 40, 60, 80, and 100 $^\circ\text{C}$ for 24 h. In order to control and monitor the growth of the produced porous Pd nanospheres, the reaction was quenched at different time intervals: 15 s, 1 min, 5 min, 10 min, 30 min, 1 h, 2 h, 4 h, 6 h, 12 h, and 24 h (several parallel reactions were carried out). The reactions were quenched by adding 100 μL of a 300 mM $\text{HCl}(\text{aq})$ solution to the reaction mixture and cooling to 0 $^\circ\text{C}$ in an ice water bath. The nanostructures were then isolated and washed three times with ethanol by successive rounds of centrifugation at 55000 rpm for 30 min and supernatant removal. After washing, the nanoparticles were then suspended in 10 mL of water

2.3. Results and Discussion

Our investigations started with the synthesis of porous Pd nanospheres by employing $\text{PdCl}_4^{2-}(\text{aq})$ as the precursor, hydroquinone as the reducing agent, water as the solvent, and PVP as

the stabilizing agent. We were interested in investigating how the reaction temperature affects the formation of porous Pd nanospheres and their sizes. To this end, we conducted reactions at 20, 40, 60, 80, and 100 °C. Figure 2.1 shows TEM images of the porous Pd nanospheres obtained by this approach as a function of the temperature obtained after 24 h of reaction.

Figure 2.1. TEM images of porous Pd nanospheres displaying controlled sizes obtained by reducing $\text{PdCl}_4^{2-}(\text{aq})$ with hydroquinone at different temperatures: (A–B) 20, (C–D) 40, (E–F) 60, (G–H) 80, and (I–J) 100 °C. All nanostructures here were isolated after a 24 h of reaction time.

In all cases, the Pd nanoparticles presented well-defined shapes and uniform sizes. However, the diameters and morphology of the product nanoparticles were strongly dependent upon the reaction temperature (Figure 2.1 A–J). For instance, the size of the porous Pd nanospheres decreased as the reaction temperature was increased, with diameter of 62 ± 6 , 39 ± 4 , 22 ± 3 , 12 ± 3 , and 7 ± 2 nm when the syntheses were carried out at 20 (Figure 2.1, A and B), 40 (Figure 2.1, C and D), 60 (Figure 2.1, E and F), 80 (Figure 2.1, G and H), and 100 °C (Figure 2.1, I and J), respectively. Regarding their morphology, the porous Pd nanospheres appeared to be comprised of aggregated Pd crystallites *ca.* 7–8 nm in size at reaction temperatures of 20, 40, and 60 °C (Figure 2.1 A–F). This observation was further supported by the high resolution secondary electron (HR-SE), HAADF-STEM, and HRTEM images obtained for Pd nanospheres synthesized at 40 °C (Figure 2.2 A–I).

Figure 2.2. HR-SE, HAADF-STEM, and HRTEM images of typical porous Pd nanospheres obtained at 40 °C. The region indicated by dashed squares at the HAADF-STEM image (H) is detailed in (I), showing lattice fringes corresponding to the {111} spacing of Pd.

Conversely, the nanostructures obtained at 80 and 100 °C were comprised of multiple aggregated Pd nanoparticles (Pd nanoparticles *ca.* 8 nm in size with several Pd satellites (1–2 nm) adhered at their surface), in which the number of aggregated crystallites, and thus outer diameters, decreased with the increase in reaction temperature. In order to gain further insights into the differences in the growth mechanisms of the Pd porous nanospheres as a function of the temperature, we performed control experiments by stopping the reactions at different times following the addition of $\text{PdCl}_4^{2-}(\text{aq})$ precursor to the reaction mixture during the synthesis performed at 20 and 100 °C. This was achieved by quenching the reducing power of hydroquinone by quickly adding HCl to the reaction mixture.²⁰ Prior to the addition of HCl, hydroquinone forms a univalent species in the solution ($\text{HQ}^-(\text{aq})$), which has a reduction rate that is more than 10^4 times faster than its protonated form (H_2Q).^{21–23} Therefore, adding small amounts of HCl into the system will shift that following reaction toward the right side:

This strategy allowed us to monitor the product formation and shape evolution as a function of time as described in Figure 2.3 and 2.4 (synthesis employing 20 and 100 °C as the reaction temperature, respectively). Figure 2.3 displays the morphology evolution of a reaction conducted at 20 °C by stopping the reaction after 1 (Figure 2.3 A), 2 (Figure 2.3 B), 4 (Figure 2.3 C), 6 (Figure 2.3 D), 12 (Figure 2.3 E), and 24 h (Figure 2.3 F), respectively.

Figure 2.3. TEM images of porous Pd nanospheres obtained at 20 °C as a function of the Pd growth time: (A) 1, (B) 2, (C) 4, (D) 6, (E) 12, and (F) 24 h.

First, clusters of Pd NPs *ca.* 7–8 nm in size each (comprised of several ultra-small nanoparticles *ca.* 1–2 nm in size) were produced after 1 h of reaction (no Pd particles could be isolated before 1 h even after centrifugation at 55000 rpm). As the reaction proceeded to $t = 2$ h (Figure 2.3 B), Pd nanoparticles appeared (formed from the fusion of these clusters of Pd NPs), which then served as seeds for the additional attachment of clusters of Pd NPs, leading to the formation of the larger porous nanoparticles (Figure 2.3 C), which increased in size up to 24 h of reaction (Figure 2.3 C–F). No further increase in size was detected after 24 h.

Interestingly, a different growth pattern was observed during the synthesis carried out at 100 °C (Figure 2.4 A–D). Here, the formation of clusters of Pd NPs could be observed after only 15 s following the addition of hydroquinone to the reaction mixture (Figure 2.4 A). After 1 min, the presence of multiple aggregated Pd nanoparticles were detected (Figure 2.4 B), indicating that the preformed clusters of Pd NPs had been consumed in a fusion process.

Figure 2.4. TEM images for Pd nanoparticles obtained at 100 °C as a function of the Pd growth time: (A) 15 s, (B) 1 min, (C) 1 h, and (D) 24 h.

In this case, all clusters of Pd NPs were consumed at 1 min and no further attachment/aggregation processes took place, resulting in unchanged morphology even after 24 h (Figure 2.4 C and D). Figure 2.5 A–D show TEM and HAADF-STEM images for the clusters of Pd NPs (Figure 2.5 A and B) and multiple aggregated Pd nanoparticles (Figure 2.5 C and D). While the clusters of Pd NPs are formed by the assembly of ultra-small Pd NPs (1–2 nm each), multiple aggregated Pd nanoparticles are polycrystalline and formed by Pd nanoparticles *ca.* 8 nm in size with several Pd satellites (1–2 nm) adhered at their surface.

Figure 2.5. HAADF-STEM images detailing the early stages on the synthesis of porous Pd nanospheres at 100 °C. Clusters of Pd NPs (A and B) fuse together to form multiple aggregated Pd nanoparticles *ca.* 8 nm in size containing several Pd satellites (1-2 nm) adhered at their surface (C and D).

In order to investigate the role played by PVP during the formation of the porous Pd nanospheres, we performed a series of experiments regarding their synthesis under the same experimental conditions as those describe in Figure 2.1 by removing hydroquinone as the reducing agent or by modifying the amount of PVP added into the reaction mixture. Without hydroquinone, no $\text{PdCl}_4^{2-}(\text{aq})$ precursor reduction could be detected, even at temperatures as high as 100 °C. Interestingly, porous Pd nanospheres still were formed in the absence of PVP (Figure 2.6 A), indicating that hydroquinone plays a key role towards the formation of porous Pd nanospheres. Specifically, porous Pd nanospheres *ca.* 120 nm in diameter were obtained (Figure 2.6 A).

Figure 2.6. TEM images of Pd porous nanospheres obtained at 40 °C as a function of the PVP amount: (A) 0 (absence of PVP), (B) 5, (C) 10, (D) 20, (E) 30 and, (F) 50 mg.

Our results indicated that the size of porous Pd nanospheres could be also controlled by the amount of PVP added into the reaction. Specifically, porous Pd nanospheres *ca.* 60 ± 5 , 39 ± 4 , 33 ± 4 , 29 ± 3 , and 25 ± 2 nm were obtained when the amount of PVP ranged from 5 to 100 mg (Figure 2.6 B–F). However, PVP could not prevent the observed attachment of Pd clusters of NPs to the formed Pd seeds. Upon increasing the amount of PVP to 400 mg, no additional decrease in Pd particle size could be detected, which might be related to the ineffective stabilization by PVP. It has been reported that PVP is less effective as a stabilizing agent in polar solvents (water, DMF, etc).^{17,24,25}

We believe that the unique growth regime observed for our porous Pd nanospheres can be explained by combining elements of the classical nucleation theory (LaMer theory) and DLVO-theory.²⁶ Over the full temperature range (20–100 °C), all reactions initially gave rise to clusters of Pd NPs, with a formation mechanism that fits well within the classical nucleation theory. After this step, what primarily differentiates the final product is the degree to which these clusters of NPs have aggregated. Our modern day understanding of nanoparticle aggregation theory is based on DLVO theory,²⁶ which states that the distance-dependent potential energy (V_T) between colloidal particles is simply defined a short range attractive van der Waals potential (V_A) and a long range repulsive electrostatic potential (V_R):

$$V_{total} = V_A + V_R \quad (2.1)$$

where:

$$V_R = -\frac{AR}{12D} + 2\pi\epsilon\epsilon_o R\psi^2 e^{-kD} \quad (2.2)$$

and where:

$$k = \left[\sum_i \frac{z_i^2 q^2 c_i}{k_B T} \right]^2 \quad (2.3)$$

In the above formulations, A is the Hamaker constant, R is the radius of the particles, ϵ_o is the permittivity of vacuum, ϵ is the dielectric constant of the solvent, ψ is the Stern potential, k is the Debye constant, z_i is the charge number of the ionic species, i is the elementary charge, c_i is the concentration of ion i (co- or counter-ions) at $x = \infty$ (in the bulk solution), k_B is the Boltzmann constant, D is the distance between the outermost surface of two colliding particles, and T is the temperature of the system. Intuitively, one may initially think that carrying out a reaction at higher temperatures (endowing the particles with higher average kinetic energies) would be more likely

to overcome this aggregation barrier and cause particle aggregation. However, this was exactly the opposite of what we experimentally observed.

To account for this behavior, we carefully analyzed all of the key DLVO-defining reactions parameters. The data in Figure 2.7 shows that at 100 °C all $\text{PdCl}_4^{2-}(\text{aq})$ precursor is reduced in the first minute of the reaction. On the other hand, at 20 °C, less than 20 % of the $\text{PdCl}_4^{2-}(\text{aq})$ precursor was reduced to Pd after 1 h. For all temperatures investigated, the rate of Pd consumption was strongly dependent on the reaction temperature (Figure 2.7 A), and all reactions could be described by a first-order rate law (Figure 2.7 B).

Figure 2.7. (A) Reduction (%) of $\text{PdCl}_4^{2-}(\text{aq})$ precursor by hydroquinone and (B) Plots of $\ln(C_t/C_0)$ as function of the reaction time for different temperatures: 20 (black line), 40 (grey line), 60 (green line), 80 (red line), and 100 °C (blue line).

The calculated rate constants (k) indicated that the reaction performed at 100 °C took place 856 times faster than the reaction at 20 °C. Therefore, when the reaction is carried out at lower temperatures, the clusters of Pd NPs are exposed to relatively high ionic strengths ($\text{PdCl}_4^{2-}_{(\text{aq})}$ and K^+ ions) throughout the reaction. Aggregation of colloids is highly sensitive to the ionic strength (defined by both valency and concentration of ions present in the system),^{27,28} where only slight increases to the ion-concentration can give rise to aggregation. Therefore, when reactions are carried out at lower temperatures, the clusters of Pd NPs are exposed to higher concentrations of the Pd-salt ($\text{PdCl}_4^{2-}_{(\text{aq})}$ and K^+ ions), which effectively decreases the repulsion potential and assists the aggregation process. At higher temperatures, the Pd-salt precursor is rapidly exhausted and the ionic-strength is low enough such that the Pd clusters remain stable in solution. The other key parameters (*e.g.*, dielectric constant, stern potential, and Hamaker constant) can be assumed constant throughout the reaction. In order to confirm this hypothesis, we performed control experiments employing 100 °C as the reaction temperature under the same conditions as those described in Figure 2.1 by adding different volumes of a 12 mM KCl solution to the reaction mixture in order to modulate the ionic strength. The results are shown in Figure 2.8. Without the addition of KCl, multiple aggregated Pd nanoparticles were formed as described in Figure 2.1 I–J. Interestingly, it was found that the size of porous Pd nanospheres could be controlled by the volume of a 12 mM KCl solution added into the reaction mixture. In this case, porous Pd nanospheres *ca.* 13 ± 3 , 23 ± 4 , 33 ± 4 , 39 ± 5 nm were obtained when the volume of a 12 mM KCl solution ranged from 20 to 200 μL (Figure 2.8 A–C), in agreement with the proposed mechanism, in which increase ionic strengths favor more aggregation of pre-formed clusters of Pd NPs and thus lead to larger outer diameters.

Figure 2.8. TEM images of Pd porous nanospheres obtained at 100 °C as a function of the volume of a 12 mM KCl solution added before starting the reactions: (A) 20, (B) 50, and (C) 200 μ L.

Based on the product morphology, crystallinity, and kinetics of formation observed in control experiments; we propose a mechanism for porous Pd nanospheres formation as depicted in Scheme 2.1. In the first step of this reported approach, the $\text{PdCl}_4^{2-}(\text{aq})$ reduction leads to the formation of clusters of Pd NPs composed of an ensemble of ultra-small Pd particles < 2 nm each. At 20 °C, when the reaction is relatively slow, the particles are formed in the presence of unreacted precursor molecules. The residual precursor gives rise to a relatively high ionic strength that causes some of

these clusters of Pd NPs to fuse together and form Pd nanoparticles, which then serve as seeds for the further attachment of clusters of Pd NPs. Then, with increasing time, the pre-formed clusters of Pd NPs continually attach to the Pd seeds leading to the formation of porous Pd nanospheres. On the other hand, when the reaction rate is too fast, as in the case when the temperature is at 100 °C, all of the $\text{PdCl}_4^{2-}(\text{aq})$ is rapidly reduced and the product formation occurs in a solution that has a low ionic strength. Since the low ionic strength leads to higher inter-particle repulsion forces, the clusters of Pd NPs do not aggregate.

Scheme 2.1. Proposed formation mechanism for the porous Pd nanospheres based on a non-classical mechanism, in which clusters of Pd NPs are produced in a first step.

2.4. Conclusion

In summary, we have reported a facile one-step route for the synthesis of size-controlled porous Pd nanospheres involving the reduction of $\text{PdCl}_4^{2-}(\text{aq})$ precursor by hydroquinone. The obtained porous Pd nanospheres presented well-defined shapes and uniform sizes. We found that the

presence of hydroquinone induced the formation of porous Pd nanospheres by a new mechanism that combines elements of classical nucleation (LaMer theory) and DLVO-theory. The control over the porous Pd nanospheres sizes was easily modulated only by changing the reaction temperature and subsequently the ionic strength, which could be explained based on the differences in the $\text{PdCl}_4^{2-}(\text{aq})$ reduction rates. In this case, when the ionic strength in the solution was relatively high (during slow reaction rates), the clusters of Pd NPs formed in the first step of the reaction serve as templates for the formation of larger porous nanospheres since the repulsion forces between them is low due to the relatively high ionic strength. When the ionic strength is relatively low (during fast reaction rates), the clusters of Pd NPs fuse to form multiple aggregated Pd nanoparticles with 1-2 nm Pd satellites adhered at the surface. We believe that the results presented here will not only provides some additional clues for rationalizing the nucleation and growth behavior of colloidal nanoparticles, but hopefully will also inspire future investigations for the development of strategies for the synthesis of metal nanoparticles with unconventional shapes and potentially improved properties for diverse applications.

2.5. References

- (1) Liu, Z.; Yang, Z.; Peng, B.; Cao, C.; Zhang, C.; You, H.; Xiong, Q.; Li, Z.; Fang, J. Highly Sensitive, Uniform, and Reproducible Surface-Enhanced Raman Spectroscopy from Hollow Au-Ag Alloy Nanourchins. *Adv. Mater.* **2014**, *26* (15), 2431–2439.
- (2) Bej, A.; Ghosh, K.; Sarkar, A.; Knight, D. W. Palladium Nanoparticles in the Catalysis of Coupling Reactions. *RSC Adv.* **2016**, *6* (14), 11446–11453.
- (3) Cheong, S.; Watt, J. D.; Tilley, R. D. Shape Control of Platinum and Palladium Nanoparticles for Catalysis. *Nanoscale* **2010**, *2* (10), 2045–2053.
- (4) Chen, A.; Ostrom, C. Palladium-Based Nanomaterials: Synthesis and Electrochemical Applications. *Chem. Rev.* **2015**, *115* (21), 11999–12044.
- (5) Wu, B.; Zheng, N. Surface and Interface Control of Noble Metal Nanocrystals for Catalytic and Electrocatalytic Applications. *Nano Today* **2013**, *8* (2), 168–197.
- (6) Zhang, H.; Jin, M.; Xiong, Y.; Lim, B.; Xia, Y. Shape-Controlled Synthesis of Pd

- Nanocrystals and Their Catalytic Applications. *Acc. Chem. Res.* **2013**, *46* (8), 1783–1794.
- (7) Shao, M.; Odell, J.; Humbert, M.; Yu, T.; Xia, Y. Electrocatalysis on Shape-Controlled Palladium Nanocrystals: Oxygen Reduction Reaction and Formic Acid Oxidation. *J. Phys. Chem. C* **2013**, *117* (8), 4172–4180.
 - (8) Xie, S.; Choi, S.-I.; Xia, X.; Xia, Y. Catalysis on Faceted Noble-Metal Nanocrystals: Both Shape and Size Matter. *Curr. Opin. Chem. Eng.* **2013**, *2* (2), 142–150.
 - (9) Fu, G.; Han, W.; Yao, L.; Lin, J.; Wei, S.; Chen, Y.; Tang, Y.; Zhou, Y.; Lu, T.; Xia, X. One-Step Synthesis and Catalytic Properties of Porous Palladium Nanospheres. *J. Mater. Chem.* **2012**, *22* (34), 17604–17611.
 - (10) Zhang, L.; Zhang, J.; Jiang, Z.; Xie, S.; Jin, M.; Han, X.; Kuang, Q.; Xie, Z.; Zheng, L. Facile Syntheses and Electrocatalytic Properties of Porous Pd and Its Alloy Nanospheres. *J. Mater. Chem.* **2011**, *21* (26), 9620–9625.
 - (11) Zhou, Y.; Wang, D.; Li, Y. Pd and Au@Pd Nanodendrites: A One-Pot Synthesis and Their Superior Catalytic Properties. *Chem. Commun.* **2014**, *50* (46), 6141–6144.
 - (12) da Silva, A. M.; Rodrigues, T.; Taguchi, L. K.; Fajardo, H.; Balzer, R.; Probst, L. D.; Camargo, P. C. Pd-Based Nanoflowers Catalysts: Controlling Size, Composition, and Structures for the 4-Nitrophenol Reduction and BTX Oxidation Reactions. *J. Mater. Sci.* **2015**, 1–12.
 - (13) Wang, F.; Li, C.; Sun, L.-D.; Xu, C.-H.; Wang, J.; Yu, J. C.; Yan, C.-H. Porous Single-Crystalline Palladium Nanoparticles with High Catalytic Activities. *Angew. Chemie Int. Ed.* **2012**, *51* (20), 4872–4876.
 - (14) Lim, B.; Jiang, M.; Camargo, P. H. C.; Cho, E. C.; Tao, J.; Lu, X.; Zhu, Y.; Xia, Y. Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction. *Sci.* **2009**, *324* (5932), 1302–1305.
 - (15) Gao, Q.; Gao, M.-R.; Liu, J.-W.; Chen, M.-Y.; Cui, C.-H.; Li, H.-H.; Yu, S.-H. One-Pot Synthesis of Branched Palladium Nanodendrites with Superior Electrocatalytic Performance. *Nanoscale* **2013**, *5* (8), 3202–3207.
 - (16) Hong, W.; Fang, Y.; Wang, J.; Wang, E. One-Step and Rapid Synthesis of Porous Pd Nanoparticles with Superior Catalytic Activity toward Ethanol/formic Acid Electrooxidation. *J. Power Sources* **2014**, *248*, 553–559.
 - (17) Lim, B.; Jiang, M.; Yu, T.; Camargo, P. C.; Xia, Y. Nucleation and Growth Mechanisms for Pd-Pt Bimetallic Nanodendrites and Their Electrocatalytic Properties. *Nano Res.* **2010**, *3* (2), 69–80.
 - (18) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chemie Int. Ed.* **2009**, *48* (1), 60–103.
 - (19) You, H.; Fang, J. Particle-Mediated Nucleation and Growth of Solution-Synthesized Metal Nanocrystals: A New Story beyond the LaMer Curve. *Nano Today* **2016**, *11* (2), 145–167.
 - (20) da Silva, A. G. M.; de Souza, M. L.; Rodrigues, T. S.; Alves, R. S.; Temperini, M. L. A.; Camargo, P. H. C. Rapid Synthesis of Hollow Ag–Au Nanodendrites in 15 Seconds by

- Combining Galvanic Replacement and Precursor Reduction Reactions. *Chem. – A Eur. J.* **2014**, *20* (46), 15040–15046.
- (21) Xu, J.; Wilson, A. R.; Rathmell, A. R.; Howe, J.; Chi, M.; Wiley, B. J. Synthesis and Catalytic Properties of Au–Pd Nanoflowers. *ACS Nano* **2011**, *5* (8), 6119–6127.
 - (22) Sirajuddin; Mechler, A.; Torriero, A. A. J.; Nafady, A.; Lee, C.-Y.; Bond, A. M.; O’Mullane, A. P.; Bhargava, S. K. The Formation of Gold Nanoparticles Using Hydroquinone as a Reducing Agent through a Localized pH Change upon Addition of NaOH to a Solution of HAuCl₄. *Colloids Surfaces A Physicochem. Eng. Asp.* **2010**, *370* (1–3), 35–41.
 - (23) da Silva, A. G. M.; Rodrigues, T. S.; Slater, T. J. A.; Lewis, E. A.; Alves, R. S.; Fajardo, H. V.; Balzer, R.; da Silva, A. H. M.; de Freitas, I.; Oliveira, D. C. de; et al. Controlling Size, Morphology, and Surface Composition of AgAu Nanodendrites in 15 S for Improved Environmental Catalysis under Low Metal Loadings. *ACS Appl. Mater. Interfaces* **2015**.
 - (24) Ewers, T. D.; Sra, A. K.; Norris, B. C.; Cable, R. E.; Cheng, C.-H.; Shantz, D. F.; Schaak, R. E. Spontaneous Hierarchical Assembly of Rhodium Nanoparticles into Spherical Aggregates and Superlattices. *Chem. Mater.* **2005**, *17* (3), 514–520.
 - (25) Pastoriza-Santos, I.; Liz-Marzán, L. M. Formation of PVP-Protected Metal Nanoparticles in DMF. *Langmuir* **2002**, *18* (7), 2888–2894.
 - (26) Polte, J. Fundamental Growth Principles of Colloidal Metal Nanoparticles - a New Perspective. *CrystEngComm* **2015**, *17* (36), 6809–6830.
 - (27) Stuart, E. J. E.; Rees, N. V.; Cullen, J. T.; Compton, R. G. Direct Electrochemical Detection and Sizing of Silver Nanoparticles in Seawater Media. *Nanoscale* **2013**, *5* (1), 174–177.
 - (28) Burrows, N. D.; Hale, C. R. H.; Penn, R. L. Effect of Ionic Strength on the Kinetics of Crystal Growth by Oriented Aggregation. *Cryst. Growth Des.* **2012**, *12* (10), 4787–4797.

Chapter 3. Rapid Single-step Synthesis of Monodisperse Sub-10 nm Pd Nanocubes and Their Evolution into Concave and Assembled Cubic Nanostructures

3.1. Introduction

Metal nanocubes have attracted increased attention over the last decades due to their unique properties, advancing their applications in catalysis, plasmonic, sensing, and imaging.¹⁻⁷ It has been well-established that the physicochemical properties of metal nanoparticles (NPs) are dependent on a set of physicochemical parameters, including particle shape, size, composition, and surface morphologies.⁸⁻¹² In particular, the precise control over the shape of a metal nanoparticle can be employed as a simple and versatile strategy for tailoring particle performance for a targeted application.^{4,13-15} For example, it has been demonstrated that Pd nanocubes bound by {100} facets are significantly more active relative to the other shapes toward the formic acid oxidation reaction.^{16,17}

In order to provide a high-level of control over particle shape, it is crucial that we begin to cultivate a rational understanding of particle nucleation and growth pathways.¹⁸⁻²² In classical models, NPs have been formed by precursor reduction, nucleation, and then growth (LaMer theory).²³ However, recent experimental and theoretical studies have demonstrated that several secondary processes (coalescence, orientated attachment, Ostwald ripening, etc.) can also play an important role in the growth process, modifying the classical pathway.²³ Despite some investigations into non-classical mechanisms, a detailed description of the nucleation and growth pathways is still missing, especially for NPs with specific shapes such as nanocubes.

Here, we demonstrate that the growth pathway of different Pd cubic nanostructures follows a non-classical mechanism that combines diffusion processes with classical elements of both LaMer and DLVO theories. This approach involves a one-step synthesis wherein the $\text{PdCl}_4^{2-}(\text{aq})$ precursor is reduced by hydroquinone to form monodisperse sub-10 nm nanocubes after only a few minutes at 100 °C. Simply by modulating the reaction temperature, it was possible to achieve fine control over the edge length and morphologies of the cubic nanostructures.

3.2. Experimental Section

3.2.1. Materials and Instrumentation

Analytical grade chemicals potassium tetrachloropalladate trihydrate ($\text{K}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$, 98%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$, 99%, Sigma-Aldrich), and potassium bromide (KBr, 99%, Sigma-Aldrich) were used as received. All solutions were prepared using deionized water (18.2 M Ω cm). Transmission electron microscope (TEM) images were obtained with a Hitachi HT 7700 microscope operated at 120 kV. High resolution secondary electron (HR-SE), high resolution transmission electron microscope (HRTEM), and high-angle annular dark-field scanning TEM (HAADF-STEM) images were obtained with a Hitachi HD 2700 microscope with a STEM aberration corrector operated at 200 kV. Samples for TEM analysis were prepared by drop-casting aqueous suspensions of the nanocrystals on a carbon-coated copper grid, followed by drying under ambient conditions. The Pd atomic percentages were measured by inductively coupled plasma mass spectrometry (ICP-MS, Perkin-Elmer, NexION 300Q).

3.2.2. Synthesis of Size-controlled Pd Cubic Nanostructures

In a typical procedure, 10 mL of an aqueous PVP solution (10 mg/mL) was transferred to a 20 mL round-bottom flask and stirred for 10 min, followed by the addition of 100 μ L of a 120 mM KBr solution and 1 mL of a 12 mM PdCl_4^{2-} (aq) solution. After 2 min, 1 mL of a 30 mM aqueous hydroquinone solution was added to this mixture. Control over the nanoparticle size was easily obtained by changing the reaction temperature. To demonstrate this control, we carried out a series of reactions performed at temperatures of 20, 40, 60, 80, and 100 $^{\circ}\text{C}$ for 24 h. In order to monitor the growth of the produced cubic Pd nanostructures, the reaction was quenched at different time points: 15 s, 1 min, 5 min, 10 min, 30 min, 1 h, 2 h, 4 h, 6 h, 12 h, and 24 h (several parallel reactions were carried out). The reactions were quenched by cooling the reaction vessel to 0 $^{\circ}\text{C}$ in an ice water bath. The product nanocrystals were then isolated and washed three times with ethanol and three times with distilled water by successive rounds of centrifugation at 55,000 rpm for 30 min and supernatant removal. After washing, the nanoparticles were then suspended in 10 mL of water.

3.3. Results and Discussion

Our investigations started with the synthesis of monodisperse sub-10 nm Pd nanocubes (Figure 3.1) by reducing PdCl_4^{2-} (aq) with hydroquinone in the presence of PVP (a colloidal stabilizer) and KBr (a {100} facet capping agent) at 100 $^{\circ}\text{C}$ for 5 min. The resultant Pd nanocubes displayed uniform cubic shapes and an average edge length of 6 ± 2 nm.

Figure 3.1. Low-magnification TEM image of monodisperse sub-10 nm Pd nanocubes obtained by reducing $\text{PdCl}_4^{2-}(\text{aq})$ with hydroquinone in the presence of KBr as a capping agent at 100 °C.

In order to investigate the role temperature played in controlling the size and shape of the Pd nanocubes, we conducted a set of experiments at different temperatures. To this end, reactions were performed at 100, 80, 60, 40, and 20 °C for 24 h, as shown in Figure 3.2 A-F. In all cases, the Pd nanoparticles presented well-defined cubic shapes and uniform sizes. However, we found that both the nanoparticle size and morphology were strongly dependent upon the reaction temperature (Figure 3.2 A-F). For instance, the particle size increased as the reaction temperature was decreased, with average sizes of 6 ± 2 , 9 ± 3 , 14 ± 4 , 18 ± 3 , 25 ± 4 , and 45 ± 4 nm observed when the syntheses were carried out at 100 (Figure 3.2 A), 80 (Figure 3.2 B), 60 (Figure 3.2 C), 50 (Figure 3.2 D), 40 (Figure 3.2 E), and 20 °C (Figure 3.2 F), respectively.

Figure 3.2. TEM images of Pd nanocubes displaying controlled sizes obtained at different temperatures: (A) 100, (B) 80, (C) 60, (D) 50, (E) 40, and (F) 20 °C.

Regarding their morphologies, HR-SE, HAADF-STEM, and HRTEM analyses (Figure 3.3 A-I) were performed to obtain further details regarding their cubic structures. The formation of monocrystalline sub-10 nm Pd nanocubes are clearly evident at 100 °C (Figure 3.3 A-B). The HRTEM image of an individual Pd nanocube *ca.* 6 nm in edge length showed the presence of

lattice fringes corresponding to the $\{100\}$ lattice spacing of *fcc* Pd (Figure 3.3 C). Interestingly, decreasing the temperature from 100 to 60 °C led to the formation of larger and noticeably concave nanocubes *ca.* 15 nm in edge length (Figure 3.3 D-E), though they also presented lattice fringes corresponding to the $\{100\}$ lattice spacing of *fcc* Pd (Figure 3.3 F).

Figure 3.3. (A,D and G) HAADF-STEM, (B, E, and H) SE-STEM, and (C, F, and I) HRTEM images for a typical Pd nanocube obtained at different temperatures: (A-C) 100, (D-F) 60, and (G-I) 20 °C, respectively. The region indicated by dashed squares at the HAADF-STEM image (H) is detailed in (I). The HRTEM images (C, F, and I) all show the lattice fringes corresponding to the $\{100\}$ spacing of Pd.

The formation of concave cubes could be explained by the differences between the relative deposition and diffusion rates as a function of reaction temperature. Our group recently demonstrated that the ratio of the atom deposition rate (V_{dep}) to the surface adatom diffusion rate

(V_{diff}) is expected to decrease with an increase in reaction temperature.²⁴ At higher temperatures (100 °C), diffusion processes tend to be accelerated, allowing newly deposited adatom at the corner sites to readily diffuse along the particle faces, leading to the formation of smooth and well-defined nanocubes.²⁴ However, upon lowering the reaction temperature to 60 °C, the rate of V_{dep} becomes substantially higher than V_{diff} , which leads to limited adatom diffusion from the corners and the formation of concave nanocubes.²⁴ When the reaction temperature was lowered even further to 20 °C, large assembled Pd nanocubes (Figure 3.3 G-H) *ca.* 45 ± 4 nm in edge length and comprised by the aggregation of multiple Pd cubic crystallites *ca.* 6–7 nm were produced. Phase-contrast HRTEM results revealed that the individual Pd cubic crystallites at the surface of the assembled nanocubes were monocrystalline (Figure 3.3 I). The presence of lattice fringes corresponding to the {100} lattice spacing of *fcc* Pd (Figure 3.3 I) could be observed in the region indicated by dashed square in the HAADF-STEM and HR-SE images (Figure 3.3 G-H).

In order to understand the different growth mechanisms occurring at different temperatures, we performed a set of control experiments by quenching the reaction at different time points directly after the addition of the $\text{PdCl}_4^{2-}(\text{aq})$ precursor to the reaction mixture. Figure 3.4 displays the morphological evolution of a reaction conducted at 60 °C when stopping the reaction after 15 s (Figure 3.4 A), 1 min (Figure 3.4 B), 2 min (Figure 3.4 C), 5 min (Figure 3.4 D), 10 min (Figure 3.4 E), and 1 h (Figure 3.4 F), respectively.

Figure 3.4. TEM images of the Pd concave nanocubes obtained at 60 °C as a function of the Pd growth time: (A) 15 s, (B) 1 min, (C) 2 min, (D) 5 min, (E) 10 min, and (F) 1 h.

After 15 s of the reaction (Figure 3.4 A), we observed clusters of Pd NPs (*ca.* 7–8 nm in size, comprised of several ultra-small nanoparticles *ca.* 1–2 nm in size) produced alongside nanocubes *ca.* 6–7 nm in size. As the reaction proceeded to $t = 1$ min (Figure 3.4 B), an increased number of Pd nanocubes appeared, believed to form from the fusion of the clusters of Pd NPs. Surprisingly, it was observed that these clusters of Pd NPs self-assembled in cubic clusters of Pd NPs (as shown in the region indicated by dashed square in Figure 3.4 B), leading to the formation of Pd nanocubes during the fusion process. After 2, 5, and 10 min of the reaction (Figure 3.4 C–E), the preformed Pd nanocubes served as seeds for the additional attachment of these cubic clusters of Pd NPs,

resulting in the larger Pd concave nanocubes (Figure 3.4 F) found after 1 h of reaction. No significant changes in particle size or shape were detected after 24 h. Figure 3.5 A–D shows HAADF-STEM, HR-SE, and HRTEM images of the cubic clusters of Pd NPs together with the preformed sub-10 nm nanocubes. While the cubic clusters of Pd NPs were generated by the assembly of ultra-small polycrystalline Pd NPs (1-2 nm each Figure 3.5 A-D), the sub-10 nm Pd nanocubes were monocrystalline (Figure 3.5 C).

Figure 3.5. HAADF-STEM, SE-STEM, and HRTEM images detailing the early stage on the synthesis of Pd nanocubes at 60 °C. (A and B) Pd cubic nanoclusters are polycrystalline (C) formed by several small Pd islands *ca.* 1-2 nm in size (D). In this mechanism, they fuse together to generate Pd nanocubes *ca.* 6 nm in size.

Interestingly, a similar growth pattern was observed during syntheses carried out at 100 °C (Figure 3.6 A-D). Here, the formation of sub-10 nm Pd nanocubes appeared almost completed after only 15 s following the addition of hydroquinone to the reaction mixture (Figure 3.6 A). After 1 and 2 min of the reaction (Figure 3.6 B-C), it should be noted that the last remaining cubic

clusters of Pd NPs fused together to form additional Pd nanocubes. At 5 min after the addition of hydroquinone, only monodisperse sub-10 nm Pd nanocubes could be detected (Figure 3.6 B-D). No further attachment/aggregation processes took place, resulting in unchanged morphology even after 24 h of reaction (Figure 3.2 A).

Figure 3.6. TEM images of sub-10 nm Pd nanocubes obtained at 100 °C as a function of the Pd growth time: (A) 15 s, (B) 1 min, (C) 2 min, and (D) 5 min.

In order to investigate the role played by KBr during the formation of the cubic nanostructures, we performed a set of experiments under the same conditions as those described in Figure 3.2 C, except modifying the amount of KBr added into the reaction mixture. Figure 3.7 displays the morphology evolution of a reaction conducted in the absence of KBr at 60 °C after 5 s (Figure 3.7 A), 15 s (Figure 3.7 B), 1 min (Figure 3.7 C), 5 min (Figure 3.7 D), 10 min (Figure 3.7 E), and 30 min (Figure 3.7 F), respectively.

Figure 3.7. TEM images for Pd nanoparticles obtained at 60 °C in absence of KBr as a function of the Pd growth time: (A) 5 s, (B) 15s, (C) 1 min, (D) 5 min, (E) 10 min, and (F) 30 min.

Interestingly, the same clusters of Pd NPs *ca.* 7–8 nm in size each were produced after 5 s reaction (Figure 3.7 A). However, without KBr available, they did not assemble into a cubic shape. Consequently, as the reaction proceeded to 15 s (Figure 3.7 B), spherical Pd nanoparticles appeared (formed from the fusion of these spherical clusters of Pd NPs), indicating that the presence of Br^- is critical for shape control in this system. In this case, while hydroquinone is responsible for the formation of the clusters of Pd NPs, the presence of KBr induced the self-assembly of the Pd

clusters into a cubic shape. Without Br^- present, spherical structures are instead formed. After 1 min of reaction, these spherical Pd nanoparticles served as seeds for the additional attachment of clusters of Pd NPs, leading to the formation of larger spherical porous nanoparticles (Figure 3.7 C). The size of the spherical porous nanoparticles continued to increase up to 30 min of the reaction (Figure 3.7 D-F) and consumed all remaining clusters of Pd NPs. No further morphological changes were detected after 24 h of reaction.

Figure 3.8 shows the effect of KBr over the size and shape of the produced Pd NPs. This was accomplished by employing the same conditions as those described in Figure 3.2 C, but with increasing volumes of 120 mM KBr added. TEM images show the product at 24 hrs after 20 (Figure 3.8 A), 50 (Figure 3.8 B), 100 (Figure 3.8 C, same volume of Figure 3.2), 200 (Figure 3.8 D), 500 (Figure 3.8 E), and 1000 μL (Figure 3.8 F) of 120 mM KBr solution was added, respectively. Our results indicate that the sizes, shapes, and uniformity strongly depend on the volume of KBr added into the reactions. Because of the preferential adsorption of Br^- onto the Pd $\{100\}$ facets, the introduction of Br^- ions would be expected to favor the formation of Pd nanocrystals enclosed by $\{100\}$ facets, such as cubes, depending on the concentration of Br^- ions.^{20,25} When only 20 μL of the 120 mM KBr solution was added to a reaction, irregular Pd nanoparticles were formed (Figure 3.8 A), likely due to an insufficient concentration of Br^- ions. This behavior has been observed previously when the concentration of Br^- ions is too low and the exposed Pd $\{100\}$ surfaces could not be fully stabilized, resulting in the formation of irregular structures.^{20,25} Next, as the amount of Br^- ions was increased to exceed the critical value (50 and 100 μL , Figure 3.8 B-C), it was possible to obtain Pd nanocubes. On the other hand, when the amount of Br^- ions greatly exceeded the critical value (500 and 1000 μL , Figure 3.8 E-F), a

preferential anisotropic growth took place leading the formation of Pd nanorods and nanobars (Figure 3.8 E-F).

Figure 3.8. TEM images for Pd concave nanocubes obtained at 60 °C as a function of different volumes of a 120 mM KBr solution added into the reactions: (A) 20 , (B) 50, (C, same amount of Figure 3.2) 100, (D) 200, (E) 500, and (F) 1000 μL .

This is also in agreement with our results obtained at 100 °C, in which $\{100\}$ -faceting of the monodisperse sub-10 nm Pd nanocubes is clearly evident after the amount of Br^- ions is increased (Figure 3.9 A-F).

Figure 3.9. TEM images for Pd nanocubes and nanorods obtained at 100 °C as a function of different volumes of a 120 mM KBr solution added into the reactions: (A) 20, (B) 50, (C, same amount of Figure 3.2) 100, (D) 200, (E) 500, and (F) 1000 μL .

Many previous reports have demonstrated that halides preferentially bind to the $\{100\}$ facets of various metals, wherein the large excess of Br^- ions inhibit the growth of $\{100\}$ and lead to the formation of nanobars fully enclosed by $\{100\}$ facets and nanorods with 5-fold twinned structure, in agreement with our results.^{20,26–28}

We also provide kinetic curves for the percent reduction of $\text{PdCl}_4^{2-}(\text{aq})$ precursor as function of the reaction time in presence of hydroquinone for reaction held at 20, 60, and 100 °C as shown in Figure 3.10.

Figure 3.10. Plots showing the (A) percent conversion of the $\text{PdCl}_4^{2-}(\text{aq})$ precursor to Pd through reduction with hydroquinone and (B) $\ln(\text{PdCl}_4^{2-}(t)/\text{PdCl}_4^{2-}(t_0))$ as function of the reaction time for temperatures of 20, 60, and 100 °C, traced by black, red, and blue lines, respectively.

As expected, the reaction rate constant for the Pd consumption was strongly dependent on the reaction temperature (Figure 3.10 A), and all of the reactions could be described by a first-order rate law (Figure 3.10 B). Remarkably, the calculated rate constants (k) indicated that the reaction

performed at 60 and 100 °C took place 11.8 and 1200 times faster, respectively, relative to the cubic nanostructures obtained at 20 °C. This indicates that all $\text{PdCl}_4^{2-}(\text{aq})$ precursor is reduced in the first minute of the reaction at 100 °C, while less than 20 and 10% of the $\text{PdCl}_4^{2-}(\text{aq})$ precursor were reduced to Pd after 1 h at 60 and 20 °C, respectively. To elucidate how the reaction temperature could have such a profound effect on the nanoparticle products, we looked into the theory to understand how nanocrystal nucleation, growth, and aggregation could all be tied together.

It is well known that colloidal aggregation is highly sensitive to the ionic strength (defined by both the valency and concentration of ions present in the system) of the reaction system,^{29,30} where only slight increases to the ion-concentration can give rise to aggregation. Our modern understanding of growth mechanisms shows that the formation of the different cubic nanostructures reported herein may be explained by combining diffusion processes with elements of both La Mer and DLVO theories.^{23,31} At the entire temperature range (20–100 °C), all reactions initially started from the formation of the cubic clusters of Pd NPs, with a nucleation mechanism that fits well within the classical La Mer theory.^{23,31} Subsequently, what primarily modifies the final morphology of the cubic nanostructures is the degree to which the cubic clusters of Pd NPs have aggregated, a process governed by the balance Derjaguin, Landau, Verwey, and Overbeek (DLVO) theory.³¹ DLVO theory states that the distance-dependent potential energy (V_T) between colloidal particles is simply defined by the sum of a short range attractive van der Waals potential (V_A) and a long range repulsive electrostatic potential (V_R): $V_T = V_A + V_R$. If $V_A > V_R$, the aggregation process will take place. At 100 °C, the Pd-salt precursor is rapidly and completely consumed as the ionic-strength is low enough such that the Pd clusters remain stable in solution. Therefore, no aggregation steps could be detected at different time intervals (see Figure 3.6 and 3.10). At 60 °C,

the $\text{PdCl}_4^{2-}(\text{aq})$ conversion and growth took place less rapidly, and the products grew under relatively high ionic strength. The high ionic strength destabilized the colloids (*i.e.*, $V_A > V_R$), and caused the attachment of the remaining preformed Pd nanocubes, resulting in the formation of larger concave Pd nanocubes (see Figure 3.4). If this proposed growth mechanism is correct, it should be expected that lowering the temperatures (e.g., 20 °C) should produce intermediates that are more aggregated as compared to those derived from reaction temperatures of 60 and 100 °C. From the TEM image in Figure 3.11, it is clearly evident that there are many more clusters of Pd NPs attached at the surface of the preformed seeds.

Figure 3.11. TEM image for an intermediate stage of the Pd nanocubes obtained at 20 °C after 3 h of reaction.

This follows the proposed mechanism, wherein products formed during reactions carried out at low reaction temperatures are exposed to/ significantly higher concentrations of the Pd-salt ($\text{PdCl}_4^{2-}(\text{aq})$ and K^+ ions), which effectively decreases the repulsion potential and assists the aggregation step. This increase in the ionic strength favors greater aggregation of pre-formed cubic clusters of Pd NPs and thus leads to the formation of different cubic nanostructures as a function of the temperature.

Based on the structural features of the nanostructures, several control experiments, and the kinetics of the $\text{PdCl}_4^{2-}(\text{aq})$ conversion, we propose a mechanism for the formation of the obtained cubic Pd nanoparticles as shown in Scheme 3.1.

Scheme 3.1. Proposed formation mechanism for Pd nanocubes based on a non-classical growth.

First, the hydroquinone reduces $\text{PdCl}_4^{2-}(\text{aq})$ to Pd atoms, which supersaturate and homogeneously nucleate to form Pd NPs. As the reaction ensues, these Pd NPs group together to form clusters, which in the presence of KBr causes these clusters to group together in a cubic shape. At 20 °C, when the reaction is relatively slow, the particles are formed in the presence of unreacted precursor molecules. The residual Pd-precursor ions gives rise to a relatively high ionic strength that accelerates the aggregation process, and causes the Pd NPs to fuse together and form Pd nanocubes. These Pd cubes then serve as seeds for the further attachment of cubic clusters of Pd NPs, and with increasing time, the pre-formed cubic clusters of Pd NPs continually attach to the Pd cubic seeds leading to the formation of large assembled nanocubes. At higher temperatures

(*e.g.*, 60 °C), the $\text{PdCl}_4^{2-}(\text{aq})$ conversion and growth regime took place faster so that the ionic strength is lower, which leads to a lower number of cubic clusters attached at the Pd nanocubes seeds. The formation of Pd concave nanocubes at this temperature can be explained by considering that the rate of deposition is greater than the rate of adatom diffusion ($V_{\text{dep}} > V_{\text{diff}}$), which induces a preferential growth at the corners of the cubic seed. On the other hand, when the reaction rate is very fast (*e.g.*, 100 °C), all of the $\text{PdCl}_4^{2-}(\text{aq})$ precursor is rapidly reduced and the product formation occurs in a reaction solution that has a low ionic strength and high surface diffusion, leading to the formation of monodisperse sub-10 nm nanocubes.

3.4. Conclusion

In summary, we have demonstrated a new strategy for producing monodisperse sub-10 nm Pd nanocubes and elucidated their temperature-dependent formation mechanism. Our approach involved the use of PdCl_4^{2-} as the precursor, hydroquinone as the reducing agent, water as the solvent, PVP as the stabilizing agent, and KBr as the capping agent. We found that both hydroquinone and KBr are crucial for the formation of the obtained cubic nanostructures. In this case, the presence of hydroquinone and KBr induced the formation of different cubic nanostructures by a new growth pathway that combines classical nucleation theory with diffusion and aggregation processes based on both La Mer and DLVO theories. The different cubic morphologies obtained as a function of the temperature could be explained based on the differences in the $\text{PdCl}_4^{2-}(\text{aq})$ reduction kinetics. In this case, when the ionic strength in the solution was relatively high (during slow reaction rates), the preformed cubic seeds formed in the first step of the reaction serve as templates for attachment/aggregation of the remaining cubic clusters of NPs,

resulting in the formation of large assembled Pd nanocubes. When reactions are carried out at 20 °C, the cubic clusters of Pd NPs are exposed to higher concentrations of the Pd-salt ($\text{PdCl}_4^{2-}(\text{aq})$ and K^+ ions), which effectively decreases the repulsion potential and assists in aggregate formation, resulting in large, assembled Pd nanocubes. At 60 °C, the $\text{PdCl}_4^{2-}(\text{aq})$ conversion and growth regime was greatly accelerated such that the ionic strength was effectively lower, which led to a lower number of cubic clusters attached at the Pd nanocubes seeds. The formation of Pd concave nanocubes at this temperature can be explained the rate of $V_{\text{dep}} > V_{\text{diff}}$, which induces a preferential deposition and growth at the corners of the cubic seed. When the reaction rate is carried out at 100 °C, all of the PdCl_4^{2-} is rapidly reduced and the product formation occurs in a solution that has a low ionic strength. Since the low ionic strength leads to higher inter-particle repulsion forces, only monodisperse sub-10 nm nanocubes were detected. We believe that the mechanisms discovered herein provide a significant advancement to the understanding of the nucleation and growth behavior in colloidal systems, which we believe should be extendable to the broad range of other inorganic nanomaterials.

3.5. References

- (1) Hsia, C.-F.; Madasu, M.; Huang, M. H. Aqueous Phase Synthesis of Au–Cu Core–Shell Nanocubes and Octahedra with Tunable Sizes and Noncentrally Located Cores. *Chem. Mater.* **2016**, 28 (9), 3073–3079.
- (2) Wang, C.; Daimon, H.; Lee, Y.; Kim, J.; Sun, S. Synthesis of Monodisperse Pt Nanocubes and Their Enhanced Catalysis for Oxygen Reduction. *J. Am. Chem. Soc.* **2007**, 129 (22), 6974–6975.
- (3) Wang, Y.; Zheng, Y.; Huang, C. Z.; Xia, Y. Synthesis of Ag Nanocubes 18–32 Nm in Edge Length: The Effects of Polyol on Reduction Kinetics, Size Control, and Reproducibility. *J. Am. Chem. Soc.* **2013**, 135 (5), 1941–1951.
- (4) Zhang, H.; Jin, M.; Xiong, Y.; Lim, B.; Xia, Y. Shape-Controlled Synthesis of Pd Nanocrystals and Their Catalytic Applications. *Acc. Chem. Res.* **2013**, 46 (8), 1783–1794.

- (5) Xu, Y.-K.; Hwang, S.; Kim, S.; Chen, J.-Y. Two Orders of Magnitude Fluorescence Enhancement of Aluminum Phthalocyanines by Gold Nanocubes: A Remarkable Improvement for Cancer Cell Imaging and Detection. *ACS Appl. Mater. Interfaces* **2014**, *6* (8), 5619–5628.
- (6) Yang, Y.; Liu, J.; Fu, Z.-W.; Qin, D. Galvanic Replacement-Free Deposition of Au on Ag for Core–Shell Nanocubes with Enhanced Chemical Stability and SERS Activity. *J. Am. Chem. Soc.* **2014**, *136* (23), 8153–8156.
- (7) Ye, J.-S.; Chen, C.-W.; Lee, C.-L. Pd Nanocube as Non-Enzymatic Glucose Sensor. *Sensors Actuators B Chem.* **2015**, *208*, 569–574.
- (8) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem. Int. Ed. Engl.* **2009**, *48* (1), 60–103.
- (9) Bastús, N. G.; Comenge, J.; Puentes, V. Kinetically Controlled Seeded Growth Synthesis of Citrate-Stabilized Gold Nanoparticles of up to 200 nm: Size Focusing versus Ostwald Ripening. *Langmuir* **2011**, *27* (17), 11098–11105.
- (10) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O'Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, *14* (4), 1921–1926.
- (11) da Silva, A. G. M.; Rodrigues, T. S.; Slater, T. J. A.; Lewis, E. A.; Alves, R. S.; Fajardo, H. V.; Balzer, R.; da Silva, A. H. M.; de Freitas, I.; Oliveira, D. C. de; et al. Controlling Size, Morphology, and Surface Composition of AgAu Nanodendrites in 15 S for Improved Environmental Catalysis under Low Metal Loadings. *ACS Appl. Mater. Interfaces* **2015**, *7* (46), 25624–25632.
- (12) da Silva, A. G. M.; Rodrigues, T. S.; Correia, V. G.; Alves, T. V.; Alves, R. S.; Ando, R. A.; Ornellas, F. R.; Wang, J.; Andrade, L. H.; Camargo, P. H. C. Plasmonic Nanorattles as Next-Generation Catalysts for Surface Plasmon Resonance-Mediated Oxidations Promoted by Activated Oxygen. *Angew. Chemie Int. Ed.* **2016**, *55* (25), 7111–7115.
- (13) Mostafa, S.; Behafarid, F.; Croy, J. R.; Ono, L. K.; Li, L.; Yang, J. C.; Frenkel, A. I.; Cuenya, B. R. Shape-Dependent Catalytic Properties of Pt Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132* (44), 15714–15719.
- (14) Xu, R.; Wang, D.; Zhang, J.; Li, Y. Shape-Dependent Catalytic Activity of Silver Nanoparticles for the Oxidation of Styrene. *Chem. – An Asian J.* **2006**, *1* (6), 888–893.
- (15) Yin, A.-X.; Min, X.-Q.; Zhang, Y.-W.; Yan, C.-H. Shape-Selective Synthesis and Facet-Dependent Enhanced Electrocatalytic Activity and Durability of Monodisperse Sub-10 nm Pt–Pd Tetrahedrons and Cubes. *J. Am. Chem. Soc.* **2011**, *133* (11), 3816–3819.
- (16) Jin, M.; Zhang, H.; Xie, Z.; Xia, Y. Palladium Nanocrystals Enclosed by {100} and {111} Facets in Controlled Proportions and Their Catalytic Activities for Formic Acid Oxidation. *Energy Environ. Sci.* **2012**, *5* (4), 6352–6357.
- (17) Habas, S. E.; Lee, H.; Radmilovic, V.; Somorjai, G. A.; Yang, P. Shaping Binary Metal Nanocrystals through Epitaxial Seeded Growth. *Nat Mater* **2007**, *6* (9), 692–697.

- (18) Thanh, N. T. K.; Maclean, N.; Mahiddine, S. Mechanisms of Nucleation and Growth of Nanoparticles in Solution. *Chem. Rev.* **2014**, *114* (15), 7610–7630.
- (19) Yoreo, J. J. De; Vekilov, P. G. Principles of Crystal Nucleation and Growth. **2003**.
- (20) Lim, B.; Kobayashi, H.; Camargo, P. H. C.; Allard, L. F.; Liu, J.; Xia, Y. New Insights into the Growth Mechanism and Surface Structure of Palladium Nanocrystals. *Nano Res.* **2010**, *3* (3), 180–188.
- (21) Yang, T.-H.; Peng, H.-C.; Zhou, S.; Lee, C.-T.; Bao, S.; Lee, Y.-H.; Wu, J.-M.; Xia, Y. Toward a Quantitative Understanding of the Reduction Pathways of a Salt Precursor in the Synthesis of Metal Nanocrystals. *Nano Lett.* **2016**.
- (22) da Silva, A. G. M.; Lewis, E. A.; Rodrigues, T. S.; Slater, T. J. A.; Alves, R. S.; Haigh, S. J.; Camargo, P. H. C. Surface Segregated AgAu Tadpole-Shaped Nanoparticles Synthesized Via a Single Step Combined Galvanic and Citrate Reduction Reaction. *Chem. – A Eur. J.* **2015**, *21* (35), 12314–12320.
- (23) You, H.; Fang, J. Particle-Mediated Nucleation and Growth of Solution-Synthesized Metal Nanocrystals: A New Story beyond the LaMer Curve. *Nano Today* **2016**, *11* (2), 145–167.
- (24) Xia, X.; Xie, S.; Liu, M.; Peng, H.-C.; Lu, N.; Wang, J.; Kim, M. J.; Xia, Y. On the Role of Surface Diffusion in Determining the Shape or Morphology of Noble-Metal Nanocrystals. *Proc. Natl. Acad. Sci.* **2013**, *110* (17), 6669–6673.
- (25) Peng, H.-C.; Xie, S.; Park, J.; Xia, X.; Xia, Y. Quantitative Analysis of the Coverage Density of Br[−] Ions on Pd{100} Facets and Its Role in Controlling the Shape of Pd Nanocrystals. *J. Am. Chem. Soc.* **2013**, *135* (10), 3780–3783.
- (26) Xiong, Y.; Cai, H.; Yin, Y.; Xia, Y. Synthesis and Characterization of Fivefold Twinned Nanorods and Right Bipyramids of Palladium. *Chem. Phys. Lett.* **2007**, *440* (4–6), 273–278.
- (27) Xiao, C.; Ding, H.; Shen, C.; Yang, T.; Hui, C.; Gao, H.-J. Shape-Controlled Synthesis of Palladium Nanorods and Their Magnetic Properties. *J. Phys. Chem. C* **2009**, *113* (31), 13466–13469.
- (28) Huang, X.; Zheng, N. One-Pot, High-Yield Synthesis of 5-Fold Twinned Pd Nanowires and Nanorods. *J. Am. Chem. Soc.* **2009**, *131* (13), 4602–4603.
- (29) Burrows, N. D.; Hale, C. R. H.; Penn, R. L. Effect of Ionic Strength on the Kinetics of Crystal Growth by Oriented Aggregation. *Cryst. Growth Des.* **2012**, *12* (10), 4787–4797.
- (30) Stuart, E. J. E.; Rees, N. V.; Cullen, J. T.; Compton, R. G. Direct Electrochemical Detection and Sizing of Silver Nanoparticles in Seawater Media. *Nanoscale* **2013**, *5* (1), 174–177.
- (31) Polte, J. Fundamental Growth Principles of Colloidal Metal Nanoparticles - a New Perspective. *CrystEngComm* **2015**, *17* (36), 6809–6830.

Section 3.

Combining Galvanic Replacement and Co-reduction: an Efficient Strategy Towards Complex Morphologies

Chapter 4. One-step Synthesis of Hollow Ag-Au Nanodendrites in 15 Seconds by Combining Galvanic Replacement and Precursor Reduction Reactions

4.1. Introduction

Silver (Ag) and gold (Au) nanostructures display remarkable optical properties in the visible range as a result of the excitation of their surface plasmon resonance (SPR).^{1,2} that enable applications in areas such as surface-enhanced Raman scattering (SERS) detection, plasmon enhanced/mediated catalysis, and the development of plasmonic solar cells.³⁻⁷ As properties in metal nanomaterials are strongly dependent upon shape, size, morphology, and structure (solid versus hollow interiors), the precise control over any or several of these parameters opens up the possibility to tailor and/or optimize properties for a target application.⁸ Among several classes of metallic nanomaterials, those displaying hollow interiors as well as sharp tips/branches at their surface (hollow nanodendrites) are especially attractive. First, hollow interiors provide larger surface-to-volume ratios than their solid counterparts.⁹⁻¹² Second, nanomaterials displaying sharp tips/branches at the surface has shown improved performances for catalytic and electrochemical applications due to higher surface areas relative to their rounded counterparts.¹³⁻¹⁵ Taking applications in surface-enhanced Raman scattering (SERS) as an example, while hollow interiors provide a larger number of sites for adsorption/interaction with a probe molecule, sharp tips enable a higher concentration of electromagnetic fields as compared to spherical particles during plasmon oscillation as a result of the lightning rod effect, in which the charges tend to concentrate at the tips.^{16,17} This, in turn, lead to higher SERS amplifications according to the electromagnetic mechanism of SERS enhancement.^{2,18}

The synthesis of hollow Ag-Au nanostructures in variety of shapes has been demonstrated by the galvanic replacement reaction between Ag nanocrystals and AuCl_4^- (aq).¹⁹ However, these materials often display smooth surfaces.^{10,20} On the other hand, Au-based nanodendrites often display solid interiors (or a core-shell morphology).^{17,21–23} While a few reports have addressed the synthesis hollow Ag-Au nanodendrites, most of the described procedures do not lead to samples displaying monodisperse sizes and controlled surface morphologies. Moreover, described protocols often require many synthetic steps and take, at least, several minutes to be completed.^{24–26} In this context, the development of facile, one-step, and fast approaches to the synthesis of hollow Ag-Au nanodendrites would be highly desirable.

We describe herein a simple strategy for the synthesis of Ag-Au nanodendrites displaying monodisperse sizes and well-defined morphologies comprised of hollow interiors and sharp tips/branches at their surface in 15 s and one synthetic step. More specifically, our approach was based on the utilization of Ag nanospheres as seeds for Au deposition by a combination of galvanic replacement reaction between Ag and AuCl_4^- (aq) and AuCl_4^- (aq) reduction using hydroquinone as a reducing agent. Moreover, water was employed as the solvent and polyvinylpyrrolidone (PVP) as the stabilizer.

4.2. Experimental Section

4.2.1. Materials and Instrumentation

Analytical grade chemicals chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich), silver nitrate (AgNO_3 , 99%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$, 99%, Vetec), L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$,

99%, Sigma-Aldrich), sodium borohydride (NaBH_4 , 98%, Sigma-Aldrich), were used as received. All solutions were prepared using deionized water (18.2 M Ω). The scanning electron microscopy (SEM) images were obtained using a JEOL field emission gun electron microscope JSM 6330F operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension containing the nanostructures over a silicon wafer, followed by drying under ambient conditions. Transmission electron microscopy (TEM) images were obtained with a JEOL 1010 microscope operating at 80 kV. Samples for TEM were prepared by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous solutions or aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 or UV-3101 PC spectrophotometer. The Au and Ag atomic percentages were measured by flame atomic absorption spectrometry (FAAS) with a Shimadzu spectrophotometer, model AA-6300, equipped with an air-acetylene flame.

4.2.2. Synthesis of Ag seeds

Ag seeds were prepared by the polyol process.²⁷ In a typical experiment, 5 mg of polyvinylpyrrolidone (PVP) was dissolved in 37.5 mL of ethylene glycol. Then, AgNO_3 (200 mg, 1.2 mmol) was added and mixed until the complete dissolution. The resulting solution was heated to 125 °C for 2.5 hours, leading to the appearance of a greenish-yellow color, allowed to cool down to room temperature, and diluted to 125 mL of water.

4.2.3. Synthesis of Ag-Au hollow nanodendrites

Ag-Au hollow nanodendrites were synthesized by seed-mediated growth approach, in which Ag seeds were employed as chemical templates for Au deposition via galvanic replacement,

hydroquinone was also employed as a reducing agent, and PVP as the stabilizer. In a typical procedure, 5 μL of the as-prepared Ag seeds suspension was added to 9.4 mL of PVP aqueous solution (0.1 wt %). This mixture was transferred to a 25 mL round-bottom flask and stirred at 50 $^{\circ}\text{C}$ for 10 min. 0.1 mL of 30 mM aqueous hydroquinone solution was added and, after 2 min, 0.1 mL of a 12 mM $\text{AuCl}_4^{-}(\text{aq})$ was added. In order to control and monitor the growth of the Ag-Au nanodendrites as a function of time, three individual reactions were performed and quenched at different intervals: 15 s, 1 min, and 5 min. The reactions could be quenched by the addition of 0.1 mL of 0.3 M $\text{HCl}_{(\text{aq})}$ solution and cooling the reaction flask in ice water. Ag-Au nanodendrites were washed three times with water by successive rounds of centrifugation at 12000 rpm and removal of the supernatant. After washing, the Ag-Au nanodendrites were suspended in 1 mL of water.

4.3. Results and Discussion

We started our investigations with the synthesis of uniform Ag nanospheres 35 ± 4 nm in diameter by a polyol method in the presence of PVP (Figure 4.1). We were interested in employing these Ag nanospheres as chemical templates for obtaining Ag-Au hollow dendrites by combining the galvanic replacement reaction between Ag and $\text{AuCl}_4^{-}(\text{aq})$ and the chemical reduction of $\text{AuCl}_4^{-}(\text{aq})$ to Au by hydroquinone employing water as the solvent and 50 $^{\circ}\text{C}$ as the reaction temperature. In this process, the hydroquinone reducing power can be quenched upon the addition of HCl to the reaction mixture, which can be employed to monitor the product formation and shape evolution as a function of time.²⁸

Figure 4.1. TEM image of Ag nanospheres 35 ± 4 nm in diameter employed as seeds for the synthesis of hollow Ag-Au nanodendrites.

Interestingly, we found that hollow Ag-Au nanodendrites could be obtained by this approach after 15 s following the addition of $\text{AuCl}_4^-_{(\text{aq})}$ to the suspension containing Ag nanospheres and hydroquinone, as illustrated in Figure 4.2. The SEM image of the Ag-Au nanodendrites obtained at this stage (Figure 4.2 A) clearly shows that the material presents well-defined shapes, monodisperse sizes, and were 66 ± 4 nm in size (outer diameter). This indicates a 31 nm growth relative to the initial Ag nanospheres. The inset in the SEM image also corroborates the formation of several branches and/or sharp tips at the surface, yielding a nanodendritic morphology. The formation of the nanodendrites is also supported by TEM results (Figure 4.2 B and C), in which the mass-thickness contrast corroborates the formation of hollow interiors. Phase-contrast HRTEM results show that the individual branches at the surface were single crystalline (Figure 4.2 D). The presence of ~ 0.23 nm lattice fringes corresponding to the $\{111\}$ spacing of Au could be observed, showing that the Au branches grow along the $\langle 111 \rangle$ direction.

Figure 4.2. SEM (A), TEM (B and C), and HRTEM (D) images of the hollow Ag-Au nanodendrites obtained by stopping the reaction after 15 s following the addition of AuCl_4^- (aq). The scale bars in the inset corresponds to 50 nm.

FAAS (flame atomic absorption spectroscopy) analysis showed that the composition of Ag and Au in the nanodendrite corresponded to 5.6 and 94.4 at. %, respectively. Figure 4.3 displays the effect of growth time over the morphology of the produced nanodendrites which were obtained by quenching the reducing power of hydroquinone by the addition of HCl and stopping the reaction after 1 (Figure 4.3 A and B) and 5 min (Figure 4.3 C and D).

Figure 4.3. SEM (A and C) and TEM (B and D) images of Ag-Au hollow nanodendrites obtained by stopping the reaction after 1 (A and B) and 5 min (C and D) following the addition of AuCl_4^- (aq). The scale bars in the insets correspond to 50 nm.

It can be observed an increase in the outer diameter of the nanodendrites to 70 ± 6 and 74 ± 6 nm by allowing the reaction to proceed for 1 and 5 min, respectively (as compared to ~ 66 for the nanodendrites obtained after 15 s). In addition to a slight increase in size, a change in the surface morphology could be observed as a function of growth time. Specifically, the branches became gradually more rounded (less spiky) as the growth time increased from 15 s to 1 and 5 min. This observation is supported by UV-VIS extinction spectra (Figure 4.4). While the surface plasmon resonance band (SPR) for the initial Ag NPs was located at ~ 407 nm, a red shift to ~ 617 nm and broadening of the signal was observed due to the formation of Ag-Au nanodendrites after

15 s, in agreement with the deposition of Au branches in the material as well as the formation of the hollow interiors.

Figure 4.4. UV-visible extinction spectra of Ag nanospheres employed as seeds (black trace) and Ag-Au nanodendrites obtained at different growth stages. The spectra for the Ag-Au nanodendrites obtained by stopping the reaction after 15 s, 1 min, and 5 min following the addition of AuCl_4^- (aq) are represented as the red, green, and blue traces, respectively.

Interestingly, a gradual blue shift in the SPR band to 605 and 603 nm was detected for the Ag-Au nanodendrites obtained after 1 and 5 min, respectively, in agreement with the formation of more rounded tips/branches. It has been established that nanostructures with corners/tips often display SPR peaks red-shifted relative to their rounded counterparts.²⁹ This can be explained due to increased charge separation enabled by sharper tips, that reduces the restoring force for electron oscillation which manifests itself in a red-shift of the resonance peak.²⁹

The FAAS analysis showed that the Au at. % in the Ag-Au nanodendrites corresponded to 95.6 and 96.4 for the samples obtained after 1 and 5 min, respectively, indicating a minor increase

in the Au at % relative to the sample obtained after 15 s (94.4). This result suggests the amounts of Ag are also similar in all materials. It is plausible to assume that, after 15 s during the reaction, shell growth is dominated by AuCl_4^- (aq) reduction by hydroquinone as Ag oxidation and dissolution due to galvanic replacement does not occur to a significant level.

In our employed approach, the formation of the hollow Ag-Au nanodendrites can be understood as a combination of galvanic replacement reaction between Ag nanospheres and AuCl_4^- (aq) ions as well as the AuCl_4^- (aq) reduction by hydroquinone as depicted in Scheme 4.1.

Scheme 4.1. Approach for the synthesis of Ag-Au nanodendrites by a combination of galvanic replacement between Ag and AuCl_4^- (aq) and AuCl_4^- (aq) reduction in the presence of hydroquinone as the reducing agent, PVP as the stabilizer, and water as the solvent.

When AuCl_4^- (aq) is introduced into an aqueous suspension containing Ag nanospheres and hydroquinone, it will be reduced by both Ag (galvanic reaction) and hydroquinone (precursor reduction) to produce Au atoms. While the galvanic reaction enables the Au deposition together with the Ag oxidation from the Ag nanospheres that work as sacrificial templates, leading to the formation of the hollow interiors, AuCl_4^- (aq) reduction by hydroquinone in the presence of PVP lead to the deposition of Au branches/islands to yield the nanodendrite morphology. In order to

gain further insights into the role played by the nature of the reducing agent, we performed control experiments by replacing hydroquinone with ascorbic acid and sodium borohydride under similar conditions (stopping the reaction after 15 s following the addition of AuCl_4^- (aq)). When the reaction was carried out in the presence of ascorbic acid as the reducing agent, the conformal Au deposition over the Ag nanospheres was observed (Figure 4.5 A). Interestingly, a Ag@Au core-shell morphology was detected without the formation of hollow interiors, as depicted by the absence of mass-thickness contrast in the TEM image (Figure 4.5 A). This result indicates that the utilization of ascorbic acid suppressed the galvanic reaction, and only precursor reduction was observed. Similar results regarding the Au deposition without galvanic replacement (by precursor reduction) in the presence of ascorbic acid to yield Ag-Au core-shell materials have been recently described in the deposition of Au over Ag nanocubes.³⁰ When sodium borohydride was employed as a reducing agent under similar conditions, the formation of hollow Ag-Au nanoparticles (nanoshells) together with the deposition of several nanoparticles below 10 nm in diameter were detected (Figure 4.5 B). Here, both galvanic replacement and precursor reduction were observed. In this case, it is possible that while the galvanic reaction led to the formation of the Ag-Au nanoshells, the utilization of a strong reducing agent such as sodium borohydride also promoted the homogeneous nucleation and growth of Au and Ag nanoparticles. It is important to note that the reaction mixture contains both AuCl_4^- (aq) and Ag^+ (produced from the oxidation of Ag during the galvanic reaction).

In order to verify the role of hydroquinone over the formation/deposition of branches/sharp tips, we performed a control experiment in the absence of Ag seeds. As shown in Figure 4.5 C, this led to the formation of polydisperse Au nanodendrites, supporting that the presence of hydroquinone can lead to the AuCl_4^- (aq) reduction under our experimental conditions to produce

Au having a dendritic morphology. However, the presence of Ag seeds seems to be important to the production of well-defined and uniform materials. Interestingly, when Ag nanospheres were replaced by Au nanoparticles as seeds, the formation of uniform and solid nanodendrites could also be observed (Figure 4.5 D). Therefore, our results demonstrate that the utilization of both Ag seeds and hydroquinone are crucial to the formation of Ag-Au nanodendrites having monodisperse sizes, well-defined surface morphologies, and hollow interiors in 15 s. In this case, while the growth time enabled the control over the surface morphologies, the nature of the seeds (Ag vs Au) allowed us to control the structure (hollow vs solid interiors).

Figure 4.5. (A-B) TEM images of the Ag-Au nanodendrites obtained by employing ascorbic acid (A) and sodium borohydride (B) as the reducing agents (instead of hydroquinone). (C) TEM image of Au nanodendrites obtained in the absence of Ag seeds, showing the formation of nanodendrites with irregular shape and large size-distribution. (D) SEM image of Au nanodendrites obtained in the presence of Au nanospheres as seeds. In (C) and (D), hydroquinone was employed as the reducing agents. All the conditions were similar as those described in Figure 4.2.

4.4. Conclusion

We described herein a simple and effective strategy to the synthesis of uniform Ag-Au nanodendrites in 15 s and one synthetic step displaying well-defined morphologies comprised of hollow interiors and sharp tips/branches at the surface. The described approach for the synthesis of the nanodendrites was based on the combination of two processes: *i*) galvanic replacement reaction between AuCl_4^- and Ag nanospheres employed as seeds; and *ii*) AuCl_4^- to Au reduction promoted by the presence of hydroquinone. Our approach also employed water as the solvent, PVP as the stabilizer, and 50 °C as the reaction temperature. The surface morphology of the Ag-Au nanodendrites could be controlled as a function of growth time, in which a slight increase in the outer diameter and the formation of more rounded tips were observed as the reaction time was increased to 1 and 5 min (as compared to the product obtained after only 15 s). We believe that the approach described herein can serve as a platform for the fast and one-step synthesis of hollow nanodendrites having a wealth of sizes, compositions, and surface morphologies for applications in SERS and catalysis.

4.5. References

- (1) Hu, M.; Chen, J.; Li, Z.-Y.; Au, L.; Hartland, G. V.; Li, X.; Marquez, M.; Xia, Y. Gold Nanostructures: Engineering Their Plasmonic Properties for Biomedical Applications. *Chem. Soc. Rev.* **2006**, 35 (11), 1084–1094.
- (2) Willets, K. A.; Van Duyne, R. P. Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annu. Rev. Phys. Chem.* **2007**, 58 (1), 267–297.
- (3) McNay, G.; Eustace, D.; Smith, W. E.; Faulds, K.; Graham, D. Surface-Enhanced Raman Scattering (SERS) and Surface-Enhanced Resonance Raman Scattering (SERRS): A Review of Applications. *Appl. Spectrosc.* **2011**, 65 (8), 825–837.
- (4) Catchpole, K. R.; Polman, A. Plasmonic Solar Cells. *Opt. Express* **2008**, 16 (26), 21793–

- 21800.
- (5) Baffou, G.; Quidant, R. Nanoplasmonics for Chemistry. *Chem. Soc. Rev.* **2014**, *43* (11), 3898–3907.
 - (6) Atwater, H. A.; Polman, A. Plasmonics for Improved Photovoltaic Devices. *Nat. Mater.* **2010**, *9* (3), 205–213.
 - (7) Huang, Y.-F.; Zhang, M.; Zhao, L.-B.; Feng, J.-M.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angew. Chemie Int. Ed.* **2014**, *53* (9), 2353–2357.
 - (8) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem. Int. Ed. Engl.* **2009**, *48* (1), 60–103.
 - (9) Lou, X. W. (David); Archer, L. A.; Yang, Z. Hollow Micro-/Nanostructures: Synthesis and Applications. *Adv. Mater.* **2008**, *20* (21), 3987–4019.
 - (10) Skrabalak, S. E.; Chen, J.; Sun, Y.; Lu, X.; Au, L.; Cobley, C. M.; Xia, Y. Gold Nanocages: Synthesis, Properties, and Applications. *Acc. Chem. Res.* **2008**, *41* (12), 1587–1595.
 - (11) An, K.; Hyeon, T. Synthesis and Biomedical Applications of Hollow Nanostructures. *Nano Today* **2009**, *4* (4), 359–373.
 - (12) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O'Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, *14* (4), 1921–1926.
 - (13) Mohanty, A.; Garg, N.; Jin, R. A Universal Approach to the Synthesis of Noble Metal Nanodendrites and Their Catalytic Properties. *Angew. Chemie Int. Ed.* **2010**, *49* (29), 4962–4966.
 - (14) Jena, B. K.; Raj, C. R. Synthesis of Flower-like Gold Nanoparticles and Their Electrocatalytic Activity Towards the Oxidation of Methanol and the Reduction of Oxygen. *Langmuir* **2007**, *23* (7), 4064–4070.
 - (15) Lim, B.; Xia, Y. Metal Nanocrystals with Highly Branched Morphologies. *Angew. Chemie Int. Ed.* **2011**, *50* (1), 76–85.
 - (16) Hao, F.; Nehl, C. L.; Hafner, J. H.; Nordlander, P. Plasmon Resonances of a Gold Nanostar. *Nano Lett.* **2007**, *7* (3), 729–732.
 - (17) Nehl, C. L.; Liao, H.; Hafner, J. H. Optical Properties of Star-Shaped Gold Nanoparticles. *Nano Lett.* **2006**, *6* (4), 683–688.
 - (18) Hermoso, W.; Alves, T. V.; de Oliveira, C. C. S.; Moriya, E. G.; Ornellas, F. R.; Camargo, P. H. C. Triangular Metal Nanoprisms of Ag, Au, and Cu: Modeling the Influence of Size, Composition, and Excitation Wavelength on the Optical Properties. *Chem. Phys.* **2013**, *423* (0), 142–150.
 - (19) Xia, X.; Wang, Y.; Ruditskiy, A.; Xia, Y. 25th Anniversary Article: Galvanic Replacement: A Simple and Versatile Route to Hollow Nanostructures with Tunable and Well-Controlled Properties. *Adv. Mater.* **2013**, *25* (44), 6313–6333.
 - (20) Sun, Y.; Xia, Y. Shape-Controlled Synthesis of Gold and Silver Nanoparticles. *Sci.* **2002**,

- 298 (5601), 2176–2179.
- (21) Xue, K.; Xu, Y.; Song, W. One-Step Synthesis of 3D Dendritic Gold@polypyrrole Nanocomposites via a Simple Self-Assembly Method and Their Electrocatalysis for H₂O₂. *Electrochim. Acta* **2012**, *60* (0), 71–77.
 - (22) Jeong, G. H.; Lee, Y. W.; Kim, M.; Han, S. W. High-Yield Synthesis of Multi-Branched Gold Nanoparticles and Their Surface-Enhanced Raman Scattering Properties. *J. Colloid Interface Sci.* **2009**, *329* (1), 97–102.
 - (23) Hrelescu, C.; Sau, T. K.; Rogach, A. L.; Jäckel, F.; Laurent, G.; Douillard, L.; Charra, F. Selective Excitation of Individual Plasmonic Hotspots at the Tips of Single Gold Nanostars. *Nano Lett.* **2011**, *11* (2), 402–407.
 - (24) Liu, Z.; Yang, Z.; Peng, B.; Cao, C.; Zhang, C.; You, H.; Xiong, Q.; Li, Z.; Fang, J. Highly Sensitive, Uniform, and Reproducible Surface-Enhanced Raman Spectroscopy from Hollow Au-Ag Alloy Nanourchins. *Adv. Mater.* **2014**, *26* (15), 2431–2439.
 - (25) Petri, M. V.; Ando, R. A.; Camargo, P. H. C. Tailoring the Structure, Composition, Optical Properties and Catalytic Activity of Ag–Au Nanoparticles by the Galvanic Replacement Reaction. *Chem. Phys. Lett.* **2012**, *531* (0), 188–192.
 - (26) Liu, Z.; Cheng, L.; Zhang, L.; Jing, C.; Shi, X.; Yang, Z.; Long, Y.; Fang, J. Large-Area Fabrication of Highly Reproducible Surface Enhanced Raman Substrate via a Facile Double Sided Tape-Assisted Transfer Approach Using Hollow Au-Ag Alloy Nanourchins. *Nanoscale* **2014**, *6* (5), 2567–2572.
 - (27) Silvert, P.-Y.; Herrera-Urbina, R.; Duvauchelle, N.; Vijayakrishnan, V.; Elhsissen, K. T. Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 1-Synthesis and Characterization. *J. Mater. Chem.* **1996**, *6* (4), 573–577.
 - (28) Xu, J.; Wilson, A. R.; Rathmell, A. R.; Howe, J.; Chi, M.; Wiley, B. J. Synthesis and Catalytic Properties of Au–Pd Nanoflowers. *ACS Nano* **2011**, *5* (8), 6119–6127.
 - (29) Wiley, B. J.; Im, S. H.; Li, Z.-Y.; McLellan, J.; Siekkinen, A.; Xia, Y. Maneuvering the Surface Plasmon Resonance of Silver Nanostructures through Shape-Controlled Synthesis. *J. Phys. Chem. B* **2006**, *110* (32), 15666–15675.
 - (30) Yang, Y.; Liu, J.; Fu, Z.-W.; Qin, D. Galvanic Replacement-Free Deposition of Au on Ag for Core–Shell Nanocubes with Enhanced Chemical Stability and SERS Activity. *J. Am. Chem. Soc.* **2014**, *136* (23), 8153–8156.

Chapter 5. Controlling Size, Morphology, and Surface Composition of AgAu Nanodendrites in 15 s for Improved Catalysis under Low Metal Loadings

5.1. Introduction

Noble metal nanomaterials are known to be highly active towards a wide variety of heterogeneous catalysis transformations, including oxidation, reduction, and coupling reactions.^{1–5} Catalytic performance can be optimized by careful control of particle size, shape, and surface composition.^{6–10} Nanoparticles with a nodular surface morphology have been shown to be particularly attractive for various catalytic and electrocatalytic applications.^{7,11–14} These ‘nanodendrites’ have shown superior performance relative to spherical and commercial nanoparticle counterparts, although details of the enhanced activity remains unclear.^{12,14–16} Attempts to understand the effect of nanodendrite morphology on catalytic performance have been hindered by a lack of experimental control during the synthesis of these structures.^{13,17–19}

We recently reported that it was possible to produce AgAu nanodendrites in only 15 s from Ag NP seeds via a combined galvanic replacement and reduction reaction in the presence of hydroquinone, in which the utilization of Ag NPs seeds was imperative to the formation of uniform nanodendrites.²⁰ Here, we further demonstrate the rapid synthesis of a range of highly controlled AgAu nanodendrite morphologies and use these materials to explore the effect of the surface morphology and composition on catalytic activity. Specifically, we focus on the catalytic gas-phase oxidation of the toxic volatile organic compounds benzene, toluene and o-xylene (BTX), which represents an important transformation for environmental remediation^{21–24} and where

improved catalytic performance could provide higher degradation efficiencies with lower energy costs.^{4,13}

Our synthesis approach employs Ag nanoparticles (NPs) as seeds and is based on a combination of the galvanic replacement reaction between Ag and AuCl_4^- (aq) with simultaneous reduction of AuCl_4^- (aq) to Au by hydroquinone. Simply by varying the number of Ag NP seeds in suspension during the synthesis, we are able to accurately control the size and surface morphology of the produced AgAu nanodendrites. We demonstrate that the size, morphology and surface composition of AgAu nanodendrites has a strong effect on their gas-phase BTX oxidation activity measured after supporting the nanoparticle catalysts on a silica substrate.

5.2. Experimental Section

5.2.1. Materials and Instrumentation

Analytical grade chemicals chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich), silver nitrate (AgNO_3 , 99%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$, 99%, Vetec), hydrochloric acid (HCl , 37%, Sigma-Aldrich), silica (SiO_2 , pore size 22 Å, 800 m²/g, CAS number 112926-00-8, Sigma-Aldrich), benzene (C_6H_6 , >99%, Vetec), toluene (C_7H_8 , >99%, Vetec) and o-xylene (C_8H_{10} , >99%, Vetec) were used as received. All solutions were prepared using deionized water (18.2 MΩ).

Scanning electron microscope (SEM) images were obtained using a JEOL field emission gun microscope, JSM 6330F, operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension containing the nanostructures over an oxidised silicon wafer, followed by drying under ambient conditions. Transmission electron microscope and high resolution

transmission electron microscope (TEM and HRTEM) images were obtained with a JEOL 1010 microscope operated at 80 kV and with a FEI Tecnai TF30 microscope operated at 300 kV. High angle annular dark field (HAADF) scanning transmission electron microscope (STEM) images were acquired using a probe-side aberration-corrected FEI Talos F200X S/TEM operated at 200 kV with a beam current of approximately 0.3 nA. Energy dispersive X-ray (EDX) spectrum images were obtained in this instrument with the Super-X EDX detector configuration which has a total solid angle of ~ 0.8 sr. Samples were prepared for TEM, HRTEM, and EDX imaging by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous suspensions of the nanoparticles with a Shimadzu UV-1700 or UV-3101 PC spectrophotometer. The Au and Ag atomic percentages were measured by flame atomic absorption spectrometry (FAAS) with a Shimadzu spectrophotometer, model AA-6300, equipped with an air-acetylene flame. X-ray photoelectron spectroscopy (XPS) data of the samples was obtained with an SPECSLAB II (Phoibos-Hsa 3500 150, 9 channeltrons) SPECS spectrometer, with Al K α source ($E = 1486.6$ eV) operating at 12 kV, pass energy ($E_{\text{pass}} = 40$ eV, 0.1 eV energy step and acquisition time of 1 s per point. The samples were placed on stainless steel sample-holders and were transferred under inert atmosphere to the XPS pre-chamber and held there for a 2 h in a vacuum atmosphere. The residual pressure inside the analysis chamber was $\sim 1 \times 10^{-9}$ Torr. The binding energies (BE) of the Ag 3d, Au 4f and C 1s spectral peaks were referenced to the C 1s peak, at 284.5 eV, providing accuracy within ± 0.2 eV. The estimation of the metallic surface area was carried out in a Micrometrics Chemisorb 2705. For the estimation of metallic surface area, the catalysts were pretreated with N₂ flow at 125 °C for 1 h. Then, the system was heated at 400 °C for 1 h under O₂ flow before being cooled to room temperature. The catalysts were then reduced at 400 °C under

H₂ flow for 1 h and cooled to room temperature under N₂ flow. Finally, H₂ pulses were provided to the samples at 40 °C until the H₂ consumption ceased. The amount of H₂ adsorbed on the catalyst was estimated considering a stoichiometric factor of 1 (1 H atom chemisorbed on 1 atom), a surface area value of 0.08 nm²/atom and with the density of Au being 19.32 g.cm⁻³.

5.2.2. *Synthesis of Ag seeds*

Ag seeds were prepared by the polyol process.²⁵ In a typical experiment, 5 mg of polyvinylpyrrolidone (PVP) was dissolved in 37.5 mL of ethylene glycol. Then, AgNO₃ (200 mg, 1.2 mmol) was added and mixed until complete dissolution. The resulting solution was heated to 125 °C for 2.5 hours, leading to the appearance of a greenish-yellow color, allowed to cool to room temperature, and then diluted to 125 mL using DI water (no further purification steps were required). The Ag nanoparticle (NP) seeds were observed using SEM imaging and found to be roughly spherical with a mean diameter of 35 ± 4 nm.

5.2.3. *Synthesis of AgAu nanodendrites*

AgAu nanodendrites were synthesized through a combination of galvanic replacement and precursor reduction, employing Ag NPs as seeds, hydroquinone as a reducing agent, polyvinylpyrrolidone (PVP) as a stabilizer, water as the solvent and AuCl₄⁻(aq) as the Au precursor.²⁰ Here, the surface morphology of the produced AgAu nanodendrites could be tailored by varying the number/concentration of Au NPs seeds in the reaction mixture. Typically, 1, 3, 5 or 10 µL of the as-prepared Ag seeds suspension (1.2×10^{17} NPs/L) were added to four different vials containing 9.4 mL of PVP aqueous solution (0.1 wt %). Each mixture was transferred to a 25 mL round-bottom flask and was vigorously stirred at 50 °C. After 10 min, 0.1 mL of 30 mM aqueous

hydroquinone solution and 0.1 mL of 12 mM AuCl_4^- (aq) were sequentially added, then after 15 s the reaction was quenched by the addition of 0.1 mL of 0.3 M HCl (aq) solution and by simultaneously cooling the reaction mixture in ice water. The AgAu nanodendrites produced were then washed three times with water by successive rounds of centrifugation at 8000 rpm and removal of the supernatant. After washing, the AgAu nanodendrites were suspended in 1 mL of water.

5.2.4. Synthesis of AgAu nanodendrites supported on silica (AgAu/SiO₂ 0.1 wt. %)

AgAu nanodendrites were supported on commercial silica by a wet impregnation method.²⁶ The AgAu content in the SiO₂ support corresponded to 0.1 % in weight (in terms of total metal content). Briefly, 300 mL of each nanodendrite suspension was concentrated to 30 mL. Then, 1 g of silica was added to the resulting suspension and vigorously stirred at 80 °C to produce a paste. After that, 50 mL of distilled water was added and the suspension was stirred until completely dry (5 h). The resulting solids were then treated at 120 °C for 2 h under air.

5.2.5. Benzene, toluene and o-xylene oxidation (BTX oxidation)

The catalytic oxidation of benzene, toluene and o-xylene was performed in a fixed bed tubular quartz reactor under atmospheric pressure. The following conditions were used: 0.030g catalyst, inlet benzene (1.2 g.m⁻³), toluene (0.7 g.m⁻³), o-xylene (0.5 g.m⁻³) in air, gas flow rate 20 cm³.min⁻¹, residence time 0.3 s, gas hourly space velocity 12000 h⁻¹ and temperature range 25-300 °C. The reaction data was collected after at least 2 h on-stream at room temperature. The reaction products were determined by gas chromatography-mass spectrometry (GC-MS). The reactant and product mixtures were analyzed using two on-line gas chromatographs equipped with flame

ionization and thermal conductivity detectors (FID and TCD, respectively) and an HP-5 column. The catalytic activity was expressed as the degree of the conversion of benzene, toluene and o-xylene, respectively. The conversion of the BTX compounds was calculated as follows:

$$\text{CBTXs (\%)} = [(\text{BTXs})_{\text{in}} - (\text{BTXs})_{\text{out}}] \cdot 100 / (\text{BTXs})_{\text{in}} \quad (1)$$

where CBTXs (%) = percentage of BTX conversion; $(\text{BTXs})_{\text{in}}$ = input quantity and $(\text{BTXs})_{\text{out}}$ = output quantity.

5.3. Results and Discussion

Varying the volume of Ag NP seed suspension (1.2×10^{17} NPs/L) employed during the synthesis caused significant changes in the AgAu nanodendrite particles produced as shown in Figures 5.1 A-H (1, 3, 5 and 10 μL , for A-D and E-H respectively). These volumes of seed solution correspond to 0.2, 0.6, 1.0 and 2.0 nM of Ag in the reaction mixture and an estimated 1.2×10^{11} , 3.6×10^{11} , 6.0×10^{11} and 1.2×10^{17} Ag NP seeds (assuming a mean nanoparticle contains 4.8×10^4 atoms). The SEM and TEM images in Figure 5.1 demonstrate that the outer diameter, as well as the surface morphology of the produced nanodendrites strongly depends upon the concentration of Ag NPs employed as seeds during synthesis. Specifically, the size of the AgAu nanodendrites decreases as the number of Ag NP seeds is increased, with mean outer diameters of 148 ± 6 , 96 ± 5 , 66 ± 4 and 45 ± 3 nm for 1, 3, 5 and 10 μL of Ag NP seed suspension. The diameter of the surface nodules (or branches) also becomes larger as the overall size of the particles increases and the individual branch tips consequently exhibit lower curvature, as shown by comparing the AgAu

nanodendrites obtained in the presence of 1 and 10 μL of Ag NP seeds (Figure 5.1 A vs. 5.1 D and 5.1 E vs. 5.1 H).

Figure 5.1. SEM (A-D) and TEM (E-H) images of AgAu nanodendrites displaying controlled surface morphologies obtained by varying the volume of Ag NP seed suspension employed during the synthesis: 1 μL (A and E), 3 μL (B and F), 5 μL (C and G), and 10 μL (D and H). The scale bars in the TEM images are 40 nm (E-H).

FAAS analysis of the nanoparticle ensembles reveals that the overall Au content in the AgAu nanodendrites is lower for the smaller nanoparticles; specifically 99, 96, 94 and 90 at. % Au and 1, 4, 6, and 10 at. % Ag for the samples obtained using 1, 3, 5 and 10 μL of the Ag NP seed suspension, respectively. These results can be explained based on the increase in the number

of sites available for Au heterogeneous nucleation, and subsequent growth, as the number of Ag NPs in the reaction mixture is increased (Scheme 5.1). A larger number of Ag NP seeds, for a fixed concentration of AuCl_4^- (aq), leads to a decrease in the amount of Au available for the growth of Au branches at the surface of each seed. This leads to a decrease in the overall diameter of the resulting individual nanodendrites and in the size of the individual branches.

Scheme 5.1. Approach to produce AgAu nanodendrites displaying controlled surface morphologies by varying the volume of Ag NP seed suspension containing 1.2×10^{17} NPs/L (1, 3, 5, and 10 μL to give 1.2×10^{11} , 3.6×10^{11} , 6.0×10^{11} , and 1.2×10^{12} NPs, respectively), while all other experimental parameters were kept unchanged. The AgAu nanodendrites were obtained by the combination of the galvanic replacement reaction between Ag seeds and AuCl_4^- (aq) and the chemical reduction of AuCl_4^- (aq) to Au by hydroquinone. An increase in the volume of Ag NP seeds in suspension leads to a decrease in the size of the particles.

In order to gain further insights into the crystalline structure of the Au branches, the AgAu nanodendrites obtained in the presence of 1 and 10 μL of Ag NP seeds suspension were analyzed by HRTEM, as depicted in Figure 5.2.

Figure 5.2. HRTEM images depicting the Au branches of AgAu nanodendrites obtained when the volume of the Ag NP seed suspension employed during the synthesis corresponded to 1 μL (A), and 10 μL (B).

HRTEM images (Figure 5.2 A and B) clearly show that some of the individual nodules at the surface of the AgAu nanodendrites are composed of single crystals, and have roughly spherical tips, displaying no obvious faceting. The average radius of curvature for the branches was higher for the smaller nanoparticles (the radius of curvature for the nanodendrite nodules shown in Figure 5.2 A and B is 17 ± 1 and 12 ± 1 nm respectively). The Au branch growth direction is observed to be along both $\langle 100 \rangle$ and $\langle 110 \rangle$ directions for nanodendrites obtained from 1 and 10 μL of the Ag NP seed suspensions.

The UV-VIS extinction spectra measured for the various AgAu nanodendrites are depicted in Figure 5.3 and show good agreement with the size and surface morphology variations observed by SEM and TEM.

Figure 5.3. UV-visible extinction spectra of Ag NP seeds and AgAu nanodendrites obtained by using 1, 3, 5 and 10 μL of the Ag NP seed suspension (represented as the black, red, purple, green and blue traces respectively).

The Ag NP seeds show the expected characteristic localized surface plasmon resonance (LSPR) band centered at 407 nm and which can be assigned to their dipolar resonant mode.²⁰ This LSPR peak is red-shifted relative to both Ag and Au NPs and broadened as a result of the formation of the AgAu nanodendrites, with the larger nanodendrites red shifted to a greater extent than the smaller nanodendrite particles. This behavior is a consequence of the larger overall diameter of the particles and of the presence of Au branches on the surface, which enable increased charge separation during plasmon oscillation, reducing the restoring force and producing a resonance peak at longer wavelengths.^{27–29} Specifically, the observed LSPR peak band is found to be centered at 690, 623, 613 and 607 nm, for the AgAu nanodendrites obtained in the presence of 1, 3, 5, and 10 μL of Ag NP seeds suspension, respectively.

We also performed STEM-EDX spectrum imaging for the AgAu nanodendrites obtained in the presence of 1 and 10 μL of Ag NP seeds suspension (shown in Figure 5.1 A and 5.1 D, respectively) in order to investigate the particles Ag and Au elemental distribution as shown in Figure 5.4. Surprisingly, while the STEM-EDX results for the nanodendrites having larger sizes (Figure 5.1 A) showed only the presence of Au (Ag was not detected in the structure, in agreement with FAAS data), we found that smaller AgAu nanodendrites (Figure 5.1 D) presented a Ag surface segregation behavior, with a fairly uniform Ag surface layer, < 2 nm thick, covering the entire surface of the nanodendrites (Figure 5.4 C and 5.4 D). This Ag surface segregation is similar to that recently observed during the synthesis of AgAu nanoparticles (nanoshells and tadpoles) by galvanic replacement between Ag and AuCl_4^- (aq), and may be assigned to the lower surface energy of Ag relative to Au and the AgAu miscibility at the nanoscale.^{6,30} Cliff Lorimer compositional analysis of the summed EDX spectrum images revealed the particles to contain 90 at % Au in agreement with the FAAS elemental analysis results.

Figure 5.4. (A-B) i) STEM-EDX spectrum of AgAu nanodendrites obtained in the presence of (A) 1 μ L and (B) 10 μ L of Ag NP seeds suspension from the NPs indicated in the inset HAADF image (ii). The spectrum depicted in (B) shows X-ray peaks associated with Ag, while the spectrum in (A) does not. (C-D) Elemental maps of Au (red) and Ag (green) displaying a clear segregation of Ag to the surface of the nanoparticle shown in (B). The elemental maps have been smoothed using a 3-pixel average window.

In order to further investigate surface composition, oxidation state and the charge transfer tendencies between Au and Ag in the AgAu nanodendrites, we performed XPS analyses for the

samples obtained in the presence of 1 and 10 μL of Ag NP seeds suspension (shown in Figure 5.1 A and D, respectively) as depicted in Figure 5.5 (XPS spectra) and Table 5.1 (XPS parameters and assignments).

Figure 5.5. XPS spectra of Ag 3d (A) and Au 4f (B) core level for AgAu nanodendrites obtained in the presence of 1 and 10 μL of Ag NP seeds (shown in Figure 5.1 A and D, respectively).

Table 5.1. Binding energies, surface compositions, and Au/Ag ratios for AgAu nanodendrites measured by XPS analyses.

Sample	Binding energy 4f _{7/2} (eV)		Relative atomic concentration (%)		Binding energy 3d _{5/2} (eV)		Relative atomic concentration (%)		Ag : Au
	Au ⁰	Au ^{δ+}	Au ⁰	Au ^{δ+}	Ag ⁰	Ag ⁺	Ag ⁰	Ag ⁺	
AgAu (Fig. 1D)	83.7	85.3	80	20	368.7	367.4	30	70	9:91
AgAu (Fig. 1A)	83.0	84.7	37	63	--	--	--	--	1:99

Ag 3d and Au 4f presented well separated spin-orbit components ($\Delta \sim 6.0$ and 3.7 eV respectively). The binding energies (BE) of Ag 3d and Au 4f regions indicated slight shifts relative to bulk Ag (368.3 eV) and Au (84.0 eV)³¹ which can be explained due to the formation of nanosized particles that generally modify the surface properties.^{31,32} No significant Ag peaks were detected for the larger nanodendrites (obtained in the presence of $1 \mu\text{L}$ of seeds) in agreement with the very low Ag content observed from STEM-EDX imaging and FAAS analysis of this sample. It is important to emphasize that FAAS analysis is an effective technique to determinate the overall composition in bimetallic nanoparticles. However, this technique provides no information about surface atomic distributions. The absence of Ag in the XPS data, therefore, demonstrates a Ag free surface layer but is not inconsistent with an overall Ag content of $\sim 1\%$ as determined by FAAS.

In contrast, the XPS spectrum for the smaller nanodendrites (obtained in the presence of $10 \mu\text{L}$ of seeds) presented BE at 368.7 and 374.6 eV assigned to Ag⁰ species at the Ag 3d_{5/2} and 3d_{3/2} regions, respectively. Two further peaks at 367.4 and 373.4 eV were also observed in the Ag 3d_{5/2} and Ag 3d_{3/2} regions which correspond to Ag⁺ species.^{31,33} Both large and small nanodendrites showed peaks in the Au 4f_{7/2} and Au 4f_{5/2} regions: those at 83.7 and 87.3 eV could be assigned to Au⁰ species while those at 85.3 and 89.1 eV related to Au^{δ+} species.^{31,34} Therefore, XPS data indicates an enhanced silver content on the surface of the small nanodendrites compared to the

monometallic Au surface observed for the larger nanodendrites. The Ag surface segregation observed in the smaller nanodendrites is in agreement with previous reports.^{6,30} However, the nanodendrites obtained using 1 μL of Ag seeds are almost 3 times bigger. Therefore, it is suggested that the increase in the particle size could inhibit Ag surface segregation. Surprisingly, differences in the $M^{\delta+}/M^0$ ratio ($M = \text{Au}$ and Ag) could also be observed between these two samples, indicating a variation in the chemical state at their surface. In order to quantify these differences, the Ag $3d_{5/2}$ and Au $4f_{7/2}$ spectra were de-convoluted into 2 peaks corresponding to Ag^0 (368.7 eV) and Ag^+ (367.4 eV), and 2 peaks corresponding to Au^0 (83.7 eV) and $\text{Au}^{\delta+}$ (85.3 eV). As depicted in Table 5.1, the $\text{Au}^0/\text{Au}^{\delta+}$ ratio increased when Ag was detected at the surface, and this behavior can be explained due to charge transfer from Ag to Au, thus leading $\text{Au}^{\delta+}$ species to reduce to Au^0 and Ag^0 to oxidize to Ag^+ .³⁵ It is important to note that experimental and theoretical studies on Ag, Au, and AgAu bimetallic materials have demonstrated that the most catalytically active sites correspond to Ag^+ and $\text{Au}^{\delta+}$ surface species relative to their Ag^0 and Au^0 counterparts, respectively.^{36,37} Therefore, the presence of relatively high Ag^+ and $\text{Au}^{\delta+}$ content at the surface is promising for the nanodendrites application as catalytic materials.

For conventional systems, $\text{Au}^{\delta+}$ and Ag^+ species can be formed at catalyst surface by heating at high temperatures ($> 500\text{ }^\circ\text{C}$) under an oxygen atmosphere. However, the AgAu nanodendrites were obtained under mild conditions and were not calcined prior to catalytic testing. Thus, the high $\text{Au}^{\delta+}$ species concentration could be related to the employed synthesis approach which is based on the combination of a galvanic replacement reaction between Ag and AuCl_4^- (aq) (producing Ag^+ species) and the reduction of AuCl_4^- (aq) to Au in the presence of hydroquinone. It is suggested that due to the short reaction time (15 s), the partial reduction of the Au precursor (AuCl_4^-) may lead to a high concentration of both $\text{Au}^{\delta+}$ and Ag^+ species at the surface as indicated

by our XPS analyses. It is important to note that the AgAu nanodendrites having smaller sizes (Fig. 1D) contained a smaller amount of $\text{Au}^{\delta+}$ species at the surface relative to the nanodendrites having larger sizes (Fig. 5.1 A), probably due to their higher Ag surface concentration (Figure 5.4 and Table 5.1) which favors the charge transfer from Ag to Au, thus reducing $\text{Au}^{\delta+}$ species to Au^0 and oxidizing Ag^0 to Ag^+ .

In order to investigate the effect of the observed differences in morphology, size, and surface composition on their catalytic activities, the AgAu nanodendrites were supported onto a commercial silica substrate to produce AgAu/SiO₂ catalysts. The metal loading in all AgAu/SiO₂ catalysts produced corresponded to 0.1 wt%. A uniform distribution of particles was produced for all supported nanodendrite samples (AgAu/SiO₂) without significant agglomeration as shown by the SEM images in Figure 5.6. The number of metallic active sites in the AgAu/SiO₂ materials was determined by hydrogen chemisorption and corresponded to 0.35, 0.28, 0.18, and 0.07 μmol per gram of catalyst for the AgAu/SiO₂ catalysts containing the AgAu nanodendrites obtained by employing 1 μL (Fig. 5.6 A and B), 3 μL (Fig. 5.6 C and D), 5 μL (Fig. 5.6 E and F) and 10 μL (Fig. 5.6 G and H) of Ag NP seeds suspension. Interestingly, these results show that the number of catalytically active sites decreases as the size of the AgAu nanodendrites decreases. This can be attributed to the variation in surface morphology among the AgAu nanodendrite samples: nanodendrites with larger outer diameters displayed greater surface roughness as a consequence of the longer branches on their surface. The larger AgAu nanodendrites consequently have a larger surface to volume ratio with the observed variations in surface morphology compensating for the increase in the overall size in order to produce more catalytically active sites. It is important to note that the presence of Ag in the nanodendrites having smaller sizes as well as the presence of

PVP (in all nanodendrite samples) may also contribute to reduce the hydrogen chemisorption results.

Figure 5.6. SEM images of AgAu nanodendrites with controlled surface morphologies supported on commercial SiO₂ (AgAu/SiO₂) by wet impregnation. The volume of Ag NP seed suspension (1.2×10^{17} NPs/L) employed during the synthesis of the AgAu nanodendrites corresponded to 1 μL (A-B), 3 μL (C-D), 5 μL (E-F), and 10 μL (G-H).

Figure 5.7 A-C depicts the conversion % for the oxidation of benzene, toluene, and *o*-xylene, respectively, as a function of reaction temperature for the AgAu/SiO₂ solid catalysts shown in Figure 5.6.

Figure 5.7. Oxidation of benzene (A), toluene (B), and *o*-xylene (C) as a function of temperature, catalyzed by the different supported nanodendrite AgAu/SiO₂ depicted in Fig. 5.6A (blue trace), Fig. 5.6C (green trace), Fig. 5.6E (purple trace), Fig. 5.6G (red trace) and pure SiO₂ (black trace).

While no significant conversion is detected for the pure SiO₂ support (control experiment), all AgAu/SiO₂ catalysts display high catalytic activities at relatively low temperatures (the BTX oxidation began just above room temperature) and low metal loadings (0.1 wt. %). The BTX % conversion increases with temperature for all catalysts and encouragingly only H₂O and CO₂ are detected as reaction products. Interestingly, the BTX % conversion decreases as the outer diameters of the AgAu nanodendrites decreases, in agreement with the detected decrease in the active surface area for smaller particles. For instance, at 300 °C, the conversion efficiency for

benzene is 97 % for the largest nanodendrites (with diameters of 148 ± 6 nm) but only 82 % for the smallest nanodendrites (45 ± 3 nm). Similarly, the % conversion for toluene and *o*-xylene drops from 82 to 60 %, and 55 to 38 %, respectively, for the smallest nanodendrites compared to the largest at 300 °C. These variations in catalytic performance are contrary to that expected for perfectly spherical particles considering only the effect of the increased surface-to-volume ratio as the particles become smaller. Therefore, we would like to propose that the greater activity that is observed here for the larger nanodendrites could be related to following factors: *i*) the unusual surface morphology, which enables higher surface areas for nanodendrites with larger outer diameters, and *ii*) the differences in electronic structure that enable different $M^{\delta+}/M^0$ ratios at the surface.

We also investigated the catalytic stability for the largest nanodendrites which showed the highest activity towards the benzene oxidation (Figure 5.8). It can be observed that no significant loss of catalytic activity was detected even after 24 h, showing that these materials may represent promising candidates for gas-phase catalytic applications.

Figure 5.8. Benzene conversion percentages as a function of time employing the AgAu/SiO₂ materials depicted in Figure 5.6 A and B as catalyst.

In order to demonstrate the high catalytic activities of the AgAu nanodendrites and the advantage of their utilization as catalysts for the BTX oxidation, their performance is compared with those from a conventional Au/SiO₂ catalyst prepared by impregnation, (see Figure 5.9).

Figure 5.9. Oxidation (conversion %) of benzene, toluene, and *o*-xylene (black, red, and blue traces, respectively) as a function of temperature employing standard Au/SiO₂ catalyst prepared by wet impregnation of AuCl₄⁻(aq) precursor followed by calcination and reduction steps at 500 °C. The Au loading corresponded to 5 % in weight.

The metal loading in the Au/SiO₂ catalyst corresponds to 5 wt. % (as opposed to 0.1 wt. %, used for the AgAu nanodendrites). It can be observed that the AgAu nanodendrites display significantly higher catalytic activities than the conventional Au/SiO₂ catalyst under far lower metal loadings. Their performance is also superior to other catalysts reported in the literature as depicted in Table 5.2 (Turnover frequency (TOF) up to 1884 h⁻¹).^{22,34,38–44}

Table 5.2. Oxidation of benzene and toluene over AgAu/SiO₂ nanodendrites (depicted in Fig. 4A) and other catalysts reported in literature.

Catalysts	Loading (wt %)	Substrate	Temperature (°C)	Conversion (%)	TOF (h ⁻¹)	Ref.
Nanodendrites (Fig. 4A)	0.1	Benzene	300	97	1756	This work
Nanodendrites (Fig. 4A)	0.1	Toluene	300	82	695	This work
Au/SiO ₂ (wet impregnation)	5.0	Benzene	300	47	1.1	This work
Au/MCM-41	5.0	Benzene	300	61	58	34
Au/MCM-41	5.0	Toluene	300	44	32	34
Au/Al ₂ O ₃	1.4	Benzene	300	78	0.8	38
Au/MgO	1.7	Benzene	300	32	0.3	38
Au/ZnO	1.3	Benzene	300	92	2.4	38
Au/TiO ₂	1.0	Toluene	300	10	130	22
Au/MgO	1.0	Toluene	300	5	-	39
Au/La ₂ O ₃	1.0	Toluene	300	3	-	39
Au/Fe ₂ O ₃	1.0	Toluene	300	40	-	39
Au/Co ₃ O ₄	1.5	Toluene	300	69	1.4	40
Au/Al ₂ O ₃	1.5	Toluene	300	37	0.5	40
Au/MgO	1.5	Toluene	300	33	0.3	40
Au-Ag/CeO ₂	1.25	Toluene	300	20	-	41
Au-Pd/MCM-41	5.6	Benzene	300	68	52	34
Au-Pd/MCM-41	5.6	Toluene	300	49	39	34
AuCeDP	5.0	Toluene	300	0	-	42
AuCeCP	4.7	Toluene	300	85	-	42
AuCo-45	3.07	Toluene	300	86	-	43
Pd-AuFeCeMM	4.0	Benzene	300	92	-	44

We believe the remarkable catalytic activities observed for the nanodendrites were related to three main factors: *i*) the high concentration of Ag⁺ and Au^{δ+} species at the surface that represent catalytically active sites towards oxidation reactions,^{35,36} *ii*) the dendritic structures that have shown superior performances towards several catalytic and electrocatalytic processes relative to spherical particle counterparts,^{7,12,16} and in supported samples (AgAu/SiO₂) *iii*) the uniform distribution of

particles without significant agglomeration, a property that is generally crucial to achieve high catalytic activities.^{7,45,46} Although the presence of Ag^+ and $\text{Au}^{\delta+}$ species at the catalyst surface have demonstrated to be the most catalytically active sites towards oxidation reactions relative to their Ag^0 and Au^0 counterparts, respectively, previous studies have only considered the role of Ag^+ and $\text{Au}^{\delta+}$ in isolation.^{36,37} Systematic studies clearly identifying the most active specie (Ag^+ or $\text{Au}^{\delta+}$) are scarce in the literature. Here, our results indicate that $\text{Au}^{\delta+}$ species lead to improved catalytic performances as compared to Ag^+ species for the BTX oxidation. The remarkable catalytic activity, stability, and low Au loadings described herein agree with the principles of Green Chemistry applied to nanoscience, which encompasses the design of safer nanomaterials.

5.4. Conclusion

We have demonstrated that altering the concentration of Ag NP seed suspensions employed during the synthesis of AgAu nanodendrites represents a simple and effective approach to accurately control their size and surface morphology. Our results have shown that the outer diameters of the AgAu nanodendrites, as well as the size of the branches on the nanodendrite surfaces, decreases as the concentration of Ag NP seeds is increased. Investigating the effect of differences in nanodendrite morphology on their catalytic activity in the gas-phase BTX oxidation reaction has demonstrated that the best results are achieved for the largest nanodendrites with diameters of approximately 150 nm. We believe the results described herein may have important implications on the design and synthesis of noble-metal nanodendrites, displaying both low loadings and optimized performance for catalytic and electrocatalytic applications.

5.5. References

- (1) Stratakis, M.; Garcia, H. Catalysis by Supported Gold Nanoparticles: Beyond Aerobic Oxidative Processes. *Chem. Rev.* **2012**, *112*, 4469–4506.
- (2) Speziali, M. G.; Silva, A. G. M. da; Miranda, D. M. V. de; Monteiro, A. L.; Robles-Dutenhefner, P. A. Air stable ligandless heterogeneous catalyst systems based on Pd and Au supported in SiO₂ and MCM-41 for Suzuki–Miyaura cross-coupling in aqueous medium. *Appl. Catal. A* **2013**, *462–463*, 39–45.
- (3) Zhang, Y.; Cui, X.; Shi, F.; Deng, Y. Nano-Gold Catalysis in Fine Chemical Synthesis. *Chem. Rev.* **2011**, *112*, 2467–2505.
- (4) Min, B. K.; Friend, C. M. Heterogeneous Gold-Based Catalysis for Green Chemistry: Low-Temperature CO Oxidation and Propene Oxidation. *Chem. Rev.* **2007**, *107*, 2709–2724.
- (5) Zhang, G.; Peng, Y.; Cui, L.; Zhang, L. Gold-Catalyzed Homogeneous Oxidative Cross-Coupling Reactions. *Angew. Chemie Int. Ed.* **2009**, *48*, 3112–3115.
- (6) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O'Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, *14*, 1921–1926.
- (7) Rodrigues, T. S.; da Silva, A. G. M.; Gonçalves, M. C.; Fajardo, H. V.; Balzer, R.; Probst, L. F. D.; Camargo, P. H. C. AgPt Hollow Nanodendrites: Synthesis and Uniform Dispersion over SiO₂ Support for Catalytic Applications. *ChemNanoMat* **2015**, *1*, 46–51.
- (8) Cheong, S.; Watt, J. D.; Tilley, R. D. Shape control of platinum and palladium nanoparticles for catalysis. *Nanoscale* **2010**, *2*, 2045–2053.
- (9) Mostafa, S.; Behafarid, F.; Croy, J. R.; Ono, L. K.; Li, L.; Yang, J. C.; Frenkel, A. I.; Cuenya, B. R. Shape-Dependent Catalytic Properties of Pt Nanoparticles. *J. Am. Chem. Soc.* **2010**, *132*, 15714–15719.
- (10) Silva, A. G. M. da; Rodrigues, T. S.; Macedo, A.; Silva, R. T. P. da; Camargo, P. H. C. An undergraduate level experiment on the synthesis of Au nanoparticles and their size-dependent optical and catalytic properties. *Quim. Nova* **2014**, *37*, 1716–1720.
- (11) Gao, Q.; Gao, M.-R.; Liu, J.-W.; Chen, M.-Y.; Cui, C.-H.; Li, H.-H.; Yu, S.-H. One-pot synthesis of branched palladium nanodendrites with superior electrocatalytic performance. *Nanoscale* **2013**, *5*, 3202–3207.
- (12) Lim, B.; Jiang, M.; Camargo, P. H. C.; Cho, E. C.; Tao, J.; Lu, X.; Zhu, Y.; Xia, Y. Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction. *Science* **2009**, *324*, 1302–1305.
- (13) Mohanty, A.; Garg, N.; Jin, R. A Universal Approach to the Synthesis of Noble Metal Nanodendrites and Their Catalytic Properties. *Angew. Chemie Int. Ed.* **2010**, *49*, 4962–4966.
- (14) Wang, W.; Wang, D.; Liu, X.; Peng, Q.; Li, Y. Pt-Ni nanodendrites with high hydrogenation activity. *Chem. Commun.* **2013**, *49*, 2903–2905.
- (15) Wang, L.; Wang, H.; Nemoto, Y.; Yamauchi, Y. Rapid and Efficient Synthesis of Platinum

- Nanodendrites with High Surface Area by Chemical Reduction with Formic Acid. *Chem. Mater.* **2010**, *22*, 2835–2841.
- (16) Li, Y.; Ding, W.; Li, M.; Xia, H.; Wang, D.; Tao, X. Synthesis of core-shell Au-Pt nanodendrites with high catalytic performance via overgrowth of platinum on in situ gold nanoparticles. *J. Mater. Chem. A* **2015**, *3*, 368–376.
 - (17) Hrelescu, C.; Sau, T. K.; Rogach, A. L.; Jäckel, F.; Laurent, G.; Douillard, L.; Charra, F. Selective Excitation of Individual Plasmonic Hotspots at the Tips of Single Gold Nanostars. *Nano Lett.* **2011**, *11*, 402–407.
 - (18) Hao, F.; Nehl, C. L.; Hafner, J. H.; Nordlander, P. Plasmon Resonances of a Gold Nanostar. *Nano Lett.* **2007**, *7*, 729–732.
 - (19) Zhang, H.; Huang, F.; Xu, S.; Xia, Y.; Huang, W.; Li, Z. Fabrication of nanoflower-like dendritic Au and polyaniline composite nanosheets at gas/liquid interface for electrocatalytic oxidation and sensing of ascorbic acid. *Electrochem. commun.* **2013**, *30*, 46–50.
 - (20) da Silva, A. G. M.; de Souza, M. L.; Rodrigues, T. S.; Alves, R. S.; Temperini, M. L. A.; Camargo, P. H. C. Rapid Synthesis of Hollow Ag–Au Nanodendrites in 15 Seconds by Combining Galvanic Replacement and Precursor Reduction Reactions. *Chem. Eur. J.* **2014**, *20*, 15040–15046.
 - (21) Wu, J. C.-S.; Lin, Z.-A.; Tsai, F.-M.; Pan, J.-W. Low-temperature complete oxidation of BTX on Pt/activated carbon catalysts. *Catal. Today* **2000**, *63*, 419–426.
 - (22) Hosseini, M.; Barakat, T.; Cousin, R.; Aboukaïs, A.; Su, B.-L.; De Weireld, G.; Siffert, S. Catalytic performance of core-shell and alloy Pd–Au nanoparticles for total oxidation of VOC: The effect of metal deposition. *Appl. Catal. B* **2012**, *111–112*, 218–224.
 - (23) Li, W. B.; Wang, J. X.; Gong, H. Catalytic combustion of VOCs on non-noble metal catalysts. *Catal. Today* **2009**, *148*, 81–87.
 - (24) Everaert, K.; Baeyens, J. Catalytic combustion of volatile organic compounds. *J. Hazard. Mater.* **2004**, *109*, 113–139.
 - (25) Silvert, P.-Y.; Herrera-Urbina, R.; Duvauchelle, N.; Vijayakrishnan, V.; Elhsissen, K. T. Preparation of colloidal silver dispersions by the polyol process. Part 1-Synthesis and characterization. *J. Mater. Chem.* **1996**, *6*, 573–577.
 - (26) Jiang, S. P. A review of wet impregnation—An alternative method for the fabrication of high performance and nano-structured electrodes of solid oxide fuel cells. *Mater. Sci. Eng. A* **2006**, *418*, 199–210.
 - (27) Wiley, B.; Sun, Y.; Xia, Y. Synthesis of silver nanostructures with controlled shapes and properties. *Acc. Chem. Res.* **2007**, *40*, 1067–1076.
 - (28) Hermoso, W.; Alves, T. V.; Ornellas, F. R.; Camargo, P. H. C. Comparative study on the far-field spectra and near-field amplitudes for silver and gold nanocubes irradiated at 514, 633 and 785 nm as a function of the edge length. *Eur. Phys. J. D* **2012**, *66*, 1–11.
 - (29) Hermoso, W.; Alves, T. V.; de Oliveira, C. C. S.; Moriya, E. G.; Ornellas, F. R.; Camargo, P. H. C. Triangular metal nanoprisms of Ag, Au, and Cu: Modeling the influence of size,

- composition, and excitation wavelength on the optical properties. *Chem. Phys.* **2013**, *423*, 142–150.
- (30) da Silva, A. G. M.; Lewis, E. A.; Rodrigues, T. S.; Slater, T. J. A.; Alves, R. S.; Haigh, S. J.; Camargo, P. H. C. Surface Segregated AgAu Tadpole-Shaped Nanoparticles Synthesized Via a Single Step Combined Galvanic and Citrate Reduction Reaction. *Chem. Eur. J.* **2015**, *21*, 12314–12320.
 - (31) Qu, Z.; Ke, G.; Wang, Y.; Liu, M.; Jiang, T.; Gao, J. Investigation of factors influencing the catalytic performance of CO oxidation over Au–Ag/SBA-15 catalyst. *Appl. Surf. Sci.* **2013**, *277*, 293–301.
 - (32) Zheng, J.; Lin, H.; Wang, Y.; Zheng, X.; Duan, X.; Yuan, Y. Efficient low-temperature selective hydrogenation of esters on bimetallic Au–Ag/SBA-15 catalyst. *J. Catal.* **2013**, *297*, 110–118.
 - (33) Harikumar, K. R.; Ghosh, S.; Rao, C. N. R. X-ray Photoelectron Spectroscopic Investigations of Cu–Ni, Au–Ag, Ni–Pd, and Cu–Pd Bimetallic Clusters. *J. Phys. Chem. A* **1997**, *101*, 536–540.
 - (34) da Silva, A. G. M.; Fajardo, H. V.; Balzer, R.; Probst, L. F. D.; Lovón, A. S. P.; Lovón-Quintana, J. J.; Valença, G. P.; Schreine, W. H.; Robles-Dutenhefner, P. A. Versatile and efficient catalysts for energy and environmental processes: Mesoporous silica containing Au, Pd and Au-Pd. *J. Power Sources* **2015**, *285*, 460–468.
 - (35) Sasirekha, N.; Sangeetha, P.; Chen, Y.-W. Bimetallic Au–Ag/CeO₂ Catalysts for Preferential Oxidation of CO in Hydrogen-Rich Stream: Effect of Calcination Temperature. *J. Phys. Chem. C* **2014**, *118*, 15226–15233.
 - (36) Casaletto, M. P.; Longo, A.; Martorana, A.; Prestianni, A.; Venezia, A. M. XPS study of supported gold catalysts: the role of Au⁰ and Au^{+δ} species as active sites. *Surf. Interface Anal.* **2006**, *38*, 215–218.
 - (37) Zhang, X.; Qu, Z.; Yu, F.; Wang, Y. High-temperature diffusion induced high activity of SBA-15 supported Ag particles for low temperature CO oxidation at room temperature. *J. Catal.* **2013**, *297*, 264–271.
 - (38) Wu, H.; Wang, L.; Zhang, J.; Shen, Z.; Zhao, J. Catalytic oxidation of benzene, toluene and p-xylene over colloidal gold supported on zinc oxide catalyst. *Catal. Commun.* **2011**, *12*, 859–865.
 - (39) Carabineiro, S. A. C.; Chen, X.; Martynyuk, O.; Bogdanchikova, N.; Avalos-Borja, M.; Pestryakov, A.; Tavares, P. B.; Órfão, J. J. M.; Pereira, M. F. R.; Figueiredo, J. L. Gold supported on metal oxides for volatile organic compounds total oxidation. *Catal. Today* **2015**, *244*, 103–114.
 - (40) Wu, H.; Wang, L.; Shen, Z.; Zhao, J. Catalytic oxidation of toluene and p-xylene using gold supported on Co₃O₄ catalyst prepared by colloidal precipitation method. *J. Mol. Catal. A Chem.* **2011**, *351*, 188–195.
 - (41) Fiorenza, R.; Crisafulli, C.; Condorelli, G.; Lupo, F.; Scirè, S. Au–Ag/CeO₂ and Au–Cu/CeO₂ Catalysts for Volatile Organic Compounds Oxidation and CO Preferential

- Oxidation. *Catal. Letters* **2015**, *145*, 1691–1702.
- (42) Scirè, S.; Minicò, S.; Crisafulli, C.; Satriano, C.; Pistone, A. Catalytic combustion of volatile organic compounds on gold/cerium oxide catalysts. *Appl. Catal. B Environ.* **2003**, *40*, 43–49.
 - (43) Solsona, B.; Pérez-Cabero, M.; Vázquez, I.; Dejoz, A.; García, T.; Álvarez-Rodríguez, J.; El-Haskouri, J.; Beltrán, D.; Amorós, P. Total oxidation of VOCs on Au nanoparticles anchored on Co doped mesoporous UVM-7 silica. *Chem. Eng. J.* **2012**, *187*, 391–400.
 - (44) Tabakova, T.; Ilieva, L.; Petrova, P.; Venezia, A. M.; Avdeev, G.; Zanella, R.; Karakirova, Y. Complete benzene oxidation over mono and bimetallic Au–Pd catalysts supported on Fe-modified ceria. *Chem. Eng. J.* **2015**, *260*, 133–141.
 - (45) da Silva, A. M.; Rodrigues, T.; Taguchi, L. K.; Fajardo, H.; Balzer, R.; Probst, L. D.; Camargo, P. C. Pd-based nanoflowers catalysts: controlling size, composition, and structures for the 4-nitrophenol reduction and BTX oxidation reactions. *J. Mater. Sci.* **2015**, asap, asap. <http://dx.doi.org/10.1007/s10853-015-9315-3>
 - (46) John, J.; Gravel, E.; Hagège, A.; Li, H.; Gacoin, T.; Doris, E. Catalytic Oxidation of Silanes by Carbon Nanotube–Gold Nanohybrids. *Angew. Chemie Int. Ed.* **2011**, *50*, 7533–7536.

Chapter 6. Pd-based Nanoflowers: Controlling Size, Composition and Structures for the 4-nitrophenol Reduction and BTX Oxidation Reactions

6.1. Introduction

Palladium (Pd) nanostructures have been employed as catalysts for a variety of transformations that include oxidation, hydrogenation, reduction, carbon-carbon coupling (Suzuki, Heck, and Stille) reactions, among others.¹⁻⁶ In catalytic applications, strategies that enable one to improve/maximize performance are of vital importance due to high costs and rare reserves of noble metals such as Pd. For instance, catalytic properties can be optimized by maneuvering size, shape (control over exposed surface facets), composition, and structure (solid versus hollow interiors) in metal nanocrystals.⁷⁻¹³ Hollow interiors, for example, may enable higher surface areas relative to their solid analogues.¹⁴ Also, it has been demonstrated that bimetallic compositions containing Pd (including Pd-Au and Pd-Ag combinations) have led to improved in catalytic activities towards oxidation and reduction reactions as compared to monometallic nanoparticles due to the synergism/combination of properties between the metal components.^{12,15-20}

Nevertheless, a precise correlation between performance and many of the physical and chemical parameters that define the catalyst (size, shape, composition and structure) is crucial to design nanostructures with desired properties and optimized performances. This remains challenging, as it requires uniform nanomaterials in which several of these parameters must be controlled.²¹ Moreover, practical applications in heterogeneous catalysis require active species to be deposited onto a solid support, as agglomeration may take place during the utilization of the unsupported nanoparticles.^{22,23} This demands the synthesis of controlled nanostructures is

relatively large amounts. Still, several protocols for the controlled synthesis of nanomaterials are limited regarding their large-scale applicability.^{24,25}

We describe herein, a facile strategy for synthesis of bimetallic nanomaterials containing Pd. More specifically, we focused on the synthesis of solid Au@Pd (core@shell) and hollow AgPd nanoflowers displaying controlled sizes and compositions followed by the investigation of their catalytic performance as a function of these parameters towards the 4-nitrophenol reduction and the BTX (benzene, toluene, and *o*-xylene) oxidation. We were interested in studying how the presence of Au in the core of the nanoparticles influence their catalytic performance towards both liquid and gas-phase transformations. In this context, the use of Ag and Au as templates represents an intuitive strategy as Ag lead to hollow interiors while Au lead to solid, core-shell systems. We focused on Pd-based nanoflowers as their surface is comprised of small Pd branches/petals, making them attractive for catalytic applications as they enable one, at least in principle, to achieve higher surface areas relative to their rounded counterparts.^{19,26–29} While their size could be controlled as a function of the Pd growth time, their structure was dependent on the nature of the seeds employed for the synthesis, i.e., Au or Ag nanoparticles. Our protocol could be scaled-up by 100 folds and the resulting nanoflowers supported onto commercial silica with highly uniform dispersion. This enabled us to investigate the catalytic performance of both unsupported and supported nanoflowers (towards the 4-nitrophenol reduction and BTX oxidation, respectively). While 4-aminophenol (product from the reduction of 4-nitrophenol) represents an important intermediate in the synthesis of several analgesic and antipyretic drugs,^{30,31} benzene, toluene, and *o*-xylene comprise volatile organic compounds that are recognized as hazardous contaminants, and their catalytic oxidation has been acknowledged as an effective approach for their removal.^{32–36} It is important to note that current challenges for the BTX oxidation include: achieve substantial

conversions at low temperature, avoid the formation of side products, and decrease the amount of noble metal in the catalyst.

6.2. Experimental Section

6.2.1. Materials and Instrumentation

Analytical grade chemicals chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich), silver nitrate (AgNO_3 , 99%, Sigma-Aldrich), potassium tetrachloropalladate trihydrate ($\text{K}_2\text{PdCl}_4 \cdot 3\text{H}_2\text{O}$, 98%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$, 99%, Vetec), L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 99%, Sigma-Aldrich), sodium borohydride (NaBH_4 , 98%, Sigma-Aldrich), sodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%, Sigma-Aldrich), silica (pore size 22 Å, 800 m^2/g , CAS number 112926-00-8, Sigma-Aldrich), benzene (C_6H_6 , >99%, Vetec), toluene (C_7H_8 , >99%, Vetec), and o-xylene (C_8H_{10} , >99%, Vetec). The scanning electron microscopy (SEM) images were obtained using a JEOL field emission gun microscope JSM 6330F operated at 5 kV. The samples were prepared by dropcasting an aqueous suspension containing the nanostructures over a silicon wafer, followed by drying under ambient conditions. Transmission electron microscopy (TEM) images were obtained with a JEOL 1010 microscope operating at 80 kV or a JEOL JEM 2100 microscope operated at 200 kV. Samples for TEM were prepared by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 or UV-3101 PC spectrophotometer. The average sizes were determined by measuring the diameter of 50 nanostructures with the quoted errors corresponding to the standard deviation of the data

from the TEM images. The Au, Ag, and Pd atomic percentages were measured by flame atomic absorption spectrometry (FAAS) with a Shimadzu spectrophotometer, model AA-6300, equipped with an air-acetylene flame. Regarding the sample preparation for FAAS, a 10 mL aliquot of a suspension containing the nanoflowers was centrifuged and the supernatant was decanted. This solid, or 10 mg of the supported catalysts, were then digested with 3 mL of aqua regia, and 7 mL of water was added. This mixture was left under stirring for 1 h, and a 1 mL aliquot was employed in the analysis.

6.2.2. Synthesis of Au and Ag NPs seeds

Au seeds were prepared by the citrate reduction approach.³⁷ In a typical procedure, 30 mL of 0.25 mM AuCl_4^- were added to a 100 mL round-bottom flask under magnetic stirring. This system was heated to 100°C for 15 minutes, followed by the addition of 0.9 mL of 1 wt. % sodium citrate dihydrate. The reaction was allowed to proceed for another 10 min, yielding a red suspension containing the Au NPs.

Ag seeds were prepared by the polyol process.³⁸ Briefly, 5 mg of polyvinylpyrrolidone (PVP) was dissolved in 37.5 mL of ethylene glycol. Then, AgNO_3 (200 mg, 1.2 mmol) was added and mixed until complete dissolution. The resulting solution was heated to 125 °C and kept at this temperature for 2.5 hours, leading to the appearance of a greenish-yellow color due to the formation of the Ag NPs. The reaction mixture was then allowed to cool to room temperature and diluted to 125 mL with water.

6.2.3. Synthesis of solid Au@Pd and hollow AgPd nanoflowers

Solid Au@Pd and hollow AgPd nanoflowers were synthesized by a seed-mediated growth approach. In a typical procedure, 10 μL or 400 μL of the as-prepared Ag or Au seeds, respectively,

was added to 9.4 mL of a PVP aqueous solution (0.1 wt %). This mixture was transferred to a 25 mL round-bottom flask and stirred at 50 °C for 10 min, followed by the addition of 0.1 mL of 30 mM aqueous hydroquinone solution. After 2 min, 170 μL of a 12 mM $\text{PdCl}_4^{2-}(\text{aq})$ solution was added to this mixture. In order to control and monitor the growth of the produced Au@Pd and AgPd nanoflowers, the reaction was quenched at different time intervals: 15 s, 1 min, 5 min, 10 min, 30 min and 1 hour (several parallel reactions were carried out). The reactions were quenched by the addition of 0.1 mL of 0.3 M $\text{HCl}(\text{aq})$ solution to the reaction mixture and cooling to 0° C in an ice water bath. The nanostructures isolated and washed three times with ethanol by successive rounds of centrifugation at 10000 rpm and removal of the supernatant. After washing, the nanoparticles were suspended in 10 mL of water. For the scale-up syntheses, the 25 mL round-bottom flask was replaced by a 2000-mL flask, and the volumes of all solutions were increased by a factor of 100. The formation of solid Au@Pd and hollow AgPd nanoflowers were not dependent on the presence of reducing agents, PVP, or ethylene glycol from the synthesis of Au or Ag NPs. The concentration of the starting Ag and Au NPs suspensions were 2.16 and 0.24 mM, respectively. This corresponded to 1.2×10^{17} and 3.0×10^{15} NPs/L, respectively. The differences in the volumes of Ag and Au NPs suspensions employed during the synthesis of the nanoflowers were chosen in order to match the number of seeds/particles in each case.

6.2.4. Catalytic activity towards the 4-nitrophenol reduction

For the catalytic tests of the 4-nitrophenol reduction, 300 μL of a 1.4×10^{-4} M 4-nitrophenol aqueous solution, 2 mL of 4.2×10^{-2} M sodium borohydride aqueous solution, and 100 μL of as-prepared nanoflowers were added into a quartz cuvette. Then, the change in absorbance at 400 nm was monitored by UV–Vis spectroscopy. In this case, the color of the solution gradually changed from yellow to transparent owing to the reduction of 4-nitrophenol to 4 aminophenol. The color

changes associated with the conversion of 4-nitrophenolate to 4-aminophenol enables one to easily monitor the reaction kinetics by UV–VIS spectroscopy. In order to estimate the product conversion, we employed a calibration curve for 4-nitrophenolate concentration as function of the Absorbance at 400 nm. The catalytic activities of Au@Pd and AgPd hollow nanoflowers were described by TOF (turnover frequency) rates.³⁹ The TOF can be defined as the number of completed catalytic cycles per atom in catalytic surface of the catalyst as a function of time, and was calculated according to the equation 1:

$$\text{TOF} = C_{4\text{NP}}/(C_{\text{M}} \cdot t) \quad (1)$$

where $C_{4\text{NP}}$ denotes the concentration of 4-nitrophenolate converted to 4-aminophenol, C_{M} the total metal concentration, and t the time.

6.2.5. Synthesis of 1 wt. % solid Au@Pd and hollow AgPd nanoflowers supported on silica

The solid Au@Pd and hollow AgPd nanoflowers supported on commercial silica by a wet impregnation method at 1 wt % (in terms of total metal content).⁴⁰ In typical experiment, 1 L of the nanoflowers suspension obtained after 30 min of reaction was concentrated to 50 mL. Then, 1 g of silica was added to resulting suspension and stirred vigorously at 80 °C until the formation of a paste. Then, 50 mL of distilled water was added and the suspension was kept under stirring to dryness (5 h). The catalysts were then treated at 120 °C for 2 h under air.

6.2.6. Catalytic activity towards benzene, toluene and o-xylene oxidation (BTX oxidation)

The catalytic oxidation of benzene, toluene and o-xylene was performed in a fixed bed tubular quartz reactor under atmospheric pressure. The following conditions were chosen: 0.030g

catalyst, inlet benzene (1.2 g.m^{-3}), toluene (0.7 g.m^{-3}), o-xylene (0.5 g.m^{-3}) in air, gas flow rate $20 \text{ cm}^3.\text{min}^{-1}$, residence time 0.3s , gas hourly space velocity 12000 h^{-1} and temperature range $25\text{-}300^\circ\text{C}$. The reaction data were collected after at least 2 h on-stream at room temperature. The reaction products were determined by GC-MS. The reactant and product mixtures were analyzed using two on-line gas chromatographs equipped with FID and TCD detector and an HP-5 column. The catalytic activity was expressed as the degree of the conversion of benzene, toluene and o-xylene, respectively. The conversion of the BTX compounds was calculated as follows:

$$\text{CBTXs (\%)} = [(\text{BTXs})_{\text{in}} - (\text{BTXs})_{\text{out}}] \cdot 100 / (\text{BTXs})_{\text{in}} \quad (2)$$

where CBTXs (%) = percentage of BTX conversion; $(\text{BTXs})_{\text{in}}$ = input quantity and $(\text{BTXs})_{\text{out}}$ = output quantity.

6.3. Results and Discussion

Our studies started with the synthesis of solid Au@Pd and hollow AgPd nanoflowers as shown in Scheme 6.1. Solid Au@Pd nanoflowers could be obtained by a seed-mediated approach, in which Au NPs were employed as seeds (physical templates) for Pd growth in the presence of hydroquinone as the reducing agent (Scheme 6.1 A).¹⁹ The synthesis of hollow AgPd nanoflowers, on the other hand, was based on the utilization of Ag NPs as chemical templates for Pd growth in the presence of hydroquinone. This approach is shown in Scheme 6.1 B and combines the galvanic replacement reaction between Ag and $\text{PdCl}_4^{2-}(\text{aq})$ (which leads to the Ag oxidation and its subsequent dissolution from the core together with $\text{PdCl}_4^{2-}(\text{aq})$ reduction and deposition) and PdCl_4^{2-}

(aq) reduction to Pd by hydroquinone (that contribute to the formation of the nanoflower morphology).⁴¹

Scheme 6.1. Approach for the synthesis of solid Au@Pd and hollow AgPd nanoflowers. Solid Au@Pd nanoflowers (A) were obtained by the utilization of Au NPs as physical templates for Pd growth, while hollow AgPd nanoflowers (B) were obtained by the combination of the galvanic replacement reaction between Ag NPs and $\text{PdCl}_4^{2-}(\text{aq})$ and the co-reduction with hydroquinone.

Figure 6.1 A shows a TEM image of Au NPs that were employed as seeds for the synthesis of Au@Pd nanoflowers. They were 15 ± 2 nm in diameter and displayed quasi-spherical shape. The Au@Pd nanoflowers obtained at different time intervals after the $\text{PdCl}_4^{2-}(\text{aq})$ addition to the reaction mixture containing the Au NPs seeds are shown in Figure 6.1 B-D. Our results show that the size of the Au@Pd nanoflowers could be controlled by varying the growth time before the

$\text{PdCl}_4^{2-}(\text{aq})$ reduction to Pd was quenched by the addition of HCl to the reaction mixture. Specifically, Figure 6.1 B-D show the Au@Pd materials obtained by quenching the $\text{PdCl}_4^{2-}(\text{aq})$ reduction after 15 s, 5 min, and 30 min of growth, respectively.

Figure 6.1. (A-D) TEM images of Au NPs (A) employed as templates for the synthesis of solid Au@Pd nanoflowers (B-D) with controlled sizes as a function of the Pd growth time: 15 s (B), 5 min (C), and 30 min (D). (E-H) TEM images of Ag NPs (E) employed as templates for the synthesis of hollow AgPd nanoflowers (F-H) with controlled sizes by adjusting the Pd growth time: 15 s (F), 5 min (G), and 30 min (H). The scale bars in the insets correspond to 10 (A-D) or 20 nm (E-H).

A more detailed morphology evolution as a function of time is depicted in Figure 6.2. In all cases, the materials displayed quasi-spherical shape and were relatively monodisperse in size. The mass-thickness contrast detected from the TEM images confirms the formation of a Au@Pd core-shell architecture. The size of the Au@Pd nanoflowers corresponded to $17 \text{ nm} \pm 2 \text{ nm}$, $29 \text{ nm} \pm 3 \text{ nm}$, and $39 \text{ nm} \pm 3 \text{ nm}$ for 15 s, 5 min, and 30 min growth, respectively (corresponding to Pd shell thicknesses of $2 \text{ nm} \pm 0.3 \text{ nm}$, $14 \pm 2 \text{ nm}$, and $25 \pm 3 \text{ nm}$ respectively).

Figure 6.2. (A-I) TEM images of Au NPs (A) employed as templates for the synthesis of solid Au@Pd nanoflowers (B-I) with controlled sizes as a function of the Pd growth time: 15 s (B), 1 min (C), 5 min (D), 10 min (E), 20 min (F), 30 min (G), 45 min (H), 1h (I).

Figure 6.1 E-H show TEM images of Ag NPs seeds (Figure 6.1 E, 35 ± 4 nm in diameter) and the corresponding AgPd nanoflowers (Figure 6.1 F-H) obtained after the addition of PdCl_4^{2-} (aq) to the reaction mixture containing the Ag NPs at different time intervals (15 s, 5 min, and 30 min, respectively). The AgPd nanoflowers also displayed quasi-spherical shape and monodisperse sizes. The mass-thickness contrast from TEM images (Figure 6.1 F-H) clearly show the formation of hollow interiors in all AgPd nanoflowers. As discussed for Au@Pd nanomaterials, the size of the hollow AgPd nanoflowers (Pd shell thickness) could also be tailored as a function of the growth time during the synthesis. Their outer diameters corresponded to $42 \text{ nm} \pm 3 \text{ nm}$, $60 \text{ nm} \pm 5 \text{ nm}$, and $77 \text{ nm} \pm 5 \text{ nm}$ when the growth time was 15 s, 5 min, and 30 min, respectively (Pd shell

thicknesses of $8 \text{ nm} \pm 2 \text{ nm}$, $26 \pm 4 \text{ nm}$, and $45 \text{ nm} \pm 4 \text{ nm}$ respectively). Here, the shell thickness in Au@Pd and AgPd nanoflowers is controlled by the growth time, the size of the Ag and Au NPs employed as seeds, and the method for Pd deposition. In the Au@Pd nanomaterials, Pd was deposited over the Au seeds only by precursor reduction in the presence of hydroquinone. However, for AgPd nanoflowers, Pd was deposited by both precursor reduction in the presence of hydroquinone and galvanic replacement reaction between Ag and PdCl_4^{2-} , which led to larger shell thicknesses relative to Au@Pd nanoflowers. Additional TEM images for AgPd nanoflowers are shown in Figure 6.3.

Figure 6.3. (A-F) TEM images of Ag NPs (A) employed as templates for the synthesis of hollow AgPd nanoflowers (B-F) with controlled sizes as a function of the Pd growth time: 15 s (B), 1 min (C), 5 min (D), 10 min (E), 30 min (F).

The UV-VIS extinction properties of solid Au@Pd and hollow AgPd nanoflowers obtained at different growth times are in agreement with a formation of a Pd shell over the Au NPs and the Pd deposition accompanied by Ag oxidation and subsequent dissolution to yield hollow interiors (Figure 6.4).

Figure 6.4. UV-VIS extinction spectra as a function of reaction/growth time during the synthesis of Au@Pd (A) and AgPd (B) nanoflowers.

The signal at 525 and 411 nm (for Au and Ag NPs, respectively) can be assigned to the dipole mode of the surface plasmon resonance (SPR) excitation.^{37,38} It can be observed that this signal disappear after 15 s growth in both materials in agreement with a formation of a Pd shell over the Au NPs and the Ag oxidation and subsequent dissolution to yield hollow interiors. Also, a strong signal at 246 nm appeared for both Au@Pd and AgPd nanoflowers after 15 s. Its signal intensity increased as function of time, and can be associated with the increased Pd deposition at the surface with time.¹⁹ Interestingly, a band at 287 nm can also be observed in the Au@Pd and AgPd spectra. This signal is often related to the presence of free Pd clusters in suspension, which suggest that Pd growth may take place by cluster attachment.¹⁹ For Au@Pd nanoflowers, this signal appeared after 15 s growth and then decreased in intensity only after 30 min. On the other hand, for AgPd nanoflowers, this peak was detected after 15 s growth and practically disappeared after 1 min. These observations agree with a faster reduction/growth kinetics for AgPd nanoflowers relative to Au@Pd, as Pd nucleation and growth is favored both by $\text{PdCl}_4^{2-}(\text{aq})$ reduction by hydroquinone and the galvanic replacement reaction between $\text{PdCl}_4^{2-}(\text{aq})$ and Ag.

Figure 6.5 shows TEM images of the Au@Pd nanoflowers obtained without washing via successive steps of centrifugation and removal of the supernatant, which shows the presence of small Pd clusters together with the nanoflowers and indicate that Pd growth occurred by cluster attachment.¹⁹

Figure 6.5. TEM images of Au@Pd nanoflowers obtained after quenching the Pd growth 15 s (A) and 1 min (B) without washing the reaction mixture by successive rounds of centrifugation and removal of the supernatant. The presence of several small Pd nanoparticles can be detected, suggesting a growth mechanism via cluster attachment in the presence of hydroquinone.

The compositional variations on Au@Pd and AgPd nanoflowers as a function of growth time determined FAAS (flame atomic absorption spectroscopy) analysis are shown in Tables 6.1 and 6.2, respectively. Specifically, the Pd at. % corresponded to 42, 73, and 88 in the Au@Pd and to 62, 80, and 92 in the AgPd nanoflowers obtained after 15 s, 5 min, 30 min growth, respectively. Therefore, the Au@Pd and AgPd nanoflowers obtained after 15 s, 5 min, and 30 min growth could be denoted as Au₅₈@Pd₄₂, Au₂₇@Pd₇₃, and Au₁₂@Pd₈₈, respectively, and Ag₃₈Pd₆₂, Ag₂₀Pd₈₀, and Ag₈Pd₉₂, respectively. The increase in the Pd at. % as a function of time is in agreement with the growth of the Pd shells as illustrated by the TEM results.

Table 6.1. Atomic percentages of Au and Pd in Au@Pd nanoflowers as a function of growth obtained by FAAS.

Growth time	Au (at. %)	Pd (at. %)	Sample
15s	58	42	Au ₅₈ @Pd ₄₂
1 min	42	58	Au ₄₂ @Pd ₅₈
5 min	27	73	Au ₂₇ @Pd ₇₃
10 min	18	82	Au ₁₈ @Pd ₈₂
30 min	12	88	Au ₁₂ @Pd ₈₈
1 h	10	90	Au ₁₀ @Pd ₉₀

Table 6.2. Atomic percentages of Ag and Pd in AgPd nanoflowers as a function of growth time obtained by FAAS.

Growth time	Ag (at. %)	Pd (at. %)	Sample
15s	38	62	Ag ₃₈ Pd ₆₂
1 min	27	73	Ag ₂₇ Pd ₇₃
5 min	20	80	Ag ₂₀ Pd ₈₀
10 min	13	87	Ag ₁₃ Pd ₈₇
30 min	8	92	Ag ₈ Pd ₉₂
1 h	4	96	Ag ₄ Pd ₉₆

Figure 6.6 shows HRTEM images for Au@Pd (Figure 6.6 A, C, and E) and AgPd (Figure 6.6 B, D, and F) nanoflowers obtained after 30 min growth. The images for individual nanoflowers (Figure 6.6 A and B) as well as zoom-in images for the core regions (Figure 6.6 C and D) clearly show the formation of solid or hollow interiors for Au@Pd and AgPd nanoflowers, respectively. Phase-contrast images for the shell regions (Figure 6.6 E and F) show the presence of Pd single crystalline domains, in which the Pd {111} lattice fringes can be clearly visualized.

Figure 6.6. HRTEM images for Au@Pd (A, C, and E) and AgPd (B, D, and F) nanoflowers obtained after 30 min growth. (A) and (B) show individual nanoflowers; (C) and (D) display their core regions; and (E) and (F) depict their shells. Solid and hollow interiors as well as single-crystalline Pd domains on their shells can be clearly observed from the images.

In order to unravel the role played by hydroquinone as a reducing agent to promote the formation of the nanoflower morphology, we performed a series of experiments regarding the synthesis of Au@Pd and AgPd nanostructures under the same experimental conditions as those describe in Figure 6.1 by replacing hydroquinone with ascorbic acid, sodium borohydride, or

sodium citrate. The effect of the reducing agent over the morphology of Au@Pd and AgPd materials results are shown in Figure 6.7 and 6.8, respectively.

Figure 6.7. TEM images of Au@Pd solid nanostructures obtained after 1 h growth by employing ascorbic acid (A) sodium borohydride (B), sodium citrate (C), and hydroquinone (D) as the reducing agents.

The utilization of ascorbic acid as the reducing agent led to the formation of Au@Pd core-shell materials containing small bumps at the surface only after 1 h of reaction (Figure 6.7 A). When sodium borohydride was employed as a reducing agent, we could observe the formation of Au@Pd nanodendrites after 1 hour (Figure 6.7 B). The presence of some uncoated nanoparticles and free Pd nanoparticles can be observed from the image. No Pd deposition was observed in presence of sodium citrate (Figure 6.7 C). It is important to emphasize that the utilization of hydroquinone led to Au@Pd nanoflowers (after 1 h of growth, Figure 6.7 D) with outer diameters

larger than those observed for Au@Pd materials obtained by using ascorbic acid and sodium borohydride. Regarding AgPd nanostructures, the formation of hollow nanoflowers was not detected when ascorbic acid, sodium borohydride, and sodium citrate were employed as reducing agents. Instead, the formation of AgPd nanoshells was observed (Figure 6.8).

Figure 6.8. TEM images of AgPd hollow nanostructures obtained after 1 h growth by employing ascorbic acid (A), sodium borohydride (B), sodium citrate (C), and hydroquinone (D) as the reducing agents.

Here, nanoshells refer to hollow nanomaterials having smooth surfaces while nanodendrites refer to hollow nanostructures having branches or tips at their surface. Moreover, the formation of Pd clusters could also be detected in the images (Figure 6.8 B-C). These results demonstrate that the utilization hydroquinone is crucial to the formation of the nanoflower morphology in both Au@Pd and AgPd materials. These data also illustrate that the nature of the

reducing agent (reducing strength) strongly affects the kinetics of Pd reduction. As citrate and ascorbic acid are weak reducing agents, it is plausible that they favor a layer-by-layer Pd deposition mechanism to give rise to core@shell (Au seeds) or hollow shell (Ag seeds) materials. On the other hand, sodium borohydride is a strong reducing agent, leading to a fast nucleation and growth kinetics of Pd over the templates and also contributing to the formation of isolated Pd NPs.

In the next step, we were interested in investigating how the catalytic activities of the solid Au@Pd and hollow AgPd nanoflowers were dependent upon size, composition, and nature of the cores (Au, Pd and Ag represent active phases for this transformation). We started our catalytic studies by employing the reduction of 4-nitrophenol by sodium borohydride as a model reaction.^{13,37,42} The calculated TOF (h^{-1}) rates for Au@Pd and AgPd nanoflowers obtained after 15 s, 1 min, and 30 min growth are depicted in Figure 6.9.

Figure 6.9. Turnover frequencies values (TOF, h^{-1}) as a function of size/composition of solid Au@Pd (red trace) and hollow AgPd (black trace) nanoflowers as catalysts towards the 4-nitrophenol reduction.

The TOF rates at stationary state corresponded to 243 ± 4 , 221 ± 3 and $160 \pm 5 \text{ h}^{-1}$ for $\text{Au}_{58}@\text{Pd}_{42}$, $\text{Au}_{27}@\text{Pd}_{73}$, and $\text{Au}_{12}@\text{Pd}_{88}$ materials, respectively. This indicates a decrease in the catalytic activity with the increase in the $\text{Au}@\text{Pd}$ size, which might be related with the reduction in the surface area of the metal nanoparticles. Conversely, TOF values for AgPd nanoflowers corresponded to 127 ± 3 , 179 ± 2 and $170 \pm 4 \text{ h}^{-1}$ for $\text{Ag}_{38}\text{Pd}_{62}$, $\text{Ag}_{20}\text{Pd}_{80}$ and $\text{Ag}_8\text{Pd}_{92}$, respectively. Interestingly, an increase in TOF values was detected with the increase in the AgPd size/shell thickness. These variations in TOF values can be explained as the Pd catalytic activity towards the 4-nitrophenolate reduction is higher relative to Ag.⁴³ Moreover, a synergic effect in bimetallic catalysts containing Au and Pd has been demonstrated for this reaction.^{44,45} Therefore, the Au contribution to the catalytic activity decreases as the Pd content in the nanoflowers increase in the $\text{Au}@\text{Pd}$ material, leading to a decrease in TOF values with an increase in size and lower Au content. Here, it is plausible that it becomes harder for 4-nitrophenolate molecules to diffuse to the Au cores as the shell thickness was gradually increased. On the contrary, the increase in TOF values as a function of size for the AgPd nanoflowers may be explained by the gradual decrease in the Ag at % (which is less active than both Au and Pd) in the AgPd materials, despite the increase in size.

When we compare the solid $\text{Au}@\text{Pd}$ and hollow AgPd nanoflowers, $\text{Au}_{58}@\text{Pd}_{42}$ and $\text{Au}_{27}@\text{Pd}_{73}$ materials displayed higher catalytic activities than $\text{Ag}_{38}\text{Pd}_{62}$ and $\text{Ag}_{20}\text{Pd}_{80}$, respectively. It is plausible that the Au cores in the $\text{Au}@\text{Pd}$ nanoflowers can contribute to improve the catalytic activities for 4-nitrophenolate reduction relative to the hollow AgPd material. As Au is much more active than Ag for this transformation, solid $\text{Au}@\text{Pd}$ become better catalysts than hollow AgPd nanoflowers. Interestingly, at bigger sizes, in which the compositions become very similar ($\text{Au}_{12}@\text{Pd}_{88}$ and $\text{Ag}_8\text{Pd}_{92}$ materials), hollow $\text{Ag}_8\text{Pd}_{92}$ nanoflowers displayed slightly higher

TOF values as compared to the solid $\text{Au}_{12}@\text{Pd}_{88}$ material, even though the $\text{Ag}_8\text{Pd}_{92}$ nanoflowers have bigger outer diameters/shell thickness than to $\text{Au}_{12}@\text{Pd}_{88}$. This observation suggests that the hollow interiors contribute for improving the catalytic performance relative to the solid material at bigger sizes. We also performed control experiments in which we compared the catalytic activities towards the reduction of 4-nitrophenol of the AgPd and Au@Pd nanoflowers obtained after 30 min growth relative to monometallic Ag (Figure 6.1 A), Au (Figure 6.1 E), and Pd nanoparticles synthesized under the same experimental conditions as those describe in Figure 6.1 without any seeds (Figure 6.10).

Figure 6.10. SEM images of Pd nanospheres obtained after 30 min growth without the use Ag or Au NPs as seeds employing the same experimental conditions as described in Figure 6.1.

The calculated TOF values (Figure 6.11) clearly show that the activity for both AgPd and Au@Pd nanoflowers were much higher relative to the sum of their individual monometallic nanoparticle counterparts, indicating that both Ag and Ag in the nanoflower structure contributed to the observed catalytic activities.

Figure 6.11. Catalytic activities expressed as TOF values (h^{-1}) for Au@Pd and AgPd nanoflowers relative to the sum of their monometallic counterparts.

Interestingly, our stability tests for the $\text{Au}_{12}\text{@Pd}_{88}$ and $\text{Ag}_8\text{Pd}_{92}$ nanoflowers showed that they could be reused with no significant loss of activity even after 5 catalytic cycles (Figure 6.12), indicating that they were stable under our employed conditions.

Figure 6.12. Catalytic activity expressed in terms of 4-nitrophenol conversion as a function of number of catalytic cycles for (A) $\text{Au}_{12}\text{@Pd}_{88}$ and (B) $\text{Ag}_8\text{Pd}_{92}$ nanoflowers.

In order to further evaluate the role played by the nature of the cores, we decided to investigate the catalytic activity of the solid Au@Pd and hollow AgPd nanoflowers obtained after 30 min ($\text{Au}_{12}\text{@Pd}_{88}$ and $\text{Ag}_8\text{Pd}_{92}$) towards the gas-phase BTX oxidation. To this end, we scaled-up the synthesis of the nanoflowers by 100 folds and supported the resulting material onto commercial silica. It can be observed that the $\text{Au}_{12}\text{@Pd}_{88}$ and $\text{Ag}_8\text{Pd}_{92}$ nanoflowers obtained after the scaled-up synthesis (Figure 6.13) displayed essentially the same morphology as those described in Figure 6.1. The yield of AgPd nanoflowers was 89.7 and 85.5 % for the typical and scaled up syntheses, respectively. For Au@Pd, these values corresponded to 92.1 and 87.7 %, respectively.

Figure 6.13. TEM images of Au@Pd (A and B) and AgPd (C and D) nanoflowers before (A and C) and after (B and D) scaling up the synthesis by 100 folds.

The nanoflowers were then supported on silica by wet impregnation to generate Au@Pd/SiO₂ and AgPd/SiO₂ catalysts as shown Figure 6.14 A and B (Au@Pd/SiO₂) and Figure 6.14 C and D (AgPd/SiO₂). The concentration in terms of metal of the nanoflowers suspensions

employed for the preparation of the supported materials were 174 and 179 μM for AgPd and Au@Pd, respectively. The metal wt. % in the supported catalysts was determined by FAAS. This approach enabled the uniform distribution (without agglomeration) of nanoflowers over the entire surface of the support. The metal loading in both materials corresponded to 1 % in weight.

Figure 6.14. SEM images of Au@Pd/SiO₂ (A and B) and AgPd/SiO₂ (C and D) materials obtained by the wet impregnation of Au@Pd and AgPd nanoflowers onto commercial SiO₂, illustrating the uniform dispersion of the nanoflowers over the silica support.

Figure 6.15 depicts the conversion for the oxidation of BTX as a function of reaction temperature employing Au@Pd/SiO₂, AgPd/SiO₂, and pure SiO₂ as the catalysts (the inset in Figure 6.15 shows a scheme for the BTX oxidation reaction). While no significant conversion was detected for the pure SiO₂ support, both Au@Pd/SiO₂ and AgPd/SiO₂ displayed good catalytic activities at relatively low temperatures. The oxidation of benzene, toluene and o-xylene began to take place at above 25, 50 and 75°C, respectively. Only H₂O and CO₂ were detected as the

oxidation products, and the BTX conversion increased with temperature for both Au@Pd/SiO₂ and AgPd/SiO₂ catalysts.

Figure 6.15. Oxidation (conversion %) of benzene (A), toluene (B), and *o*-xylene (C) as a function of temperature catalyzed by Au@Pd/SiO₂, AgPd/SiO₂, and SiO₂.

Solid Au@Pd/SiO₂ was more active than the hollow AgPd/SiO₂ nanoflowers for the BTX oxidation reactions mainly at the higher temperatures. Specifically, 81 and 72 % conversion for benzene, 68 and 53 % conversion for toluene, and 41 and 36 % conversion for *o*-xylene were detected at 300 °C when Au@Pd/SiO₂ and AgPd/SiO₂ nanoflowers were employed as catalysts, respectively. Assuming the same noble metal content for both catalysts (1 wt%), the larger size of the hollow Ag₈Pd₉₂ nanoflower can lead to a poorer dispersion on the SiO₂ support. Thus, the higher conversion percentages presented by the Au@Pd/SiO₂ catalyst can be explained by the better dispersion of the Au₁₂@Pd₈₈ nanoflower on the SiO₂ support and also the fact that Au and Pd display higher catalytic activities than Ag towards the BTX oxidation (Figure 6.14).⁴⁶ Besides, the oxidation of organic compounds promoted by noble metal catalysts is recognized as a catalyst structure sensitive reaction.^[47] As discussed for the 4-nitrophenol reduction, Au nanomaterials can also catalyze the BTX conversion. Therefore, it is plausible that, as the diffusion of gas molecules through the Pd shells in both Au@Pd and AgPd nanoflowers may be easier relative to liquid species, the Au core in the Au@Pd material can contribute to improve the catalytic activity towards BTX oxidation relative to the hollow AgPd nanoflowers. This shows that the nature and structure of the core can influence the catalytic performance in bimetallic core-shell architectures. For instance, a catalytically active core may contribute to boost the catalytic activity for a gas-phase reaction relative to the hollow (shell) material. Some authors have reported high catalytic activities for Au-Pd based catalysts having a core-shell morphology (Au-rich core and a Pd-rich shell) towards oxidation reactions due to the synergetic effect between the noble metals.^{48,49} We believe that our results represent an important improvement in terms of performance relative to conventional systems. For instance, the conversion percentages reported in our paper are significantly higher (at lower metal loadings) as compared to conventional Au, Pd and Au-Pd/SiO₂

catalysts employing the same experimental conditions.²³ Specifically, while ~ 5 nm conventional Pd nanoparticles deposited over SiO₂ at 5 wt. % loading having high dispersion displayed < 50% conversion towards the benzene oxidation at 300°C, the Au@Pd and AgPd nanoflowers deposited over SiO₂ at 1 wt. % loading displayed 81 and 72 % conversions at this temperature, respectively.²³

6.4. Conclusion

In summary, we described the synthesis of Au@Pd and AgPd nanoflowers displaying well-defined and controlled sizes, compositions, and structure (solid versus hollow interiors), which enabled us to investigate how the presence of Au in the nanoflower's core affected their catalytic performance. Regarding the catalytic activities for the reduction of 4-nitrophenol, our data suggested that the Au in the core of the particles was capable of boosting the catalytic performance relative to the hollow material when the Pd at. % in the nanoflowers were up to 80. Above this value, the hollow Ag₈Pd₉₂ nanoflowers had a slightly higher catalytic activity than the solid Au₁₂@Pd₈₈. On the contrary, solid Au₁₂@Pd₈₈ nanoflowers displayed higher catalytic activities towards the BTX oxidation as compared to the Ag₈Pd₉₂ material. In this case, the Au content from the core of the nanoflowers could contribute to the catalytic activity even at higher Pd at. % values (larger sizes/shell thickness). These results indicate that the catalytic activities in core-shell and hollow systems are also sensitive to the type of reaction (liquid vs. gas phases). Therefore, we believe that our results may serve as a platform not only to the synthesis of bimetallic nanomaterials based on Pd displaying controlled compositions, architectures, and structures (both supported and unsupported), but also to understand how these parameters affect their catalytic activity for different classes of reactions.

6.5. References

- (1) Cheong, S.; Watt, J. D.; Tilley, R. D. Shape Control of Platinum and Palladium Nanoparticles for Catalysis. *Nanoscale* **2010**, 2 (10), 2045–2053.
- (2) Yin; Liebscher, J. Carbon–Carbon Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts. *Chem. Rev.* **2006**, 107 (1), 133–173.
- (3) Long, R.; Mao, K.; Ye, X.; Yan, W.; Huang, Y.; Wang, J.; Fu, Y.; Wang, X.; Wu, X.; Xie, Y.; et al. Surface Facet of Palladium Nanocrystals: A Key Parameter to the Activation of Molecular Oxygen for Organic Catalysis and Cancer Treatment. *J. Am. Chem. Soc.* **2013**, 135 (8), 3200–3207.
- (4) Speziali, M. G.; Silva, A. G. M. da; Miranda, D. M. V. de; Monteiro, A. L.; Robles-Dutenhefner, P. A. Air Stable Ligandless Heterogeneous Catalyst Systems Based on Pd and Au Supported in SiO₂ and MCM-41 for Suzuki–Miyaura Cross-Coupling in Aqueous Medium. *Appl. Catal. A Gen.* **2013**, 462–463 (0), 39–45.
- (5) Saldan, I.; Semenyuk, Y.; Marchuk, I.; Reshetnyak, O. Chemical Synthesis and Application of Palladium Nanoparticles. *J. Mater. Sci.* **2015**, 50 (6), 2337–2354.
- (6) da Silva, A. M.; Robles-Dutenhefner, P.; Dias, A.; Fajardo, H.; Lovón, A. P.; Lovón-Quintana, J.; Valença, G. Gold, Palladium and Gold–palladium Supported on Silica Catalysts Prepared by Sol–gel Method: Synthesis, Characterization and Catalytic Behavior in the Ethanol Steam Reforming. *J. Sol-Gel Sci. Technol.* **2013**, 67 (2), 273–281.
- (7) Crespo-Quesada, M.; Yarulin, A.; Jin, M.; Xia, Y.; Kiwi-Minsker, L. Structure Sensitivity of Alkynol Hydrogenation on Shape- and Size-Controlled Palladium Nanocrystals: Which Sites Are Most Active and Selective? *J. Am. Chem. Soc.* **2011**, 133 (32), 12787–12794.
- (8) Jin, M.; Zhang, H.; Xie, Z.; Xia, Y. Palladium Nanocrystals Enclosed by {100} and {111} Facets in Controlled Proportions and Their Catalytic Activities for Formic Acid Oxidation. *Energy Environ. Sci.* **2012**, 5 (4), 6352–6357.
- (9) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O’Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, 14 (4), 1921–1926.
- (10) Bai, S.; Wang, X.; Hu, C.; Xie, M.; Jiang, J.; Xiong, Y. Two-Dimensional G-C₃N₄: An Ideal Platform for Examining Facet Selectivity of Metal Co-Catalysts in Photocatalysis. *Chem. Commun.* **2014**, 50 (46), 6094–6097.
- (11) Long, R.; Zhou, S.; Wiley, B. J.; Xiong, Y. Oxidative Etching for Controlled Synthesis of Metal Nanocrystals: Atomic Addition and Subtraction. *Chem. Soc. Rev.* **2014**, 43 (17), 6288–6310.
- (12) Rodrigues, T.; da Silva, A. M.; Macedo, A.; Farini, B.; Alves, R.; Camargo, P. C. Probing the Catalytic Activity of Bimetallic versus Trimetallic Nanoshells. *J. Mater. Sci.* **2015**, 50 (16), 5620–5629.
- (13) Wang, X.; Fu, J.; Wang, M.; Wang, Y.; Chen, Z.; Zhang, J.; Chen, J.; Xu, Q. Facile Synthesis of Au Nanoparticles Supported on Polyphosphazene Functionalized Carbon

- Nanotubes for Catalytic Reduction of 4-Nitrophenol. *J. Mater. Sci.* **2014**, *49* (14), 5056–5065.
- (14) Lou, X. W. (David); Archer, L. A.; Yang, Z. Hollow Micro-/Nanostructures: Synthesis and Applications. *Adv. Mater.* **2008**, *20* (21), 3987–4019.
 - (15) Scott, R. W. J.; Datye, A. K.; Crooks, R. M. Bimetallic Palladium–Platinum Dendrimer-Encapsulated Catalysts. *J. Am. Chem. Soc.* **2003**, *125* (13), 3708–3709.
 - (16) Wang, D.; Villa, A.; Porta, F.; Prati, L.; Su, D. Bimetallic Gold/Palladium Catalysts: Correlation between Nanostructure and Synergistic Effects. *J. Phys. Chem. C* **2008**, *112* (23), 8617–8622.
 - (17) Song, H. M.; Anjum, D. H.; Sougrat, R.; Hedhili, M. N.; Khashab, N. M. Hollow Au@Pd and Au@Pt Core-Shell Nanoparticles as Electrocatalysts for Ethanol Oxidation Reactions. *J. Mater. Chem.* **2012**, *22* (48), 25003–25010.
 - (18) Zhang, S.; Metin, Ö.; Su, D.; Sun, S. Monodisperse AgPd Alloy Nanoparticles and Their Superior Catalysis for the Dehydrogenation of Formic Acid. *Angew. Chemie Int. Ed.* **2013**, *52* (13), 3681–3684.
 - (19) Xu, J.; Wilson, A. R.; Rathmell, A. R.; Howe, J.; Chi, M.; Wiley, B. J. Synthesis and Catalytic Properties of Au–Pd Nanoflowers. *ACS Nano* **2011**, *5* (8), 6119–6127.
 - (20) Kuai, L.; Yu, X.; Wang, S.; Sang, Y.; Geng, B. Au–Pd Alloy and Core–Shell Nanostructures: One-Pot Coreduction Preparation, Formation Mechanism, and Electrochemical Properties. *Langmuir* **2012**, *28* (18), 7168–7173.
 - (21) Xiong, Y.; Xia, Y. Shape-Controlled Synthesis of Metal Nanostructures: The Case of Palladium. *Adv. Mater.* **2007**, *19* (20), 3385–3391.
 - (22) Phan, N. T. S.; Van Der Sluys, M.; Jones, C. W. On the Nature of the Active Species in Palladium Catalyzed Mizoroki–Heck and Suzuki–Miyaura Couplings – Homogeneous or Heterogeneous Catalysis, A Critical Review. *Adv. Synth. Catal.* **2006**, *348* (6), 609–679.
 - (23) da Silva, A. G. M.; Fajardo, H. V.; Balzer, R.; Probst, L. F. D.; Lovón, A. S. P.; Lovón-Quintana, J. J.; Valença, G. P.; Schreine, W. H.; Robles-Dutenhefner, P. A. Versatile and Efficient Catalysts for Energy and Environmental Processes: Mesoporous Silica Containing Au, Pd and Au–Pd. *J. Power Sources* **2015**, *285* (0), 460–468.
 - (24) Lim, B.; Jiang, M.; Tao, J.; Camargo, P. H. C.; Zhu, Y.; Xia, Y. Shape-Controlled Synthesis of Pd Nanocrystals in Aqueous Solutions. *Adv. Funct. Mater.* **2009**, *19* (2), 189–200.
 - (25) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chemie Int. Ed.* **2009**, *48* (1), 60–103.
 - (26) Fu, G.; Wu, K.; Lin, J.; Tang, Y.; Chen, Y.; Zhou, Y.; Lu, T. One-Pot Water-Based Synthesis of Pt–Pd Alloy Nanoflowers and Their Superior Electrocatalytic Activity for the Oxygen Reduction Reaction and Remarkable Methanol-Tolerant Ability in Acid Media. *J. Phys. Chem. C* **2013**, *117* (19), 9826–9834.
 - (27) Yin, Z.; Zheng, H.; Ma, D.; Bao, X. Porous Palladium Nanoflowers That Have Enhanced Methanol Electro-Oxidation Activity. *J. Phys. Chem. C* **2008**, *113* (3), 1001–1005.

- (28) Mohanty, A.; Garg, N.; Jin, R. A Universal Approach to the Synthesis of Noble Metal Nanodendrites and Their Catalytic Properties. *Angew. Chemie Int. Ed.* **2010**, *49* (29), 4962–4966.
- (29) Gao, Q.; Gao, M.-R.; Liu, J.-W.; Chen, M.-Y.; Cui, C.-H.; Li, H.-H.; Yu, S.-H. One-Pot Synthesis of Branched Palladium Nanodendrites with Superior Electrocatalytic Performance. *Nanoscale* **2013**, *5* (8), 3202–3207.
- (30) Damato, T. C.; de Oliveira, C. C. S.; Ando, R. A.; Camargo, P. H. C. A Facile Approach to TiO₂ Colloidal Spheres Decorated with Au Nanoparticles Displaying Well-Defined Sizes and Uniform Dispersion. *Langmuir* **2013**, *29* (5), 1642–1649.
- (31) Saha, S.; Pal, A.; Kundu, S.; Basu, S.; Pal, T. Photochemical Green Synthesis of Calcium-Alginate-Stabilized Ag and Au Nanoparticles and Their Catalytic Application to 4-Nitrophenol Reduction. *Langmuir* **2009**, *26* (4), 2885–2893.
- (32) Khan, F. I.; Kr. Ghoshal, A. Removal of Volatile Organic Compounds from Polluted Air. *J. Loss Prev. Process Ind.* **2000**, *13* (6), 527–545.
- (33) Iranpour, R.; Cox, H. H. J.; Deshusses, M. A.; Schroeder, E. D. Literature Review of Air Pollution Control Biofilters and Biotrickling Filters for Odor and Volatile Organic Compound Removal. *Environ. Prog.* **2005**, *24* (3), 254–267.
- (34) Everaert, K.; Baeyens, J. Catalytic Combustion of Volatile Organic Compounds. *J. Hazard. Mater.* **2004**, *109* (1–3), 113–139.
- (35) Rezlescu, N.; Rezlescu, E.; Popa, P. D.; Doroftei, C.; Ignat, M. Nanostructured GdAlO₃ Perovskite, a New Possible Catalyst for Combustion of Volatile Organic Compounds. *J. Mater. Sci.* **2013**, *48* (12), 4297–4304.
- (36) Gennequin, C.; Lamallem, M.; Cousin, R.; Siffert, S.; Idakiev, V.; Tabakova, T.; Aboukaïs, A.; Su, B. L. Total Oxidation of Volatile Organic Compounds on Au/Ce–Ti–O and Au/Ce–Ti–Zr–O Mesoporous Catalysts. *J. Mater. Sci.* **2009**, *44* (24), 6654–6662.
- (37) Silva, A. G. M. da; Rodrigues, T. S.; Macedo, A.; Silva, R. T. P. da; Camargo, P. H. C. An Undergraduate Level Experiment on the Synthesis of Au Nanoparticles and Their Size-Dependent Optical and Catalytic Properties. *Quím. Nova*, **2014**, *37* (10), 1716–1720.
- (38) Silvert, P.-Y.; Herrera-Urbina, R.; Duvauchelle, N.; Vijayakrishnan, V.; Elhsissen, K. T. Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 1-Synthesis and Characterization. *J. Mater. Chem.* **1996**, *6* (4), 573–577.
- (39) Boudart, M. Turnover Rates in Heterogeneous Catalysis. *Chem. Rev.* **1995**, *95* (3), 661–666.
- (40) Jiang, S. P. A Review of Wet impregnation—An Alternative Method for the Fabrication of High Performance and Nano-Structured Electrodes of Solid Oxide Fuel Cells. *Mater. Sci. Eng. A* **2006**, *418* (1–2), 199–210.
- (41) da Silva, A. G. M.; de Souza, M. L.; Rodrigues, T. S.; Alves, R. S.; Temperini, M. L. A.; Camargo, P. H. C. Rapid Synthesis of Hollow Ag–Au Nanodendrites in 15 Seconds by Combining Galvanic Replacement and Precursor Reduction Reactions. *Chem. – A Eur. J.* **2014**, *20* (46), 15040–15046.

- (42) Wang, S.; Zhang, J.; Yuan, P.; Sun, Q.; Jia, Y.; Yan, W.; Chen, Z.; Xu, Q. Au Nanoparticle Decorated N-Containing Polymer Spheres: Additive-Free Synthesis and Remarkable Catalytic Behavior for Reduction of 4-Nitrophenol. *J. Mater. Sci.* **2015**, *50* (3), 1323–1332.
- (43) Esumi, K.; Isono, R.; Yoshimura, T. Preparation of PAMAM- and PPI-Metal (Silver, Platinum, and Palladium) Nanocomposites and Their Catalytic Activities for Reduction of 4-Nitrophenol. *Langmuir* **2003**, *20* (1), 237–243.
- (44) Oh, S.-D.; Kim, M.-R.; Choi, S.-H.; Chun, J.-H.; Lee, K.-P.; Gopalan, A.; Hwang, C.-G.; Sang-Ho, K.; Hoon, O. J. Radiolytic Synthesis of Pd-M (M=Ag, Au, Cu, Ni and Pt) Alloy Nanoparticles and Their Use in Reduction of 4-Nitrophenol. *J. Ind. Eng. Chem.* **2008**, *14* (5), 687–692.
- (45) Endo, T.; Kuno, T.; Yoshimura, T.; Esumi, K. Preparation and Catalytic Activity of Au-Pd, Au-Pt, and Pt-Pd Binary Metal Dendrimer Nanocomposites. *Journal of Nanoscience and Nanotechnology*, **2005**, *5* (11), 1875–1882.
- (46) Abbasi, Z.; Haghighi, M.; Fatehifar, E.; Saedy, S. Synthesis and Physicochemical Characterizations of Nanostructured Pt/Al₂O₃-CeO₂ Catalysts for Total Oxidation of VOCs. *J. Hazard. Mater.* **2011**, *186* (2–3), 1445–1454.
- (47) Liotta, L. F. Catalytic Oxidation of Volatile Organic Compounds on Supported Noble Metals. *Appl. Catal. B Environ.* **2010**, *100* (3–4), 403–412.
- (48) Hosseini, M.; Barakat, T.; Cousin, R.; Aboukaïs, A.; Su, B.-L.; De Weireld, G.; Siffert, S. Catalytic Performance of Core-shell and Alloy Pd-Au Nanoparticles for Total Oxidation of VOC: The Effect of Metal Deposition. *Appl. Catal. B Environ.* **2012**, *111–112* (0), 218–224.
- (49) Enache, D. I.; Barker, D.; Edwards, J. K.; Taylor, S. H.; Knight, D. W.; Carley, A. F.; Hutchings, G. J. Solvent-Free Oxidation of Benzyl Alcohol Using Titania-Supported Gold-palladium Catalysts: Effect of Au-Pd Ratio on Catalytic Performance. *Catal. Today* **2007**, *122* (3–4), 407–411.

Chapter 7. Surface Segregated AgAu Tadpole Nanoparticles Synthesized by a Single-step Combining Galvanic Replacement Reaction and Citrate Reduction

7.1. Introduction

One dimension (1D) nanomaterials based on Au have attracted considerable attention for applications that include catalysis,^{1,2} surface-enhanced Raman scattering (SERS) detection,^{3–5} biosensors,⁶ and the development of nanomotors.^{7,8} Among several 1D morphologies, tadpoles are particularly interesting as a result of their unique shape comprising a spherical head and a high aspect ratio tail.^{9–11} Although several papers have described the synthesis of Au tadpoles by reducing AuCl_4^- ions in the presence of citrate or polyvinylpyrrolidone (PVP), a mechanistic understanding of their formation and growth remains unclear and similar bimetallic noble metal systems are largely unexplored.^{9,12} A deeper understanding is imperative to enable the rational design of nanomaterials with well-controlled features and thus the desired chemical and optical properties.

Bimetallic nanomaterials often show enhanced performance compared to single element systems.^{13–17} For instance, bimetallic nanomaterials containing Au and Ag have displayed improved performances in catalysis, electrocatalysis, plasmon-mediated catalysis, and SERS.^{13,18–}

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It has been established that the galvanic replacement reaction between Ag NPs and AuCl_4^- (aq) represents an effective strategy to the synthesis of AgAu nanomaterials with hollow interiors and ultrathin walls in a single step reaction, employing water as the solvent.^{22,23} However, the morphology of the AgAu nanomaterials produced by this approach are usually restricted to shapes

that are hollow analogues of the Ag nanocrystals employed as templates.²² For example, AgAu shells, cages, frames, and tubes have been obtained by using, Ag spheres, cubes, prisms, and wires as starting materials.^{22–25}

Surprisingly, we demonstrate that the addition of citrate in the galvanic replacement reaction between Ag spheres and AuCl_4^- (aq) induces anisotropic growth of Au from the surface of the Ag seeds, providing a facile one-step strategy for the synthesis of hollow headed AgAu tadpoles. Our approach is based on the combination of a galvanic replacement reaction between Ag and AuCl_4^- (aq) and the reduction of AuCl_4^- (aq) to Au in the presence of citrate. The obtained AgAu tadpoles have nodular hollow heads. A ~ 1 nm thick Ag layer is found to cover the entire surface of the tadpoles. A number of control experiments were performed to reveal the mechanism of this reaction.

Although AgAu bimetallic and hollow nanomaterials have been synthesized in a variety of shapes and compositions (such as shells, cages, frames, and tubes),²² we believe this is the first demonstration of the synthesis of AgAu tadpoles. It is noteworthy that, more generally, there are few reports of the synthesis of bimetallic particles with the characteristic tadpole morphology.^{26–}

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7.2. Experimental Section

7.2.1. Materials and Instrumentation

Analytical grade chemicals chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich), silver nitrate (AgNO_3 , 99%, Sigma-Aldrich), ethylene glycol (EG, 99.8%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), sodium citrate

dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%, Sigma-Aldrich), hydroquinone ($\text{C}_6\text{H}_6\text{O}_2$, 99%, Vetec), L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$, 99%, Sigma-Aldrich), sodium borohydride (NaBH_4 , 98%, Sigma-Aldrich), 4-nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$, 99,8%, Merck) were used as received. All solutions were prepared using deionized water (18.2 M Ω).

Transmission electron microscope (TEM) images were obtained with a JEOL 1010 microscope operating at 80 kV. Analysis of the nanoparticle size was performed by measurement of TEM images considering populations of ~ 20 tadpoles with the quoted errors corresponding to the standard deviation of the data. High angle annular dark field (HAADF) scanning transmission electron microscope (STEM) images, and energy dispersive X-ray (EDX) spectrum images were acquired using a probe-side aberration-corrected FEI Titan G2 80-200 S/TEM operated at 200 kV. STEM images were collected using a convergence angle of 18 mrad and a high angle annular dark-field (HAADF) detector with an inner angle of 55 mrad. EDX compositional analysis was performed using the Super-X detector configuration ($4 \times 30 \text{ mm}^2$ SDDs) with a solid angle of ~ 0.7 sr and a beam current of ~ 0.2 nA. Samples were prepared by drop-casting an aqueous suspension of the nanostructures on a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 spectrophotometer. The Au and Ag atomic percentages were measured by flame atomic absorption spectrometry (FAAS) with a Shimadzu spectrophotometer, model AA-6300, equipped with an air-acetylene flame.

7.2.2. Synthesis of Ag NPs seeds

Ag NPs seeds were prepared by the polyol process.²⁹ Briefly, 5 mg of polyvinylpyrrolidone (PVP) was dissolved in 37.5 mL of ethylene glycol. Then, AgNO_3 (200 mg, 1.2 mmol) was added

and mixed until complete dissolution. The resulting solution was heated to 125 °C and kept at this temperature for 2.5 hours, leading to the appearance of a greenish-yellow color due to the formation of the Ag NPs. The reaction mixture was then allowed to cool to room temperature and diluted to 125 mL with water.

7.2.3. *Synthesis of AgAu tadpoles*

AgAu tadpoles were synthesized by combination of galvanic replacement and precursor reduction reactions employing Ag NPs as seeds. In a typical procedure, 10 μL of the as-prepared Ag NPs seeds were added to 9.4 mL of a PVP aqueous solution (0.1 wt %). This mixture was transferred to a 25 mL round-bottom flask and stirred at 50 °C for 10 min, followed by the addition of 0.1 mL of 30 mM aqueous citrate solution. After 2 min, 170 μL of a 12 mM AuCl_4^- (aq) solution was added to this mixture. In order to control and monitor the growth of the produced AgAu tadpoles, the reaction was quenched at different time intervals: 15 s, 5 min, 10 min, 20 min and, 30 min (several parallel reactions were carried out). The reactions were quenched by cooling to 0 °C in an ice-water bath. The nanostructures were isolated and washed three times with ethanol by successively centrifuging at 15000 rpm, removing the supernatant, and then re-dispersing the nanoparticles. After washing, the nanoparticles were suspended in 10 mL of water.

7.3. Results and Discussion

AgAu tadpoles were obtained from Ag nanoparticle (NP) seeds by combining the galvanic replacement reaction between Ag and AuCl_4^- (aq) and the reduction of AuCl_4^- (aq) to Au by citrate ions in the presence of PVP, the reaction was carried out in water at 50 °C for 5 min as depicted in Scheme 7.1.

Scheme 7.1. Approach for the synthesis of AgAu tadpoles by a combination of galvanic replacement between Ag and AuCl_4^- and AuCl_4^- reduction in the presence of citrate as the reducing agent.

Figure 7.1 shows HAADF STEM images of a typical AgAu tadpole. The tadpole displays a nodular head ~ 40 nm in diameter with a hollow void region at the center (~ 12 nm in diameter). The hollow head provides evidence that, even with citrate present, galvanic replacement plays a role in the growth mechanism. The tail of this tadpole is ~ 55 nm in length and ~ 15 nm in width.

Figure 7.1. (a) HAADF images of a typical AgAu tadpole structures, regions indicated by dashed squares are shown at atomic resolution in the middle column with their corresponding Fourier transform (FT). (b) Elemental maps extracted from a STEM-EDX spectrum image of the AgAu tadpole shown in (a). The combined Ag and Au map and the line scan demonstrate a ~ 1 nm thick Ag-rich surface layer over the entire structure.

High resolution HAADF STEM imaging of AgAu tadpoles (Figure 7.2) shows that, despite having undulating or bent shapes and rounded surfaces, the tadpoles' tails are generally single crystals.

Figure 7.2. HAADF STEM images of two AgAu tadpoles, fused at the head. The left tadpole was imaged at atomic resolution, confirming that the head is polycrystalline, while the entire tail is a single crystal. Regions highlighted by dashed boxes in the low magnification image are shown at atomic resolution with their FFT.

Figure 7.3 shows low magnification TEM image of multiple tadpoles from this sample. Conversely, the head regions contains multiple crystal orientations probably stemming from the polycrystalline nature of the Ag NPs used as seeds (Figure 7.1 a).¹⁰ This behavior has also been observed in the synthesis of Au nanotadpoles, in which a single-crystalline tail can grow from a polycrystalline Au NP seed (head).¹¹

Figure 7.3. Low magnification TEM image of AgAu tadpoles obtained following the addition of AuCl_4^- to the reaction mixture after 5 min.

It is not possible to simply distinguish between Au and Ag metals by using high resolution imaging due to the similarity in crystal structure, lattice parameter and atomic number. We therefore performed STEM-EDX spectrum imaging to investigate the Ag and Au elemental distributions in the tadpoles. Surprisingly, we find that the AgAu tadpoles display Ag surface segregation, with a fairly uniform surface layer of Ag, approximately 1 nm thick, covering the entire surface of the tadpoles (Figure 7.1 b and Figure 7.4). This Ag surface segregation is similar to that recently observed during the synthesis of AgAu nanoparticles by galvanic replacement between Ag and AuCl_4^- .³⁰ Intuitively one might predict that the Ag would be located in the head as the only source of Ag is the seed particle, so it is interesting that Ag is able to cover the entire

surface of the tadpole, including the ~ 50 nm long tail. The hollow 3D morphology of the head region makes the 2D elemental maps more difficult to interpret. However, analysis of extracted line scans suggests that this structure is a hollow nodular Au structure with a central void and that, like the tail, the head is also covered by a ~ 1 nm Ag surface layer (inside and out).

Figure 7.4. EDX spectrum imaging of the AgAu tadpoles shown in Figure 7.2, as with the tadpole studied in Figure 7.1, elemental maps and line scans confirms that a ~ 1 nm thick layer of silver covers the surface of the entire tadpole.

Cliff Lorimer quantification of EDX spectra extracted from the spectrum images in Figure 7.1 and Figure 7.4 reveals that the Ag/Au ratio is higher in the head region than in the tail (Figure 7.5), this may be due to the presence of residual silver from the seed particle or merely reflect the higher surface to volume ratio of the hollow head region. EDX spectroscopy analysis revealed the

overall composition of the tadpoles shown in Figure 7.1 and Figure 7.4 to be 13 and 16 at. % Ag, respectively. By comparison the average Ag and Au composition for the entire nanoparticle population, as determined by flame atomic absorption spectrometry (FAAS), corresponded to 9 at. % Ag (91 at% Au) suggesting there are a range of compositions within the nanoparticle population (possibly corresponding to tadpoles with different tail lengths).

Figure 7.5. EDX quantification was performed on the spectrum images shown in figures 7.1 and 7.3 using the Cliff Lorimer approach. In both cases summed spectra were extracted and evaluated for three regions: region 1, the entire tadpole; region 2, the head region; region 3, the tail region. In both cases the Ag/Au ratio is found to be higher in the head than in the tail. Ag:Au at. % ratios for the upper image are: region 1, 16.4:83.6; region 2, 18.8:81.2; region 3, 8.7:91.3. Ag:Au at. % ratios for the lower image are: region 1, 13.1:86.9; region 2, 17.6: 82.4.

Based on the observations of product morphology, crystallinity, and elemental distribution gained from high, resolution imaging and spectrum imaging we propose a mechanism for tadpole formation. We suggest that the morphologies observed may be the result of a non-classical growth mechanism. Classical growth assumes that crystals grow by monomer addition. In such a reaction two growth regimes can exist. If the rate of reduction is rapid, growth will occur in a diffusion limited regime with precursor species reducing as soon as they reach the surface of the growing nanocrystal leading to the isotropic growth of spherical nanocrystals.³¹ Alternatively, in a reaction limited regime where reduction is slower, precursors may not immediately reduce upon reaching the surface of a growing nanocrystal and instead seek the lowest energy facets, resulting in anisotropic growth of faceted nanostructures.³¹ While the products seen here are anisotropic, they lack the faceted shapes and clear crystallographic direction of elongation expected to arise from monomer addition to a favorable crystal facet. The formation of anisotropic nanostructures by the coalescence of multiple nanocrystal sub-units, termed oriented attachment, has also been widely reported.^{2,4,32-34} Such non-classical growth mechanisms can yield single crystalline nanorods and nanowires, sometimes with non-faceted shapes similar to the tails observed in this work.³⁵⁻³⁷ The ability for spherical gold nanocrystals to assemble into 1D chains in water has been directly observed with *in situ* electron microscopy, with their anisotropic assembly attributed to dipole-dipole and Van der Waals interactions.³⁸ Studies of Pt₃Fe nanowire growth show that the nanocrystals are able to change their orientation in the initial winding chain, rotating until a common crystallographic face is found with their neighbor, at which point a neck is formed and subsequently smoothed.³⁵ It is feasible that gold nanocrystal chains can transform into a single crystal tails by such a mechanism.^{35,39}

We believe that citrate reduction initially forms numerous small gold nanocrystals which assemble to form 1D chains attached to the presynthesised silver seeds in the manner previously observed.³⁸ The gold nanocrystals in the chain then rotate and restructure to form a single crystalline tail which still retains some of the undulating, kinked character typical of a nanoparticle chain.^{35,38} Simultaneously the silver seed reacts with AuCl_4^- (aq) in a galvanic reaction, as evidenced by the hollow head.⁴⁰ The Ag^+ (aq) ions released into solution by the galvanic reaction may be re-reduced by the citrate once AuCl_4^- (aq) has been depleted, forming the Ag shell observed.⁴¹ However, surface diffusion of silver metal from the head could also explain the presence of silver layer covering the entire surface of the structure. A thermodynamic driving force for the formation of a silver surface layer is expected as silver has a significantly lower surface energy than gold for the low energy {100}, {110}, and {111} faces.⁴² While alloyed solid solutions are known to be the thermodynamically stable phase in bulk AgAu, the high surface area of these nanoparticles provides a strong driving force for reducing surface energy by surface segregation of Ag.^{43–45} Furthermore, recent work on heating of AgAu nanocrystals has shown that the spontaneous formation of alloyed structures requires higher temperatures than those employed in this work.⁴⁵ It is known that surface-diffusion is an important process in nanocrystal growth and plays a critical role in elemental re-distribution in bimetallic particles.^{46,47} We hypothesize that the nanoparticle's exceptionally high surface area provides a strong driving force for this segregation while simultaneously offering a fast path for elemental redistribution via surface diffusion.⁴⁵

In order to gain further insights into the growth mechanism of these unusual AgAu tadpole structures, we have performed a series of control experiments, stopping the reaction at different time intervals following the addition of AuCl_4^- (aq) to the reaction mixture containing the Ag NPs seeds. Figure 7.6 shows the TEM image of the initial spherical Ag NPs (34 ± 2 nm in diameter)

employed as seeds, and the AgAu nanomaterials obtained by stopping the reaction after 15 seconds, 5 minutes, 10 minutes, and 30 minutes (Figures 7.6 B, C, D, and E respectively).

Figure 7.6. TEM images of Ag seeds (A) and AgAu structures obtained following the addition of $\text{AuCl}_4^-_{(\text{aq})}$ to the reaction mixture after: 15 s (B), 5 min (C), 10 min (D), and 30 min (E). The selected regions in (D) illustrate the formation of plate-like heads which accompanies the elongation of the tails.

After 15 s, nodules are already observed on the particles (now with an average diameter of 43 ± 5 nm), although for most particles clear tails have not yet developed. In line with the previously proposed mechanism, the nodular appearance may be the result of the attachment of multiple small Au particles to the Ag seed. Longer reaction times lead to an increase in the length of the tails due to anisotropic growth (tail lengths of ~ 50 nm, ~ 120 nm, and ~ 180 nm for 5, 10 and 30 mins respectively). However, as the tails elongate the diameter of the heads remains roughly constant. Interestingly, for some particles in populations observed after 10 and 30 min growth the formation of a second head with a plate-like morphology can be observed (as highlighted in red in Figure 7.6 D) similar to what has been previously observed for the growth of Au tadpoles and kites

in the presence of PVP.⁹ Between 10 and 30 minutes the tails also become noticeable straighter, this is consistent with previous accounts of growth by oriented attachment, where nanowires formed from chains of nanocrystals are initially bent but straighten as the reaction proceeds.³⁵ These results indicate that both the size and morphology of the AgAu tadpoles can be further manipulated by controlling the growth time.

In order to investigate the role-played by the presence of citrate in the reaction, we performed control experiments by removing the citrate (Figure 7.7 A), by replacing citrate with ascorbic acid, sodium borohydride or hydroquinone (Figure 7.7 B-D, respectively), and by removing the Ag NPs seeds (Figure 7.7 E).

Figure 7.7. TEM images of the different AgAu nanomaterial structures obtained by performing control experiments under the same experimental conditions as those describe in Figure 7.1 but in the absence of the citrate (A) or by replacing the citrate with sodium borohydride (B), ascorbic acid (C), or hydroquinone (D), and in the absence of Ag NPs as templates (E).

In the absence of citrate, AgAu nanoshells are obtained as a result of the galvanic replacement reaction between Ag and AuCl_4^- (Figure 7.7 A).⁴⁰ Similarly, AgAu nanoshells were

obtained by replacing citrate with borohydride (Figure 7.7 B). In contrast, ascorbic acid led to the formation of spherical Ag@Au nanoparticles (Figure 7.7 C). In this case, TEM images of the nanoparticles show no hollow interiors, suggesting that the use of ascorbic acid suppressed the galvanic reaction, and only precursor reduction occurs. This is in agreement with the results reported recently on the synthesis of Ag@Au core-shell nanocubes promoted by ascorbic acid.⁴⁸ Finally, the utilization of hydroquinone instead of citrate has led to the formation of particles with multiple Au branches at their surface (Figure 7.7 D), in agreement with previous findings that hydroquinone promoted the deposition of Au branches on the surface of Ag NPs seeds.¹⁸ We also studied the importance of the NP seeds in determining the AgAu tadpole morphology. When the synthesis was carried out in the absence of Ag NP seeds, spherical Au NPs were produced (Figure 7.7 E). These results demonstrate that the growth of tadpoles requires both the use of seeds and citrate.

In order to confirm that the presence of seeds was imperative to the formation of the tadpoles, we also performed a control experiment in which Ag NPs were replaced by Au NPs as seeds. Interestingly, the use of Au NP seeds led to the formation of double-headed tadpoles, as illustrated in Figures 7.8. Solid heads are produced, as no galvanic replacement is involved, and the resulting tadpoles are monometallic as illustrated by the HAADF STEM and EDX elemental maps shown in Figure 7.8 C and D. High resolution HAADF STEM images and the corresponding Fourier transforms (Figure 7.8 E) show that, as in the AgAu tadpoles, the undulating tail is a single crystal.

Figure 7.8. Low magnification HAADF STEM (a) and BF TEM (b) images of Au tadpoles. (c) and (d) show a HAADF STEM image and an Au elemental map of the same region. The central tadpole in image (c) was imaged at atomic resolution, it is found to have a single crystal tail and a polycrystalline head; regions indicated by dashed squares in (c) are shown at atomic resolution in (e) with their corresponding FT.

7.4. Conclusion

In summary, we have demonstrated a fast, facile and low temperature synthesis route for the production of AgAu tadpoles from Ag NP seeds. Our approach is based on a combination of the galvanic replacement reaction between Ag and AuCl_4^- (aq) and AuCl_4^- (aq) reduction to Au in the presence of citrate and PVP. The AgAu tadpoles formed consist of a hollow nodular head and

elongated undulating tail with a ~ 1 nm thick Ag shell covering the entire surface of the structure. We found that both the presence of citrate and nanocrystal seeds are crucial for the formation of the tadpole morphology. The tadpole heads were found to be polycrystalline while the tails were single crystals with lengths that could be controlled as a function of growth time. We believe that the morphologies observed point towards an oriented attachment growth mechanism and that the lower surface energy of Ag relative to Au may drive the formation of the silver shell via surface diffusion from the head region. By varying the nature of the seeds (Au NPs), double-headed monometallic Au tadpoles could be obtained. The combined galvanic-citrate approach presented here provides new routes to nanomaterials with novel morphologies. The hollow headed AgAu tadpoles may be also inspire the design of novel nanomotor and drug-delivery systems having encapsulation capabilities as well as catalytic and optical (plasmonic) properties.

7.5. References

- (1) Hong, X.; Tan, C.; Chen, J.; Xu, Z.; Zhang, H. Synthesis, Properties and Applications of One- and Two-Dimensional Gold Nanostructures. *Nano Res.* **2015**, *8* (1), 40–55.
- (2) Hu, L.; Cao, X.; Yang, J.; Li, M.; Hong, H.; Xu, Q.; Ge, J.; Wang, L.; Lu, J.; Chen, L.; et al. Oxidation of Benzylic Compounds by Gold Nanowires at 1 Atm O₂. *Chem. Commun.* **2011**, *47* (4), 1303–1305.
- (3) Jones, S. T.; Taylor, R. W.; Esteban, R.; Abo-Hamed, E. K.; Bomans, P. H. H.; Sommerdijk, N. A. J. M.; Aizpurua, J.; Baumberg, J. J.; Scherman, O. A. Gold Nanorods with Sub-Nanometer Separation Using Cucurbit[n]uril for SERS Applications. *Small* **2014**, *10* (21), 4298–4303.
- (4) Huang, H.; Wang, J.-H.; Jin, W.; Li, P.; Chen, M.; Xie, H.-H.; Yu, X.-F.; Wang, H.; Dai, Z.; Xiao, X.; et al. Competitive Reaction Pathway for Site-Selective Conjugation of Raman Dyes to Hotspots on Gold Nanorods for Greatly Enhanced SERS Performance. *Small* **2014**, *10* (19), 4012–4019.
- (5) Jana, N. R.; Pal, T. Anisotropic Metal Nanoparticles for Use as Surface-Enhanced Raman Substrates. *Adv. Mater.* **2007**, *19* (13), 1761–1765.
- (6) Li, N.; Zhao, P.; Astruc, D. Anisotropic Gold Nanoparticles: Synthesis, Properties,

- Applications, and Toxicity. *Angew. Chemie Int. Ed.* **2014**, 53 (7), 1756–1789.
- (7) Gao, W.; Wang, J. Synthetic Micro/nanomotors in Drug Delivery. *Nanoscale* **2014**, 6 (18), 10486–10494.
 - (8) Abdelmohsen, L. K. E. A.; Peng, F.; Tu, Y.; Wilson, D. A. Micro- and Nano-Motors for Biomedical Applications. *J. Mater. Chem. B* **2014**, 2 (17), 2395–2408.
 - (9) Lim, B.; Camargo, P. H. C.; Xia, Y. Mechanistic Study of the Synthesis of Au Nanotadpoles, Nanokites, and Microplates by Reducing Aqueous H₂AuCl₄ with Poly(vinyl Pyrrolidone). *Langmuir* **2008**, 24 (18), 10437–10442.
 - (10) Hu, J.; Zhang, Y.; Liu, B.; Liu, J.; Zhou, H.; Xu, Y.; Jiang, Y.; Yang, Z.; Tian, Z.-Q. Synthesis and Properties of Tadpole-Shaped Gold Nanoparticles. *J. Am. Chem. Soc.* **2004**, 126 (31), 9470–9471.
 - (11) Wu, H.; Ji, X.; Zhao, L.; Yang, S.; Xie, R.; Yang, W. Shape Evolution of Citrate Capped Gold Nanoparticles in Seeding Approach. *Colloids Surfaces A Physicochem. Eng. Asp.* **2012**, 415 (0), 174–179.
 - (12) Ravi Kumar, D. V.; Kumavat, S. R.; Chamundeswari, V. N.; Patra, P. P.; Kulkarni, A. A.; Prasad, B. L. V. Surfactant-Free Synthesis of Anisotropic Gold Nanostructures: Can Dicarboxylic Acids Alone Act as Shape Directing Agents? *RSC Adv.* **2013**, 3 (44), 21641–21647.
 - (13) Singh, A. K.; Xu, Q. Synergistic Catalysis over Bimetallic Alloy Nanoparticles. *ChemCatChem* **2013**, 5 (3), 652–676.
 - (14) Jiang, H.-L.; Akita, T.; Ishida, T.; Haruta, M.; Xu, Q. Synergistic Catalysis of Au@Ag Core–Shell Nanoparticles Stabilized on Metal–Organic Framework. *J. Am. Chem. Soc.* **2011**, 133 (5), 1304–1306.
 - (15) Speziali, M. G.; Silva, A. G. M. da; Miranda, D. M. V. de; Monteiro, A. L.; Robles-Dutenhefner, P. A. Air Stable Ligandless Heterogeneous Catalyst Systems Based on Pd and Au Supported in SiO₂ and MCM-41 for Suzuki–Miyaura Cross-Coupling in Aqueous Medium. *Appl. Catal. A Gen.* **2013**, 462–463 (0), 39–45.
 - (16) Rodrigues, T. S.; da Silva, A. G. M.; Gonçalves, M. C.; Fajardo, H. V.; Balzer, R.; Probst, L. F. D.; Camargo, P. H. C. AgPt Hollow Nanodendrites: Synthesis and Uniform Dispersion over SiO₂ Support for Catalytic Applications. *ChemNanoMat* **2015**, 1 (1), 46–51.
 - (17) Silva, A. G. M.; Rodrigues, T. S.; Dias, A.; Fajardo, H. V.; Goncalves, R. F.; Godinho, M.; Robles-Dutenhefner, P. A. Ce_{1-x}Sm_xO_{1.9-δ} Nanoparticles Obtained by Microwave-Assisted Hydrothermal Processing: An Efficient Application for Catalytic Oxidation of α-Bisabolol. *Catal. Sci. Technol.* **2014**, 4 (3), 814–821.
 - (18) da Silva, A. G. M.; de Souza, M. L.; Rodrigues, T. S.; Alves, R. S.; Temperini, M. L. A.; Camargo, P. H. C. Rapid Synthesis of Hollow Ag–Au Nanodendrites in 15 Seconds by Combining Galvanic Replacement and Precursor Reduction Reactions. *Chem. – A Eur. J.* **2014**, 20 (46), 15040–15046.
 - (19) Liu, Z.; Yang, Z.; Peng, B.; Cao, C.; Zhang, C.; You, H.; Xiong, Q.; Li, Z.; Fang, J. Highly Sensitive, Uniform, and Reproducible Surface-Enhanced Raman Spectroscopy from

- Hollow Au-Ag Alloy Nanourchins. *Adv. Mater.* **2014**, 26 (15), 2431–2439.
- (20) Lim, B.; Jiang, M.; Camargo, P. H. C.; Cho, E. C.; Tao, J.; Lu, X.; Zhu, Y.; Xia, Y. Pd-Pt Bimetallic Nanodendrites with High Activity for Oxygen Reduction. *Sci.* **2009**, 324 (5932), 1302–1305.
 - (21) Rodrigues, T.; da Silva, A. M.; Macedo, A.; Farini, B.; Alves, R.; Camargo, P. C. Probing the Catalytic Activity of Bimetallic versus Trimetallic Nanoshells. *J. Mater. Sci.* **2015**, 50 (16), 5620–5629.
 - (22) Xia, X.; Wang, Y.; Ruditskiy, A.; Xia, Y. 25th Anniversary Article: Galvanic Replacement: A Simple and Versatile Route to Hollow Nanostructures with Tunable and Well-Controlled Properties. *Adv. Mater.* **2013**, 25 (44), 6313–6333.
 - (23) Sun, Y.; Mayers, B.; Xia, Y. Metal Nanostructures with Hollow Interiors. *Adv. Mater.* **2003**, 15 (7–8), 641–646.
 - (24) An, K.; Hyeon, T. Synthesis and Biomedical Applications of Hollow Nanostructures. *Nano Today* **2009**, 4 (4), 359–373.
 - (25) Lou, X. W. (David); Archer, L. A.; Yang, Z. Hollow Micro-/Nanostructures: Synthesis and Applications. *Adv. Mater.* **2008**, 20 (21), 3987–4019.
 - (26) Camargo, P. H. C.; Xiong, Y.; Ji, L.; Zuo, J. M.; Xia, Y. Facile Synthesis of Tadpole-like Nanostructures Consisting of Au Heads and Pd Tails. *J. Am. Chem. Soc.* **2007**, 129 (50), 15452–15453.
 - (27) Mao, J.; Cao, X.; Zhen, J.; Shao, H.; Gu, H.; Lu, J.; Ying, J. Y. Facile Synthesis of Hybrid Nanostructures from Nanoparticles, Nanorods and Nanowires. *J. Mater. Chem.* **2011**, 21 (31), 11478–11481.
 - (28) Wu, J.; Hou, Y.; Gao, S. Controlled Synthesis and Multifunctional Properties of FePt-Au Heterostructures. *Nano Res.* **2011**, 4 (9), 836–848.
 - (29) Silvert, P.-Y.; Herrera-Urbina, R.; Duvauchelle, N.; Vijayakrishnan, V.; Elhsissen, K. T. Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 1-Synthesis and Characterization. *J. Mater. Chem.* **1996**, 6 (4), 573–577.
 - (30) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O'Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, 14 (4), 1921–1926.
 - (31) Woehl, T. J.; Evans, J. E.; Arslan, I.; Ristenpart, W. D.; Browning, N. D. Direct in Situ Determination of the Mechanisms Controlling Nanoparticle Nucleation and Growth. *ACS Nano* **2012**, 6 (10), 8599–8610.
 - (32) Schliehe, C.; Juarez, B. H.; Pelletier, M.; Jander, S.; Greshnykh, D.; Nagel, M.; Meyer, A.; Foerster, S.; Kornowski, A.; Klinke, C.; et al. Ultrathin PbS Sheets by Two-Dimensional Oriented Attachment. *Sci.* **2010**, 329 (5991), 550–553.
 - (33) Pacholski, C.; Kornowski, A.; Weller, H. Self-Assembly of ZnO: From Nanodots to Nanorods. *Angew. Chemie Int. Ed.* **2002**, 41 (7), 1188–1191.
 - (34) Banfield, J. F.; Welch, S. A.; Zhang, H.; Ebert, T. T.; Penn, R. L. Aggregation-Based Crystal Growth and Microstructure Development in Natural Iron Oxyhydroxide Biomineralization

- Products. *Sci.* **2000**, 289 (5480), 751–754.
- (35) Liao, H.-G.; Cui, L.; Whitlam, S.; Zheng, H. Real-Time Imaging of Pt₃Fe Nanorod Growth in Solution. *Sci.* **2012**, 336 (6084), 1011–1014.
 - (36) Cho, K.-S.; Talapin, D. V.; Gaschler, W.; Murray, C. B. Designing PbSe Nanowires and Nanorings through Oriented Attachment of Nanoparticles. *J. Am. Chem. Soc.* **2005**, 127 (19), 7140–7147.
 - (37) Akhtar, J.; Malik, M. A.; O'Brien, P.; Revaprasadu, N. The Oriented Self-Assembly of Small PbSe Nanocrystals into Extended Structures “nanoworms.” *Mater. Lett.* **2012**, 77 (0), 78–81.
 - (38) Liu, Y.; Lin, X.-M.; Sun, Y.; Rajh, T. In Situ Visualization of Self-Assembly of Charged Gold Nanoparticles. *J. Am. Chem. Soc.* **2013**, 135 (10), 3764–3767.
 - (39) Aabdin, Z.; Lu, J.; Zhu, X.; Anand, U.; Loh, N. D.; Su, H.; Mirsaidov, U. Bonding Pathways of Gold Nanocrystals in Solution. *Nano Lett.* **2014**, 14 (11), 6639–6643.
 - (40) Petri, M. V.; Ando, R. A.; Camargo, P. H. C. Tailoring the Structure, Composition, Optical Properties and Catalytic Activity of Ag–Au Nanoparticles by the Galvanic Replacement Reaction. *Chem. Phys. Lett.* **2012**, 531 (0), 188–192.
 - (41) Rivas, L.; Sanchez-Cortes, S.; García-Ramos, J. V.; Morcillo, G. Growth of Silver Colloidal Particles Obtained by Citrate Reduction To Increase the Raman Enhancement Factor. *Langmuir* **2001**, 17 (3), 574–577.
 - (42) Vitos, L.; Skriver, H. L.; Kollár, J. The Formation Energy for Steps and Kinks on Cubic Transition Metal Surfaces. *Surf. Sci.* **1999**, 425 (2–3), 212–223.
 - (43) Mallard, W. C.; Gardner, A. B.; Bass, R. F.; Slifkin, L. M. Self-Diffusion in Silver-Gold Solid Solutions. *Phys. Rev.* **1963**, 129 (2), 617–625.
 - (44) White, J. L.; Orr, R. L.; Hultgren, R. The Thermodynamic Properties of Silver-Gold Alloys. *Acta Metall.* **1957**, 5 (12), 747–760.
 - (45) Lewis, E. A.; Slater, T. J. A.; Prestat, E.; Macedo, A.; O'Brien, P.; Camargo, P. H. C.; Haigh, S. J. Real-Time Imaging and Elemental Mapping of AgAu Nanoparticle Transformations. *Nanoscale* **2014**, 6 (22), 13598–13605.
 - (46) Langlois, C.; Li, Z. L.; Yuan, J.; Alloyeau, D.; Nelayah, J.; Bochicchio, D.; Ferrando, R.; Ricolleau, C. Transition from Core-Shell to Janus Chemical Configuration for Bimetallic Nanoparticles. *Nanoscale* **2012**, 4 (11), 3381–3388.
 - (47) Baletto, F.; Mottet, C.; Ferrando, R. Molecular Dynamics Simulations of Surface Diffusion and Growth on Silver and Gold Clusters. *Surf. Sci.* **2000**, 446 (1–2), 31–45.
 - (48) Yang, Y.; Liu, J.; Fu, Z.-W.; Qin, D. Galvanic Replacement-Free Deposition of Au on Ag for Core–Shell Nanocubes with Enhanced Chemical Stability and SERS Activity. *J. Am. Chem. Soc.* **2014**, 136 (23), 8153–8156.

Section 4.

Optimizing Both Active Phase and the Support: Achieving Efficient Heterogeneous Catalysts

Chapter 8. MnO₂ Nanowires Decorated with Au Ultrasmall Nanoparticles for the Green Oxidation of Silanes and Hydrogen Production under Ultralow Loadings

8.1. Introduction

Gold nanoparticles (Au NPs) have attracted increased interest in the field of heterogeneous catalysis due to their high catalytic activity and selectivity, being employed in a variety of organic reactions that include oxidation, reduction, and C-C coupling.¹⁻⁴ Among these transformations, the oxidation of hydrosilanes has attracted particular attention. Silanols are a key element in the production of silicon-containing materials (i.e. polymers).⁵⁻⁷ Generally, hydrosilanes are classically converted into silanols using strong and toxic oxidizing agents such as permanganate, dichromate, and peracids that lead to significant amounts of siloxanes and toxic byproducts.^{7,8} On the other hand, Au supported materials have been reported as promising catalysts for the oxidation of hydrosilanes using mild and non-toxic oxidants such as water and oxygen.^{5,6,8-10}

The green oxidation of organic compounds^{2,11-13} has emerged as a new frontier in heterogeneous catalysis as this transformation represents an eco-friendly approach based on the use of dioxygen (O₂), water, or hydrogen peroxide as the oxidant, non-toxic solvents such as water, low catalyst loadings, and mild temperature and pressure conditions.¹⁴⁻¹⁷ Despite these very attractive features, green oxidations remain challenging owing to the low conversion percentages, selectivities, and substrate versatility.¹² Therefore, the development of novel catalysts displaying high activities towards green transformations, such as oxidation, becomes highly desirable.

Here, we describe the catalytic activity of MnO₂ nanowires decorated with ultrasmall Au NPs (NPs having diameters of 3 nm or less)¹⁸ towards the green oxidation of hydrosilanes, which produces silanols and hydrogen gas (H₂). Owing to their morphology comprised of ultrasmall Au NPs (3 nm), we found that the MnO₂-Au NPs displayed high catalytic performances under ultralow Au loadings (0.001 - 0.0002 mol %). Interestingly, the MnO₂-Au NPs were synthesized by a facile approach, which was based on the utilization of MnO₂ nanowires as physical templates for Au deposition without the need of any prior surface modification/functionalization steps. This method enabled the uniform deposition of monodisperse Au NPs over the entire surface of the support (MnO₂). MnO₂ was chosen as a model support material due to their low cost, stability, and low toxicity.^{19,20} Moreover, various methodologies have been reported for the synthesis of MnO₂ displaying controlled shapes.^{21–24} Although approaches to the synthesis of hybrids between MnO₂ and metal NPs have been reported, most of them generally do not lead a precise control over particle size, monodispersity, particle distribution, and composition, which is crucial to optimize activities.^{25–29}

8.2. Experimental Section

8.2.1. Materials and Instrumentation

Analytical grade chemicals chloroauric acid trihydrate (HAuCl₄·3H₂O, 99.9%, Sigma-Aldrich), manganese sulfate monohydrate (MnSO₄·H₂O, 99%, Sigma-Aldrich), potassium permanganate (KMnO₄, 99%, Sigma-Aldrich), ethylene glycol (EG, 99.8%, Sigma Aldrich), sodium borohydride (NaBH₄, 98%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), dimethyl(phenyl)silane (C₈H₁₂Si, 98%, Sigma Aldrich),

dimethyl(phenethyl)silane ($C_{10}H_{16}Si$, 98%, Sigma Aldrich) cyclohexyldimethylsilane ($C_8H_{18}Si$, 98%, Sigma Aldrich) were used without further purification. Dimethyl(1-phenylethyl)silane ($C_8H_{12}Si$) and dimethyl(1-(naphthalen-2-yl)ethyl)silane ($C_{14}H_{18}Si$) were synthesized according to previously reported protocols.³⁰ All solutions were prepared using deionized water (18.2 M Ω).

The scanning electron microscopy (SEM) images were obtained using a JEOL field emission gun microscope JSM 6330F operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension containing the nanostructures over a silicon wafer, followed by drying under ambient conditions. The high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM2100 microscope operated at 200 kV. Samples for HRTEM were prepared by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 spectrophotometer. The Au atomic percentage was measured by flame atomic absorption spectrometry (FAAS) with a Shimadzu spectrophotometer, model AA-6300, equipped with an air-acetylene flame.

8.2.2. *Synthesis of MnO₂ nanowires*

The MnO₂ nanowires were obtained by a hydrothermal approach.²³ In a typical procedure, 0.4 g of MnSO₄·H₂O and 1.0 g of KMnO₄ were dissolved in 30 mL of deionized water. This solution was transferred to an 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated and stirred at 140 °C for 19 h and then allowed to cooled down to room temperature. The nanowires were washed three times with ethanol (15 mL) and three times with water (15 mL) by

successive rounds of centrifugation and removal of the supernatant, and finally dried at 80°C for 6 h in air.

8.2.3. *Synthesis of MnO₂ nanowires decorated with Au NPs (MnO₂-Au NPs)*

Typically, 40 mg of MnO₂ nanowires and 13 mg of PVP were added to 10 mL of EG. The obtained suspension was transferred to a 25 mL round-bottom flask and kept under vigorous stirring at 90 °C for 20 min. Then, 1 mL of an 120 mM NaBH_{4(aq)} and 1 mL of a 24 mM AuCl₄⁻_(aq) solutions were sequentially added to the reaction flask. This mixture was kept under vigorous stirring for another 1 h to produce MnO₂-Au NPs, which were washed three times with ethanol (15 mL) and water (15 mL) by successive rounds of centrifugation at 6000 rpm for 5 min and removal of the supernatant. After washing, the MnO₂-Au NPs were suspended in 40 mL of water.

8.2.4. *Oxidation of hydrosilanes catalyzed by MnO₂-Au NPs*

In a typical experiment, a mixture of the hydrosilane (0.025mmol), H₂O (0.5 mL), and 50 µL of the suspension containing MnO₂-Au NPs (0.001 mol % in terms of Au) were transferred to a 2 mL microtube (*eppendorf*®). This system was kept under stirring at room temperature for 1 h, in a *Thermomixer*®. Then, the MnO₂-Au NPs was recovered from the reaction mixture by centrifugation and the supernatant was analyzed by GC-MS. GCM-QP2010SE Shimadzu instrument with low-resolution electron impact (EI, 70eV) equipped with a RTx®-5MS capillary column. GC/MS conditions: injector 260 °C; detector: 110 °C pressure: 100kPa. Column temperature: 80 °C, 1 °C/min up to 280 °C). The reaction products, when needed, were purified by a column chromatography (silica gel). The recovered catalyst was washed with water (3 x 1 mL) and re-used for the recycling studies.

8.3. Results and Discussion

Our studies started with the synthesis of MnO_2 nanowires by a hydrothermal approach. The nanowires displayed well-defined shapes and uniform sizes, being 34 ± 5 nm in width and > 1 μm in length (Figure 8.1).

Figure 8.1. SEM images of MnO_2 nanowires employed as physical templates for Au deposition.

The MnO_2 nanowires could be directly employed as physical templates for the nucleation and growth of Au NPs over their surface without the need of any surface modification/functionalization steps as depicted in Figure 8.2 A. Our approach employed AuCl_4^- (aq) as the Au precursor, PVP as the stabilizer, BH_4^- (aq) as the reducing agent, EG (ethylene glycol) as the solvent, and 90°C as the reaction temperature.

Figure 8.2. (A) Strategy for the synthesis of MnO₂ nanowires decorated with ultrasmall Au NPs, which was based on the reduction of AuCl₄⁻(aq) to Au by BH₄⁻ in presence of PVP, EG as the solvent, and 90 °C as the reaction temperature. (B-E) HRTEM images of MnO₂-Au NPs depicting the ultrasmall and monodisperse Au NPs size as well as their uniform distribution over the MnO₂ surface. The lattice fringes orientation in the phase-contrast HRTEM images (D and E) show that both the MnO₂ nanowires and Au NPs were single crystalline.

Figure 8.2 B-E shows HRTEM images of the MnO₂ nanowires decorated with Au NPs (MnO₂-Au NPs) obtained by this procedure. The uniform deposition (without agglomeration) of monodisperse, spherical, and ultrasmall (3 ± 1 nm) Au NPs over the entire surface of the MnO₂ nanowires could be clearly detected. Figure 8.2 D and E suggest that the Au NPs were directly

deposited over the surface of the MnO₂ nanowires, and no morphology changes at the surface of the MnO₂ upon the formation of Au NPs could be observed. The MnO₂ were crystallized as β -MnO₂ and were single-crystalline, with its growing direction corresponding to {110}.^{23,31} The characteristic lattice fringes from *fcc* Au can also be observed in Fig. 8.2 E, and indicate that the Au NPs were single-crystalline. The Au content in the MnO₂-Au NPs suspension as determined by FAAS analysis corresponded to 0.17 mg/L. The XRD pattern for the MnO₂-Au NPs (Figure 8.3) showed four peaks corresponding to the (110), (101), (211) and (200) reflections of the β -MnO₂ phase (JCPDS 24-0735). Only a small and broad peak assigned to the (111) reflection of *fcc* Au can be detected, in agreement with their ultrasmall sizes and low loading on the MnO₂ nanowires.

Figure 8.3. XRD pattern for MnO₂-Au NPs.

Owing to the well-defined morphology comprised of micrometer long MnO₂ nanowires and ultrasmall Au NPs sizes, the MnO₂-Au NPs are very attractive for catalytic applications. We

were particularly interested in investigating the catalytic activities of the MnO₂-Au NPs under ultralow Au loading conditions towards the green oxidation of hydrosilanes to silanol and gaseous hydrogen (H₂), using water as the solvent and under room temperature. Figure 8.4 and Table 8.1 (entry 1) depict the conversion percentages (%) for the oxidation of dimethyl(phenyl)silane, employed as a model substrate, catalyzed by MnO₂-Au NPs. The catalyst loading in terms of Au corresponded to 0.001 mol %.

Table 8.1. Green oxidation of silanes catalyzed by MnO₂-Au NPs.^a

Entry	R ¹	Au loading (mol %)	Time (min)	Conversion ^[b] (%)	Selectivity to silanol ^[b] (%)
1		0.0002	60	90	100
2		0.001	10	100	100
3		0.001	60	100	100
4		0.001	60	100	100
5		0.001	60	100	100
6		0.001	60	99	100

^a Reactions conditions: silane (0.025 mmol), H₂O (0.5 mL), 25 °C, 800 rpm. All reactions were performed in duplicate. The percentage of catalyst was calculated based on the Au loading. ^[b] The conversion and selectivity % were calculated using GC-MS analysis.

Figure 8.4. Green oxidation of dimethyl(phenyl)silane catalyzed by MnO₂-Au NPs (black trace) and pure MnO₂ nanowires (red trace).

While no significant conversion was detected for the MnO₂ nanowires after 10 min of reaction (control experiment), the MnO₂-Au NPs catalyst displayed high catalytic activities, achieving 97% of conversion after only 2 min, and 100 % after 10 min. When the catalyst loading in terms of Au was further reduced to 0.0002 mol % (entry 2, Table 8.1), the MnO₂-Au NPs were still exceptionally active under our employed conditions, in which 90 % conversion could be achieved after 60 min.

In order to demonstrate the versatility of the MnO₂-Au NPs as catalysts for the oxidation of hydrosilanes, we varied the nature of the groups attached to the Si atom, from aryl to benzylic groups (entry 3, Table 8.1). In this case, 100 % conversion could be achieved after 60 min. This slightly difference in the silane structure possibly increases the steric hindrance at silicon atom, which could decrease the catalytic activity, since benzyldimethylsilanol was obtained in 100 % after 10 min. The same behavior was observed for dimethyl(1-phenylethyl)silane (entry 4, Table

8.1). The dimethyl(naphthalen-2-yl)silane and cyclohexyldimethylsilane were also investigated as substrates (entries 5 and 6, Table 8.1, respectively). Both compounds were also successfully oxidized to silanol after 1 h (100% yield), suggesting that the MnO_2 -Au NPs were efficient and versatile as catalysts in the oxidation of a variety of hydrosilanes under ultralow Au loading conditions. Ultralow can be defined as reactions catalyzed employing less than 0.1 mol % in terms of metal loadings.^{32,33}

One of the main advantages of heterogeneous as compared to homogeneous catalysis is the easy separation of the catalysts from the reaction mixture and its subsequent reusability. Here, the stability and recycling of the MnO_2 -Au NPs catalysts towards the oxidation of dimethyl(phenyl)silane were investigated as depicted in Figure 8.5.

Figure 8.5. Recycling/stability studies employing MnO_2 -Au NPs as catalysts in the green oxidation of dimethylphenylsilane under the same conditions as described in Figure 8.4. No significant loss of activity was observed even after 10 reaction cycles.

After each reaction cycle, the MnO₂-Au NPs catalysts were removed from the reaction mixture by centrifugation and washed before being reused in the next reaction cycle. In this case, the catalytic reactions were scaled-up by 20 folds. It can be observed that almost 100 % conversion was achieved even after the 10th cycle, suggesting that the catalytic activities remained unaffected and the successive reaction cycles did not lead to any detrimental structural modifications on the MnO₂-Au NPs catalysts. The SEM images of the MnO₂-Au NPs before and after the catalytic tests (Figure 8.6 A and B, respectively) are in agreement with this observation, showing no change on the morphological features after the stability studies.

Figure 8.6. SEM images of MnO₂-Au NPs catalysts before (A) and after (B) the recycling/stability studies described in Figure 8.5, suggesting no significant morphological changes and indicating the robustness of the catalysts.

We also evaluated the absence of Au leaching from the MnO₂-Au NPs under our experimental conditions by a series of control experiments. In this case, MnO₂-Au NPs were rapidly isolated during the course of the reaction (after 1 min of reaction) to avoid re-deposition of potentially leached metal ions onto the solid. Then, the supernatant was allowed to react even further. As expected for a heterogeneous mechanism, no further conversion of dimethyl(phenyl)silane was observed after removing the MnO₂-Au NPs catalyst from the reaction mixture (Figure 8.7). Moreover, the supernatant obtained from these leaching tests and also from the recycling experiments were quantified by FAAS analyses and Au was not detected.

Figure 8.7. Evaluation of Au leaching during dimethylphenylsilane oxidation by MnO₂-Au NPs as catalysts. Reaction profile was expressed as the conversion % as a function of time. At 1 min, the catalysts were removed from the reaction mixture and no further conversion was observed.

No silane conversion was observed in the absence of H₂O, indicating that H₂O may act as the main oxidant in agreement with previous results.³⁴ In absence of O₂, a significant decrease in the reaction rate was observed (~50 % in the dimethyl(phenyl)silane oxidation). This result suggests that O₂ molecules could react with the hydride species adsorbed at the catalyst surface,

making them reactive for the next silane insertion according to the proposed mechanism depicted in Scheme 8.1.^{34,35}

Scheme 8.1. Proposed mechanism for silane oxidation and hydrogen production reactions catalyzed by MnO₂-Au NPs.

The deposition of noble metals over MnO₂ enabled improved electrocatalytic and surface-enhanced Raman scattering performances due to metal-support interactions.^{36,37} Moreover, Au NPs can interact with metal oxides to facilitate the oxidative processes, in which the reducibility of the support material can play an important role over the observed performances.²⁵ Therefore, in order to gain further insights into the role played by the metal-support interactions over the high catalytic activities observed herein, the MnO₂ nanowires and MnO₂-Au NPs were investigated by

temperature programmed reduction (TPR) and Raman and UV-VIS spectroscopies (Figure 8.8 A-C, respectively).

Figure 8.8. Temperature programmed reduction profiles (A), Raman (B), and UV-Vis (C) spectra for MnO_2 nanowires and MnO_2 -Au NPs.

The TPR profile for the MnO₂ nanowires exhibited only a single and narrow reduction peak centered at 373 °C. Interestingly, the TPR profile was dramatically different for the MnO₂-Au NPs. In this case, reduction of MnO₂ support was facilitated and three main reduction steps corresponding to the reduction of MnO₂ to Mn₂O₃ (233 °C), Mn₂O₃ to Mn₃O₄ (305 °C), and then Mn₃O₄ to MnO (362 °C) could be observed.²⁵ This result clearly suggests that strong metal-support interactions take place in the MnO₂-Au NPs, in which the presence of ultrasmall Au NPs facilitated/promoted the MnO₂ reduction.^{25,38} Raman and UV-VIS spectroscopies (Figure 8.8 B and C, respectively) are in agreement with these observations. The Raman spectra for MnO₂ (Figure 8.8 B) displayed 522 and 646 nm signals assigned to the characteristic MnO₂ vibration modes. On the other hand, only a broad band centered at 592 nm was observed for the MnO₂-Au NPs, which can be explained by the distortion of the Mn-O-Mn chain in the octahedral manganese oxide lattice by the presence of Au, leading to loss of translational symmetry that activates otherwise Raman-forbidden oxygen vibrations.³⁶ Therefore, this broad band in the Raman spectra due to the presence Au reflect the phonon density of states rather than the Raman-allowed zone center phonons in MnO₂.³⁶ The UV-VIS spectra for MnO₂ nanowires displayed a broad band at 448 nm assigned to the d-d transitions (Figure 8.8 C).³⁹ This signal was suppressed for MnO₂-Au NPs, while a broad and peak centered at 538 nm which is assigned to the dipole mode of the localized surface plasmon resonance excitation SPR in Au,⁴⁰ in agreement with the Au NPs deposition over MnO₂ nanowires.

In order to gain further insights into the surface composition, oxidation state and the charge transfer tendencies between Au and MnO₂, both MnO₂ nanowires and MnO₂-Au NPs were investigated by XPS as depicted in Figure 8.9 A-C (XPS spectra) and Table 8.2 (XPS parameters and assignments).

Figure 8.9. XPS spectra of Mn 2p (A), O 1s (B) and Au 4f core levels for MnO₂ nanowires and MnO₂-Au NPs.

Table 8.2. Binding energies, surface composition, and Au:Mn ratio for MnO₂ nanowires and MnO₂-Au NPs measured by XPS analyses.

Catalyst	BE of Au 4f _{7/2} (eV)		BE of Mn 2p _{3/2} (eV)	BE of O 1s (eV)			Au:Mn
	Au ⁰	Au ^{δ+}		O _L	O _S	O _W	
MnO ₂	no signal	no signal	642.9	529.9 (59)*	532.0 (28)*	533.9 (13)*	N/A
MnO ₂ -Au	83.7 (80)*	85.2 (20)*	641.8	529.5 (51)*	531.4 (35)*	533.6 (14)*	0.30

* Percent of Au or O species

Mn 2p and Au 4f core levels presented well-separated spin-orbit components at $\Delta \sim 11.5$ and 3.7 eV, respectively. The binding energies (BE) of Au 4f_{7/2} and Mn 2p_{3/2} regions indicated slight shifts relative to bulk Au (84.0 ± 0.2 eV) and Mn (462.4 ± 0.2 eV) which can be explained due to the formation of nanosized particles that generally modify surface properties. In order to probe the surface structural and compositional changes that may occur during the Au deposition onto the MnO₂ surface, the Mn 2p, and O 1s XPS spectra were included for MnO₂ nanowires and MnO₂-Au NPs. The XPS spectrum for the MnO₂ nanowires (Figure 8.9 A) displays its main peak at the Mn 2p_{3/2} region centered at 642.9 eV, which can be to the presence of Mn⁴⁺ species in good agreement with XRD analysis.^{38,41} Interestingly, a variation in the oxidation states of Mn species was observed after the Au NPs deposition at MnO₂ surface. In this case, the main peak at the Mn 2p_{3/2} region was shifted and broadened to 641.8 eV, which indicates the presence of Mn species in lower oxidation states, and thus the partial reduction of Mn⁴⁺ to Mn ^{δ +} ($\delta < 4$) at the surface.⁴² One plausible explanation for the observed reduction of Mn⁴⁺ species at the surface is the utilization of sodium borohydride (a reducing agent) during the Au NPs deposition step. However, this detected shift to lower binding energy region is also expected due to the charge transfer at the metal-support interface as a result of metal-support interactions.^{42,43}

The O 1s XPS spectra obtained from MnO₂ and MnO₂-Au NPs catalysts are shown in Figure 8.9 B. Three surface oxygen species could be observed in the O 1s XPS spectra. The binding energy between 529.9-529.5 eV was characteristic of the lattice oxygen (denoted as O_L), the binding energies between 532.0-531.4 eV were assigned to oxygen vacancies or the surface oxygen ions (denoted as O_s), and the binding energies around 533.9 eV were characteristic of adsorbed water (O_w).⁴¹ As expected, the analyses of O 1s XPS spectra are in agreement with the Mn 2p_{3/2} XPS results. The Au NPs deposition led to a decrease in the O_L/O_s ratio, demonstrating

the enrichment of oxygen vacancies or the surface oxygen ions probably induced by the partial reduction of MnO₂ in presence of sodium borohydride during the Au NPs deposition step and/or charge transfer from Au to MnO₂ due to metal-support interactions.^{37,42,43}

In addition to partial MnO₂ reduction that led to an increase concentration of oxygen ions at their surface, the Au 4f XPS spectra (Figure 8.9 C) for the MnO₂-Au NPs displayed broad peaks in the Au 4f region, suggesting the presence of different oxidation states (Au⁰ and Au^{δ+} species).⁴⁴ In order to quantify these differences, the Au 4f_{7/2} region was de-convoluted into 2 peaks: one at 83.7 eV assigned to Au⁰ species and other at 85.2 eV related to Au^{δ+} species. As depicted in Table 8.2, the Au NPs deposition at the MnO₂ surface led to the formation of a significant concentration of Au^{δ+} species. For instance, the Au^{δ+}/Au⁰ ratio was ~20 % in the MnO₂-Au NPs. Experimental and theoretical studies on Au-based catalysts have demonstrated that the most catalytically active sites in oxidation reactions correspond to Au^{δ+} surface species.^{44,45} Remarkably, our catalyst displayed a higher number of Au^{δ+} surface species relative to other reported Au-based catalysts displaying high activities towards oxidation reactions.^{4,38,46,47}

Therefore, we believe that the improved catalytic activities observed for the MnO₂-Au NPs can be assigned to: *i*) the metal-support interactions, in which the presence of Au NPs could facilitate oxidative processes and thus yield high performances towards the oxidation of hydrosilanes; *ii*) the significant concentration of Au^{δ+} species and oxygen vacancies at the catalyst surface that represent highly catalytically active sites towards oxidation reactions, and *iii*) the Au NPs ultrasmall sizes at the MnO₂ surface that enable the exposure of high energy Au surface/facets (Figure 8.10), high surface-to-volume ratios, and their uniform dispersion. The catalytic activity, reusability, and low Au loadings described herein for the MnO₂-Au catalysts agree with the principles of Green Chemistry applied to nanoscience, which encompasses the design of safer

nanomaterials that can both meet performance specifications and may pose minimal health/environmental impacts.⁴⁸

Figure 8.10. HRTEM image showing an ultrasmall Au nanoparticle at the MnO₂ surface. The presence of a faceted surface can be clearly identified from the image.

Although Au NPs supported on different substrates can also catalyze this transformation, the MnO₂-Au NPs catalysts described in this paper displayed significantly improved catalytic performances relative to conventional Au-SiO₂ material and other systems containing Au NPs described in the literature as depicted in Table 8.3.^{5,7–10,34}

Table 8.3. Oxidation of dimethyl(phenyl)silane in different solvents over MnO₂-Au NPs^[a] and other catalysts reported in literature.

Catalysts	Au loading (mol %)	Solvent	Time (min)	Conversion (%)	TOF (h ⁻¹)	Ref.
MnO ₂ -Au	0.001	water	10	>99	590000 ^b	This work
Au-SiO ₂	0.1	water	10	23	1534	This Work
Au-SiO ₂	0.1	water	60	>99	983	This Work
AuHPA	0.83	water	180	>99	40 ^b	5
SBA-PIL-Au	0.4	water	180	>99	83 ^b	7
AuCNT	0.1	THF	45	98	72000	8
Au/SiO ₂	0.4	THF	10	>99	14850 ^b	9
AuNPore	1.0	acetone	60	>99	10800 ^b	10
Au-2	0.1	water	40	>99	10167 ^b	34

^[a] Reactions conditions: silane (0.025 mmol), H₂O (0.5 mL), 25 °C, 800 rpm. All reactions were performed in duplicate

^[b] TOF based on the gold loading.

For example, MnO_2 -Au NPs displayed significantly higher catalytic activities than the conventional Au/ SiO_2 material under far lower metal loadings in the catalytic reaction (0.001 mol Au % vs 0.1 mol % used for the Au/ SiO_2). This catalyst was obtained by conventional wet impregnation according previous protocol.⁴⁹ Moreover, Au loading and the TOF value obtained for the MnO_2 -Au NPs catalysts ($\text{TOF} = 590000 \text{ h}^{-1}$) were much higher relative to conventional Au- SiO_2 catalyst prepared by wet impregnation, and Au NPs supported on carbon nanotubes, SiO_2 , SBA-15, $\text{AlO}(\text{OH})$, and hydroxyapatite.^{5,7-10,34} While the synthetic routes to produce these systems were relatively complicated and presented several steps, our approach to MnO_2 -Au NPs was straightforward and enabled the synthesis of a relatively large amount of nanomaterial (40 mg per batch; reaction volume: 12 mL). In addition, by using the same amount of MnO_2 nanowires and by changing only the volumes of 120 mM BH_4^- (aq) and 24 mM AuCl_4^- (aq) added during the Au deposition step, the Au loading/coverage at the surface of the nanowires could be controlled. For example, when 100 μL of 120 mM NaBH_4 (aq) and 100 μL of 24 mM AuCl_4^- (aq) solutions were added to 40 mg of MnO_2 nanowires during the Au deposition, the Au content in the suspension corresponded to 0.02 mg/L. However, if 500 μL of each solutions were employed during the synthesis, an Au content corresponded to 0.96 mg/L would be observed. Figure 8.11 shows SEM images of MnO_2 -Au NPs with different Au weight percentage (Figure 8.11 A and B).

— 40 nm

Figure 8.11. SEM images of MnO₂-Au NPs showing the control over the loading/coverage of Au NPs over the MnO₂ surface as a function of the amount of BH₄⁻_(aq) and AuCl₄⁻_(aq) employed during the synthesis. The MnO₂-Au NPs depicted in (A) and (B) were obtained under similar conditions as described in Figure 8.1, except that the same volume of 120 mM BH₄⁻_(aq) and 24 mM AuCl₄⁻_(aq) added during the synthesis was changed, corresponding to 100 and 500 μL (A and B, respectively).

8.4. Conclusions

We have demonstrated that MnO₂ nanowires decorated with ultrasmall Au NPs (NPs having diameters of 3 nm) can be employed as heterogeneous catalysts towards the green oxidation

of hydrosilanes and H₂ production. Surprisingly, we observed that high catalytic performances (TOF = 590000 h⁻¹) could be achieved towards hydrosilane oxidation employing ultralow Au loadings (0.001 – 0.0002 mol % in terms of Au), water as solvent and oxidant, and at room temperature. Moreover, the MnO₂-Au NPs displayed good stability/recyclability, and no morphological changes or loss of activity were observed even after 10 reaction cycles. The MnO₂-Au NPs catalysts were comprised of MnO₂ nanowires 34 ± 5 nm in width and > 1 μm in length, which could be directly employed as templates for the deposition of ultrasmall Au NPs over their surface employing AuCl₄⁻_(aq) as the Au precursor, BH₄⁻_(aq) as the reducing agent, PVP as the stabilizer, and ethylene glycol as the solvent. The Au NPs were uniformly deposited over the entire surface of the MnO₂ nanowires, displayed spherical shape, and were monodisperse. Moreover, their coverage/loading could be controlled by adjusting the amount of AuCl₄⁻_(aq) and BH₄⁻_(aq) added during the synthesis. Our results show that the utilization of supported ultrasmall Au NPs having controlled sizes and dispersion may inspire the design of novel catalysts capable of pushing the limits of Au heterogeneous catalysis, in which high catalytic performances towards green transformations can be achieved even at ultralow metal loadings.

8.5. References

- (1) Zhang, Y.; Cui, X.; Shi, F.; Deng, Y. Nano-Gold Catalysis in Fine Chemical Synthesis. *Chem. Rev.* **2011**, *112* (4), 2467–2505.
- (2) Min, B. K.; Friend, C. M. Heterogeneous Gold-Based Catalysis for Green Chemistry: Low-Temperature CO Oxidation and Propene Oxidation. *Chem. Rev.* **2007**, *107* (6), 2709–2724.
- (3) Zhang, G.; Peng, Y.; Cui, L.; Zhang, L. Gold-Catalyzed Homogeneous Oxidative Cross-Coupling Reactions. *Angew. Chemie Int. Ed.* **2009**, *48* (17), 3112–3115.
- (4) da Silva, A. G. M.; Fajardo, H. V.; Balzer, R.; Probst, L. F. D.; Lovón, A. S. P.; Lovón-Quintana, J. J.; Valença, G. P.; Schreine, W. H.; Robles-Dutenhefner, P. A. Versatile and Efficient Catalysts for Energy and Environmental Processes: Mesoporous Silica Containing

- Au, Pd and Au-Pd. *J. Power Sources* **2015**, 285 (0), 460–468.
- (5) Mitsudome, T.; Noujima, A.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Supported Gold Nanoparticle catalyst for the Selective Oxidation of Silanes to Silanols in Water. *Chem. Commun.* **2009**, 35, 5302–5304.
 - (6) Jeon, M.; Han, J.; Park, J. Transformation of Silanes into Silanols Using Water and Recyclable Metal Nanoparticle Catalysts. *ChemCatChem* **2012**, 4 (4), 521–524.
 - (7) Ma, L.; Leng, W.; Zhao, Y.; Gao, Y.; Duan, H. Gold Nanoparticles Supported on the Periodic Mesoporous Organosilica SBA-15 as an Efficient and Reusable Catalyst for Selective Oxidation of Silanes to Silanols. *RSC Adv.* **2014**, 4 (13), 6807–6810.
 - (8) John, J.; Gravel, E.; Hagège, A.; Li, H.; Gacoin, T.; Doris, E. Catalytic Oxidation of Silanes by Carbon Nanotube–Gold Nanohybrids. *Angew. Chemie Int. Ed.* **2011**, 50 (33), 7533–7536.
 - (9) Li, W.; Wang, A.; Yang, X.; Huang, Y.; Zhang, T. Au/SiO₂ as a Highly Active Catalyst for the Selective Oxidation of Silanes to Silanols. *Chem. Commun.* **2012**, 48 (73), 9183–9185.
 - (10) Asao, N.; Ishikawa, Y.; Hatakeyama, N.; Menggenbateer; Yamamoto, Y.; Chen, M.; Zhang, W.; Inoue, A. Nanostructured Materials as Catalysts: Nanoporous-Gold-Catalyzed Oxidation of Organosilanes with Water. *Angew. Chemie Int. Ed.* **2010**, 49 (52), 10093–10095.
 - (11) Hill, C. L. Homogeneous Catalysis: Controlled Green Oxidation. *Nature* **1999**, 401 (6752), 436–437.
 - (12) Sheldon, R. A. Fundamentals of Green Chemistry: Efficiency in Reaction Design. *Chem. Soc. Rev.* **2012**, 41 (4), 1437–1451.
 - (13) Parmeggiani, C.; Cardona, F. Transition Metal Based Catalysts in the Aerobic Oxidation of Alcohols. *Green Chem.* **2012**, 14 (3), 547–564.
 - (14) Wen, C.; Yin, A.; Dai, W.-L. Recent Advances in Silver-Based Heterogeneous Catalysts for Green Chemistry Processes. *Appl. Catal. B Environ.* **2014**, 160–161 (0), 730–741.
 - (15) Polshettiwar, V.; Varma, R. S. Green Chemistry by Nano-Catalysis. *Green Chem.* **2010**, 12 (5), 743–754.
 - (16) Sheldon, R. A.; Arends, I. W. C. E.; ten Brink, G.-J.; Dijkman, A. Green, Catalytic Oxidations of Alcohols. *Acc. Chem. Res.* **2002**, 35 (9), 774–781.
 - (17) Rodrigues, T. S.; da Silva, A. G. M.; Gonçalves, M. C.; Fajardo, H. V; Balzer, R.; Probst, L. F. D.; Camargo, P. H. C. AgPt Hollow Nanodendrites: Synthesis and Uniform Dispersion over SiO₂ Support for Catalytic Applications. *ChemNanoMat* **2015**, 1 (1), 46–51.
 - (18) Kim, B. H.; Hackett, M. J.; Park, J.; Hyeon, T. Synthesis, Characterization, and Application of Ultrasmall Nanoparticles. *Chem. Mater.* **2014**, 26 (1), 59–71.
 - (19) Yang, P.; Ding, Y.; Lin, Z.; Chen, Z.; Li, Y.; Qiang, P.; Ebrahimi, M.; Mai, W.; Wong, C. P.; Wang, Z. L. Low-Cost High-Performance Solid-State Asymmetric Supercapacitors Based on MnO₂ Nanowires and Fe₂O₃ Nanotubes. *Nano Lett.* **2014**, 14 (2), 731–736.
 - (20) Lu, X.; Zhai, T.; Zhang, X.; Shen, Y.; Yuan, L.; Hu, B.; Gong, L.; Chen, J.; Gao, Y.; Zhou, J.; et al. WO_{3-x}@Au@MnO₂ Core–Shell Nanowires on Carbon Fabric for High-

- Performance Flexible Supercapacitors. *Adv. Mater.* **2012**, *24* (7), 938–944.
- (21) Xiao, W.; Wang, D.; Lou, X. W. Shape-Controlled Synthesis of MnO₂ Nanostructures with Enhanced Electrocatalytic Activity for Oxygen Reduction. *J. Phys. Chem. C* **2010**, *114* (3), 1694–1700.
 - (22) Truong, T. T.; Liu, Y.; Ren, Y.; Trahey, L.; Sun, Y. Morphological and Crystalline Evolution of Nanostructured MnO₂ and Its Application in Lithium–Air Batteries. *ACS Nano* **2012**, *6* (9), 8067–8077.
 - (23) Wang, X.; Li, Y. Selected-Control Hydrothermal Synthesis of α - and β -MnO₂ Single Crystal Nanowires. *J. Am. Chem. Soc.* **2002**, *124* (12), 2880–2881.
 - (24) Chen, W.-M.; Qie, L.; Shao, Q.-G.; Yuan, L.-X.; Zhang, W.-X.; Huang, Y.-H. Controllable Synthesis of Hollow Bipyramid β -MnO₂ and Its High Electrochemical Performance for Lithium Storage. *ACS Appl. Mater. Interfaces* **2012**, *4* (6), 3047–3053.
 - (25) Alhumaimess, M.; Lin, Z.; He, Q.; Lu, L.; Dimitratos, N.; Dummer, N. F.; Conte, M.; Taylor, S. H.; Bartley, J. K.; Kiely, C. J.; et al. Oxidation of Benzyl Alcohol and Carbon Monoxide Using Gold Nanoparticles Supported on MnO₂ Nanowire Microspheres. *Chem. – A Eur. J.* **2014**, *20* (6), 1701–1710.
 - (26) Thapa, A. K.; Shin, T. H.; Ida, S.; Sumanasekera, G. U.; Sunkara, M. K.; Ishihara, T. Gold–Palladium Nanoparticles Supported by Mesoporous β -MnO₂ Air Electrode for Rechargeable Li-Air Battery. *J. Power Sources* **2012**, *220* (0), 211–216.
 - (27) Jung, K.-N.; Riaz, A.; Lee, S.-B.; Lim, T.-H.; Park, S.-J.; Song, R.-H.; Yoon, S.; Shin, K.-H.; Lee, J.-W. Urchin-like α -MnO₂ Decorated with Au and Pd as a Bi-Functional Catalyst for Rechargeable Lithium–oxygen Batteries. *J. Power Sources* **2013**, *244* (0), 328–335.
 - (28) Liu, S.-Y.; Wang, G.; Xie, J.; Tu, F.; Yang, H.; Zhang, S.; Zhu, T.; Cao, G. S.; Zhao, X. B. Au-Nanocrystals-Decorated δ -MnO₂ as Efficient Catalytic Cathode for High-Performance Li-O₂ Batteries. *Nanoscale* **2015**, *2015*, *7*, 9589–9596.
 - (29) Qiu, T.; Luo, B.; Giersig, M.; Akinoglu, E. M.; Hao, L.; Wang, X.; Shi, L.; Jin, M.; Zhi, L. Au@MnO₂ Core–Shell Nanomesh Electrodes for Transparent Flexible Supercapacitors. *Small* **2014**, *10* (20), 4136–4141.
 - (30) Bassindale, A. R.; Lau, J. C.-Y.; Taylor, P. G. Nucleophile-Assisted Racemisation of Halosilanes; an Alternative Pathway Involving Halide Exchange. *J. Organomet. Chem.* **1988**, *341* (1–3), 213–224.
 - (31) Débart, A.; Paterson, A. J.; Bao, J.; Bruce, P. G. α -MnO₂ Nanowires: A Catalyst for the O₂ Electrode in Rechargeable Lithium Batteries. *Angew. Chemie* **2008**, *120* (24), 4597–4600.
 - (32) Jin, Y.; Xi, J.; Zhang, Z.; Xiao, J.; Xiao, F.; Qian, L.; Wang, S. An Ultra-Low Pd Loading Nanocatalyst with Efficient Catalytic Activity. *Nanoscale* **2015**, *7* (12), 5510–5515.
 - (33) Hierso, J.-C.; Beaupérin, M.; Meunier, P. Ultra-Low Catalyst Loading as a Concept in Economical and Sustainable Modern Chemistry: The Contribution of Ferrocenylpolyphosphane Ligands. *Eur. J. Inorg. Chem.* **2007**, *2007* (24), 3767–3780.
 - (34) Liu, T.; Yang, F.; Li, Y.; Ren, L.; Zhang, L.; Xu, K.; Wang, X.; Xu, C.; Gao, J. Plasma Synthesis of Carbon Nanotube-Gold Nanohybrids: Efficient Catalysts for Green Oxidation

- of Silanes in Water. *J. Mater. Chem. A* **2014**, 2 (1), 245–250.
- (35) Shang, C.; Liu, Z.-P. Origin and Activity of Gold Nanoparticles as Aerobic Oxidation Catalysts in Aqueous Solution. *J. Am. Chem. Soc.* **2011**, 133 (25), 9938–9947.
 - (36) Jana, S.; Pande, S.; Sinha, A. K.; Sarkar, S.; Pradhan, M.; Basu, M.; Saha, S.; Pal, T. A Green Chemistry Approach for the Synthesis of Flower-like Ag-Doped MnO₂ Nanostructures Probed by Surface-Enhanced Raman Spectroscopy. *J. Phys. Chem. C* **2009**, 113 (4), 1386–1392.
 - (37) Gorlin, Y.; Chung, C.-J.; Benck, J. D.; Nordlund, D.; Seitz, L.; Weng, T.-C.; Sokaras, D.; Clemens, B. M.; Jaramillo, T. F. Understanding Interactions between Manganese Oxide and Gold That Lead to Enhanced Activity for Electrocatalytic Water Oxidation. *J. Am. Chem. Soc.* **2014**, 136 (13), 4920–4926.
 - (38) Wang, L.-C.; Liu, Y.-M.; Chen, M.; Cao, Y.; He, Fan, K.-N. MnO₂ Nanorod Supported Gold Nanoparticles with Enhanced Activity for Solvent-Free Aerobic Alcohol Oxidation. *J. Phys. Chem. C* **2008**, 112 (17), 6981–6987.
 - (39) Li, W.; Cui, X.; Zeng, R.; Du, G.; Sun, Z.; Zheng, R.; Ringer, S. P.; Dou, S. X. Performance Modulation of α -MnO₂ Nanowires by Crystal Facet Engineering. *Sci. Rep.* **2015**, 5.
 - (40) Silva, A. G. M. da; Rodrigues, T. S.; Macedo, A.; Silva, R. T. P. da; Camargo, P. H. C. An Undergraduate Level Experiment on the Synthesis of Au Nanoparticles and Their Size-Dependent Optical and Catalytic Properties. *Quím. Nova* **2014**, 37 (10), 1716–1720.
 - (41) Liang, S.; Teng, F.; Bulgan, G.; Zong, R.; Zhu, Y. Effect of Phase Structure of MnO₂ Nanorod Catalyst on the Activity for CO Oxidation. *J. Phys. Chem. C* **2008**, 112 (14), 5307–5315.
 - (42) Chang, L.-H.; Sasirekha, N.; Chen, Y.-W.; Wang, W.-J. Preferential Oxidation of CO in H₂ Stream over Au/MnO₂–CeO₂ Catalysts. *Ind. Eng. Chem. Res.* **2006**, 45 (14), 4927–4935.
 - (43) Zhang, H.; Lin, C.; Du, F.; Zhao, Y.; Gao, P.; Chen, H.; Jiao, Z.; Li, X.; Zhao, T.; Sun, Y. Enhanced Interactions between Gold and MnO₂ Nanowires for Water Oxidation: A Comparison of Different Chemical and Physical Preparation Methods. *ACS Sustain. Chem. Eng.* **2015**, 3 (9), 2049–2057.
 - (44) Casaletto, M. P.; Longo, A.; Martorana, A.; Prestianni, A.; Venezia, A. M. XPS Study of Supported Gold Catalysts: The Role of Au⁰ and Au^{+δ} Species as Active Sites. *Surf. Interface Anal.* **2006**, 38 (4), 215–218.
 - (45) Chen, L.; Chabu, J. M.; Liu, Y. Bimetallic AgM (M = Pt, Pd, Au) Nanostructures: Synthesis and Applications for Surface-Enhanced Raman Scattering. *RSC Adv.* **2013**, 3 (13), 4391–4399.
 - (46) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O'Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, 14 (4), 1921–1926.
 - (47) Sudarsanam, P.; Malleshram, B.; Reddy, P. S.; Großmann, D.; Grünert, W.; Reddy, B. M. Nano-Au/CeO₂ Catalysts for CO Oxidation: Influence of Dopants (Fe, La and Zr) on the Physicochemical Properties and Catalytic Activity. *Appl. Catal. B Environ.* **2014**, 144, 900–

908.

- (48) Gilbertson, L. M.; Zimmerman, J. B.; Plata, D. L.; Hutchison, J. E.; Anastas, P. T. Designing Nanomaterials to Maximize Performance and Minimize Undesirable Implications Guided by the Principles of Green Chemistry. *Chem. Soc. Rev.* **2015**, *44*, 5758-5777.
- (49) da Silva, A. G. M.; Rodrigues, T. S.; Slater, T. J. A.; Lewis, E. A.; Alves, R. S.; Fajardo, H. V; Balzer, R.; da Silva, A. H. M.; de Freitas, I.; Oliveira, D. C. de; et al. Controlling Size, Morphology, and Surface Composition of AgAu Nanodendrites in 15 S for Improved Environmental Catalysis under Low Metal Loadings. *ACS Appl. Mater. Interfaces* **2015**, *7* (46), 25624-25632.

Chapter 9. Boosting Catalysts by the Concerted Design of the Support and Active Phase: Achieving High Activities for MnO₂-Au Nanoflowers Towards Green Oxidations

9.1. Introduction

The main goal of nanocatalysis is the development of materials displaying active sites that selectively drive target transformations with high conversion percentages under green and mild experimental conditions.^{1–5} However, in practice, the identification and optimization of these active sites is challenging.^{1,6–8} This is because chemical reactions often take place at poorly defined solid–gas or solid–liquid interfaces, making it difficult to unravel the exact structure of catalytically active sites. This intrinsic limitation on the design and utilization of simple models catalysts for green chemical transformations have motivated researchers to employ an observation-driven approach in nanocatalysis, in which advances in the field have mainly occurred by a combination of accumulated knowledge and trial and error.^{9–13}

Among several types of transformations, the green oxidation of organic compounds has emerged as an important topic in nanocatalysis as it represents an eco-friendly approach based on the use of dioxygen (O₂), water, or hydrogen peroxide as the oxidants, low catalyst loadings, low-temperatures, and atmospheric pressure conditions.^{14–18} Although the concepts of the green chemistry applied in catalysis are very appealing, examples of truly green oxidations remain limited due to the low activity and selectivity of most reported catalysts.^{1,16,19} Therefore, the combination of fundamental knowledge in chemistry, nanoscience, and catalysis is essential to

enable the design and investigation of nanocatalysts displaying improved performances towards green oxidation reactions.

Here, we investigated the concerted optimization of both the support material and active phase in order to achieve superior catalytic performances towards green oxidations in catalysts comprised of ultrasmall Au NPs deposited onto MnO₂ nanoflowers. MnO₂ nanomaterials obtained by hydrothermal synthesis are attractive as supports in oxidation reactions.^{20–22} This is because they often display oxygen vacancies at their surface, which represent attractive sites towards oxidations.^{23–26} On the other hand, Au NPs were chosen as it has been established that they are active towards oxidation of a variety of molecules/substrates.^{27–29} Therefore, we aimed at combining the attractive features of both MnO₂ and Au NPs to achieve high catalytic performances towards green oxidation reactions. Owing to their hierarchical morphology, large specific surface area, ultrasmall Au NPs sizes, and high concentration of oxygen vacancies and Au^{δ+} species at their surface, we found that the MnO₂-Au nanoflowers displayed improved performances towards the green oxidation of CO, benzene, toluene, xylene, glucose, and fructose under mild conditions relative to other reported catalysts as well as MnO₂-Au nanowires and commercial MnO₂-Au NPs obtained under similar conditions.

9.2. Experimental Section

9.2.1. Materials and Instrumentation

Analytical grade chemicals chloroauric acid trihydrate (HAuCl₄.3H₂O, 99.9%, Sigma-Aldrich), manganese sulfate monohydrate (MnSO₄.H₂O, 99%, Sigma-Aldrich), potassium permanganate (KMnO₄, 99%, Sigma-Aldrich), ethylene glycol (EG, 99.8%, Sigma Aldrich),

sodium borohydride (NaBH_4 , 98%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), manganese oxide (MnO_2 , ReagentPlus®, $\geq 99\%$, Sigma-Aldrich), benzene (C_6H_6 , $>99\%$, Vetec), toluene (C_7H_8 , $>99\%$, Vetec) and o-xylene (C_8H_{10} , $>99\%$, Vetec) were used as received. All solutions were prepared using deionized water (18.2 M Ω).

The scanning electron microscopy (SEM) images were obtained using a JEOL field emission gun microscope JSM 6330F operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension containing the nanostructures over a silicon wafer, followed by drying under ambient conditions. The high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL JEM2100 microscope operated at 200 kV. High angle annular dark field (HAADF) and energy dispersive x-ray spectroscopy (EDS) images were acquired using a FEI TECNAI G2 F20 operated at 200 kV. Samples for HRTEM, STEM-HAADF, and STEM-EDX were prepared by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 spectrophotometer. The Au atomic percentage was measured by flame atomic absorption spectrometry (FAAS) with a Shimadzu spectrophotometer, model AA-6300, equipped with an air-acetylene flame. Temperature-programmed reduction with hydrogen (H_2 -TPR) was carried out in a Micrometrics Chemisorb 2705. Usually, 0.1 g of a catalyst was dried with N_2 flow at 125 °C for 1h. Then, the sample was cooled down to room temperature and then reduced at 1000 °C under H_2 flow (30 mL min $^{-1}$). X-ray photoelectron spectroscopy (XPS) data of the samples was obtained with an SPECSLAB II (Phoibos-Hsa 3500 150, 9 channeltrons) SPECS spectrometer, with Al K α source ($E = 1486.6$ eV) operating at 12 kV, pass energy (E_{pass}) = 40 eV, 0.1 eV energy step and acquisition time of 1 s per point. The samples were placed on stainless steel sample-holders and

were transferred under inert atmosphere to the XPS pre-chamber and held there for a 2 h in a vacuum atmosphere. The residual pressure inside the analysis chamber was $\sim 1 \times 10^{-9}$ Torr. The binding energies (BE) of the Ag 3d, Au 4f and C 1s spectral peaks were referenced to the C 1s peak, at 284.5 eV, providing accuracy within ± 0.2 eV. Textural characteristics for the catalysts were determined from nitrogen adsorption isotherms, recorded at -196°C in a Quantachrome Nova 1000. The samples (ca. 100 mg) were degassed for 3 h at 150°C before analysis. Specific surface areas were determined by the Brunauer-Emmett-Teller equation (BET method) from adsorption isotherm generated in a relative pressure range $0.07 < P/P_0 < 0.3$. The total pore volume was calculated from the amount of N_2 adsorbed at a relative pressure close to unity. The average pore diameter was determined by the Barrett-Joyner-Halenda (BJH) method from the N_2 desorption isotherms.

9.2.2. Synthesis of MnO_2 nanoflowers and nanowires (MnO_2 NFs and NWs, respectively)

The MnO_2 nanoflowers and nanowires were obtained by a hydrothermal approach.^{20,22} In a typical procedure for the synthesis of nanoflowers, 0.4 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and 1.0 g of KMnO_4 were dissolved in 30 mL of deionized water. This solution was transferred to an 100 mL Teflon-lined stainless steel autoclave. The autoclave was heated and stirred at 140°C for 1 h and then allowed to cooled down to room temperature. For the synthesis of MnO_2 nanowires, the same procedure was employed but the autoclave was heated and stirred at 140°C for 18 h. The products were collected by centrifugation and washed three times with ethanol (15 mL) and three times with water (15 mL) by successive rounds of centrifugation and removal of the supernatant, Then, they were dried at 80°C for 6 h in air.

9.2.3. Synthesis of MnO_2 -Au nanoflowers, MnO_2 -Au nanowires, and commercial MnO_2 -Au NPs

Typically, 200 mg of MnO_2 nanoflowers and 260 mg of PVP were added to 200 mL of EG. The obtained suspension was transferred to a 25 mL round-bottom flask and kept under vigorous stirring at 90 °C for 20 min. Then, 3.0 mL of an 120 mM $NaBH_4(aq)$ and 3 mL of a 24 mM $AuCl_4^-$ solutions were sequentially added to the reaction flask. This mixture was kept under vigorous stirring for another 1 h to produce MnO_2 -Au NPs. After cooling down to room temperature, the MnO_2 -Au NFs were isolated by centrifugations and washed three times with acetic acid (15 mL), three times with ethanol (15 mL), and three times with water (15 mL) by successive rounds of centrifugation at 6000 rpm for 5 min and removal of the supernatant. After washing, the MnO_2 -Au NFs were dried at 120 °C for 6 h in air. For the synthesis of MnO_2 -Au nanowires and commercial MnO_2 -Au, the same procedure was employed as abovementioned.

9.2.4. CO, Benzene, toluene and o-xylene (BTX) oxidation

The catalytic oxidation of CO was carried out under atmospheric pressure in a fixed-bed quartz tubular reactor with 5 mm of inner diameter. Then the catalysts exposed to the reactant gases mixture, composed by 2% CO, 16% O_2 balanced by N_2 (flow/mass = 500 ml min⁻¹ gcat⁻¹). The catalytic tests were performed at a temperature range from 20 to 150 °C. The reaction products were analyzed by an in-line chromatograph (GC 3800-VARIAN), with two thermal conductivity detectors and three separation packed columns (two Porapak N and one 13X molecular sieve). The CO conversion (X_{CO}) for all the reactions was calculated as follows:

$$X_{CO} (\%) = [(CO_{in} - CO_{out})] / CO_{in} \times 100 \quad (1)$$

where X_{CO} (%) is the CO conversion percentage; CO_{in} is the CO input and CO_{out} is the CO output.

The catalytic oxidation of benzene, toluene and o-xylene was performed in a fixed bed tubular quartz reactor under atmospheric pressure. The following conditions were used: 0.030g catalyst, inlet benzene (1.2 g.m^{-3}), toluene (0.7 g.m^{-3}), o-xylene (0.5 g.m^{-3}) in air, gas flow rate $20 \text{ cm}^3.\text{min}^{-1}$, residence time 0.3 s, gas hourly space velocity 12000 h^{-1} and temperature range 25-300 °C. The reaction data was collected after at least 2 h on-stream at room temperature. The reaction products were determined by gas chromatography-mass spectrometry (GC-MS). The reactant and product mixtures were analyzed using two on-line gas chromatographs equipped with flame ionization and thermal conductivity detectors (FID and TCD, respectively) and an HP-5 column. The catalytic activity was expressed as the degree of the conversion of benzene, toluene and o-xylene, respectively. The conversion of the BTX compounds was calculated as follows:

$$CBTXs (\%) = [(BTXs)_{in} - (BTXs)_{out}] \cdot 100 / (BTXs)_{in} \quad (2)$$

where $CBTXs (\%)$ = percentage of BTX conversion; $(BTXs)_{in}$ = input quantity and $(BTXs)_{out}$ = output quantity.

9.5. Glucose and fructose oxidation

Glucose and fructose oxidation was carried out in a SPR multi reactor equipped with the 24 vials for high throughput screening of the catalytic materials. The catalysts (50 mg) were placed in each reactor. Then, 3 mL of an aqueous sugar solution (1.0 wt.%) was injected. The catalytic tests were performed under air atmosphere or molecular oxygen, at 80°C, and for 4 hours. After the reactions, the reactors were cooled down to room temperature. The reactant mixture was

filtered and analyzed on DIONEX HPLC using Aminex HPX-87H Ion Exclusion column and employing 0.005 mol H₂SO₄ as the eluent (0,45 mL/min).

9.3. Results and Discussion

Our investigations began with the hydrothermal synthesis of MnO₂ nanoflowers. They displayed well-defined shapes, uniform sizes, and a hierarchical structure assembled from petal nanosheets around 15 nm in thicknesses (Figure 9.1 A-B).

Figure 9.1. (A-D) SEM images of pure MnO₂ (A-B) and MnO₂-Au nanoflowers (C-D) depicting the ultrasmall Au NPs as well as their uniform distribution over the MnO₂ surface.

This material was then employed as physical templates for the deposition of Au NPs at their surface. We developed herein a facile procedure in which the MnO₂ nanoflowers were directly employed as physical templates for deposition of ultrasmall Au NPs at their surface. No surface modification/functionalization steps were required. Our strategy was based on chemical reduction of AuCl₄⁻_(aq) by BH₄⁻_(aq) in the presence of MnO₂ nanoflowers, PVP as the stabilizing agent, EG (ethylene glycol) as the solvent, and 90 °C as the reaction temperature. The MnO₂-Au nanoflowers obtained by this route are shown in Figures 9.1 C-D. The deposited Au NPs were monodisperse, had ultrasmall sizes (2.6 ± 0.8 nm), and were uniformly dispersed onto the MnO₂ surface. Therefore, no significant agglomeration, which often lead to detrimental catalytic properties, was detected.

Figure 9.2 shows STEM (Figure 9.2 A), HAADF-STEM (Figure 9.2 B), STEM-EDX elemental mapping (Figure 9.2 C and D), and HRTEM (Figure 9.2 E) images for the MnO₂-Au nanoflowers. These results further confirm the uniform deposition of monodisperse and ultrasmall Au NPs over the entire outer surface of the MnO₂ nanoflowers (Figure 9.2 A and B). Moreover, no morphological changes in the MnO₂ shape could be detected after Au NPs deposition. The STEM-EDX maps revealed that Mn and Au are well distributed over the entire extension of the nanoflowers (Figure 9.2 C and D). HRTEM images (Figure 9.2 E) revealed that each Au nanoparticle was single-crystalline and displayed the characteristic *fcc* Au lattice spacings.

Figure 9.2. HRTEM (A) and HAADF (B) images of MnO₂-Au nanoflowers showing the uniform distribution of the deposited Au NPs over the MnO₂ surface. Regions indicated by dashed squares are shown at the elemental maps (C and D) extracted from a STEM-EDX spectrum image of the MnO₂-Au nanoflowers. The lattice fringes orientation in the phase-contrast HRTEM image (E) show that Au NPs were single crystalline.

In addition to the MnO₂-Au nanoflowers, we were interested on the understanding of how the structural, electronic, textural, and catalytic properties in MnO₂-Au would change as a function of the support morphology. To this end, we also prepared MnO₂ nanowires and commercial MnO₂ decorated with ultrasmall Au NPs materials by a similar experimental approach. Figure 9.3 shows

HRTEM and SEM images for MnO₂ nanowires (Figure 9.3 A and B) and commercial MnO₂ (Figure 9.3 C and D) decorated with ultrasmall Au NPs.

Figure 9.3. (A-B) TEM and (C-D) SEM images of MnO₂-Au nanowires (A-B) and MnO₂-Au commercial (C-D) obtained by the same approach described in Figure 9.1.

They also displayed an uniform distribution of Au NPs at their surface with no significant agglomeration of particles. However, the Au NPs sizes increased when the deposition was performed in the presence of MnO₂ nanowires and commercial MnO₂ as supports relative to the nanoflowers. Specifically, the Au NPs sizes corresponded to 3.2 ± 0.9 nm and 16 ± 4 nm in diameter in the catalyst containing MnO₂ nanowires and commercial MnO₂, respectively. These variations in the Au NPs size agree with a heterogeneous nucleation and growth mechanism for Au deposition.^{30,31} As MnO₂ nanoflowers are expected to have a larger surface areas relative to their

nanowires and commercial analogues, there would be more sites available for the heterogeneous nucleation, leading to smaller sizes under the same concentration of AuCl_4^- (aq) precursor. The values for the surface area, pore volume, and average pore size were obtained by BET analysis and are shown in Table 9.1.

Table 9.1. Chemical and textural properties measured by FAAS and N_2 -physisorption for the MnO_2 and MnO_2 -Au nanoflowers, nanowires, and commercial materials.

Catalyst	Au Content (wt%)	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter ($\text{\AA}$)
MnO_2 -Au nanoflowers	1.3	196	0.42	6.1
MnO_2 nanoflowers	n/a	194	0.41	6.1
MnO_2 -Au nanowires	1.3	125	0.16	6.9
MnO_2 nanowires	n/a	122	0.16	6.8
MnO_2 -Au commercial	1.4	15	0.05	17.8
MnO_2 commercial	n/a	14	0.05	17.8

The specific surface area for the MnO_2 nanoflowers was higher ($194 \text{ m}^2/\text{g}$) relative to MnO_2 nanowires ($122 \text{ m}^2/\text{g}^{-1}$) and MnO_2 commercial ($14 \text{ m}^2/\text{g}^{-1}$). This agrees with the Au NPs size variations as a function of the support. The deposition of Au NPs over MnO_2 materials led to a slight increase in the surface area for all samples as a result of the intrinsic high surface area of Au NPs (Table 9.1). The MnO_2 -Au nanoflowers also displayed a smaller average BJH pore diameter (6.1 nm) relative to MnO_2 -Au nanowires (6.9 nm), and commercial MnO_2 -Au (17.8 nm). The Au content in the MnO_2 -Au materials as determined by FAAS analysis was similar for all samples, corresponding to 1.3, 1.3, and 1.4 wt. %, for the MnO_2 -Au materials containing the nanoflowers, nanowires, and commercial MnO_2 , respectively.

The reducibility of the support material represents an important parameter in the context of catalytic applications.^{32–34} This is because Au NPs (active phase) can strongly interact with

metal oxides (support), changing their redox properties.^{32–34} This, in turn, can affect catalytic activities.^{24,35} We investigated their reducibility of the prepared MnO₂-Au materials by temperature programmed reduction (TPR) as illustrated in Figure 9.4.

Figure 9.4. Temperature reduction programmed (TPR) profiles for pure MnO₂ and MnO₂-Au, nanowires, nanoflowers, and commercial materials showing the greater reducibility property of MnO₂-Au nanoflowers.

The TPR profile for the pure MnO₂ nanoflowers displayed two peaks centered at 323 and 284 °C, assigned to the reduction of MnO₂ to Mn_xO_y (displaying lower oxidation states).^{32–34} After the deposition of the ultrasmall Au NPs at the nanoflowers surface, a marked change in the TPR profile was observed. In this case, the reduction of MnO₂ was shifted to lower temperatures and

three main reduction peaks corresponding to the reduction of MnO_2 to Mn_2O_3 (287 °C), Mn_2O_3 to Mn_3O_4 (252 °C), and then Mn_3O_4 to MnO (113 °C) could be observed.^{32–34} This result suggests that strong metal-support interactions take place in the MnO_2 -Au nanoflowers, in which the presence of ultrasmall Au NPs facilitated the MnO_2 reduction.^{32–34} The same overall behavior was observed for the MnO_2 nanowires and commercial MnO_2 . However, the reduction temperature values were higher as compared to the materials containing the nanoflowers. These results agree with previous observations that smaller Au NPs and high surface area supports lead to stronger metal-support interactions due to the higher interfacial perimeter between Au and the oxide support. This allows for a more effective gas adsorption and fast surface reduction processes.^{32,36}

In order to investigate the surface composition, oxidation state, and the charge transfer tendencies between Au NPs and MnO_2 materials, we performed XPS analyses as depicted in Figure 9.5 (XPS spectra) and Table 9.2 (XPS parameters and assignments). We were interested in probing the surface structural changes that possibly could be observed after the deposition of Au NPs at the MnO_2 surface. Figure 9.5 shows the Mn 2p (Figure 9.5 A), O 1s (Figure 9.5 B), and Au 4f (Figure 9.5 C) core-level spectra for MnO_2 nanoflowers, MnO_2 nanowires, and commercial MnO_2 before and after the deposition of Au NPs at their surface. The Mn 2p and Au 4f core levels presented well-separated spin-orbit components at $\Delta \sim 11.5$ and 3.7 eV, respectively. The binding energies (BE) of Au 4f_{7/2} and Mn 2p_{3/2} regions indicated slight shifts relative to bulk Au (84.0 ± 0.2 eV) and Mn (642.5 ± 0.2 eV), which can be explained due to the formation of nanosized particles that generally modify the surface properties.^{33,37}

Figure 9.5. XPS spectra of Mn 2p (A), O 1s (B) and Au 4f (C) core levels for the MnO₂ and MnO₂-Au nanoflowers, MnO₂-Au nanowires, commercial MnO₂-Au materials.

Table 9.2. Binding energies, surface composition, and Au:Mn ratio for the MnO₂ and MnO₂-Au bulk, nanowires and nanoflowers measured by XPS analyses.

Sample	BE of Au 4f _{7/2} (eV)		BE of Mn 2p _{3/2} (eV)	BE of O 1s (eV)			Au 4f / Mn 2p
	I (Au ⁰)	II (Au ^{δ+})		O _L	O _S	O _W	
MnO ₂ -Au nanoflowers	83.6 (74)*	85.5 (26)*	641.7	529.8 (41)*	531.6 (47)*	533.7 (12)*	0.4
MnO ₂ nanoflowers	no signal	no signal	642.6	530.0 (61)*	532.0 (28)*	534.1 (11)*	
MnO ₂ -Au nanowires	83.7 (80)*	85.4 (20)*	641.7	530.1 (46)*	532.0 (39)*	534.5 (15)*	0.4
MnO ₂ nanowires	no signal	no signal	642.6	529.5 (52)*	531.5 (34)*	533.5 (14)*	
Commercial MnO ₂ -Au	84.5 (80)*	86.5 (18)*	642.0	530.1 (56)*	532.0 (30)*	534.2 (14)*	0.3
Commercial MnO ₂	no signal	no signal	642.7	530.0 (56)*	532.2 (29)*	534.3 (15)*	

* Percent of Au or O species

The XPS spectrum for the MnO₂ nanoflowers displayed its main peak at the Mn 2p_{3/2} region centered at 642.6 eV, which can be assigned to the presence of Mn⁴⁺ species. Interestingly, a variation in the oxidation state for the Mn species was observed after the Au NPs deposition. In this case, the main peak at the Mn 2p_{3/2} region was shifted and broadened to 641.7 eV, which indicates the presence of Mn species in lower oxidation states, and thus the partial reduction of Mn⁴⁺ to Mn^{δ+} (δ < 4) at the surface.³⁸ Previous investigations have assigned this detected shift to lower binding energy region to strong metal-support interactions,^{23,24,35,39} in which charge transfer at the metal-support interface takes place. The same behavior was observed for the MnO₂ nanowires and commercial MnO₂. However, lower binding energy shifts were detected as compared to the MnO₂-Au nanoflowers sample, indicating a stronger metal-support interaction in the nanoflowers relative to the other materials and in agreement with the TPR data.

The O 1s XPS spectra obtained from MnO₂ and MnO₂-Au NPs materials are shown in Figure 9.5 B. Three surface oxygen species could be observed in the O 1s XPS spectra. The binding energy between 529.9-529.5 eV was characteristic of the lattice oxygen (denoted as O_L), the binding energies between 532.0-531.4 eV were assigned to oxygen vacancies or the surface

oxygen ions (denoted as O_s), and the binding energies around 533.9 eV were characteristic of adsorbed water (O_w).^{23,33} As expected, the analyses of O 1s XPS spectra agrees with the Mn 2p_{3/2} XPS results. The Au NPs deposition over the MnO₂ nanoflowers led to a more significant decrease in the O_L/O_s ratio relative to the MnO₂ nanowires and commercial MnO₂. This demonstrates that the enrichment of oxygen vacancies or the surface oxygen ions was probably induced by the partial reduction of Mn⁴⁺ species during the Au NPs deposition step, which occurred in a higher extent in the nanoflowers support aa compared to the nanowires and commercial MnO₂.

In addition to partial MnO₂ reduction at the surface that led to an increase concentration of oxygen ions, the Au 4f XPS spectra (Figure 9.5 C) displayed broad peaks in the Au 4f region, suggesting the presence of different oxidation states (Au^0 and $Au^{\delta+}$ species).⁴⁰ We quantified these species by the deconvolution of the Au 4f_{7/2} into 2 peaks: *i*) 83.7 eV assigned to Au^0 species and *ii*) 85.2 eV related to $Au^{\delta+}$ species. As observed in Table 9.2, the deposition of Au NPs led to the formation of a significant amount of $Au^{\delta+}$ species. Specifically, the $Au^{\delta+}$ species ratio was ~26 % in the MnO₂-Au nanoflowers. Previous experimental and theoretical investigations on supported Au catalysts have indicated that the most catalytically active sites in oxidation reactions correspond to surface $Au^{\delta+}$ species,^{34,40,41} making this material particularly attractive. It is important to emphasize that the MnO₂-Au nanoflowers presented the higher concentration of these species relative to the MnO₂-Au nanowires, commercial MnO₂-Au, and other reported supported Au catalysts displaying good performances in oxidation transformations.^{23,29,42,43}

Owing to their morphology comprised of ultrasmall Au NPs, large surface areas (hierarchical nanoflowers), high concentration of oxygen vacancies, and $Au^{\delta+}$ species at their surface (strong metal-support interactions), we decided to investigate the catalytic activities of the MnO₂-Au nanoflowers towards the gas-phase green oxidation of organic compounds (benzene,

toluene, o-xylene - BTX), CO, and sugars using molecular oxygen and mild conditions. We also compared their catalytic activities with those employing MnO₂-Au nanowires and commercial MnO₂-Au under similar conditions.

Figure 9.6 depicts the conversion (%) for the CO and BTX oxidation as a function of reaction temperature employing MnO₂-Au nanoflowers, MnO₂-Au nanowires, and commercial MnO₂-Au materials as catalysts.

Figure 9.6. Oxidation (conversion %) of CO (A), benzene (B), toluene (C), and xylene (D) as a function of temperature, catalyzed by MnO₂-Au nanoflowers, MnO₂-Au nanowires, and commercial MnO₂-Au.

While CO is very important in the purification of hydrogen streams from organic compounds reforming and environmental remediation,⁴⁴ BTX comprise volatile organic compounds that are recognized as hazardous contaminants, and their catalytic oxidation has been acknowledged as an effective approach for their removal.⁴⁵ Current challenges in the CO and BTX oxidation include the possibility to achieve substantial conversions at low temperatures and avoiding the formation of side products and coke (which usually leads to the catalyst poisoning).^{44,45} Figure 9.6 A depicts the conversion % for the CO oxidation employing the MnO₂-Au materials as catalysts. In all cases, the conversion % increased with temperature. However, the MnO₂-Au nanoflowers displayed higher conversion % at lower temperatures and thus higher catalytic activities as compared to MnO₂-Au nanowires and commercial MnO₂-Au NPs. In the MnO₂-Au nanoflowers, most of the substrate could be converted at room temperature, and 100 % conversion was achieved at 40 °C. This value corresponded to 64 and 7 for the MnO₂-Au nanowires and commercial MnO₂-Au NPs, respectively. The same trend on the catalytic activities was observed for the BTX oxidation as illustrated in Figure 9.6 B-D (conversion % for the oxidation of benzene, toluene, and xylene, respectively). While the conversion % increased with temperature for all materials, the MnO₂-Au nanoflowers displayed the highest activities in all temperature range, being able to convert most of benzene, toluene and xylene in temperatures below 150 °C. This represents a low temperature, as BTX molecules are well-known for their high thermal stabilities. Specifically, 100%, 69%, 36% conversion for benzene, 94, 58 and 30 % conversion for toluene, and 78, 56, 27 % conversion for o-xylene were detected at 200 °C employing MnO₂-Au nanoflowers, nanowires, and commercial MnO₂-Au materials as catalysts, respectively. It is noteworthy that low conversion % were detected for all MnO₂ supports (Figure 9.7).

Figure 9.7. Oxidation (conversion %) of (A) benzene, (B) toluene, and (C) xylene as a function of temperature, catalyzed by the pure MnO₂ nanoflowers, MnO₂-Au nanowires, and commercial MnO₂-Au materials (depicted in black, red, and blue respectively).

Table 9.3 and 9.4 depicts a comparison on the catalytic activities of the MnO₂-Au nanoflowers relative to other catalysts reported in the literature towards the CO (Table 9.3) and BTX (Table 9.4) oxidation.

Table 9.3. Oxidation of CO over MnO₂-Au nanoflowers and other catalysts reported in literature.

Catalysts	Metal loading (wt %)	Temperature (°C)	Conversion (%)	Ref.
MnO ₂ -Au nanoflowers	1.3	40	100	This work
MnO ₂ -Au nanowires	1.3	50	100	This work
Commercial MnO ₂ -Au	1.4	120	100	This work
Au ₁₄₄ (SR) ₆₀ /CeO ₂	1.0	80	100	46
CeO ₂ /Au/TiO ₂	1.5	89	100	47
Au/t-Co ₃ O ₄	2.6	75	100	48
Au/c-Co ₃ O ₄	2.6	90	100	48
Au/h-Co ₃ O ₄	2.6	40	100	48
Au/TiO ₂ -CO	1.0	80	100	49
Au/TiO ₂ -H	1.0	100	100	49
Au/TiO ₂ APD1	5.0	80	100	50
Au/TiO ₂ APD3	5.0	150	100	50
beta-MnO ₂	n/a	180	100	51
Au/beta-MnO ₂ (Na ₂ CO ₃)	4.75	100	100	51
Au/beta-MnO ₂ (ureia))	4.0	150	100	51
Au/beta-MnO ₂ (NaOH)	4.0	70	100	51
Au-CeO ₂	1.0	70	100	52
Au-CeO _x /TiO ₂	1.0	50	100	52
Au/TiO ₂ -Ni 1	2.0	120	100	53
Au/TiO ₂ -Ni 5	2.0	180	100	53
Au/P25	2.0	130	100	53
Au/TNT-T	4.0	150	100	54
Au/TNT	4.0	180	100	54
Au@FeO _x	0.94	200	100	55
AuZnO-60	4.9	60	100	56
AuZnO-120	4.9	40	100	56

Table 9.4. Oxidation of benzene, and toluene over MnO₂-Au nanoflowers and other catalysts reported in literature.

Catalysts	Metal loading (wt %)	Area BET (m ² /g)	Substrate	T _{90%} of conversion (°C)	Ref.
MnO ₂ -Au nanoflowers	1.3	196	Benzene	<170	This work
MnO ₂ -Au nanoflowers	1.3	196	Toluene	<200	This work
Au/CeO ₂	1.3	79	Toluene	270	57
Au/Ce _{7.5} /Al ₂ O ₃	1.1	139	Toluene	300	57
Au/TiO ₂	1.3	121	Toluene	340	57
PdAu/TiO ₂ core-shell	1.2	151	Toluene	220	58
Pd-Au (alloy)/TiO ₂	1.2	149	Toluene	240	58
Au/bulk Al ₂ O ₃	0.72	12	Toluene	360	59
Au/3DOM Al ₂ O ₃	0.71	118	Toluene	317	59
Au/3DOM CeO ₂ -Al ₂ O ₃	0.74	108	Toluene	279	59
Au ₅ CeTi	2.4	146	Toluene	320 °C	60
Au ₅ FeTi	2.9	107	Toluene	340 °C	60
Au/beta-MnO ₂ (Na ₂ CO ₃)	4.75	160	Benzene	260 °C	51
Au/beta-MnO ₂ (ureia))	4.0	95	Benzene	360 °C	51
Au/beta-MnO ₂ (NaOH)	4.0	120	Benzene	230 °C	51
Au/CuO	1.0	10	Toluene	293 °C	61
Au/Fe ₂ O ₃	1.0	5	Toluene	330 °C	61
Au/La ₂ O ₃	1.0	10	Toluene	>400 °C	61
Au/MgO	1.0	31	Toluene	379 °C	61
Au/NiO	1.0	75	Toluene	313 °C	61
Au/Y ₂ O ₃	1.0	8	Toluene	394 °C	61
Au-Pd/MCM-41	2.9	580	Benzene	450 °C	29
Au-Pd/MCM-41	2.9	580	Toluene	>600 °C	29

These results demonstrate the high catalytic activities the MnO₂-Au nanoflowers for both transformations, in which higher activities (as expressed by higher conversion percentages at lower

temperatures) were detected relative to previously reported catalysts. Furthermore, the MnO₂-Au nanoflowers displayed good catalytic stability towards the CO and BTX oxidations (Figure 9.8). Here, no significant loss of catalytic activity was detected even after 24 h for the CO and benzene oxidation, showing that this nanomaterial may represent promising candidates as catalysts for gas-phase transformations.

Figure 9.8. CO (A) and benzene (B) conversion percentages as a function of time employing MnO₂-Au nanoflowers (Fig.1) as heterogeneous catalysts.

We also employed the obtained MnO₂-Au nanomaterials as catalysts for the oxidation of low molecular weight carbohydrates such as glucose and fructose. The catalytic oxidation of

sugars is highly attractive as several produced sugar acids have applications in the detergent, food, pharmaceutical and cosmetic industries.^{62,63} In this transformation, it is crucial to use highly active and selective catalysts, as sugar oxidations can lead to the formation of multiple products as depicted in Scheme 9.1.

Scheme 9.1. Different possible products for the oxidation of glucose as a model sugar substrate.

Table 9.5 depicts the conversion and selectivity percentages (%) for the oxidation of glucose (employed as a model substrate) catalyzed by MnO₂-Au nanomaterials.

Table 9.5. Oxidation (conversion %) of glucose catalyzed by MnO₂-Au nanomaterials.

Catalyst	Temp. (°C)	Oxidant	Conv. ^a (%)	Selectivity ^a (%)			
				Oxalic	Formic	Gluconic	Others
				ac. (%)	ac. (%)	ac. (%)	(%)
MnO ₂ -Au nanoflowers	25	O ₂	11	7	-	93	-
MnO ₂ -Au nanoflowers	50	O ₂	36	3	-	97	-
MnO ₂ -Au nanoflowers	80	O ₂	96	3	-	97 (93) ^b	-
MnO ₂ -Au nanoflowers	80	Air	52	67	-	33	-
MnO ₂ -Au nanowires	80	O ₂	46	6	-	94	-
Commercial Au/MnO ₂	80	O ₂	6	1	9	99	-
Commercial Au/MnO ₂	80	Air	-	-	-	-	-

^aReaction conditions: 1.0 wt% glucose aqueous solution, catalyst = 0.050g, H₂O (3 mL), T = 25, 50 or 80 °C, and air atmosphere or molecular oxygen as the oxidants. Conversion and Selectivity were determined by HPLC, GC-FID and GC-MS based on the peak area of glucose and the respective products.

^bThe value in parenthesis represents the yield for the isolated product.

Surprisingly, we found that MnO₂-Au nanoflowers displayed high catalytic activities and selectivity for the glucose oxidation in mild conditions (low temperatures, and atmospheric air or oxygen as the oxidants). The oxidation of glucose began to take place at room temperature (11 % of conversion). The conversion % increased with temperature, achieving 96 % at 80 °C using molecular oxygen as the oxidant. The MnO₂-Au nanoflowers were highly selective for the formation of gluconic acid (97 % at 80 °C using oxygen as the oxidant). Moreover, the MnO₂-Au nanoflowers were much more active than the MnO₂-Au nanowires and commercial MnO₂-Au NPs under the same reaction conditions (6 and 46 % of glucose conversion at 80 °C and using oxygen as oxidant). When atmospheric air was employed as the oxidant, MnO₂-Au nanoflowers still displayed a good catalytic activity. In this case, 56 % conversion was achieved, and only oxalic

and gluconic acids were generated as the products. Similar results were obtained using fructose as the substrate. In this case, 49 % of fructose conversion was obtained using the MnO₂-Au nanoflowers as catalysts under atmospheric air and 80 °C. Considering how challenging is to reach high activities under the described mild conditions,^{62,63} MnO₂-Au nanoflowers are very promising for green oxidation transformations in the liquid phase.

As aforementioned, we can assign the improved catalytic activities observed for the MnO₂-Au nanoflowers to a variety of interesting and unique features: *i*) the morphology comprised of a hierarchical structure containing ultrasmall Au NPs that lead to a large specific surface area; *ii*) strong metal–support interactions, in which the presence of Au NPs could facilitate oxidative processes and thus high performances towards oxidations; *iii*) the significant concentration of Au^{δ+} species and oxygen vacancies that represent highly active sites towards oxidation reactions; and *iv*) the uniform shapes and sizes of Au NPs displaying a good dispersion over MnO₂ support that is generally crucial to achieve high catalytic activities. The catalytic activity, stability, and mild/green reaction conditions described herein meet the principles of Green Chemistry, which we believe is crucial to envision a sustainable future through nanocatalysis.

9.4. Conclusion

We have demonstrated that the catalytic activities in MnO₂-Au materials can be maximized by the optimization of both the MnO₂ support and the Au NPs structure. Specifically, we developed a simple and efficient strategy to deposit ultrasmall Au NPs onto the surface of MnO₂ nanoflowers, nanowires, and commercial MnO₂. In all the materials, the NPs were uniformly distributed over the surface of the support. However, the Au NPs size as well as the structural, electronic, and

textural properties of the produced catalysts were strongly dependent on the support. In this case, the MnO₂-Au nanoflowers displayed the highest surface areas, smaller pore diameters, higher number of oxygen vacancies, and higher proportion of Au^{δ+} species at the surface. These attributes led to significantly improved catalytic performances towards green oxidations under mild conditions in both the gas and liquid phases relative not only to MnO₂-Au nanowires and commercial MnO₂-Au, but also other Au-based catalysts described in the literature. Specifically, the MnO₂-Au nanoflowers could be employed as highly active towards CO and BTX oxidation in the gas phase. Moreover, they presented excellent catalytic activities for the selective oxidation of sugars (glucose and fructose) in mild conditions, producing only oxalic and gluconic acids as the products. We believe that the results described herein may provide new insights towards the design of supported catalysts displaying improved catalytic performances to target important chemical transformations. In which the combined optimization of both the support and metal nanoparticles can lead to even better catalytic activities relative to the optimization of the support or metal NPs.

9.5. References

- (1) Corma, A. Heterogeneous Catalysis: Understanding for Designing, and Designing for Applications. *Angew. Chemie Int. Ed.* **2016**, *55* (21), 6112–6113.
- (2) Zhang, Z.; Xu, B.; Wang, X. Engineering Nanointerfaces for Nanocatalysis. *Chem. Soc. Rev.* **2014**, *43* (22), 7870–7886.
- (3) Mahmoud, M. A.; Narayanan, R.; El-Sayed, M. A. Enhancing Colloidal Metallic Nanocatalysis: Sharp Edges and Corners for Solid Nanoparticles and Cage Effect for Hollow Ones. *Acc. Chem. Res.* **2013**, *46* (8), 1795–1805.
- (4) Schlögl, R. Heterogeneous Catalysis. *Angew. Chemie Int. Ed.* **2015**, *54* (11), 3465–3520.
- (5) Dai, Y.; Wang, Y.; Liu, B.; Yang, Y. Metallic Nanocatalysis: An Accelerating Seamless Integration with Nanotechnology. *Small* **2015**, *11* (3), 268–289.
- (6) Fortunelli, A.; Vajda, S. Editorial: Nanocatalysis. *Catal. Sci. Technol.* **2016**, *6* (18), 6763–6765.
- (7) Mudiyansele, K.; Senanayake, S. D.; Faria, L.; Kundu, S.; Baber, A. E.; Graciani, J.; Vidal, A. B.; Agnoli, S.; Evans, J.; Chang, R.; et al. Importance of the Metal–Oxide Interface in Catalysis: In Situ Studies of the Water–Gas Shift Reaction by Ambient-Pressure

- X-Ray Photoelectron Spectroscopy. *Angew. Chemie Int. Ed.* **2013**, 52 (19), 5101–5105.
- (8) Norskov, J. K.; Bligaard, T.; Hvolbaek, B.; Abild-Pedersen, F.; Chorkendorff, I.; Christensen, C. H. The Nature of the Active Site in Heterogeneous Metal Catalysis. *Chem. Soc. Rev.* **2008**, 37 (10), 2163–2171.
 - (9) An, K.; Somorjai, G. A. Nanocatalysis I: Synthesis of Metal and Bimetallic Nanoparticles and Porous Oxides and Their Catalytic Reaction Studies. *Catal. Letters* **2015**, 145 (1), 233–248.
 - (10) Chng, L. L.; Erathodiyil, N.; Ying, J. Y. Nanostructured Catalysts for Organic Transformations. *Acc. Chem. Res.* **2013**, 46 (8), 1825–1837.
 - (11) Zaera, F. Nanostructured Materials for Applications in Heterogeneous Catalysis. *Chem. Soc. Rev.* **2013**, 42 (7), 2746–2762.
 - (12) da Silva, A. G. M.; Rodrigues, T. S.; Wang, J.; Yamada, L. K.; Alves, T. V.; Ornellas, F. R.; Ando, R. A.; Camargo, P. H. C. The Fault in Their Shapes: Investigating the Surface-Plasmon-Resonance-Mediated Catalytic Activities of Silver Quasi-Spheres, Cubes, Triangular Prisms, and Wires. *Langmuir* **2015**, 31 (37), 10272–10278.
 - (13) da Silva, A. G. M.; Rodrigues, T. S.; Correia, V. G.; Alves, T. V.; Alves, R. S.; Ando, R. A.; Ornellas, F. R.; Wang, J.; Andrade, L. H.; Camargo, P. H. C. Plasmonic Nanorattles as Next-Generation Catalysts for Surface Plasmon Resonance-Mediated Oxidations Promoted by Activated Oxygen. *Angew. Chemie Int. Ed.* **2016**, 55 (25), 7111–7115.
 - (14) Gilbertson, L. M.; Zimmerman, J. B.; Plata, D. L.; Hutchison, J. E.; Anastas, P. T. Designing Nanomaterials to Maximize Performance and Minimize Undesirable Implications Guided by the Principles of Green Chemistry. *Chem. Soc. Rev.* **2015**, 44, 5758–5777.
 - (15) Polshettiwar, V.; Varma, R. S. Green Chemistry by Nano-Catalysis. *Green Chem.* **2010**, 12 (5), 743–754.
 - (16) Sheldon, R. A. Recent Advances in Green Catalytic Oxidations of Alcohols in Aqueous Media. *Catal. Today* **2015**, 247, 4–13.
 - (17) Lam, F. L.-Y.; Li, M. C. L.; Chau, R. S. L.; Arancon, R. A. D.; Hu, X.; Luque, R. Catalysis at Room Temperature: Perspectives for Future Green Chemical Processes. *Wiley Interdiscip. Rev. Energy Environ.* **2015**, 4 (4), 316–338.
 - (18) Dunn, P. J. The Importance of Green Chemistry in Process Research and Development. *Chem. Soc. Rev.* **2012**, 41 (4), 1452–1461.
 - (19) Sheldon, R. A. Fundamentals of Green Chemistry: Efficiency in Reaction Design. *Chem. Soc. Rev.* **2012**, 41 (4), 1437–1451.
 - (20) Wang, X.; Li, Y. Selected-Control Hydrothermal Synthesis of α - and β -MnO₂ Single Crystal Nanowires. *J. Am. Chem. Soc.* **2002**, 124 (12), 2880–2881.
 - (21) Cheng, F.; Su, Y.; Liang, J.; Tao, Z.; Chen, J. MnO₂-Based Nanostructures as Catalysts for Electrochemical Oxygen Reduction in Alkaline Media. *Chem. Mater.* **2010**, 22 (3), 898–905.
 - (22) Truong, T. T.; Liu, Y.; Ren, Y.; Trahey, L.; Sun, Y. Morphological and Crystalline Evolution of Nanostructured MnO₂ and Its Application in Lithium–Air Batteries. *ACS Nano* **2012**, 6 (9), 8067–8077.
 - (23) Zhang, H.; Lin, C.; Du, F.; Zhao, Y.; Gao, P.; Chen, H.; Jiao, Z.; Li, X.; Zhao, T.; Sun, Y. Enhanced Interactions between Gold and MnO₂ Nanowires for Water Oxidation: A Comparison of Different Chemical and Physical Preparation Methods. *ACS Sustain. Chem. Eng.* **2015**, 3 (9), 2049–2057.
 - (24) Gu, D.; Tseng, J.-C.; Weidenthaler, C.; Bongard, H.-J.; Spliethoff, B.; Schmidt, W.;

- Soulimani, F.; Weckhuysen, B. M.; Schüth, F. Gold on Different Manganese Oxides: Ultra-Low-Temperature CO Oxidation over Colloidal Gold Supported on Bulk-MnO₂ Nanomaterials. *J. Am. Chem. Soc.* **2016**, *138* (30), 9572–9580.
- (25) Cheng, F.; Zhang, T.; Zhang, Y.; Du, J.; Han, X.; Chen, J. Enhancing Electrocatalytic Oxygen Reduction on MnO₂ with Vacancies. *Angew. Chemie Int. Ed.* **2013**, *52* (9), 2474–2477.
- (26) Liu, S.-Y.; Wang, G.; Xie, J.; Tu, F.; Yang, H.; Zhang, S.; Zhu, T.; Cao, G. S.; Zhao, X. B. Au-Nanocrystals-Decorated δ -MnO₂ as Efficient Catalytic Cathode for High-Performance Li-O₂ Batteries. *Nanoscale* **2015**.
- (27) Li, N.; Zhao, P.; Astruc, D. Anisotropic Gold Nanoparticles: Synthesis, Properties, Applications, and Toxicity. *Angew. Chemie Int. Ed.* **2014**, *53* (7), 1756–1789.
- (28) Min, B. K.; Friend, C. M. Heterogeneous Gold-Based Catalysis for Green Chemistry: Low-Temperature CO Oxidation and Propene Oxidation. *Chem. Rev.* **2007**, *107* (6), 2709–2724.
- (29) da Silva, A. G. M.; Fajardo, H. V.; Balzer, R.; Probst, L. F. D.; Lovón, A. S. P.; Lovón-Quintana, J. J.; Valença, G. P.; Schreine, W. H.; Robles-Dutenhefner, P. A. Versatile and Efficient Catalysts for Energy and Environmental Processes: Mesoporous Silica Containing Au, Pd and Au-Pd. *J. Power Sources* **2015**, *285* (0), 460–468.
- (30) Granasy, L.; Podmaniczky, F.; Toth, G. I.; Tegze, G.; Pusztai, T. Heterogeneous Nucleation Of/on Nanoparticles: A Density Functional Study Using the Phase-Field Crystal Model. *Chem. Soc. Rev.* **2014**, *43* (7), 2159–2173.
- (31) Yoreo, J. J. De; Vekilov, P. G. Principles of Crystal Nucleation and Growth. **2003**.
- (32) Alhumaimess, M.; Lin, Z.; He, Q.; Lu, L.; Dimitratos, N.; Dummer, N. F.; Conte, M.; Taylor, S. H.; Bartley, J. K.; Kiely, C. J.; et al. Oxidation of Benzyl Alcohol and Carbon Monoxide Using Gold Nanoparticles Supported on MnO₂ Nanowire Microspheres. *Chem. – A Eur. J.* **2014**, *20* (6), 1701–1710.
- (33) Wang, L.-C.; Liu, Y.-M.; Chen, M.; Cao, Y.; He; Fan, K.-N. MnO₂ Nanorod Supported Gold Nanoparticles with Enhanced Activity for Solvent-Free Aerobic Alcohol Oxidation. *J. Phys. Chem. C* **2008**, *112* (17), 6981–6987.
- (34) da Silva, A. G. M.; Kisukuri, C. M.; Rodrigues, T. S.; Candido, E. G.; de Freitas, I. C.; da Silva, A. H. M.; Assaf, J. M.; Oliveira, D. C.; Andrade, L. H.; Camargo, P. H. C. MnO₂ Nanowires Decorated with Au Ultrasmall Nanoparticles for the Green Oxidation of Silanes and Hydrogen Production under Ultralow Loadings. *Appl. Catal. B Environ.* **2016**, *184*, 35–43.
- (35) Gorlin, Y.; Chung, C.-J.; Benck, J. D.; Nordlund, D.; Seitz, L.; Weng, T.-C.; Sokaras, D.; Clemens, B. M.; Jaramillo, T. F. Understanding Interactions between Manganese Oxide and Gold That Lead to Enhanced Activity for Electrocatalytic Water Oxidation. *J. Am. Chem. Soc.* **2014**, *136* (13), 4920–4926.
- (36) Tana; Wang, F.; Li, H.; Shen, W. Influence of Au Particle Size on Au/CeO₂ Catalysts for CO Oxidation. *Catal. Today* **2011**, *175* (1), 541–545.
- (37) Liang, S.; Teng, F.; Bulgan, G.; Zong, R.; Zhu, Y. Effect of Phase Structure of MnO₂ Nanorod Catalyst on the Activity for CO Oxidation. *J. Phys. Chem. C* **2008**, *112* (14), 5307–5315.
- (38) Fiorenza, R.; Crisafulli, C.; Condorelli, G.; Lupo, F.; Scirè, S. Au–Ag/CeO₂ and Au–Cu/CeO₂ Catalysts for Volatile Organic Compounds Oxidation and CO Preferential Oxidation. *Catal. Letters* **2015**, *145* (9), 1691–1702.
- (39) Campbell, C. T. Catalyst-Support Interactions: Electronic Perturbations. *Nat Chem* **2012**, *4*

- (8), 597–598.
- (40) Casaletto, M. P.; Longo, A.; Martorana, A.; Prestianni, A.; Venezia, A. M. XPS Study of Supported Gold Catalysts: The Role of Au⁰ and Au^{+δ} Species as Active Sites. *Surf. Interface Anal.* **2006**, *38* (4), 215–218.
 - (41) Yang, M.; Allard, L. F.; Flytzani-Stephanopoulos, M. Atomically Dispersed Au–(OH)_x Species Bound on Titania Catalyze the Low-Temperature Water-Gas Shift Reaction. *J. Am. Chem. Soc.* **2013**, *135* (10), 3768–3771.
 - (42) Chang, L.-H.; Sasirekha, N.; Chen, Y.-W.; Wang, W.-J. Preferential Oxidation of CO in H₂ Stream over Au/MnO₂–CeO₂ Catalysts. *Ind. Eng. Chem. Res.* **2006**, *45* (14), 4927–4935.
 - (43) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O’Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, *14* (4), 1921–1926.
 - (44) Royer, S.; Duprez, D. Catalytic Oxidation of Carbon Monoxide over Transition Metal Oxides. *ChemCatChem* **2011**, *3* (1), 24–65.
 - (45) Huang, H.; Xu, Y.; Feng, Q.; Leung, D. Y. C. Low Temperature Catalytic Oxidation of Volatile Organic Compounds: A Review. *Catal. Sci. Technol.* **2015**, *5* (5), 2649–2669.
 - (46) Li, W.; Ge, Q.; Ma, X.; Chen, Y.; Zhu, M.; Xu, H.; Jin, R. Mild Activation of CeO₂-Supported Gold Nanoclusters and Insight into the Catalytic Behavior in CO Oxidation. *Nanoscale* **2016**, *8* (4), 2378–2385.
 - (47) del Río, E.; Hungria, A. B.; Tinoco, M.; Manzorro, R.; Cauqui, M. A.; Calvino, J. J.; Pérez-Omil, J. A. CeO₂-Modified Au/TiO₂ Catalysts with Outstanding Stability under Harsh CO Oxidation Conditions. *Appl. Catal. B Environ.* **2016**, *197*, 86–94.
 - (48) Yao, Y.; Gu, L. L.; Jiang, W.; Sun, H. C.; Su, Q.; Zhao, J.; Ji, W. J.; Au, C. T. Enhanced Low Temperature CO Oxidation by Pretreatment: Specialty of the Au–Co₃O₄ Oxide Interfacial Structures. *Catal. Sci. Technol.* **2016**, *6* (7), 2349–2360.
 - (49) Ohyama, J.; Koketsu, T.; Yamamoto, Y.; Arai, S.; Satsuma, A. Preparation of TiO₂-Supported Twinned Gold Nanoparticles by CO Treatment and Their CO Oxidation Activity. *Chem. Commun.* **2015**, *51* (87), 15823–15826.
 - (50) Kim, S. H.; Jung, C.-H.; Sahu, N.; Park, D.; Yun, J. Y.; Ha, H.; Park, J. Y. Catalytic Activity of Au/TiO₂ and Pt/TiO₂ Nanocatalysts Prepared with Arc Plasma Deposition under CO Oxidation. *Appl. Catal. A Gen.* **2013**, *454*, 53–58.
 - (51) Ye, Q.; Zhao, J.; Huo, F.; Wang, D.; Cheng, S.; Kang, T.; Dai, H. Nanosized Au Supported on Three-Dimensionally Ordered Mesoporous β-MnO₂: Highly Active Catalysts for the Low-Temperature Oxidation of Carbon Monoxide, Benzene, and Toluene. *Microporous Mesoporous Mater.* **2013**, *172*, 20–29.
 - (52) Rodriguez, J. A.; Si, R.; Evans, J.; Xu, W.; Hanson, J. C.; Tao, J.; Zhu, Y. Active Gold-Ceria and Gold-Ceria/titania Catalysts for CO Oxidation: From Single-Crystal Model Catalysts to Powder Catalysts. *Catal. Today* **2015**, *240*, 229–235.
 - (53) Hinojosa-Reyes, M.; Zanella, R.; Maturano-Rojas, V.; Rodríguez-González, V. Gold-TiO₂-Nickel Catalysts for Low Temperature-Driven CO Oxidation Reaction. *Appl. Surf. Sci.* **2016**, *368*, 224–232.
 - (54) Sandoval, A.; Zanella, R.; Klimova, T. E. Titania Nanotubes Decorated with Anatase Nanocrystals as Support for Active and Stable Gold Catalysts for CO Oxidation. *Catal. Today* **2017**, *282*, Part 2, 140–150.
 - (55) Najafshirvari, S.; Guardia, P.; Scarpellini, A.; Prato, M.; Marras, S.; Manna, L.; Colombo, M. The Effect of Au Domain Size on the CO Oxidation Catalytic Activity of Colloidal Au–

- FeOx Dumbbell-like Heterodimers. *J. Catal.* **2016**, *338*, 115–123.
- (56) Liu, X.; Liu, M.-H.; Luo, Y.-C.; Mou, C.-Y.; Lin, S. D.; Cheng, H.; Chen, J.-M.; Lee, J.-F.; Lin, T.-S. Strong Metal–Support Interactions between Gold Nanoparticles and ZnO Nanorods in CO Oxidation. *J. Am. Chem. Soc.* **2012**, *134* (24), 10251–10258.
- (57) Ousmane, M.; Liotta, L. F.; Carlo, G. D.; Pantaleo, G.; Venezia, A. M.; Deganello, G.; Retailleau, L.; Boreave, A.; Giroir-Fendler, A. Supported Au Catalysts for Low-Temperature Abatement of Propene and Toluene, as Model VOCs: Support Effect. *Appl. Catal. B Environ.* **2011**, *101* (3–4), 629–637.
- (58) Hosseini, M.; Barakat, T.; Cousin, R.; Aboukaïs, A.; Su, B.-L.; De Weireld, G.; Siffert, S. Catalytic Performance of Core–shell and Alloy Pd–Au Nanoparticles for Total Oxidation of VOC: The Effect of Metal Deposition. *Appl. Catal. B Environ.* **2012**, *111–112* (0), 218–224.
- (59) Yang, H.; Deng, J.; Liu, Y.; Xie, S.; Wu, Z.; Dai, H. Preparation and Catalytic Performance of Ag, Au, Pd or Pt Nanoparticles Supported on 3DOM CeO₂–Al₂O₃ for Toluene Oxidation. *J. Mol. Catal. A Chem.* **2016**, *414*, 9–18.
- (60) Barakat, T.; Idakiev, V.; Cousin, R.; Shao, G.-S.; Yuan, Z.-Y.; Tabakova, T.; Siffert, S. Total Oxidation of Toluene over Noble Metal Based Ce, Fe and Ni Doped Titanium Oxides. *Appl. Catal. B Environ.* **2014**, *146*, 138–146.
- (61) Carabineiro, S. A. C.; Chen, X.; Martynyuk, O.; Bogdanchikova, N.; Avalos-Borja, M.; Pestryakov, A.; Tavares, P. B.; Órfão, J. J. M.; Pereira, M. F. R.; Figueiredo, J. L. Gold Supported on Metal Oxides for Volatile Organic Compounds Total Oxidation. *Catal. Today* **2015**, *244* (0), 103–114.
- (62) Lee, J.; Saha, B.; Vlachos, D. G. Pt Catalysts for Efficient Aerobic Oxidation of Glucose to Glucaric Acid in Water. *Green Chem.* **2016**, *18* (13), 3815–3822.
- (63) Wojcieszak, R.; Cuccovia, I. M.; Silva, M. A.; Rossi, L. M. Selective Oxidation of Glucose to Glucuronic Acid by Cesium-Promoted Gold Nanoparticle Catalyst. *J. Mol. Catal. A Chem.* **2016**, *422*, 35–42.

Section 5.

Merging Optical and Catalytic Properties: Plasmonic Catalysis

Chapter 10. The Fault in Their Shapes: Investigating the SPR-Mediated Catalytic Activities of Silver Quasi-Spheres, Cubes, Triangular Prisms and Wires

10.1. Introduction

Silver (Ag) nanostructures have been employed as catalysts for reduction, oxidation, and oxidative coupling reactions.^{1–7} Ag also exhibits remarkable optical properties in the visible region as a result of the surface plasmon resonance (SPR) excitation, which has enabled applications in surface-enhanced Raman scattering (SERS), contrast agents, optical labeling, near-field probing, and plasmonic solar cells.^{8–12} Fascinatingly, it has been recently demonstrated that these two areas (catalysis and optical properties) can be merged together: the SPR excitation in plasmonic nanomaterials can be put to work to mediate or enhance catalytic processes, the so-called SPR-mediated or SPR-enhanced catalysis.¹³

SPR-mediated/enhanced processes represent a relatively new frontier in catalysis in which an incoming electromagnetic wave, such as visible light, is employed as an eco-friendly energy input to drive chemical reactions.^{13–15} Generally, the SPR excitation can mediate/enhance chemical processes by three main mechanisms. In the first, the high electric fields generated close to the surface as a result of SPR excitation leads to higher absorption at the metal-molecule interface, which is important in the context of photochemical transformations. Secondly, the SPR excitation leads to the formation of electron–hole pairs that can promote charge-transfer processes at the metal-molecule interface under proper conditions. Finally, local heating generated in the vicinity of the metal surface can provide energy input to drive photothermal conversions.^{14–17} Although

many papers have reported on the SPR mediated catalytic activities of Ag, Au, and AgAu NPs,^{14,15,18–20} the effect of shape and crystalline structure over activities remain unclear. Generally, it is believed that the improved matching between the SPR and excitation wavelength may lead to higher SPR-mediated catalytic activities. However, a better understanding on the factors that govern SPR-mediated processes is imperative to the rational design of optimized catalysts for target transformations.

We provide herein, new insights regarding the various factors that affect SPR-mediated catalytic activities in plasmonic nanostructures. Interestingly, it was found that the crystal structure plays an important role over the SPR-mediated catalytic activity of Ag nanomaterials. More specifically, we investigated the catalytic activity of Ag quasi-spheres, cubes, triangular prisms, and wires towards the oxidation of p-aminothiophenol (PATP) to p,p'-dimercaptoazobenzene (DMAB) by activated O₂ (³O₂) as a model reaction. We observed that the activities at 632.8 nm excitation followed the order: triangular prisms and quasi-spheres > wires >> cubes, indicating that variations in the optical properties (matching between the SPR and excitation wavelength) was not the only factor responsible for the observed differences in SPR-mediated catalytic activities and also displayed a shape dependent behavior.

10.2. Experimental Section

10.2.1. Materials and Instrumentation

Analytical grade chemicals silver nitrate (AgNO₃, 99%, Sigma-Aldrich), silver trifluoroacetate (CF₃COOAg, 98%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), ethylene glycol (EG, 99,8%, Sigma Aldrich), sodium citrate dihydrate

($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%, Sigma-Aldrich), sodium borohydride (NaBH_4 , 98%, Sigma-Aldrich), sodium hydrosulfide monohydrate (NaHS , Sigma-Aldrich), hydrochloric acid (HCl , 37%, Sigma-Aldrich), p-aminothiophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{SH}$, >97.0%, Sigma-Aldrich). The scanning electron microscopy (SEM) images were obtained using a JEOL field emission gun microscope JSM 6330F operated at 5 kV. The samples were prepared by drop-casting an aqueous suspension containing the nanostructures over a silicon wafer, followed by drying under ambient conditions. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL 1010 microscope operating at 80 kV or a JEOL JEM 2100 microscope operated at 200 kV. Samples for TEM and HRTEM were prepared by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 spectrophotometer. Raman spectra were acquired on a Renishaw Raman InVia equipped with a CCD detector and coupled to a Leica microscope that allows a rapid accumulation of Raman spectra with a spatial resolution of about 1 μm (micro-Raman technique). The laser beam was focused on the sample using a 50x lens. The experiments were performed under ambient conditions using a back-scattering geometry. The samples were irradiated with the 633 and 785 nm lines of a He-Ne laser (Renishaw RL633 laser), and a solid-state diode laser, respectively, using controlled laser power outputs of 0.02-0.66 mW and employing the exposure time up to 30 s.

10.2.2. Synthesis of Ag quasi-spheres

Ag seeds were prepared by the polyol process.²¹ Briefly, 5 mg of polyvinylpyrrolidone (PVP) was dissolved in 37.5 mL of ethylene glycol. Then, AgNO_3 (200 mg, 1.2 mmol) was added

and mixed until complete dissolution. The resulting solution was heated to 125 °C and kept at this temperature for 2.5 hours, leading to the appearance of a greenish-yellow color due to the formation of the Ag NPs. The reaction mixture was then allowed to cool to room temperature and diluted to 125 mL with water.

10.2.3. Synthesis of Ag cubes

In typical procedure,²² Ag seeds were prepared adding 5 mL of ethylene glycol into a 100 mL round flask and pre-heated at 150 °C with vigorous stirring, and then 0.06 mL of NaHS (3 mM in EG) was quickly injected. After 2 min, 0.5 mL of HCl (3 mM in EG) was injected, followed by the addition of 1.25 mL of poly(vinyl pyrrolidone) (PVP, 20 mg/mL in EG). After 2 min, 0.4 mL of CF₃COOAg (282 mM in EG) was added into the mixture and the reaction was allowed to proceed for 30 min. For the synthesis of Ag nanocubes, 1.25 mL of EG was heated 20 mL glass flask at 150 °C under magnetic stirring. After 1.5 min, 0.3 mL of a PVP solution in EG (20 mg/mL) was added, followed the addition of 50 µL of the as-prepared Ag seeds. After 2 min, 200 µL of silver nitrate solution in EG (282 mM) and the reaction was allowed to proceed for 60 min. All the products were centrifuged at 10000 rpm, followed by washing with ethanol and water to remove excess EG and PVP.

10.2.4. Synthesis of Ag triangular prisms

In a typical synthesis,²³ 50 mL of 0.2 mM AgNO₃(aq) were added to a 250 mL round flask, followed by 50 mL of 0.6 mM aqueous trisodium citrate and 2 mL of aqueous 5 mM PVP (MW 55,000). Under rapid stirring, 1 mL of 50 mM NaBH₄(aq) was quickly added to this mixture, leading to the formation of a yellow suspension. After that, a 40 W lamp was placed near the flask and the

reaction was allowed to proceed for 7 days. The Ag nanoprimers suspension was washed three times with water by successive rounds of centrifugation and removal of the supernatant.

10.2.5. Synthesis of Ag wires

In a typical procedure,²⁴ 5 mL of EG was pre-heated for 1 hour at 140 °C with vigorous stirring, followed by the addition of 0.2 mL of 3 mM HCl (in EG). After 10 min, 3 mL of 94 mM AgNO₃ and 3 mL of 147 mM PVP (both in EG) were simultaneously added dropwise to this mixture (at a speed of 45 mL/h) and left overnight, yielding a beige suspension. The reaction flask was then allowed to cool down to room temperature, and the suspension containing the Ag nanowires was washed three times with deionized water to remove excess PVP by successive rounds of centrifugation and removal of the supernatant.

10.2.6. SPR-mediated oxidation of p-aminothiophenol catalyzed by Ag nanostructures

A 1.5 mL suspension containing the Ag nanostructures were centrifuged and the supernatant was removed, followed by the addition of 10 µL of water to yield concentrated suspensions. The suspensions containing the Ag nanomaterials (10 µL) were dropcasted onto a 1 cm × 1 cm Si wafer (001 surface) followed by drying under ambient conditions. Then, 40 µL of a 1.0 mM p-aminothiophenol ethanolic solution was dropped over the Si wafer containing the NPs and dried under ambient conditions. The substrates containing the Ag NPs functionalized with PATP were then taken to the Raman spectrophotometer. All samples were used immediately for SERS measurements after preparation. All spectra were normalized with respect to the Raman band at 1081 cm⁻¹ for the ease of comparison.

10.3. Results and Discussion

We started our studies with the synthesis of Ag nanomaterials displaying controllable morphologies. Specifically, we focused on Ag quasi-spheres, cubes, triangular prisms and wires, as shown by the SEM, TEM, and HRTEM images in Figure 10.1.

Figure 10.1. TEM (A), SEM (B-D), and HRTEM (E-L) images for Ag quasi-spheres (A, E, and I), cubes (B, F, and J), triangular prisms (C, G, and K), and wires (D, H, and L). The quasi-spheres, cubes, wires, and prisms were 36 ± 4 nm in diameter, 35 ± 5 nm in edge length, 64 ± 9 nm in edge length, and 153 ± 15 nm in width, respectively.

The quasi-spheres were 36 ± 4 nm in diameter (Figure 10.1 A), the cubes were 35 ± 5 nm in edge length (Figure 10.1 B), the triangular prisms were 64 ± 9 nm in edge length (Figure 10.1 C), and the wires 153 ± 15 nm in width (Figure 10.1 D).

While the synthesis of Ag quasi-spheres, cubes, and wires followed the well-established polyol approach, the triangular prisms were obtained by the visible-light photo-induced conversion route.^{23,25} It is noteworthy that Ag quasi-spheres obtained by the described polyol method are

polycrystalline (mix of $\{100\}$ and $\{111\}$ facets),²⁶ while the cubes are single crystalline enclosed by $\{100\}$ side facets.^{22,27,28} Although the triangular prisms contain a twin plane parallel to the $\{111\}$ top and bottom surfaces, solution-prepared Ag triangular prisms are single crystalline with face-centered cubic (fcc) lattice structures.^{29,30} Their edges are typically $\{110\}$, $\{111\}$, or $\{100\}$ facets.²⁹ Finally, the Ag wires are polycrystalline, in which each wire can be described as being assembled from five $\{100\}$ monocrystalline sides subunits separated by $\{111\}$ twin planes.^{25,26,31} HRTEM images from Ag quasi-spheres (Fig. 10.1 E and I), cubes (Fig. 10.1 F and J), triangular prisms (Figure 10.1 G and K) and wires (Figure 10.1 H and L) support these observations.

The optical properties of Ag are strongly dependent on both size and shape, and the UV-VIS extinction spectra recorded from aqueous suspension containing the Ag nanomaterials are shown in Figure 10.2. The UV-VIS extinction spectra for the wires, quasi-spheres, cubes, and triangular prisms displayed their most intense peaks assigned to the SPR excitation at 379, 407, 438, and 794 nm, respectively (black, red, green, and blue traces, respectively). For the wires, quasi-spheres, and cubes, these peaks can be assigned to the dipole mode of their SPR.^{23,32,33} For the wires, this peak refer to the transverse SPR mode, and no peaks due to the longitudinal SPR excitation were detected as a result of their large aspect ratios.²⁴ It is important to note that, while the Ag quasi-spheres and cubes displayed similar sizes, the SPR resonance for the cubes was red-shifted relative to the quasi-spheres (407 and 450 nm, respectively). This red shift is due to their sharp corners, that enable increased charge separation during plasmon oscillation, which reduces its restoring force and manifests itself in the red shift of the SPR.^{34,35} The SPR extinction band for the triangular prisms were further red-shifted to 790 nm. This peak is assigned to the in-plane dipole mode resonance.^{23,35} The spectra for the Ag triangular prisms also displayed a peak at 328 nm assigned to the out-of-plane SPR resonance.^{23,35}

Figure 10.2. UV-VIS extinction spectra as a function of different Ag shapes. The spectra for the wires, quasi-spheres, cubes, and triangular prisms are represented as the black, red, green, and blue traces, respectively.

After their synthesis, we turned our attention to the investigation of the SPR-mediated catalytic activities of the Ag nanomaterials as a function of their shape and optical properties. To this end, we employed the SPR-mediated oxidation of p-aminothiophenol (PATP) to p,p'-dimercaptoazobenzene (DMAB) by $^3\text{O}_2$ as a model reaction according to the following equation (Scheme 10.1):

It has been established that the SPR excitation in Ag nanomaterials can lead to the formation of hot electrons, i.e., electrons that transiently occupy energy states above the Fermi level during plasmon oscillation.^{36–38} These hot electrons can be transferred to an adsorbed molecule displaying suitable empty energy levels available, and thus trigger charge-transfer transformations. In the context of the SPR-mediated PATP oxidation, hot electrons produced from SPR-excited Ag nanomaterials can be transferred to adsorbed O₂ molecules (from air), that are activated to ³O₂ that subsequently contribute to the PATP oxidation to DMAB at the metal surface (Scheme 10.1).³⁸

Scheme 10.1. Strategy for SPR-mediated oxidation of PATP to form DMAB catalyzed by Ag nanostructures. PATP molecules strongly bind to the Ag surface via Ag-S covalent bonds. The catalytic performances of the Ag NPs were monitored by Raman spectrophotometer using 633 nm (or 785 nm) as the incoming electromagnetic radiation.

Other advantages of using the oxidation of PATP to DMAB as a model reaction to probe SPR-mediated processes is that both PATP and DMAB adsorb strongly on Ag surfaces via the formation of strong M-S covalent bonds, which are not broken during the PATP oxidation to DMAB.^{14,19} Thus, any surfactants present at the surface of Ag nanocrystals prior to the PATP functionalization step should be readily replaced by the thiol (PATP) molecules, not affecting the detected catalytic activities (PATP to DMAB oxidation).^{39–41} Moreover, the conversion of PATP to DMAB can be easily monitored by the relative intensity ratios in the SERS spectra, as PATP and DMAB show Raman bands at distinct spectral positions.^{17,19} As the product conversion can

be monitored by the relative DMAB to DMAB+PATP intensity ratios, our estimation of catalytic activity should not be influenced by the number of adsorbed molecules on Ag nanocrystals having different shapes (and thus the number of molecules being probed), different exposed facets, or the distinct density/number of metal nanoparticles in each substrate.^{14,42}

Figure 10.3 A shows the laser-power-dependent SERS spectra of Ag quasi-spheres that had been functionalized with PATP, while Figure 10.3 B shows the DMAB:(DMAB+PATP) 1433:1081 cm^{-1} intensity ratios as a function of the laser power. The bands assigned to PATP and/or DMAB could be clearly identified in all spectra as a result of the SERS effect. For instance, the bands at 1081, 1188, 1489, and 1593 cm^{-1} corresponded to A_1 modes of PATP while the bands at 1081, 1142, 1390, 1433, and 1575 cm^{-1} were assigned to the A_g modes of DMAB.^{19,20} The relative Raman intensities of A_g modes corresponding to DMAB as well as DMAB⊗DMAB+PATP) 1433:1081 cm^{-1} intensity ratios increased with the laser power, which confirms a SPR-mediated reaction mechanism.¹⁴ Figure 10.3 C and D show the irradiation-time-dependent SERS spectra and DMAB:(DMAB+PATP) 1433:1081 cm^{-1} intensity ratios recorded employing 0.33 mW as the laser power. It can be clearly observed that the Raman intensities assigned to DMAB increase with the laser irradiation time, which is also in agreement with a SPR-mediated mechanism.

Figure 10.3. (A) Laser-power-dependent SERS spectra and (B) and DMAB:(DMAB+PATP) 1433:1081 cm⁻¹ intensity ratios for Ag quasi-spheres that had been functionalized with PATP employing 30 s as the exposure time. (C) Irradiation-time-dependent SERS spectra and (D) and DMAB:(DMAB+PATP) 1433:1081 cm⁻¹ intensity ratios for Ag quasi-spheres that had been functionalized with PATP employing 0.66 mW as the laser power. All spectra were recorded under 633 nm excitation.

Figure 10.4 A shows the SERS spectra recorded under 632.8 nm excitation for Ag cubes, wires, quasi-spheres, and triangular prisms that had been functionalized with PATP (bottom to top, black, red, green, and blue traces, respectively). The relative DMAB:(DMAB+PATP) 1433:1081 cm⁻¹ intensity ratios, that can be employed to monitor the PATP to DMAB conversion,^{19,20} were strongly dependent on the shape of the Ag nanomaterials as catalysts.

Figure 10.4. SERS (A) spectra as a function of Ag shape (cube, wire, quasi-sphere and triangle) functionalized with PATP. (B) Obtained DMAB:PATP 1433:1081 cm^{-1} intensity ratios as a function of the Ag content in the NPs. The spectra were recorded under 633 nm excitation, 30 s exposure, and 0.66 mW as the laser power. All intensities were normalized with respect to the signal at 1181 cm^{-1} .

For Ag cubes (black trace), the SERS spectra displayed only peaks assigned to PATP, indicating that this sample presented the lowest catalytic activities for the SPR-mediated oxidation of PATP under our employed conditions. Nevertheless, the DMAB:(DMAB+PATP) intensity ratios became more intense for wires, quasi-spheres, and triangular prisms (red, green, and blue traces, respectively), indicating an increase in activity for these samples. The DMAB:(PATP+DMAB) $1433:1081\text{ cm}^{-1}$ intensity ratios for all samples are plotted in Figure 10.4B. While the DMAB:(PATP+DMAB) intensity ratio was 0 for cubes (0% of PATP conversion), it increased to 0.50, 1.23 and 1.25 for wires, quasi-spheres, triangular prisms, respectively. These results indicate that Ag quasi-spheres and triangular prisms showed the highest SPR-mediated catalytic activities.

In principle, the observed variations in the catalytic activity of Ag nanostructures could be explained based on the matching between the SPR position and the wavelength of the incoming electromagnetic radiation employed as the excitation source (632.8 nm in Figure 10. 4). In this case, a stronger matching would lead to a stronger SPR excitation, that could lead to the generation of a larger population of hot electrons that would participate in the SPR-mediated oxidation of PATP. While this factor may account for the higher activity of the triangular prisms (the only shape having some extinction intensities at 632.8 nm), it fails to explain the variation observed for the Ag wire, quasi-spheres, and cubes. In fact, the SPR for the wires, quasi-spheres, and cubes were positioned at 379, 407, 438 nm respectively, being significantly blue-shifted relative to 632.8 nm (Figure 10.5). If the increased matching between the SPR in each nanostructure and the excitation wavelength was the dominant factor to dictate the SPR-mediated catalytic activities, one would expect that the activities for the cubes were higher relative to the quasi-spheres and wires. However, this did not correlate with the experimental results (quasi-spheres > wires >> cubes).

Figure 10.5. Electric field enhancement contours ($|E|/|E_0|$) calculated by the DDA method for Ag cubes 36 nm in edge length (A and B), Ag spheres 35 nm in diameter (C), and Ag triangular prisms 65 nm in edge length (D). In all cases, the wavelength of the incoming electromagnetic wave corresponded to 633 nm. The incident light was along the x-axis and E-field was along the [010] and [011] direction for Ag cubes shown in (A) and (B), respectively. In (C), the incident light was along the x-axis and the E-field along the [010] direction. Finally, in (D) incident light was along the y-axis and the E-field along the [100] direction.

Here, we would like to suggest that these variations in catalytic activity may be explained based on the different shapes of the Ag nanocrystals employed as catalysts. As aforementioned, the Ag cubes are enclosed by {100} facets, the wires by {100} side facets and {111} end facets, the quasi-spheres by a mix of {100} and {111} facets, and the prisms by {111} top and bottom facets. Therefore, our catalytic results suggest a strong shape-dependent behavior, in which the

SPR-mediated catalytic activities increased as fraction of {111} surface facets in the Ag nanocrystals employed as catalysts increased (cubes < wires < quasi-spheres and prisms). In this context, it is well established that the surface energies associated with different crystallographic planes follows the order: $\gamma(110) > \gamma(100) > \gamma(111)$.⁴³ Also, several reports indicate that and that the adsorption of molecular O₂ is more favorable on Ag (100) than Ag (111) surfaces (crystal planes with higher surface energy).²⁷ As the electron transfer from Ag to adsorbed O₂ producing the activated ³O₂ followed their desorption that subsequently leads to the PATP oxidation represents the crucial step for the DMAB formation, it is plausible that the weaker adsorption of O₂ on Ag {111} surface facets favors the O₂ desorption step after activation, and thus contribute to better catalytic performances. Similar facet-dependent electrocatalytic behavior has been observed for the oxygen reduction reaction over Ag nanocrystals.²⁷ In addition to the facet-dependent catalytic activities, grain boundaries at the surface of polycrystalline samples (Ag quasi-spheres and wires), represent high energy sites relative to single crystal surfaces that can also contribute to improved catalytic activities relative to single-crystal surfaces.⁶ As PATP molecules adsorb strongly over Ag surfaces via the formation of Ag-S bonds, no significant changes in the interaction between substrate molecules (PATP) and Ag nanocrystals as a function of shape (having different exposed surface facets) are expected. Therefore, it is plausible that the variations in catalytic activity can be understood in terms of the differences in the interaction with O₂ molecules.

It is important to note that, for Ag triangular prisms, the better matching between the between the SPR and the 633 nm excitation wavelength relative to the quasi-spheres, cubes and wires may also contribute to the improved catalytic performances (Figure 10.5). In order to support

this observation, we investigated the SPR-mediated catalytic activities of both quasi-spheres and triangular prisms employing 785 nm as the excitation wavelength (Figure 10.6).

Figure 10.6. SERS spectra of PATP-capped Ag quasi-spheres and triangular prisms replacing 633 nm laser excitation by 785 nm. Here, a laser irradiation near to triangular prisms SPR clearly shows a high enhancement of catalytic activity of Ag triangular prisms. As expected, opposite effect was observed for Ag quasi-spheres.

The SPR-mediated catalytic activities of the triangular prisms was significantly increased relative to the 632.8 nm excitation. However, the oxidation of PATP over the Ag quasi-spheres was not observed. As 785 nm was further red shifted from the SPR excitation, it is plausible that is not able to excite the SPR of the Ag quasi-spheres to the point to induce the PATP to DMAB conversion.

10.4. Conclusions

We described a systematic investigation on the SPR-mediated catalytic activities for Ag nanomaterials as a function of their shape. Specifically, we employed Ag quasi-spheres, cubes, wires and triangular prisms and the SPR-mediated oxidation of PATP to DMAB by activated O₂ as a model reaction. Our data showed that the catalytic activities under 632.8 nm excitation displayed a shape-dependent behavior, following the order: triangular prisms and quasi-spheres > wires >> cubes. As the Ag cubes are enclosed by {100} facets, the wires by {100} side facets and {111} end facets, the quasi-spheres by a mix of {100} and {111} facets, and the prisms by {111} top and bottom facets, our results suggested that the SPR-mediated catalytic activities increased as fraction of {111} surface facets in the Ag nanocrystals employed as catalysts increased. The higher activity enabled by {111} facets was explained based on its weaker interaction with O₂ relative to {100} facets, which favors O₂ desorption after activation via the transfer of hot electrons from SPR-excited Ag nanocrystals. The higher activity of the triangular prisms could also be explained based on the better matching between the SPR and the excitation wavelength. Also, grain boundaries at the surface of polycrystalline samples may also contribute to improved catalytic activities relative to single-crystal surfaces. We believe the results presented herein offer new insights regarding the various parameters that dictate SPR-mediated catalytic activities in plasmonic nanostructures, showing that shape plays an important role over the optimization of activity and design of new catalysts for a variety of SPR-mediated transformations.

10.5. References

- (1) Dong, Z.; Le, X.; Li, X.; Zhang, W.; Dong, C.; Ma, J. Silver Nanoparticles Immobilized on

- Fibrous Nano-Silica as Highly Efficient and Recyclable Heterogeneous Catalyst for Reduction of 4-Nitrophenol and 2-Nitroaniline. *Appl. Catal. B Environ.* **2014**, *158–159* (0), 129–135.
- (2) Liang, Y. Q.; Cui, Z. D.; Zhu, S. L.; Liu, Y.; Yang, X. J. Silver Nanoparticles Supported on TiO₂ Nanotubes as Active Catalysts for Ethanol Oxidation. *J. Catal.* **2011**, *278* (2), 276–287.
 - (3) Zidki, T.; Bar-Ziv, R.; Green, U.; Cohen, H.; Meisel, D.; Meyerstein, D. The Effect of the Nano-Silica Support on the Catalytic Reduction of Water by Gold, Silver and Platinum Nanoparticles - Nanocomposite Reactivity. *Phys. Chem. Chem. Phys.* **2014**, *16* (29), 15422–15429.
 - (4) Yang, G.-W.; Gao, G.-Y.; Wang, C.; Xu, C.-L.; Li, H.-L. Controllable Deposition of Ag Nanoparticles on Carbon Nanotubes as a Catalyst for Hydrazine Oxidation. *Carbon N. Y.* **2008**, *46* (5), 747–752.
 - (5) Mitsudome, T.; Arita, S.; Mori, H.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K. Supported Silver-Nanoparticle-Catalyzed Highly Efficient Aqueous Oxidation of Phenylsilanes to Silanols. *Angew. Chemie* **2008**, *120* (41), 8056–8058.
 - (6) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chemie Int. Ed.* **2009**, *48* (1), 60–103.
 - (7) Zhu, M.; Wang, C.; Meng, D.; Diao, G. In Situ Synthesis of Silver Nanostructures on Magnetic Fe₃O₄@C Core-Shell Nanocomposites and Their Application in Catalytic Reduction Reactions. *J. Mater. Chem. A* **2013**, *1* (6), 2118–2125.
 - (8) Homan, K. A.; Souza, M.; Truby, R.; Luke, G. P.; Green, C.; Vreeland, E.; Emelianov, S. Silver Nanoplate Contrast Agents for in Vivo Molecular Photoacoustic Imaging. *ACS Nano* **2011**, *6* (1), 641–650.
 - (9) Cobley, C. M.; Skrabalak, S. E.; Campbell, D. J.; Xia, Y. Shape-Controlled Synthesis of Silver Nanoparticles for Plasmonic and Sensing Applications. *Plasmonics* **2009**, *4* (2), 171–179.
 - (10) Tan, H.; Santbergen, R.; Smets, A. H. M.; Zeman, M. Plasmonic Light Trapping in Thin-Film Silicon Solar Cells with Improved Self-Assembled Silver Nanoparticles. *Nano Lett.* **2012**, *12* (8), 4070–4076.
 - (11) Emory, S. R.; Nie, S. Near-Field Surface-Enhanced Raman Spectroscopy on Single Silver Nanoparticles. *Anal. Chem.* **1997**, *69* (14), 2631–2635.
 - (12) Atwater, H. A.; Polman, A. Plasmonics for Improved Photovoltaic Devices. *Nat. Mater.* **2010**, *9* (3), 205–213.
 - (13) Baffou, G.; Quidant, R. Nanoplasmonics for Chemistry. *Chem. Soc. Rev.* **2014**, *43* (11), 3898–3907.
 - (14) Wang, J. L.; Ando, R. A.; Camargo, P. H. C. Investigating the Plasmon-Mediated Catalytic Activity of AgAu Nanoparticles as a Function of Composition: Are Two Metals Better than One? *ACS Catal.* **2014**, *4* (11), 3815–3819.

- (15) Christopher, P.; Xin, H.; Linic, S. Visible-Light-Enhanced Catalytic Oxidation Reactions on Plasmonic Silver Nanostructures. *Nat Chem* **2011**, *3* (6), 467–472.
- (16) Gonzalez-Bejar, M.; Peters, K.; Hallett-Tapley, G. L.; Grenier, M.; Scaiano, J. C. Rapid One-Pot Propargylamine Synthesis by Plasmon Mediated Catalysis with Gold Nanoparticles on ZnO under Ambient Conditions. *Chem. Commun.* **2013**, *49* (17), 1732–1734.
- (17) Huang, Y.-F.; Wu, D.-Y.; Zhu, H.-P.; Zhao, L.-B.; Liu, G.-K.; Ren, B.; Tian, Z.-Q. Surface-Enhanced Raman Spectroscopic Study of P-Aminothiophenol. *Phys. Chem. Chem. Phys.* **2012**, *14* (24), 8485–8497.
- (18) Linic, S.; Christopher, P.; Ingram, D. B. Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nat Mater* **2011**, *10* (12), 911–921.
- (19) Fang, Y.; Li, Y.; Xu, H.; Sun, M. Ascertaining P,p'-Dimercaptoazobenzene Produced from P-Aminothiophenol by Selective Catalytic Coupling Reaction on Silver Nanoparticles. *Langmuir* **2010**, *26* (11), 7737–7746.
- (20) Sun, M.; Xu, H. A Novel Application of Plasmonics: Plasmon-Driven Surface-Catalyzed Reactions. *Small* **2012**, *8* (18), 2777–2786.
- (21) Silvert, P.-Y.; Herrera-Urbina, R.; Duvauchelle, N.; Vijayakrishnan, V.; Elhsissen, K. T. Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 1-Synthesis and Characterization. *J. Mater. Chem.* **1996**, *6* (4), 573–577.
- (22) Zhang, Q.; Li, W.; Moran, C.; Zeng, J.; Chen, J.; Wen, L.-P.; Xia, Y. Seed-Mediated Synthesis of Ag Nanocubes with Controllable Edge Lengths in the Range of 30–200 nm and Comparison of Their Optical Properties. *J. Am. Chem. Soc.* **2010**, *132* (32), 11372–11378.
- (23) Hermoso, W.; Alves, T. V.; de Oliveira, C. C. S.; Moriya, E. G.; Ornellas, F. R.; Camargo, P. H. C. Triangular Metal Nanoprisms of Ag, Au, and Cu: Modeling the Influence of Size, Composition, and Excitation Wavelength on the Optical Properties. *Chem. Phys.* **2013**, *423* (0), 142–150.
- (24) de Oliveira, C. C. S.; Ando, R. A.; Camargo, P. H. C. Size-Controlled Synthesis of Silver Micro/nanowires as Enabled by HCL Oxidative Etching. *Phys. Chem. Chem. Phys.* **2013**, *15* (6), 1887–1893.
- (25) Wiley, B.; Sun, Y.; Xia, Y. Synthesis of Silver Nanostructures with Controlled Shapes and Properties. *Acc. Chem. Res.* **2007**, *40* (10), 1067–1076.
- (26) Cobley, C. M.; Xia, Y. Engineering the Properties of Metal Nanostructures via Galvanic Replacement Reactions. *Mater. Sci. Eng. R Reports* **2010**, *70* (3–6), 44–62.
- (27) Wang, Q.; Cui, X.; Guan, W.; Zhang, L.; Fan, X.; Shi, Z.; Zheng, W. Shape-Dependent Catalytic Activity of Oxygen Reduction Reaction (ORR) on Silver Nanodecahedra and Nanocubes. *J. Power Sources* **2014**, *269*, 152–157.
- (28) Xu, R.; Wang, D.; Zhang, J.; Li, Y. Shape-Dependent Catalytic Activity of Silver Nanoparticles for the Oxidation of Styrene. *Chem. – An Asian J.* **2006**, *1* (6), 888–893.
- (29) Millstone, J. E.; Hurst, S. J.; Métraux, G. S.; Cutler, J. I.; Mirkin, C. A. Colloidal Gold and

- Silver Triangular Nanoprisms. *Small* **2009**, 5 (6), 646–664.
- (30) Courty, A.; Henry, A.-I.; Goubet, N.; Pileni, M.-P. Large Triangular Single Crystals Formed by Mild Annealing of Self-Organized Silver Nanocrystals. *Nat Mater* **2007**, 6 (11), 900–907.
 - (31) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chem. Int. Ed. Engl.* **2009**, 48 (1), 60–103.
 - (32) da Silva, A. G. M.; de Souza, M. L.; Rodrigues, T. S.; Alves, R. S.; Temperini, M. L. A.; Camargo, P. H. C. Rapid Synthesis of Hollow Ag–Au Nanodendrites in 15 Seconds by Combining Galvanic Replacement and Precursor Reduction Reactions. *Chem. – A Eur. J.* **2014**, 20 (46), 15040–15046.
 - (33) Wang, Y.; Zheng, Y.; Huang, C. Z.; Xia, Y. Synthesis of Ag Nanocubes 18–32 nm in Edge Length: The Effects of Polyol on Reduction Kinetics, Size Control, and Reproducibility. *J. Am. Chem. Soc.* **2013**, 135 (5), 1941–1951.
 - (34) Wiley, B. J.; Im, S. H.; Li, Z.-Y.; McLellan, J.; Siekkinen, A.; Xia, Y. Maneuvering the Surface Plasmon Resonance of Silver Nanostructures through Shape-Controlled Synthesis. *J. Phys. Chem. B* **2006**, 110 (32), 15666–15675.
 - (35) Cobley, C.; Skrabalak, S.; Campbell, D.; Xia, Y. Shape-Controlled Synthesis of Silver Nanoparticles for Plasmonic and Sensing Applications. *Plasmonics* **2009**, 4 (2), 171–179.
 - (36) Mukherjee, S.; Libisch, F.; Large, N.; Neumann, O.; Brown, L. V.; Cheng, J.; Lassiter, J. B.; Carter, E. A.; Nordlander, P.; Halas, N. J. Hot Electrons Do the Impossible: Plasmon-Induced Dissociation of H₂ on Au. *Nano Lett.* **2012**, 13 (1), 240–247.
 - (37) Clavero, C. Plasmon-Induced Hot-Electron Generation at Nanoparticle/metal-Oxide Interfaces for Photovoltaic and Photocatalytic Devices. *Nat Phot.* **2014**, 8 (2), 95–103.
 - (38) Huang, Y.-F.; Zhang, M.; Zhao, L.-B.; Feng, J.-M.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angew. Chemie Int. Ed.* **2014**, 53 (9), 2353–2357.
 - (39) Hu, X.; Wang, T.; Wang, L.; Dong, S. Surface-Enhanced Raman Scattering of 4-Aminothiophenol Self-Assembled Monolayers in Sandwich Structure with Nanoparticle Shape Dependence: Off-Surface Plasmon Resonance Condition. *J. Phys. Chem. C* **2007**, 111 (19), 6962–6969.
 - (40) Jiang, C.; Elliott, J. M.; Cardin, D. J.; Tsang, S. C. An Electrochemical Study of 4-Aminothiophenol/Pt Nanoparticle Multilayers on Gold Electrodes. *Langmuir* **2009**, 25 (1), 534–541.
 - (41) Bhattacharya, T.; Sarma, T. K.; Samanta, S. Self-Assembled Monolayer Coated Gold-Nanoparticle Catalyzed Aerobic Oxidation of α -Hydroxy Ketones in Water: An Efficient One-Pot Synthesis of Quinoxaline Derivatives. *Catal. Sci. Technol.* **2012**, 2 (11), 2216–2220.
 - (42) Wang, J.; Ando, R. A.; Camargo, P. H. C. Controlling the Selectivity of the Surface Plasmon Resonance Mediated Oxidation of P-Aminothiophenol on Au Nanoparticles by Charge

- Transfer from UV-Excited TiO₂. *Angew. Chemie Int. Ed.* **2015**, *127* (23), 7013-7016.
- (43) Wang, Z. L. Transmission Electron Microscopy of Shape-Controlled Nanocrystals and Their Assemblies. *J. Phys. Chem. B* **2000**, *104* (6), 1153–1175.

Chapter 11. Plasmonic Nanorattles as Next-Generation Catalysts for SPR-mediated Oxidations Promoted by Activated Oxygen

11.1. Introduction

Oxidation reactions play a pivotal role in industrial processes and academic research,^{1–3} in which the activation of molecular oxygen (O_2) at the catalyst surface represents a promising alternative to achieve high activities.^{4–6} Interestingly, it has been demonstrated that the surface plasmon resonance (SPR) excitation in silver (Ag) and gold (Au) nanostructures can generate activated O_2 at the metal surface.^{7–12} This process occurs via the charge-transfer of SPR-excited hot electrons to adsorbed O_2 molecules, allowing the use of visible-light to drive oxidation reactions.^{7–12}

Most studies on SPR-mediated transformations have focused on first-generation plasmonic catalysts, i.e., conventional Ag and Au nanoparticles such as quasi-spheres, cubes, wires, plates, among others.^{7–12} Herein, we propose the utilization of metallic nanorattles, comprised of a nanosphere inside of a nanoshell, as the next generation of plasmonic catalysts towards SPR-mediated oxidations by taking advantage of the plasmon hybridization concept.^{13,14} In nanorattles, plasmon hybridization between the nanoshell and nanosphere components can lead to much higher electric field (E-field) enhancements relative to its individual counterparts.^{15–17} Nanorattles also enable the generation of electromagnetic hot spots in a controllable manner without relying on the uncontrolled aggregation among individual nanostructures.^{18,19} This is not possible in first-generation plasmonic catalysts, and aggregation leads to a decrease in surface area and thus catalytic performance. Previously, high efficiencies towards SPR-mediated transformations were

described at junctions between Ag nanocubes supported over Al_2O_3 .²⁰ Although these junctions could present higher E-field enhancements relative to the nanorattles, their formation still relies on the uncontrolled aggregation and the synthesis of nanocubes is more complex relative to spherical nanoparticles. Finally, procedures for the synthesis of nanorattles have been reported, and their optical properties can be easily tuned as a function of size and wall-thickness.^{14,21,22}

11.2. Experimental Section

11.2.1. Materials and Instrumentation

Analytical grade chemicals silver nitrate (AgNO_3 , 99%, Sigma-Aldrich), chloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich, M.W. 55,000 g/mol), ethylene glycol (EG, 99.8%, Sigma Aldrich), sodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, 99%, Sigma-Aldrich), ethylene glycol (EG, 99.8%, Sigma Aldrich), p-aminothiophenol ($\text{H}_2\text{NC}_6\text{H}_4\text{SH}$, >97.0%, Sigma-Aldrich), aniline ($\text{H}_2\text{NC}_6\text{H}_5$ >97.0%, Sigma-Aldrich) were used as received. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained with a JEOL 1010 microscope operating at 80 kV or a JEOL JEM 2100 microscope operated at 200 kV. Samples for TEM and HRTEM were prepared by drop-casting an aqueous suspension of the nanostructures over a carbon-coated copper grid, followed by drying under ambient conditions. UV-VIS spectra were obtained from aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 spectrophotometer. Raman spectra were acquired on a Renishaw Raman InVia equipped with a CCD detector and coupled to a Leica microscope that allows a rapid accumulation of Raman spectra with a spatial resolution of about 1 μm (micro-Raman technique). The laser beam was

focused on the sample using a 50x lens. The experiments were performed under ambient conditions using a back-scattering geometry. The samples were irradiated with the 633 line of a He-Ne laser (Renishaw RL633 laser), and a solid-state diode laser, respectively, using controlled laser power outputs of 0.02-0.66 mW and employing the exposure time up to 30 s.

11.2.2. Synthesis of Au and Ag NPs seeds

Au seeds were prepared by the citrate reduction approach.²³ In a typical procedure, 30 mL of 0.25 mM AuCl_4^- were added to a 100 mL round-bottom flask under magnetic stirring. This system was heated to 100°C for 15 minutes, followed by the addition of 0.9 mL of 1 wt. % sodium citrate dihydrate. The reaction was allowed to proceed for another 10 min, yielding a red suspension containing the Au NPs. Ag seeds were prepared by the polyol process.²⁴ Briefly, 5 mg of polyvinylpyrrolidone (PVP) was dissolved in 37.5 mL of ethylene glycol. Then, AgNO_3 (200 mg, 1.2 mmol) was added and mixed until complete dissolution. The resulting solution was heated to 125 °C and kept at this temperature for 2.5 hours, leading to the appearance of a greenish-yellow color due to the formation of the Ag NPs. The reaction mixture was then allowed to cool to room temperature and diluted to 125 mL with water. The concentration of particles for the starting Ag and Au NPs suspensions corresponded to 1.26×10^{17} and 1.56×10^{17} NPs/L.

11.2.3. Synthesis of Au@Ag core-shell

Au@Ag core-shell NPs were obtained using Au NPs as seeds for Ag deposition by a stepwise seeded-growth process, in which several deposition cycles were performed in order to achieve the desired sizes for the Ag shell. In the first deposition step, a mixture containing 10 mL of as-prepared suspension containing the Au NPs, 150 μL of 100 mM NaOH, and 120 μL of 100

mM ascorbic acid was quickly stirred in a 25 mL round-bottom flask for 5 min. Then, 30 μ L of 100 mM AgNO₃ was added to the reaction mixture and the reaction was allowed to proceed for 30 min. Then, a second reduction step was performed by adding another 150 μ L of 100 mM NaOH, and 120 μ L of 100 mM ascorbic acid, and 30 μ L of 100 mM AgNO₃ to the reaction mixture and the reaction allowed to proceed for another 30 min. This procedure was repeated to a total of 8 deposition steps. After this procedure was complete, the reaction mixture containing the Au@Ag NPs was allowed to cool down to room temperature before being employed as the starting material for the synthesis of the Au@AgAu nanorattles.

11.2.4. Synthesis of Au@AgAu nanorattles and AgAu nanoshells

The synthesis of Au@AgAu nanorattles and AgAu nanoshells was based on the galvanic replacement reaction between Au@Ag core-shell or Ag nanospheres (for nanorattles and nanoshells, respectively) and AuCl₄⁻_(aq). Typically, a mixture containing 5 mL of PVP aqueous solution (0.1 wt %) and 1 mL of as-prepared suspension containing the Au@Ag core-shell or Ag NPs ($\sim 1.26 \times 10^{17}$ NPs/L for both suspensions) was stirred at 100 °C for 10 min in a 25 mL round-bottom flask. Then, 2 mL of 0.8 mM AuCl₄⁻_(aq) was added dropwise and the reaction allowed to proceed at 100 °C for another 10 min. After that, the suspension was allowed to cool down to room temperature and the product washed three times with ethanol and three times with water by successive rounds of centrifugation at 15000 rpm and removal of the supernatant. After washing, the nanoparticles were suspended in 10 mL of H₂O.

11.2.5. SPR-mediated oxidation of p-aminothiophenol

A 1.5 mL suspension containing the nanostructures (AgAu nanoshells, and Au@AgAu nanorattles) and 1.2 mL suspension containing the Au nanoparticles were centrifuged and the supernatant was removed, followed by the addition of 10 μL of water to yield concentrated suspensions. The suspensions containing the nanomaterials (10 μL) were dropcasted onto a 1 cm $\times$ 1 cm Si wafer (001 surface) followed by drying under ambient conditions. Then, 40 μL of a 1.0 mM p-aminothiophenol ethanolic solution was dropped over the Si wafer containing the NPs and dried under ambient conditions. The substrates containing the Ag NPs functionalized with PATP were then taken to the Raman spectrophotometer. All samples were used immediately for SERS measurements after preparation. All spectra were normalized with respect to the Raman band at 1081 cm^{-1} for the ease of comparison.

11.2.6. SPR-mediated oxidation of aniline

A 10 mL suspension containing the nanostructures (AgAu nanoshells, and Au@AgAu nanorattles) and 8 mL suspension containing the Au nanoparticles were centrifuged and the supernatant was removed, followed by the addition of 2 mL of DMSO to yield concentrated suspensions. In this case, the concentration of all nanomaterials employed as catalysts was kept the same (6.3×10^{17} NPs/L) for catalytic studies. In a typical experiment, a mixture of the aniline (1 mmol) and 2 mL of the suspension containing the catalysts (Au NPs, AgAu nanoshells, and Au@AgAu nanorattles) was transferred to a 15 mL round-bottom flask connected to an oxygen balloon (1 atm). This system was kept under stirring for 30 h at room temperature and irradiated with a 300 W halogen tungsten lamp (OSRAM) mounted at 10 cm from the glass reactor. During the reaction, 100 μL aliquots were taken and centrifuged at 15,000 rpm for 10 min to separate the catalysts and monitor the conversion by a Shimadzu GC-2014 equipment. After the reaction was

complete, the products were purified by column chromatography (silica gel) and analyzed by CG-MS GCM-QP2010SE Shimadzu instrument with low-resolution electron impact (EI, 70eV) equipped with a RTx®-5MS capillary column. GC/MS conditions: injector 260 °C; detector: 110 °C pressure: 100kPa. Column temperature: 80 °C, 1 °C/min up to 280 °C).

11.2.7. DDA calculations

The discrete dipole approximation (DDA) was employed to calculate the extinction spectrum in the 350-800 nm range and E-field distributions for Au sphere, shell and rattle with 20, 40 and 40 nm in diameter, respectively. Based on the experimental evidence, the thickness in sphere and rattle were kept at 5 nm. For the near-fields, the local electric field distribution were calculated considering a plane at a 2 nm away distance from the metallic surface. The excitation wavelength used in the near-fields calculations was 633 nm and the polarization direction for sphere and shell along the y-axis. For the rattle, the calculations were carried out under two different directions: [010] (along the y-axis) and [001] (along the z-axis). For the cubic grid, we employed a spacing of 0.5 nm for all nanostructures. The medium refraction index was 1.0 (air) in all cases. The near-fields were described by a grid of 4.0×10^4 points on the yz plane, the dielectric constants for Au was obtained from the literature.²⁵

11.3. Results and Discussion

Theoretical simulations indicate that the $|E_{max}|^2/|E_0|^2$ values were significantly higher for a nanorattle as compared to a nanoshell and a nanosphere having similar sizes (Figure 11.1). In our calculations, the nanorattle dimensions corresponded to 40 nm in outer diameter, 5 nm in

shell thickness, and contained a nanosphere 20 nm within its void. The $|E_{max}|^2/|E_0|^2$ values at 633 nm excitation corresponded to 570.30 and 867.10 (polarization along the y- and z-axis, respectively) for the nanorattle, 49.87 for the nanoshell, and 11.26 for the nanosphere, indicating that $|E_{max}|^2/|E_0|^2$ for the nanorattle was up ~ 14 -fold higher relative to the nanoshell and nanosphere. This observation is in agreement with previous reports,^{13,14} and originates from the plasmon hybridization between the nanoshell and nanosphere,^{13,26} in which the plasmon modes of the elementary nanoparticles combine leading to increased electric field intensities at the junction of neighboring nanoparticles, i.e., the so-called electromagnetic hot spots.¹⁴

Figure 11.1. Electric field enhancement contours $|E|^2/|E_0|^2$ calculated by the DDA method for AgAu nanorattles 40 nm in outer diameter, 5 nm in shell thickness, and having a Au nanosphere 20 nm inside its core (A and B), AgAu nanoshells 40 nm in diameter and 5 nm in shell thickness (C), and Au nanospheres 20 nm in diameter (D).

The calculated UV-VIS extinction spectra for the nanorattle, nanoshell and nanosphere are shown in Figure 11.2 A-C, respectively, and agree with the plasmon hybridization phenomenon.

Figure 11.2. Calculated extinction spectra for a single nanorattle (40 nm in outer diameter and 5 nm in shell thickness containing a Au nanoparticle 20 nm in diameter within its void), a single nanoshell (40 nm in outer diameter and 5 nm in shell thickness) and a single Au nanosphere 20 nm in diameter.

While the spectra for the nanoshell and nanosphere displayed single bands centered at 508 and 576 nm, respectively, the spectra for the nanorattle was comprised of a shoulder around 500-600 nm and a band at 630 nm.^{14,22} It is important to note that $|E_{max}|^2/|E_0|^2$ values for the nanoshell and nanospheres employing 576 and 508 nm as the excitation wavelength, respectively, corresponded to 15.01 and 53.73, being still inferior to that observed for the nanorattles under 633 nm excitation.

In order to experimentally investigate how the increased E-field enhancements observed for the nanorattle can be employed to achieve higher SPR-mediated performances relative to a nanoshell and a nanosphere, we synthesized Au@AgAu nanorattles as well as their AgAu nanoshells and Au nanoparticles counterparts having similar sizes (Scheme 11.1).²⁷

Scheme 11.1. Approach for the synthesis of Au@AgAu nanorattles and AgAu nanoshells. Firstly, Au nanoparticles were employed as physical templates for Ag growth in presence of citrate, leading to the formation of a Au@Ag core-shell. Then, the Au@AgAu nanorattles were obtained by a galvanic replacement reaction between Au@Au core-shell and $\text{AuCl}_4^-_{(\text{aq})}$. The AgAu nanoshells were obtained by a galvanic replacement reaction between Ag NPs and $\text{AuCl}_4^-_{(\text{aq})}$.

The Au@AgAu nanorattles were 39 ± 5 nm in outer diameter and ~ 5 nm in shell thickness, while the size of the Au nanoparticles located inside the voids corresponded to 19 ± 3 nm (Figure 11.3 A and 1D). Likewise, the AgAu nanoshells were 38 ± 4 nm in outer diameter and ~ 5 nm in shell thickness (Figure 11.3 B and 1E). Figure 11.3 C and 1F show TEM and HRTEM images of Au nanoparticles employed as seeds for the synthesis of the nanorattles. They were 19 ± 3 nm in diameter.

Figure 11.3. (A-C) TEM and HRTEM (D-F) images for Au@AgAu nanorattles (A and D), AgAu nanoshells (B and E), and Au nanoparticles (C and F). The EDX spectra from the regions indicated by black dashed squares in (D) and (E) are shown in (G) and (H), respectively. (I) Normalized UV-VIS extinction spectra recorded from aqueous suspensions containing Au@AgAu nanorattles, AgAu nanoshells and Au nanoparticles (black, blue, and red traces, respectively).

The EDX spectra registered from the regions indicated by black dashed rectangles (Figure 11.3 G and H, respectively) confirmed that the nanorattles and nanoshells display similar wall compositions (66 ± 4 and 63 ± 3 Au wt. %, respectively). Figure 11.3 I depicts the UV-VIS extinction spectra recorded from aqueous suspensions containing the Au@AgAu nanorattles, AgAu nanoshells, and Au nanoparticles (black, blue, and red traces, respectively). The spectra for AgAu nanoshells and Au nanoparticles displayed one dipole mode LSPR extinction band centered at 640 and 521 nm,^{28,29} respectively. Conversely, the presence of two extinction bands at 519 and 638 nm was observed for the nanorattles. This is in agreement with the calculated spectra shown in Figure 11.2.

In the next step, we were interested in the following question: Would the higher E-field enhancements enabled by the nanorattle morphology relative to nanoshells and nanospheres translate into improved properties in SPR-mediated transformations? In order to address this challenge, we employed SPR-mediated oxidation of PATP functionalized at the surface of the nanomaterials as a proof-of-concept transformation to benchmark the performance of the nanorattles relative to nanoshells and nanospheres according to the following equation:^{10,30}

It has been proposed that this reaction takes place as SPR-excited hot electrons are transferred to adsorbed O₂ molecules (from air). This leads to the generation of [•]O₂ species which participate in the PATP oxidation.¹⁰ Interestingly, this model reaction can be monitored in a Raman spectrometer, in which the incoming laser is employed as both the excitation source and to monitor the DMAB formation by SERS.^{8,10} Interestingly, both PATP and DMAB adsorb strongly on Ag

and Au surfaces via M-S covalent bonds, leading to the formation of a monolayer which enable PATP molecules to be in close proximity at the surface in all nanostructures.^{8,10} Therefore, due to the formation of a monolayer at the surface, it is plausible that in all nanoparticles the probability for two neighboring PATP molecules to interact should be similar.

Figure 11.4 A and B show the SERS spectra registered from Au@AgAu nanorattles that had been functionalized with PATP as a function of the laser power (Figure 11.4 A) and exposure time (Figure 11.4 B). The bands assigned to PATP and DMAB could be clearly detected in all spectra: the bands at 1081, 1188, 1489, and 1593 cm^{-1} corresponded to A_1 modes of PATP while the bands at 1081, 1142, 1390, 1433, and 1575 cm^{-1} were assigned to the A_g modes of DMAB.³¹ The intensities of the DMAB bands as well as DMAB:(DMAB+PATP) 1433:1081 intensity ratios (plotted in Figure 11.4 C and D) increased with the laser power and exposure time in agreement with a SPR-mediated reaction mechanism.³² Although localized heating due to SPR excitation can contribute to the oxidation reaction, the absence of an exponential dependence between laser power (illumination intensity) and photocatalytic rate suggest that the reaction was not driven by a thermal process, in agreement with an electron driven pathway in which hot electrons are transferred to adsorbed O_2 species.³³ In this context, it has been demonstrated that macroscopically observable photocatalytic rate dependence on illumination intensity can provide important mechanistic insights over the transformations mediated by the SPR excitation.³³ Specifically, while exponential relationships between photon-induced rates and illumination intensities can be associated with mechanisms that are driven by a thermal process, a linear rate dependence on intensity is associated with an electron driven process.³³

Figure 11.4. Laser-power (A) and irradiation-time (B) dependent SERS spectra for Au@AgAu nanorattles that had been functionalized with PATP employing 30 s as the exposure time (A) and 0.33 mW as the laser power (B). (C) and (D) show the DMAB:(DMAB+PATP) 1433:1081 intensity ratios obtained from (A) and (B), respectively.

Figure 11.5 A displays the SERS spectra acquired from nanorattles, nanoshells and nanoparticles that had been functionalized with PATP employing 0.33 mW as the laser power and 30 s as the acquisition time (these conditions correspond to the point at which the PATP to DMAB conversion was maximized in all cases). The intensity of the DMAB signals as well as the relative DMAB:(DMAB+PATP) 1433:1081 intensity ratios (Figure 11.5 B) were significantly higher for the nanorattles as compared to the nanoshells and nanoparticles. Specifically, the

DMAB:(PATP+DMAB) 1433:1081 intensity ratios turned out to be 1.19, 0.13, and 0.03 for the nanorattles, nanoshells, and nanoparticles, respectively. This represents an increase of ~ 9.2 - and ~ 40 -fold in the PATP conversion for the nanorattles compared to the nanoshells and nanoparticles, respectively, and an enhancement of ~ 7.4 -fold relative to the sum of nanoshell and nanosphere performances.

Figure 11.5. SERS spectra (A) and DMAB:(DMAB+PATP) 1433:1081 intensity ratios (B) for Au@AgAu nanorattles (black trace), AgAu nanoshells (blue trace), and Au nanoparticles (red trace) that had been functionalized with PATP employing 30 s as the exposure time and 0.33 mW as the laser power.

After demonstrating that the higher E-field enhancements as enabled by plasmon hybridization in the nanorattle structure led to remarkably higher SPR-mediated oxidation of PATP functionalized at the surface, we turned our attention to the utilization of the nanorattles as plasmonic catalysts for the oxidation of aniline driven by visible-light under ambient conditions as shown in Figure 11.6 A (room temperature, 1 atm of O₂, and employing a 300 W tungsten lamp as the excitation source). As the visible-light excitation comprises the entire visible region, it can excite the SPR of nanorattles, nanoshells, and nanoparticles (whose SPR maxima are centered at

different laser wavelengths). This, in turn, allowed us to systematically investigate the concept of plasmon hybridization in Au@AgAu nanorattles towards SPR-mediated oxidation reactions promoted by activated O_2 .

Figure 11.6. (A) SPR-mediated oxidation of aniline catalyzed by the nanorattles. (B) Conversion (%) of aniline as a function of time catalyzed by Au@AgAu nanorattles, AgAu nanoshells, and Au nanoparticles (black, blue, and red traces, respectively) (C) Conversion (%) of aniline employing nanorattles as catalysts in the absence of visible light or by turning the light off after 3 h. Chromatograms (D) and digital photographs (E) obtained from the reaction mixture solutions catalyzed by the nanorattles as a function of time.

It is noteworthy that the conventional synthesis of aromatic azocompounds from amines requires several reaction steps and stoichiometric amounts of nitrite salts (NaNO_2) as well as toxic oxidants.³⁴ Although the use of inorganic oxides and metal nanoparticles as catalysts to produce azobenzene in good yields has been reported, the utilization of harsh conditions (strong oxidizing agents, high pressures of O_2 and/or temperatures up to 150°C) are still required.^{34–37}

Figure 11.6 B shows the conversion (%) for the oxidation of aniline as a function of time by employing the Au@AgAu nanorattles (black trace), AgAu nanoshells (blue trace), and Au nanoparticles (red trace) as catalyst. The utilization of the Au@AgAu nanorattles led to $> 90\%$ of conversion after 10 h. This conversion (%) was significantly higher relative to nanoshells and nanoparticles (23 and 14 %, respectively). The temperature of the reaction mixture at the end of the reaction corresponded to 34°C and no significant conversion was obtained in the absence of any catalyst (blank reaction, green trace). The orange trace depicts the conversion (%) considering the sum of AgAu nanoshells and Au NPs. Here, as all the catalytic experiments were carried out under the same loading of nanoparticles, their dimensions are comparable, and the shells have similar compositions, the variations in the catalytic performances of the nanorattles relative to the sum of nanoshells and nanoparticles enables us to isolate the contribution of the SPR excitation over the catalytic performance, as the same amount of surface area is available in this case. It can be observed that, after 10 h, the conversion (%) for the nanorattles was ~ 3 -fold higher relative to the sum of nanoshells and nanoparticles (same available surface areas), confirming the role of the SPR excitation over the enhancement of catalytic activities in the nanorattles.

In order to demonstrate that this transformation was mediated by the SPR excitation in the Au@AgAu nanorattles and estimate the contribution from external thermal effects, we compared the conversion (%) with and without the visible-light excitation as shown in Figure 11.6 C. Low

conversion (%) were obtained without visible-light excitation (red trace, employing 34 °C as the reaction temperature). In this case, only 15 % of conversion was observed after 10 h as compared to > 90 % under visible-light excitation (black trace). The role of visible-light excitation was further confirmed by monitoring the catalytic conversion under visible light excitation for 3 h and then turning off the light source as depicted in Figure 11.6 D, blue trace. In this case, no significant conversion took place after the light source was turned off. In order to gain further insight over contribution of the thermal effect, we also performed control experiments at 60 and 80 °C (without light excitation) and no improvement in the conversion (%) were observed as compared to the reaction performed at 34° C. It would be expected that the conversion (%) should be improved if this effect was imperative in this transformation, in agreement with previous results demonstrating that the reaction occurs via a charge-transfer electrons mechanism.^[10, 31]

Encouragingly, only azobenzene was detected as reaction product as confirmed by the chromatograms collected from the reaction mixture at different times intervals, which revealed the gradual aniline consumption and concomitant appearance of a single reaction product as depicted in Figure 11.6 D. Figure 11.6 E shows the digital photographs from the reaction mixture isolated at different time-intervals, which shows the gradual appearance of an orange-red color in the solution that is characteristic of the azobenzene formation. The chemical structure of azobenzene was confirmed by CG-MS, RMN and UV-VIS analyses from the isolated product. No aniline conversion was detected when the reaction was carried out in the absence of O₂. Moreover, the utilization of air (instead of O₂) led to a decrease in the conversion (%) by ~3-fold.

Scheme 11.2 shows the proposed mechanism for the SPR-mediated oxidation of aniline catalyzed by the plasmonic nanorattles according to our reported results and the literature.^{10,34,38–}

(A) Generation of $\cdot\text{O}_2$ by the transfer of SPR-excited hot electrons

(B) Proposed mechanism for the SPR-mediated oxidation of aniline

Scheme 11.2. Proposed mechanism for the SPR-mediated oxidation of aniline. After $\cdot\text{O}_2$ species are generated as a result of SPR excitation (A), they participate in the catalytic cycle by a radical mechanism (B).

First, $^1\text{O}_2$ species are generated from SPR excitation (Scheme 11.2 A). Then, these species enter the catalytic cycle (Scheme 11.2 B) and oxidize the nitrogen atom of aniline, leading to an aniline radical cation ($^1\text{O}_2$ molecules often lead to radical mechanism). In the next step, the coupling between the aniline radical cation and an aniline molecule may lead to the formation of a three-electron σ bond intermediate. This intermediate could lose hydrogen atoms in the presence of $\text{OH}^-_{(\text{aq})}$ species forming H_2O . This is supported by the fact that the formation of azobenzene could not be detected when the reaction was carried out in the absence of $\text{OH}^-_{(\text{aq})}$.⁴¹ Finally, the produced hydrazine can quickly be converted to azobenzene product by a superoxide species regenerating the catalyst. In order to check the reusability of the nanorattles as catalyst, they were recovered from the reaction mixture by centrifugation at the end of the reaction. The recovered catalyst could be re-used at least three times without a significant loss of performance (96 % of conversion after the 3rd cycle). It is important to note that, although the local electromagnetic field generated due to plasmon hybridization in the nanorattles is within the void region, they can contribute the described oxidation processes as the nanorattles outer shell is porous and enable the diffusion of molecules to their interior (Figures 11.7 and 11.8).⁴² Moreover, as the SPR catalytic properties are strongly dependent on size and optical properties, the control over the nanorattle dimensions (such as shell thickness, void gap, and Au nanoparticles size) may be employed to further optimize the catalytic performances.

Figure 11.7. HRTEM images of individual nanorattles (A and D) and zoomed-in images (B, C, E, and F) of regions marked by the dashed squares in (A) and (D) depicting the presence of various pores at the nanorattle shell's surface.

Figure 11.8. HRTEM images of individual nanoshells (A and D) and zoomed-in images (B, C, E, and F) of regions marked by the dashed squares in (A) and (D) depicting the presence of various pores at the shell's surface.

11.4. Conclusion

In summary, we demonstrated that the concept of plasmon hybridization in Au@AgAu nanorattles led to improved performances towards SPR-mediated oxidation reactions promoted by activated O₂. Firstly, we compared the E-field enhancements for the nanorattles relative to nanoshells and nanospheres and benchmarked their performances using the oxidation of PATP functionalized at the surface as a proof-of-concept transformation. Then, the nanorattles were employed as plasmonic catalysts to the synthesis of azobenzene from aniline under ambient conditions. As the nanorattle morphology enables the formation of electromagnetic hot spots, in a well-defined and controlled manner (as opposed to the uncontrolled aggregation of nanoparticles), they represent the next-generation of plasmonic catalysts for applications in oxidation reactions and potentially other transformations.

11.5. References

- (1) Zaera, F. Nanostructured Materials for Applications in Heterogeneous Catalysis. *Chem. Soc. Rev.* **2013**, 42 (7), 2746–2762.
- (2) Stratakis, M.; Garcia, H. Catalysis by Supported Gold Nanoparticles: Beyond Aerobic Oxidative Processes. *Chem. Rev.* **2012**, 112 (8), 4469–4506.
- (3) da Silva, A. G. M.; Kisukuri, C. M.; Rodrigues, T. S.; Candido, E. G.; de Freitas, I. C.; da Silva, A. H. M.; Assaf, J. M.; Oliveira, D. C.; Andrade, L. H.; Camargo, P. H. C. MnO₂ Nanowires Decorated with Au Ultrasmall Nanoparticles for the Green Oxidation of Silanes and Hydrogen Production under Ultralow Loadings. *Appl. Catal. B Environ.* **2016**, 184, 35–43.
- (4) Long, R.; Mao, K.; Ye, X.; Yan, W.; Huang, Y.; Wang, J.; Fu, Y.; Wang, X.; Wu, X.; Xie, Y.; et al. Surface Facet of Palladium Nanocrystals: A Key Parameter to the Activation of Molecular Oxygen for Organic Catalysis and Cancer Treatment. *J. Am. Chem. Soc.* **2013**, 135 (8), 3200–3207.
- (5) Woodham, A. P.; Meijer, G.; Fielicke, A. Activation of Molecular Oxygen by Anionic Gold Clusters. *Angew. Chemie Int. Ed.* **2012**, 51 (18), 4444–4447.
- (6) Hinde, C. S.; Ansovini, D.; Wells, P. P.; Collins, G.; Aswegen, S. Van; Holmes, J. D.; Hor, T. S. A.; Raja, R. Elucidating Structure–Property Relationships in the Design of Metal

- Nanoparticle Catalysts for the Activation of Molecular Oxygen. *ACS Catal.* **2015**, *5* (6), 3807–3816.
- (7) Christopher, P.; Xin, H.; Linic, S. Visible-Light-Enhanced Catalytic Oxidation Reactions on Plasmonic Silver Nanostructures. *Nat Chem* **2011**, *3* (6), 467–472.
 - (8) Wang, J.; Ando, R. A.; Camargo, P. H. C. Controlling the Selectivity of the Surface Plasmon Resonance Mediated Oxidation of P-Aminothiophenol on Au Nanoparticles by Charge Transfer from UV-Excited TiO₂. *Angew. Chemie Int. Ed.* **2015**, *127* (23), 7013–7016
 - (9) Wang, J. L.; Ando, R. A.; Camargo, P. H. C. Investigating the Plasmon-Mediated Catalytic Activity of AgAu Nanoparticles as a Function of Composition: Are Two Metals Better than One? *ACS Catal.* **2014**, *4* (11), 3815–3819.
 - (10) Huang, Y.-F.; Zhang, M.; Zhao, L.-B.; Feng, J.-M.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. Activation of Oxygen on Gold and Silver Nanoparticles Assisted by Surface Plasmon Resonances. *Angew. Chemie Int. Ed.* **2014**, *53* (9), 2353–2357.
 - (11) da Silva, A. G. M.; Rodrigues, T. S.; Wang, J.; Yamada, L. K.; Alves, T. V; Ornellas, F. R.; Ando, R. A.; Camargo, P. H. C. The Fault in Their Shapes: Investigating the Surface-Plasmon-Resonance-Mediated Catalytic Activities of Silver Quasi-Spheres, Cubes, Triangular Prisms, and Wires. *Langmuir* **2015**, *31* (37), 10272–10278.
 - (12) Zhao, L.-B.; Zhang, M.; Huang, Y.-F.; Williams, C. T.; Wu, D.-Y.; Ren, B.; Tian, Z.-Q. Theoretical Study of Plasmon-Enhanced Surface Catalytic Coupling Reactions of Aromatic Amines and Nitro Compounds. *J. Phys. Chem. Lett.* **2014**, *5* (7), 1259–1266.
 - (13) Prodan, E.; Radloff, C.; Halas, N. J.; Nordlander, P. A Hybridization Model for the Plasmon Response of Complex Nanostructures. *Science*. **2003**, *302* (5644), 419–422.
 - (14) Mahmoud, M. A. Plasmon Resonance Hybridization of Gold Nanospheres and Palladium Nanoshells Combined in a Rattle Structure. *J. Phys. Chem. Lett.* **2014**, *5* (15), 2594–2600.
 - (15) Liu, K.-K.; Tadeipalli, S.; Tian, L.; Singamaneni, S. Size-Dependent Surface Enhanced Raman Scattering Activity of Plasmonic Nanorattles. *Chem. Mater.* **2015**, *27* (15), 5261–5270.
 - (16) Mahmoud, M. A. Optical Properties of Gold Nanorattles: Evidences for Free Movement of the Inside Solid Nanosphere. *J. Phys. Chem. C* **2014**, *118* (19), 10321–10328.
 - (17) Khalavka, Y.; Becker, J.; Sönnichsen, C. Synthesis of Rod-Shaped Gold Nanorattles with Improved Plasmon Sensitivity and Catalytic Activity. *J. Am. Chem. Soc.* **2009**, *131* (5), 1871–1875.
 - (18) Kleinman, S. L.; Frontiera, R. R.; Henry, A.-I.; Dieringer, J. A.; Van Duyne, R. P. Creating, Characterizing, and Controlling Chemistry with SERS Hot Spots. *Phys. Chem. Chem. Phys.* **2013**, *15* (1), 21–36.
 - (19) Mahmoud, M. A.; El-Sayed, M. A. Aggregation of Gold Nanoframes Reduces, Rather Than Enhances, SERS Efficiency Due to the Trade-Off of the Inter- and Intraparticle Plasmonic Fields. *Nano Lett.* **2009**, *9* (8), 3025–3031.
 - (20) Christopher, P.; Xin, H.; Marimuthu, A.; Linic, S. Singular Characteristics and Unique Chemical Bond Activation Mechanisms of Photocatalytic Reactions on Plasmonic Nanostructures. *Nat Mater* **2012**, *11* (12), 1044–1050.
 - (21) Sun, Y.; Wiley, B.; Li, Z.-Y.; Xia, Y. Synthesis and Optical Properties of Nanorattles and Multiple-Walled Nanoshells/Nanotubes Made of Metal Alloys. *J. Am. Chem. Soc.* **2004**, *126* (30), 9399–9406.
 - (22) Priebe, M.; Fromm, K. M. Nanorattles or Yolk–Shell Nanoparticles—What Are They, How Are They Made, and What Are They Good For? *Chem. – A Eur. J.* **2015**, *21* (10), 3854–

- 3874.
- (23) Silva, A. G. M. da; Rodrigues, T. S.; Macedo, A.; Silva, R. T. P. da; Camargo, P. H. C. An Undergraduate Level Experiment on the Synthesis of Au Nanoparticles and Their Size-Dependent Optical and Catalytic Properties. *Quím. Nova* **2014**, 37 (10), 1716-1720.
 - (24) Silvert, P.-Y.; Herrera-Urbina, R.; Duvauchelle, N.; Vijayakrishnan, V.; Elhissien, K. T. Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 1-Synthesis and Characterization. *J. Mater. Chem.* **1996**, 6 (4), 573-577.
 - (25) Johnson, P. B.; Christy, R. W. Optical Constants of the Noble Metals. *Phys. Rev. B* **1972**, 6 (12), 4370-4379.
 - (26) Nordlander, P.; Prodan, E. Plasmon Hybridization in Nanoparticles near Metallic Surfaces. *Nano Lett.* **2004**, 4 (11), 2209-2213.
 - (27) Xia, X.; Wang, Y.; Ruditskiy, A.; Xia, Y. 25th Anniversary Article: Galvanic Replacement: A Simple and Versatile Route to Hollow Nanostructures with Tunable and Well-Controlled Properties. *Adv. Mater.* **2013**, 25 (44), 6313-6333.
 - (28) Skrabalak, S. E.; Chen, J.; Sun, Y.; Lu, X.; Au, L.; Cobley, C. M.; Xia, Y. Gold Nanocages: Synthesis, Properties, and Applications. *Acc. Chem. Res.* **2008**, 41 (12), 1587-1595.
 - (29) Jana, N. R.; Gearheart, L.; Murphy, C. J. Seeding Growth for Size Control of 5-40 nm Diameter Gold Nanoparticles. *Langmuir* **2001**, 17 (22), 6782-6786.
 - (30) Sun, M.; Xu, H. A Novel Application of Plasmonics: Plasmon-Driven Surface-Catalyzed Reactions. *Small* **2012**, 8 (18), 2777-2786.
 - (31) Kang, L.; Xu, P.; Zhang, B.; Tsai, H.; Han, X.; Wang, H.-L. Laser Wavelength- and Power-Dependent Plasmon-Driven Chemical Reactions Monitored Using Single Particle Surface Enhanced Raman Spectroscopy. *Chem. Commun.* **2013**, 49 (33), 3389-3391.
 - (32) Linic, S.; Christopher, P.; Ingram, D. B. Plasmonic-Metal Nanostructures for Efficient Conversion of Solar to Chemical Energy. *Nat Mater* **2011**, 10 (12), 911-921.
 - (33) Kale, M. J.; Avanesian, T.; Christopher, P. Direct Photocatalysis by Plasmonic Nanostructures. *ACS Catal.* **2014**, 4 (1), 116-128.
 - (34) Dutta, B.; Biswas, S.; Sharma, V.; Savage, N. O.; Alpay, S. P.; Suib, S. L. Mesoporous Manganese Oxide Catalyzed Aerobic Oxidative Coupling of Anilines To Aromatic Azo Compounds. *Angew. Chemie* **2016**, 128 (6), 2211-2215.
 - (35) Monir, K.; Ghosh, M.; Mishra, S.; Majee, A.; Hajra, A. Phenyliodine(III) Diacetate (PIDA) Mediated Synthesis of Aromatic Azo Compounds through Oxidative Dehydrogenative Coupling of Anilines: Scope and Mechanism. *European J. Org. Chem.* **2014**, 2014 (5), 1096-1102.
 - (36) Grirrane, A.; Corma, A.; García, H. Gold-Catalyzed Synthesis of Aromatic Azo Compounds from Anilines and Nitroaromatics. *Science (80-.)*. **2008**, 322 (5908), 1661-1664.
 - (37) Ghosh, S.; Acharyya, S. S.; Sasaki, T.; Bal, R. Room Temperature Selective Oxidation of Aniline to Azoxybenzene over a Silver Supported Tungsten Oxide Nanostructured Catalyst. *Green Chem.* **2015**, 17 (3), 1867-1876.
 - (38) Cai, S.; Rong, H.; Yu, X.; Liu, X.; Wang, D.; He, W.; Li, Y. Room Temperature Activation of Oxygen by Monodispersed Metal Nanoparticles: Oxidative Dehydrogenative Coupling of Anilines for Azobenzene Syntheses. *ACS Catal.* **2013**, 3 (4), 478-486.
 - (39) Xu, P.; Kang, L.; Mack, N. H.; Schanze, K. S.; Han, X.; Wang, H.-L. Mechanistic Understanding of Surface Plasmon Assisted Catalysis on a Single Particle: Cyclic Redox of 4-Aminothiophenol. *Sci. Rep.* **2013**, 3, 2997.
 - (40) Wu, D.-Y.; Zhao, L.-B.; Liu, X.-M.; Huang, R.; Huang, Y.-F.; Ren, B.; Tian, Z.-Q. Photon-

- Driven Charge Transfer and Photocatalysis of P-Aminothiophenol in Metal Nanogaps: A DFT Study of SERS. *Chem. Commun.* **2011**, 47 (9), 2520–2522.
- (41) Hong, X.; Wang, D.; Cai, S.; Rong, H.; Li, Y. Single-Crystalline Octahedral Au–Ag Nanoframes. *J. Am. Chem. Soc.* **2012**, 134 (44), 18165–18168.
- (42) Slater, T. J. A.; Macedo, A.; Schroeder, S. L. M.; Burke, M. G.; O’Brien, P.; Camargo, P. H. C.; Haigh, S. J. Correlating Catalytic Activity of Ag–Au Nanoparticles with 3D Compositional Variations. *Nano Lett.* **2014**, 14 (4), 1921–1926.

Section 6.

Controlled Synthesis and Education: Introducing Nanoscience to Undergraduate Students

Chapter 12. An Undergraduate Level Experiment on the Synthesis of Au Nanoparticles and their Size-Dependent Optical and Catalytic Properties

12.1. Introduction

Nanoscience encompasses the study and manipulation of nanomaterials, which display feature sizes of < 100 nm in at least one dimension.¹ Among nanomaterials, metals are particularly interesting due to their unique optical, chemical, and electronic properties allow applications in areas such as plasmonics, catalysis, biomedicine, information storage, and sensing.^{2,3}

The optical and catalytic behavior of gold nanoparticles (Au NPs) relative to the bulk element represents a remarkable example of how properties change as we move from the macroscopic to the nanoscopic dimension.^{4,5} While the optical properties of Au NPs in the visible range have been exploited for centuries (such as in stained glass windows and the Lycurgus cup),⁴ the demonstration of their catalytic activity towards CO oxidation in 1987⁴ represented a milestone in the field of nanocatalysis, followed by a burst on the utilization of Au NPs as catalysts for a wide range of transformations.⁶

The catalytic activity of Au NPs is largely due to the increase in the particles surface-to-volume ratio.^{3,5} On the other hand, the unique optical properties of Au NPs arise from the interaction of their free electrons with light, in which the oscillating electric field component from the incoming electromagnetic wave drives the free electrons in the metal into collective oscillations, which is the surface plasmon resonance (SPR) excitation.^{4,7} The SPR excitation leads to adsorption and scattering of the incident electromagnetic wave close to the resonance frequency

(in the far field) as well as the generation of intense electromagnetic fields close to the surface of the nanostructure (in the near field).⁷⁻⁹

It has been established that many properties (including optical and catalytic) in metal NPs are dependent upon several physical and chemical parameters that include size, shape, composition, and structure (solid or hollow interiors).^{3,10} Thus, the understanding on how properties vary as a function of these parameters is crucial to optimize performance and enable new applications.

Although undergraduate level laboratory experiments have been proposed on the synthesis of metal nanoparticles and investigation of their optical and/or catalytic properties,¹¹⁻¹⁶ activities in which students can establish a correlation between size and observed properties remains limited. Here, we present an undergraduate level experiment in which the students synthesize Au NPs having three different sizes, followed by an investigation on how their optical and catalytic properties change as a function of size. Specifically, the proposed experiment consists of three main parts. In the first, students perform the synthesis of three Au NPs samples having increasingly bigger sizes by a seeded growth approach. In the second, students qualitatively and quantitatively investigate the variations in the optical properties due to the formations of Au NPs and also as a function of their size (by both visual inspection and UV-VIS spectroscopy). In the third, students employ the hydrogenation of 4-nitrophenol by sodium borohydride as a model reaction to investigate the size-dependent catalytic activity of the synthesized Au NPs.^{17,18} This activity should be performed by groups of two or three students in three lab sessions of 3 h each. The first, second and third lab sessions should be organized as follows: *i*) the synthesis of Au NPs having different sizes and investigation of their optical properties; *ii*) evaluation of the catalytic activity; and *iii*) data analysis and discussion. This experiment covers concepts on the synthesis, stabilization, and

characterization of Au NPs, their size-dependent optical and catalytic properties at the nanoscale, chemical kinetics, and the role of catalyst.

12.2. Experimental

12.2.1. Experimental Overview

Full experimental details regarding the synthesis of Au NPs having different sizes, the investigation of their optical properties and catalytic activity are given in the student guide. In summary, the synthesis of aqueous suspensions containing Au NPs 15 ± 2.2 , 26 ± 2.4 , and 34 ± 3.0 nm in diameter was performed by a seeded growth approach²³. The change in optical properties due to the formation of Au NPs as compared to the AuCl_4^- precursor solution and the bulk metal should be first detected by visualizing the change in color for the suspension containing the Au NPs relative to the solution containing the AuCl_4^- precursor. Furthermore, the size dependent optical properties of the Au NPs can be directly visualized as the change in color of the Au NPs suspensions, in which the red color becomes darker as the size of the Au NPs increases. In order to quantify the change in optical properties due to the formation of Au NPs and also their dependence on size, UV-VIS spectra in the 300-800 nm range were obtained from an aqueous solution containing the AuCl_4^- precursor and also from aqueous suspensions containing the Au NPs. The catalytic activities as a function of Au NPs size was investigated employing the hydrogenation of 4-nitrophenol to 4-aminophenol as a model reaction. In this case, the reaction kinetics was monitored by UV-VIS spectroscopy in the 350 to 500 nm range,¹⁹ in which the variations in the absorbance at 400 nm were monitored as a function of time. The same concentration of Au was employed in all cases.

12.2.2. Materials and Instrumentation

Analytical grade chemicals gold(III) chloride trihydrate (HAuCl_4 , 99% - Sigma-Aldrich), trisodium citrate dehydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$, >99% - Synth), 4-nitrophenol ($\text{C}_6\text{H}_5\text{NO}_3$, 98% - Merk), and sodium borohydride (NaBH_4 , 95% - Vetec) will be used as received. All solutions were prepared using deionized water (18.2 M Ω). UV-VIS spectra will be obtained from aqueous solutions or aqueous suspensions containing the nanostructures with a Shimadzu UV-1700 spectrophotometer. Transmission electron microscopy (TEM) images were obtained with a JEOL 1010 microscope at 80 kV. The samples for TEM were prepared by drop-casting aqueous suspensions containing the nanoparticles over a carbon-coated copper grid, followed by drying under ambient conditions.

12.2.3. Synthesis of Au NPs with controlled sizes

The synthesis of Au NPs should be performed by a seeded growth approach.²⁰ In the first step, Au NPs can be prepared by adding 150 mL of a 2.2 mM sodium citrate aqueous solution to a 250 mL round-bottom flask under magnetic stirring. This system should be heated to 100°C for 15 minutes. Then, 1 mL of a 25 mM AuCl_4^- (aq) solution should be added, and the reaction mixture kept at 100°C under vigorous stirring for another 30 minutes. This procedure yields an aqueous suspension containing the Au NPs, which will be employed as seeds for the synthesis of Au NPs having larger sizes by successive Au deposition steps. For the first deposition step, add 1 mL of a 60 mM sodium citrate solution to same 250 mL round-bottom flask containing the Au NPs seeds under magnetic stirring at 100 °C. After 5 min, add 1 mL of a 25 mM AuCl_4^- (aq) solution to the reaction mixture containing the Au NPs seeds and keep the reaction mixture at 100 °C for another 30 min. This will produce a suspension containing the Au NPs (first deposition step). Similarly, a

second deposition step should be performed by adding another 1 mL of a 60 mM sodium citrate solution and 1 mL of a 25 mM AuCl_4^- (aq) solution to the reaction mixture obtained after the first deposition step, in which the Au NPs produced after the first deposition step serve as seeds for further growth. In these reactions, each Au NPs sample could be isolated by stopping the reaction at the end of each corresponding reduction/deposition step. In order to minimize the synthesis time of Au NPs with different sizes, it is recommended to perform three independent/parallel reactions, one for each desired Au NPs size (seed, first and second deposition steps). The average diameters of the Au NPs were determined by individually measuring the width of 20 nanoparticles from the TEM images.

12.2.4. Optical Properties

The change on optical properties due to the formation of Au NPs as compared to the AuCl_4^- precursor solution and the bulk metal should be first detected by visualizing the change in color for the suspension containing the Au NPs relative to the solution containing the AuCl_4^- precursor. Furthermore, the size dependent optical properties of the Au NPs can be directly visualized as the change in color of the Au NPs suspensions. In order to quantify the change in optical properties due to the formation of Au NPs and also their dependence on size, UV-VIS spectra should be measured from an aqueous solution containing the AuCl_4^- precursor and also from aqueous suspensions containing the Au NPs with a Shimadzu UV-1700 spectrophotometer in the 300-800 nm range.

12.2.5. Study of catalytic activities: 4-nitrophenol reduction reaction

The hydrogenation of 4-nitrophenol was monitored by UV-VIS absorption spectroscopy in the 350 to 500 nm range.¹⁹ In order to perform this procedure, add 2 mL of a 42 mM sodium borohydride solution to 0.3 mL of 0.14 mM 4-nitrophenol aqueous solution in a quartz cuvette, which should then be inserted into the spectrophotometer. Register the initial spectrum. Considering that the Au concentration (mM) employed in each reaction (growing step) was different, each of the resulting Au NPs suspension (Au NPs seeds, Au NPs after the first deposition step, and Au NPs after second deposition step) should be diluted so that the Au concentration is the same in all cases (8.2 mM, based on the amount of AuCl_4^- employed in the reaction). Specifically, dilute 500, 250 and, 170 μL of the suspensions containing Au NPs seeds, Au NPs after the first deposition step, and Au NPs after the second deposition step, respectively, to 2 mL with deionized water. The catalytic performances of Au NPs with different sizes should be evaluated by adding 200 μL of this aqueous suspension containing the Au NPs to the quartz cuvette containing 4-nitrophenol and sodium borohydride solution. Monitor the variations in the absorbance at 400 nm as a function of time employing a time interval of 13 s between each spectrum (for the sake of comparison, observe what happens to a mixture of 4-nitrophenol and sodium borohydride solution without the addition of Au NPs). A calibration curve for the concentration of 4-nitrophenolate ions will be provided. This curve was obtained by registering the absorbance at 400 nm from 0.16, 0.82, 1.65, 4.1, 8.2, 12.36, 16.47, and 24.71 μM standard aqueous solutions (prepared in the presence of an excess of sodium borohydride as described in the catalytic tests).

The variations in the absorbance with time should be employed to calculate the rate constants. The turnover frequency (TOF),²¹ a common parameter to describe catalytic activity, should also be estimated from the 4-nitrophenol calibration curve and the following expression:

$$\text{TOF} = N_{4\text{NP}}/(N_{\text{Au}} \cdot t) \quad (1)$$

where $N_{4\text{NP}}$ denotes the amount in mols of 4-nitrophenol converted to 4-aminophenol, N_{Au} the amount in mols of Au, and t the time.

12.2.6. Hazards

Chloroauric acid trihydrate is corrosive and hygroscopic. It can cause eyes and skin burns upon contact. It also causes gastrointestinal tract burns if swallowed and burns to the respiratory tract by inhalation. Sodium citrate may cause irritation to skin, eyes, and respiratory tract. Sodium borohydride is flammable and toxic. It is also a strong reducing agent, is corrosive, and may cause burns to any area of contact. 4-nitrophenol is poisonous via inhalation, swallowing, and contact with the skin. The experiment described in this work uses dilute solutions, which may be prepared ahead of time to minimize the risk that the solids and concentrated solutions pose to students. Labeled waste containers should be made available. Gloves, lab coat, and safety glasses should be worn throughout the experiment. All laboratory exercises should be carried out under the supervision of trained and qualified personnel.

12.2.7. Student Learning Objectives

The key learning objectives of this multidisciplinary experiment are: *i*) synthesis of metal nanoparticles with controlled sizes; *ii*) stabilization of nanoparticles; *iii*) introduce the concept of surface plasmon resonance to describe the unique optical properties of Au NPs in the visible range, which gives a visual example on the change in properties in nanoscaled systems relative to their macroscopic counterparts; *iv*) chemical kinetics (pseudo-first-order rate laws, role of catalyst,

calculation of rate constants and turnover frequencies); and v) investigation of Au NPs optical properties and catalytic activities as a function of size.

12.2.8. Lab Report

The report should follow the format of a scientific paper, comprising an introduction, experimental, results and discussion, and conclusion sections.

12.3. Results and Discussion

Figure 12.1 A-C shows TEM images for the Au NPs samples obtained after the three stages of growth. First, Au NPs seeds were obtained by the reduction of AuCl_4^- (aq) in the presence of citrate,²⁰ as depicted in Figure 12.1 A. Then, they served as physical templates for further Au growth by producing Au NPs that are larger in diameter relative to the Au NPs seeds (Figure 12.1 B). Similarly, a second deposition step was carried out employing the Au NPs obtained after the first deposition step as seeds for further growth (Figure 12.1 C). As shown in the TEM images (Fig. 12.1 A-C), the diameter of the Au NPs corresponded to 15 ± 2.2 , 26 ± 2.4 , and 34 ± 3.0 nm for the Au NPs seeds, Au NPs after the first deposition step and, Au NPs after the second deposition step, respectively. This result indicates that the described approach was effective to produce Au NPs with well-controlled sizes. It is important to note that, in all cases, the Au NPs were spherical and relatively monodisperse.

Figure 12.1. TEM images of Au NPs seeds (A) and Au NPs after the first (B) and second (C) deposition steps. In (A-C), the Au NPs diameters corresponded to 15 ± 2.2 , 26 ± 2.4 , and 34 ± 3.0 nm, respectively.

Figure 12.2 A shows digital photographs from the starting AuCl_4^- (aq) solution (shown on the left) and aqueous suspensions containing Au NPs 15 ± 2.2 , 26 ± 2.4 , and 34 ± 3.0 nm in diameter (shown from left to right, respectively).

Figure 12.2. (A) Digital photographs of the AuCl_4^- (aq) solution and aqueous suspensions containing Au NPs 15 ± 2.2 , 26 ± 2.4 , and 34 ± 3.0 nm in diameter (shown from left to right, respectively). (B) UV-VIS extinction spectra recorded for the AuCl_4^- (aq) solution and aqueous suspensions containing Au NPs 15 ± 2.2 , 26 ± 2.4 , and 34 ± 3.0 nm in diameter (blue, black, red, and green traces, respectively).

The red color displayed by the suspensions containing Au NPs (while the solution containing AuCl_4^- was light yellow) illustrate the change in optical properties due to the formation of Au NPs. The vivid color difference between bulk and nanosized Au NPs makes the SPR excitation easy to measure and visually appealing to undergraduate students. It can also be visualized that the Au NPs suspension became gradually darker as their size was increased. The

UV-VIS extinction spectra are in agreement with these observations (Figure 12.2B). While the starting AuCl_4^- (aq) solution did not display any detected signals in the visible range in the employed concentration range, all Au NPs displayed a relatively broad band centered at 522 nm. This band is assigned to the dipole mode of the localized surface plasmon resonance (LSPR) excitation in Au NPs.^{22,23} The LSPR band became more intense with size as expected from the increased contribution from scattering to the extinction.²⁰ Therefore, both the digital photographs and UV-VIS spectra could be employed to illustrate the size-dependent optical properties of Au NPs.

It is important to note that, as the syntheses are reproducible, only one set of samples (from one group, for example) can be submitted to TEM analysis so that the entire class can use the same TEM results. This can be performed from one week to another and be provided to the students for the second part of the experiment. In addition to TEM, the students can also calculate the NPs size from the UV-VIS extinction spectra according to the following equation:

$$d = \ln[(\lambda - 512)/6.53]/0.0216 \quad (1)$$

where d is the diameter and λ the SPR wavelength.²⁴ Indeed, the results calculated from this equation agreed with those obtained from the TEM results ($d = 14.8, 24.1$, and 31.8 nm for Au NPs $15 \pm 2.2, 26 \pm 2.4$, and 34 ± 3.0 nm, respectively).

The catalytic activities of Au NPs were evaluated employing the reduction of 4-nitrophenol by sodium borohydride as a model reaction. The hydrogenation of 4-nitrophenol was chosen due to several factors: *i*) it is well-established that it can be catalyzed by noble metal nanoparticles due to the particle-mediated electron transfer from borohydride ions to 4-nitrophenol;^{19,25,26} *ii*) the product from this transformation, 4-aminophenol, is an important intermediate in the synthesis of analgesic and antipyretic drugs;^{19,27} *iii*) wastewaters generated from several industries (such as

explosives and dyestuffs) contain 4-nitrophenol;²⁸ and *iv*) the color changes associated with the conversion of 4-nitrophenol to 4-aminophenol enables one to easily monitor the reaction kinetics by UV-VIS spectroscopy.^{19,29,30} Here, an excess of sodium borohydride was employed so that 4-nitrophenol is converted to 4-nitrophenolate ions, as shown in Figure 12.3 A (the concentration of sodium borohydride was 2000 folds higher relative to 4-nitrophenol). This transformation is accompanied by a change in color from pale yellow to dark yellow as well as a shift in the absorbance peak from 317 nm (for 4-nitrophenol) to 400 nm (for 4-nitrophenolate ions) in the UV-VIS spectra (Figure 12.3 B).

Figure 12.3. (A) Scheme for the formation of 4-nitrophenolate ions upon the addition of an excess of sodium borohydride to a 4-nitrophenol aqueous solution, leading to a change in color from light to dark yellow. (B) UV-VIS spectra and digital micrographs obtained from aqueous solutions of 4-nitrophenol (red trace) and 4-nitrophenolate ions (black trace).

Under this condition, the reaction kinetics approaches the pseudo-first-order regime, in which the variation in the concentration of sodium borohydride during the reaction becomes negligible. Thus, the decrease in the absorbance for the band at 400 nm can be employed to monitor the reaction kinetics (extent of the reaction) and the rate constants can be estimated from the slope of the linear correlation between $\ln(C_t/C_0)$ and time according to the following equation, which represents the pseudo-first-order rate law:

$$\ln(A_t/A_0) = -k \cdot t \quad (2)$$

where A_t correspond to the absorbance at 400 nm as a function of the time t ; A_0 the initial absorbance, and k the rate constant. The pseudo-first-order rate law can be expressed as:

$$d[C]/dt = k[C] \quad (3)$$

where C is the concentration, and integrated to give:

$$\ln(C_t/C_0) = -kt \quad (4)$$

As the Beer-Lambert law gives:

$$A = \epsilon bC \quad (5)$$

Where ϵ is the molar absorptivity of the substance and b the optical path. Equation 2 is then obtained by replacing 5 into 4.

Figure 12.4 shows the plots of $\ln(C_t/C_0)$ and the UV-VIS absorption spectra as a function of time for the Au NPs that were 15 ± 2.2 (Fig. 12.4 A and B), 26 ± 2.4 (Fig. 12.4 C and D), and 34 ± 3.0 nm in diameter (Fig. 12.4 E and F).

Figure 12.4. Plots of $\ln(C/C_0)$ and UV-VIS spectra recorded as a function of time for Au NPs 15 ± 2 (A and B), 26 ± 2 (C and D), and 34 ± 3 nm in diameter (E and F). The rate constants (k) were calculated from the slope of the curves shown in red in (A), (C), and (E).

As all catalytic investigations were performed employing the same concentration of Au, and the differences in catalytic activity can be associated with the variations in size and thus available surface area for catalysis. In all cases, the decrease in the intensity of the band at 400 nm with time was observed due to the consumption of 4-nitrophenolate ions. It can be detected that the disappearance of the band at 400 nm became slower as the Au NPs size increased, in agreement with the decrease in catalytic activity with size. The calculated rate constants (k) decreased as the Au NPs size increased, and corresponded to 0.0150 ± 0.0008 , 0.0146 ± 0.0012 , and $0.0107 \pm 0.0010 \text{ s}^{-1}$ for Au NPs 15 ± 2.2 , 26 ± 2.4 , and $34 \pm 3.0 \text{ nm}$ in diameter, respectively. Interestingly, the decrease in the catalytic activity as the size increased from 15 to 26 nm was less pronounced as compared to the decrease in catalytic activity as the size increased from 26 to 34 nm. It is noteworthy that no changes in the 400 nm band intensity were observed under similar conditions in the absence of Au NPs, indicating that the presence of the catalyst is essential for the reaction to take place in this timeframe (no reaction occurs in the absence of catalyst under similar conditions).

Another parameter that can be employed to describe the catalytic activity of Au NPs is the TOF (*turnover frequency*).²¹ The TOF can be defined as the number of completed catalytic cycles per atom of the catalyst as a function of time³⁰. Here, the TOF was calculated according to the equation 2:

$$\text{TOF} = N_{4\text{NP}} / (N_{\text{Au}} \cdot t) \quad (2)$$

where $N_{4\text{NP}}$ denotes the amount in mols of 4-nitrophenol converted to 4-aminophenol, N_{Au} the amount in mols of Au, and t the time. $N_{4\text{NP}}$ was calculated from a UV-VIS calibration curve for

4-nitrophenolate concentration as depicted in Figure 12.5A. Figure 12.5B shows the calculated TOF as a function of time for Au NPs.

Figure 12.5. (A) UV-VIS calibration curve for 4-nitrophenolate concentration and (B) calculated TOFs as a function of time for Au NPs 15 ± 2 , 26 ± 2 , and 34 ± 3 nm in diameter (red, black, and blue traces, respectively).

TOF values decreased with the increase in the Au NPs size, in agreement with the decrease in catalytic activity with size. In this case, while a slight decrease in the TOF values was observed

as the Au NPs size increased from 15 to 26 nm, TOFs for Au NPs 34 nm in diameter were notably smaller. While Au NPs 15 and 26 nm in diameter reached the maximum TOF (TOF_{MAX}) at ~ 26 s, this value corresponded to 91 s for Au NPs 34 nm in size. Table 12.1 summarizes the catalytic activities estimated as a function of Au NPs size and specific surface area.

Table 12.1. Calculated specific surface areas, rate constants, and turnover frequencies for Au NPs as a function of size.

Au NPs size (nm)	Calculated specific surface area (m^2/g)	Pseudo-first order rate constant (s^{-1})	TOF_{MAX} (s^{-1})
15	20.7	0.0150	68.6
26	11.9	0.0146	64.6
34	9.1	0.0107	24.5

The specific surface area (S) was calculated according to the equation 3:

$$S = 3/(R_{\text{Au}} \cdot d_{\text{Au}}) \quad (3)$$

Where R corresponds to the Au NPs radius, and d_{Au} to the density of gold ($19.32 \times 10^6 \text{ g/m}^3$). Because in the proposed laboratory experiment we wanted to demonstrate students how the catalytic activity is dependent upon the size of metal nanoparticle catalysts, we believe this concept can be more easily visualized/illustrated by calculating the turnover frequency as a function of the Au concentration. In this case, as the diameter of the Au NPs increased, the surface area and thus the catalytic activity decreased (as expressed by the TOF and pseudo-first order rate constants).

It is important to note that students are encouraged to experiment with Au NPs of all size regimes. While the rate constants were similar for Au NPs 15 and 26 nm in size, a decrease was still observed. Moreover, it is worth showing students that the rate constants do not simply decrease linearly as the Au NPs size increases. Finally, there is a noticeable change in optical properties as Au NPs size increase from 15 to 26 nm.

12.4. Conclusions

We proposed herein an undergraduate level activity that consists on three main parts, involving the synthesis of Au NPs of controllable sizes followed by the investigation of their size-dependent optical properties and catalytic activity. In the first part of the activity, students perform the synthesis of three Au NPs samples having different (increasingly bigger) sizes by a seeded growth approach. In this case, spherical Au NPs 15 ± 2 , 26 ± 2 , and 34 ± 3 nm in diameter were obtained. In the second part of this activity, students qualitatively and quantitatively investigate the variations in the optical properties due to the formations of Au NPs and also as a function of their size (by both visual inspection and UV-VIS spectroscopy). In the last part of the experiment, students employ the reduction of 4-nitrophenol by sodium borohydride as a model reaction to investigate the size-dependent catalytic activity of the synthesized Au NPs suspensions. The reduction of 4-nitrophenol to 4-aminophenol can be monitored by the decrease in the absorbance at 400 nm (assigned to 4-nitrophenolate ions) in the UV-VIS spectrum as a function of time, and the rate constants can be calculated by a pseudo-first-order rate law. This experiment encompasses concepts on the synthesis, stabilization, and characterization of Au NPs, their unique size-dependent optical properties and catalytic

activities, the role of catalyst, and chemical kinetics. This provides students the opportunity to integrate these multidisciplinary concepts in a single activity and to get introduced/familiarized with an active research field and current literature in the areas of nanoparticle synthesis and catalysis.

12.5. References

- (1) Guo, S.; Wang, E. Noble Metal Nanomaterials: Controllable Synthesis and Application in Fuel Cells and Analytical Sensors. *Nano Today* **2011**, 6 (3), 240–264.
- (2) Daniel, M.-C.; Astruc, D. Gold Nanoparticles: Assembly, Supramolecular Chemistry, Quantum-Size-Related Properties, and Applications toward Biology, Catalysis, and Nanotechnology. *Chem. Rev.* **2004**, 104 (1), 293–346.
- (3) Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E. Shape-Controlled Synthesis of Metal Nanocrystals: Simple Chemistry Meets Complex Physics? *Angew. Chemie Int. Ed.* **2009**, 48 (1), 60–103.
- (4) Eustis, S.; El-Sayed, M. A. Why Gold Nanoparticles Are More Precious than Pretty Gold: Noble Metal Surface Plasmon Resonance and Its Enhancement of the Radiative and Nonradiative Properties of Nanocrystals of Different Shapes. *Chem. Soc. Rev.* **2006**, 35 (3), 209–217.
- (5) Shang, C.; Liu, Z.-P. Origin and Activity of Gold Nanoparticles as Aerobic Oxidation Catalysts in Aqueous Solution. *J. Am. Chem. Soc.* **2011**, 133 (25), 9938–9947.
- (6) Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel Gold Catalysts for the Oxidation of Carbon Monoxide at a Temperature Far Below 0 °C. *Chem. Lett.* **1987**, 16 (2), 405–408.
- (7) Willets, K. A.; Van Duyne, R. P. Localized Surface Plasmon Resonance Spectroscopy and Sensing. *Annu. Rev. Phys. Chem.* **2007**, 58 (1), 267–297.
- (8) Jain, P. K.; Huang, X.; El-Sayed, I. H.; El-Sayed, M. A. Review of Some Interesting Surface Plasmon Resonance-Enhanced Properties of Noble Metal Nanoparticles and Their Applications to Biosystems. *Plasmonics* **2007**, 2 (3), 107–118.
- (9) Huang, X.; El-Sayed, M. A. Gold Nanoparticles: Optical Properties and Implementations in Cancer Diagnosis and Photothermal Therapy. *J. Adv. Res.* **2010**, 1 (1), 13–28.
- (10) Xia, X.; Wang, Y.; Ruditskiy, A.; Xia, Y. 25th Anniversary Article: Galvanic Replacement: A Simple and Versatile Route to Hollow Nanostructures with Tunable and Well-Controlled Properties. *Adv. Mater.* **2013**, 25 (44), 6313–6333.
- (11) Sharma, R. K.; Gulati, S.; Mehta, S. Preparation of Gold Nanoparticles Using Tea: A Green Chemistry Experiment. *J. Chem. Educ.* **2012**, 89 (10), 1316–1318.
- (12) Frank, A. J.; Cathcart, N.; Maly, K. E.; Kitaev, V. Synthesis of Silver Nanoprisms with

- Variable Size and Investigation of Their Optical Properties: A First-Year Undergraduate Experiment Exploring Plasmonic Nanoparticles. *J. Chem. Educ.* **2010**, 87 (10), 1098–1101.
- (13) Dungey, K. E.; Muller, D. P.; Gunter, T. Preparation of Dppe-Stabilized Gold Nanoparticles. *J. Chem. Educ.* **2005**, 82 (5), 769.
 - (14) Sereda, G.; Rajpara, V. Exploration of Solid-Supported Reactions with Gold Nanoparticles. *J. Chem. Educ.* **2010**, 87 (9), 978–980.
 - (15) Mulfinger, L.; Solomon, S. D.; Bahadory, M.; Jeyarajasingam, A. V.; Rutkowsky, S. A.; Boritz, C. Synthesis and Study of Silver Nanoparticles. *J. Chem. Educ.* **2007**, 84 (2), 322.
 - (16) McFarland, A. D.; Haynes, C. L.; Mirkin, C. A.; Van Duyne, R. P.; Godwin, H. A. Color My Nanoworld. *J. Chem. Educ.* **2004**, 81 (4), 544A.
 - (17) Chen, J.; Zhang, Q.; Wang, Y.; Wan, H. Size-Dependent Catalytic Activity of Supported Palladium Nanoparticles for Aerobic Oxidation of Alcohols. *Adv. Synth. Catal.* **2008**, 350 (3), 453–464.
 - (18) Watanabe, Y.; Wu, X.; Hirata, H.; Isomura, N. Size-Dependent Catalytic Activity and Geometries of Size-Selected Pt Clusters on TiO₂(110) Surfaces. *Catal. Sci. Technol.* **2011**, 1 (8), 1490–1495.
 - (19) Zhao, P.; Feng, X.; Huang, D.; Yang, G.; Astruc, D. Basic Concepts and Recent Advances in Nitrophenol Reduction by Gold- and Other Transition Metal Nanoparticles. *Coord. Chem. Rev.* **2015**, 287 (0), 114–136.
 - (20) Bastús, N. G.; Comenge, J.; Puentes, V. Kinetically Controlled Seeded Growth Synthesis of Citrate-Stabilized Gold Nanoparticles of up to 200 nm: Size Focusing versus Ostwald Ripening. *Langmuir* **2011**, 27 (17), 11098–11105.
 - (21) Boudart, M. Turnover Rates in Heterogeneous Catalysis. *Chem. Rev.* **1995**, 95 (3), 661–666.
 - (22) Lu, X.; Rycenga, M.; Skrabalak, S. E.; Wiley, B.; Xia, Y. Chemical Synthesis of Novel Plasmonic Nanoparticles. *Annu. Rev. Phys. Chem.* **2009**, 60, 167–192.
 - (23) Xia, Y.; Halas, N. J.; Editors, G. Shape-Controlled Surface Plasmonic Nanostructures. **2005**, 30 (5), 338–348.
 - (24) Haiss, W.; Thanh, N. T. K.; Aveyard, J.; Fernig, D. G. Determination of Size and Concentration of Gold Nanoparticles from UV–Vis Spectra. *Anal. Chem.* **2007**, 79 (11), 4215–4221.
 - (25) Damato, T. C.; de Oliveira, C. C. S.; Ando, R. A.; Camargo, P. H. C. A Facile Approach to TiO₂ Colloidal Spheres Decorated with Au Nanoparticles Displaying Well-Defined Sizes and Uniform Dispersion. *Langmuir* **2013**, 29 (5), 1642–1649.
 - (26) Wang, X.; Fu, J.; Wang, M.; Wang, Y.; Chen, Z.; Zhang, J.; Chen, J.; Xu, Q. Facile Synthesis of Au Nanoparticles Supported on Polyphosphazene Functionalized Carbon Nanotubes for Catalytic Reduction of 4-Nitrophenol. *J. Mater. Sci.* **2014**, 49 (14), 5056–5065.
 - (27) Zhu, M.; Wang, C.; Meng, D.; Diao, G. In Situ Synthesis of Silver Nanostructures on Magnetic Fe₃O₄@C Core-Shell Nanocomposites and Their Application in Catalytic

- Reduction Reactions. *J. Mater. Chem. A* **2013**, *1* (6), 2118–2125.
- (28) Chang, Y.-C.; Chen, D.-H. Catalytic Reduction of 4-Nitrophenol by Magnetically Recoverable Au Nanocatalyst. *J. Hazard. Mater.* **2009**, *165* (1–3), 664–669.
- (29) Harish, S.; Mathiyarasu, J.; Phani, K. L. N.; Yegnaraman, V. Synthesis of Conducting Polymer Supported Pd Nanoparticles in Aqueous Medium and Catalytic Activity Towards 4-Nitrophenol Reduction. *Catal. Letters* **2009**, *128* (1–2), 197–202.
- (30) Oh, S.-D.; Kim, M.-R.; Choi, S.-H.; Chun, J.-H.; Lee, K.-P.; Gopalan, A.; Hwang, C.-G.; Sang-Ho, K.; Hoon, O. J. Radiolytic Synthesis of Pd–M (M=Ag, Au, Cu, Ni and Pt) Alloy Nanoparticles and Their Use in Reduction of 4-Nitrophenol. *J. Ind. Eng. Chem.* **2008**, *14* (5), 687–692.

Chapter 13. Controlled Synthesis of Nanomaterials at the Undergraduate Laboratory: Cu(OH)₂ and CuO Nanowires

13.1. Introduction

Nanomaterials have received tremendous interest towards a wide range of applications in areas such as catalysis, energy conversion and storage, electronics, plasmonics, photonics, and biomedicine due to their unique optical, electronic, chemical, and magnetic properties.^{1–4} Moreover, nanomaterials are versatile, as it is well established that most of their properties are strongly dependent on their sizes, shapes, compositions, and architectures (core-shell, core-satellite, alloy, or hollow interiors, for example).^{5–9} Therefore, it becomes very important to introduce both nanoscience and the synthesis/characterization of nanomaterials having controlled physical chemical features, such as size, shape, and composition, to undergraduate students to prepare them for academic research and industry innovation.

In this context, several laboratory protocols have been reported aiming to introduce nanoscience to undergraduate students.^{10–18} Many of the described experiments are based on the synthesis of noble metal nanoparticles (such as gold and silver),^{10,11,13,14,19} demand the use of transmission electron microscopy (TEM),^{10,11,14,19–21} which is rarely available for undergraduate students, and focus on conventional nanoparticles, such as quasi-spherical shapes. Conversely, experiments concerning the controlled synthesis of nanomaterials, such as structures having shapes other than quasi-spheres, remain scarce. Therefore, undergraduate level experiments that involve the synthesis of nanomaterials with well-defined/controlled shapes and that are inexpensive become very attractive under the umbrella of nanotechnology education.

We describe herein a simple laboratory experiment for the synthesis of $\text{Cu}(\text{OH})_2$ and CuO nanowires displaying uniform sizes and shapes comprising three main parts. In the first, students perform the synthesis of $\text{Cu}(\text{OH})_2$ nanowires by a precipitation approach,²² followed by a calcination step that converts $\text{Cu}(\text{OH})_2$ to CuO while retaining the nanowire morphology. In the second part, students employ the obtained $\text{Cu}(\text{OH})_2$ and CuO nanowires as model systems to explore a variety of characterization techniques relevant in the context of solid-state, materials chemistry, and nanoscience. These include: scanning electron microscopy (SEM) and Fourier transform infrared (FTIR), Raman, and ultraviolet–visible (UV-VIS) spectroscopies. Specifically, by employing these techniques, students are able to qualitatively and quantitatively investigate the variations in the structural and surface properties for $\text{Cu}(\text{OH})_2$ and CuO nanowires. In the last part of the experiment, students present and discuss their obtained data with the instructor and the class, detailing the mechanisms involved in the syntheses of the nanowires (employing concepts from coordination and solid-state chemistry) and the information that every characterization technique provides as well as how they complement each other. This laboratory experiment was successfully performed by 48 undergraduate students that were in their first-year (Chemistry major) during a general chemistry course. This course is part of the basic education in chemistry at the University of São Paulo, Brazil. Students were divided in 16 groups (having 3 students each).

13.2. Experimental

13.2.1. Experimental Overview

Full experimental procedures regarding the synthesis of $\text{Cu}(\text{OH})_2$ and CuO nanowires as well as the investigation of their morphological, thermal, structural, and spectroscopic properties

are given in the student guide. Briefly, the synthesis of an aqueous suspension containing $\text{Cu}(\text{OH})_2$ nanowires was performed by precipitation method. Then, after washing, the aqueous suspension containing the $\text{Cu}(\text{OH})_2$ nanowires was dried and calcined at 180°C to generate CuO nanowires. This transformation can be qualitatively monitored by visualizing the change in color for the suspensions containing the light blue $\text{Cu}(\text{OH})_2$ and the dark brown CuO crystalline nanowires relative to the $\text{Cu}^{2+}_{(\text{aq})}$ precursor. More quantitatively, the formation of CuO nanowires from $\text{Cu}(\text{OH})_2$ could also be investigated by SEM imaging, powder XRD, and UV-VIS, Raman, and FTIR spectroscopies.

13.2.2. Materials and Instrumentation

Analytical grade chemicals Copper(II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99%, Sigma-Aldrich), Sodium hydroxide (NaOH , $\geq 98\%$, Sigma-Aldrich), ammonium hydroxide solution (NH_4OH , 28-30 wt%, Sigma-Aldrich) were used as received. All solutions were prepared using deionized water ($18.2\text{ M}\Omega$). The SEM images should be obtained using benchtop scanning electron microscope operating at 5 kV (we employed a MEV JEOL Neoscope JCM-5000). The samples can be prepared by drop-casting an aqueous suspension containing the $\text{Cu}(\text{OH})_2$ or CuO nanowires (1 mg/100 μL) over a silicon wafer, followed by drying under ambient conditions. UV-VIS spectra should be measured from the starting aqueous solution containing the $\text{Cu}^{2+}_{(\text{aq})}$ precursor and also from aqueous suspensions containing the $\text{Cu}(\text{OH})_2$ and CuO nanowires (1 mg/mL) with a spectrophotometer in the 200-900 nm range (we employed a Shimadzu UV-1700 equipment). The change on optical properties due to the formation of $\text{Cu}(\text{OH})_2$ and CuO nanowires as compared to the $\text{Cu}^{2+}_{(\text{aq})}$ precursor solution can be easily evidenced. XRD patterns should be acquired on a diffractometer with $\text{Cu K}\alpha$ radiation. The diffractograms of $\text{Cu}(\text{OH})_2$ and CuO nanowires (30 mg)

should be collected in the 20-80° range and a scanning rate of 5°/min. We also employed a Rigaku D/max-kA equipment, 30kv, 15mA). Raman spectra should be acquired on a Raman microscope equipped with a 532 nm laser and a CCD detector (we employed a WITEC alpha 300R equipment) in the 100-3200 cm⁻¹ range. The laser beam should be focused on the Cu(OH)₂ and CuO nanowires (~5 mg) using a 20x lens with laser power output of 5 m.W.cm⁻² for 10 s. The experiments should be performed under ambient conditions using a back-scattering geometry. FTIR spectra should be recorded using spectrophotometer in the 4000-400 cm⁻¹ range (we employed a Bruker Eco-ATR). Cu(OH)₂ and CuO nanowires should be diluted in KBr pellets before the measurements.

13.2.3. Hazards

The experiment described herein uses dilute solutions, which may be prepared ahead of time to minimize the risk that solids and concentrated solutions pose to students. Labeled waste containers should be made available. Gloves, lab coat, and safety glasses should be worn throughout the experiment. All laboratory activities should be carried out under the supervision of trained and qualified personnel. Copper(II) nitrate may cause eye and skin irritations. It may be harmful if absorbed through the skin, if swallowed, if inhaled. Sodium hydroxide is corrosive and hygroscopic. It can cause eye and skin burns as well as severe damage to the digestive tract when ingested. Sodium citrate may cause irritation to skin, eyes, and respiratory tract. Ammonium hydroxide is corrosive, irritant, and permeate upon skin contact. Inhalation of the spray mist may produce severe irritation of respiratory tract.

13.2.4. Synthesis of Cu(OH)₂ and CuO nanowires having controlled sizes and shapes

The synthesis of Cu(OH)₂ nanowires can be performed by a controlled precipitation method. In a typical synthesis, 1 g of Cu(NO₃)₂ should be dissolved in 100 mL of distilled water in a 250 mL round-bottom flask under magnetic stirring. Then, 30 mL of an NH₄OH solution (0.15 M) should be added into the reaction mixture under constant stirring. A blue precipitate consisting of Cu(OH)₂ should be produced when NaOH (1 M) solution is added by dropwise into the reaction mixture until the pH value reaches 9–10. This procedure yields an aqueous suspension containing the Cu(OH)₂ nanowires, which will be employed for the synthesis of CuO nanowires. Cu(OH)₂ nanowires should be filtered and washed with ethanol several times to obtain a blue solid product. The solid product should be separated into two parts. One part should be dried at room temperature (denoted Cu(OH)₂ nanowires) and the second part should be heated 180 °C for 1 h.

13.2.5. Student Learning Objectives

The key learning objectives of this laboratory experiment comprise: *i*) facile synthesis of nanostructures with controlled shapes (Cu(OH)₂ and CuO nanowires); *ii*) the use of concepts borrowed from coordination chemistry to explain/understand the formation mechanism of Cu(OH)₂ and CuO crystalline nanowires from a Cu²⁺_(aq) precursor; *iii*) investigation of the chemical transformations at the nanoscale; *iv*) allow for a hands on experience with a variety of characterization techniques; and *v*) demonstration of how different characterization techniques can be put to work to probe and understand the properties and transformation of nanostructured materials.

13.2.6. Instructor Notes

SEM: Sample preparations for SEM is dependent upon several factors (instrument configurations, nature of the samples and sample holders). Videos describing the SEM technique can be found at: (<https://www.youtube.com/watch?v=GY9lfO-tVfE>, accessed in January 2017) and (<https://www.youtube.com/watch?v=VWxYsZPtTsI>, accessed in January 2017). A protocol for sample preparation for SEM analysis can be found at: (<https://www.youtube.com/watch?v=ArPXfPjOJQc>, accessed in January 2017). Instructors should refer to the manual for their particular instrument. Institutions that have access to XRD equipment but don't have a standard library to use in this experiment, they can employ the Mercury® software that is freely available from the Cambridge Crystallographic Data Centre (CCDC) (available at <http://www.ccdc.cam.ac.uk/Solutions/FreeSoftware/Pages/FreeMercury.aspx>, accessed in January, 2017) and can compute X-ray powder diffractograms from the Crystallographic Information File (CIF) file of any phase. Instructors can prepare their own library of phases for students to search visually.

XRD: Sample preparation for XRD is dependent upon several factors (instrument configuration and sample holder) Instructors should refer to the manual for their particular instrument. A video describing the XRD technique, including sample preparation can be found at: (<http://www.youtube.com/watch?v=lwV5WCBh9a0>, accessed in January 2017). Institutions that have access to XRD equipment but don't have a standard library to use in this experiment, they can employ the Mercury® software that is freely available from the Cambridge Crystallographic Data Centre (CCDC) (it is available in: <http://www.ccdc.cam.ac.uk/Solutions/FreeSoftware/Pages/FreeMercury.aspx>, accessed in January 2017) and can compute X-ray powder diffractograms from the Crystallographic

Information File (CIF) file of any phase. Instructors can prepare their own library of phases for students to search visually.

Optical Properties: Students should be encourage to take digital photographs of the suspensions containing the $\text{Cu}(\text{OH})_2$, and CuO nanowires as well as from the initial $\text{Cu}^{2+}_{(\text{aq})}$ solution to use in the lab report. A general description of UV-VIS spectroscopy can be found on the following website: (https://www.agilent.com/cs/library/primers/public/59801397_020660.pdf, accessed in January 2017). A video describing the sample preparation for UV-VIS spectroscopy can be found at: (https://www.youtube.com/watch?v=nr3uyW1_QbM, accessed in January 2017).

FTIR: Sample preparation for IR is dependent on the physic state of the sample and instrument configuration. A video describing the technique of Infrared Spectrometry, including sample preparation can be found at: (<https://www.youtube.com/watch?v=6Jo3AZd7NIk>, accessed january 2017). A general description of Infrared Spectrometry and how analyze Infrared spectra can be found on the following link: (<https://www.youtube.com/watch?v=XIWc9eT476c>, accessed January 2017)

Raman: A video describing the technique of Infrared Spectrometry, including sample preparation and operation can be found at: (<https://www.youtube.com/watch?v=T5z2M3vxyH8>, accessed January 2017). A general description of Raman spectroscopy and operational conditions can be found on the following website: (<http://users.abo.fi/mhotokka/mhotokka/lecturenotes/ms04.d/ms04-raman-eng.pdf>, accessed January 2017).

13.2.7. Lab Report

The report should follow the format of a scientific paper, comprising an introduction, experimental, results and discussion, and conclusion sections.

13.3. Results and Discussion

The experiment reported herein involves a simple protocol for the synthesis of $\text{Cu}(\text{OH})_2$ and CuO nanomaterials with controlled shapes. Specifically, we focused on nanowires, which represent an important class of 1D nanostructures.²³ Interestingly, the synthesis involves concepts from coordination as well as solid-state chemistry. After the synthesis, the nanowires can be investigated by a variety of characterization techniques including SEM, XRD, and FTIR, Raman, and UV-VIS spectroscopies, that are widely employed in the fields of inorganic chemistry, materials, and nanoscience. In this context, the students can be introduced to the different concepts, protocols for the sample preparation, and data interpretation regarding all these characterization techniques. Finally, the color changes associated with the $\text{Cu}(\text{OH})_2$ formation and $\text{Cu}(\text{OH})_2$ to CuO transformation can be employed as a good visual aid for a chemical reactions taking place at the nanoscale. We believe that the reported experiment can also be part of an upper-level inorganic, solid-state, or materials chemistry classes. Besides, it is proposed that this experiment can be divided into three different lab sections having 3 h each as follows: *i*) synthesis of $\text{Cu}(\text{OH})_2$ and CuO crystalline nanowires and characterization by SEM and UV-VIS spectroscopy; *ii*) characterization by XRD, and FTIR and Raman spectroscopies; *iii*) presentation/ discussion of the experimental data and write-up of the lab report.

It is important to note that this experiment can also be further adapted for application in smaller schools without SEM or XRD or for certain combinations of available instrumentation. This makes this experiment very versatile and adaptable in a variety of conditions. For example, in the institutions that do not have access to SEM or XRD, they could provide all characterizations which they have access in their departments and provide students with SEM images and XRD results reported from this paper. Alternatively, a deeper focus on the available techniques, such as UV-VIS, FTIR, and Raman spectroscopies can be given.

The experiment started with the synthesis of $\text{Cu}(\text{OH})_2$ and CuO nanowires having uniform sizes and shapes as shown in Scheme 13.1.

Scheme 13.1. Approach for the synthesis of $\text{Cu}(\text{OH})_2$ and CuO nanowires. In the first step, $\text{Cu}(\text{OH})_2$ nanowires are obtained by a controlled precipitation from $\text{Cu}^{2+}_{(\text{aq})}$ in the presence of $\text{NH}_3_{(\text{aq})}$ and $\text{OH}^{-}_{(\text{aq})}$ solutions under controlled pH conditions. Then, CuO nanowires are produced from the heat treatment of solid $\text{Cu}(\text{OH})_2$ at $180\text{ }^{\circ}\text{C}$ for 30 min.

In this strategy, $\text{Cu}(\text{OH})_2$ nanowires can be prepared by a controlled precipitation method (step 1),²² in which $\text{NH}_3_{(\text{aq})}$ and $\text{NaOH}_{(\text{aq})}$ solutions were added to a $\text{Cu}^{2+}_{(\text{aq})}$ precursor under controlled pH conditions. As the reactants are mixed, it is possible to observe the formation of the deep blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex as a transient species. In the presence of hydroxide ions in excess, this complex is gradually converted into the less soluble $\text{Cu}(\text{OH})_2$ species, precipitating as a light

blue nanocrystalline product. Then, CuO nanowires were produced by the thermal decomposition of Cu(OH)₂ by heating the dried nanowires at 180 °C for 30 min (step 2).

Figure 13.1 A-D shows SEM images for the Cu(OH)₂ and CuO nanowires obtained in a FEG-SEM (Figure 13.1 A and C, respectively) as well as in a benchtop SEM equipment (Figure 13.1 B and 1D, respectively). The SEM images (Fig. 11.1 A-D) clearly demonstrate that the described approach was effective to produce Cu(OH)₂ and CuO nanowires with well-defined sizes and shapes.

Figure 13.1. SEM images of Cu(OH)₂ (A and B), and CuO (C and D) nanowires. employing a FEG-SEM (A and C) and a benchtop SEM (B and D).

Specifically, Cu(OH)₂ and CuO nanowires had similar sizes, being 18 ± 4 nm in diameter and > 500 nm in length. It is noteworthy that the nanowires can be clearly employing a benchtop SEM microscope. As the operation of a benchtop SEM (low-cost alternative relative to other conventional SEM, TEM and HRTEM microscopes) is relatively simple and does not require

experience or special skills, this experiment serves as a platform to enable undergraduate students to have hands-on experience with an electron microscope. Furthermore, it allows the application of this experiment in courses/schools where a FEG-SEM equipment is not available and/or accessible to undergraduate students.

Figure 13.2 shows the SEM images that were obtained from the CuO nanowires that were prepared by the 16 groups of students. It can be observed that the nanowires were obtained in good yields by all groups, indicating that this procedure is robust and reproducible.

Figure 13.2. SEM images of CuO nanowires prepared by the student groups during the laboratory experiment. Images in (A-P) correspond to the samples synthesized by groups 1-16, respectively.

In the next step, $\text{Cu}(\text{OH})_2$ and CuO nanowires can be employed as model materials to study a variety of other characterization techniques such as XRD, FTIR, Raman, and UV-VIS

spectroscopies. The instructor notes provide educational materials (videos and texts) describing these characterization techniques, procedures for sample preparation, and data analyses. In this case, students may perform their own sample preparations under the supervision of the instructor and staff. In the context of the described experiment, $\text{Cu}(\text{OH})_2$ and CuO nanowires represent excellent materials to demonstrate how these techniques could be employed to the study of nanomaterials and transformations at the nanoscale because their structural and spectroscopic properties are considerably different.

The powder XRD patterns for $\text{Cu}(\text{OH})_2$ and CuO nanowires are shown in Figure 13.3 (top and bottom traces, respectively). The diffractogram for the $\text{Cu}(\text{OH})_2$ nanowires displayed peaks assigned to the orthorhombic $\text{Cu}(\text{OH})_2$ structure (lattice constants $a = 0.295 \text{ nm}$, $b = 1.06 \text{ nm}$, and $c = 0.527 \text{ nm}$, JCPDS card #35-0505).²⁴

Figure 13.3. XRD diffratograms for $\text{Cu}(\text{OH})_2$ and CuO nanowires (top and bottom traces, respectively), suggesting that $\text{Cu}(\text{OH})_2$ nanowires (orthorhombic structure) were converted to CuO (monoclinic structure). Only peaks assigned to the monoclinic CuO structure could be observed after the heating step.

XRD results indicate that the heat treatment step could be employed to produce CuO as detected according to the X-ray data. This is because only peaks assigned to the monoclinic CuO

structure could be observed (lattice constants $a = 0.469$ nm, $b = 0.343$ nm, $c = 0.513$ nm, and $\beta = 99.549^\circ$, JCPDS card #45-0937), with no remaining $\text{Cu}(\text{OH})_2$ reflections.²²

Here, it is important to note the study and discussion of the nanowire formation mechanism, the $\text{Cu}(\text{OH})_2$ to CuO conversion, and the actual crystal structures for $\text{Cu}(\text{OH})_2$ and CuO represent a nice extension of this experiment. These issues are discussed in the next paragraphs.

As aforementioned, $\text{Cu}(\text{OH})_2$ structure is orthorhombic, space group $Cmc2_1$ (No. 36). Its structure is represented in Scheme 13.2 A. It presents corrugated layers perpendicular to the b -axis. In the layers, Cu^{2+} has a square pyramid geometry comprised of five OH^- ions, with four short Cu-O bonds (Cu–O: 1.95, 1.95, 1.97, and 1.97 Å) and a longer one at 2.36 Å. CuO , on the other hand, is monoclinic belonging to space group $C2/c$ (No. 15). Its structure is shown in Scheme 13.2 B and can be described by possessing crossing bands of Cu^{2+} with square planar CuO_4 units bound together by two opposite edges and spreading out in the $[110]$ and $[\bar{1}\bar{1}0]$ directions.²⁵

Scheme 13.2. Crystal structures of $\text{Cu}(\text{OH})_2$ (A, orthorhombic) and CuO nanowires (B, monoclinic).

Most reports on the synthesis of nanomaterials have established that use of stabilizing agents is crucial to the control over size and shape. Interestingly, the synthesis of the nanowires described in this experiment does not require the use of any stabilizing agent. The proposed mechanism for the formation of $\text{Cu}(\text{OH})_2$ nanowires is depicted in Scheme 13.3. Firstly, $\text{NH}_{3(\text{aq})}$ enter into the first coordination sphere of the $\text{Cu}^{2+}_{(\text{aq})}$ ions to generate the square-planar tetraamminecopper complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$.^{22,24,26} Next, $\text{OH}^-_{(\text{aq})}$ replace the $\text{NH}_{3(\text{aq})}$ ligands to generate $[\text{Cu}(\text{OH})_4]^{2-}$ with a square planar geometry. The $[\text{Cu}(\text{OH})_4]^{2-}$ units then undergo a coordination assembly growth via the formation of Cu-OH-Cu bridging bonds, leading to the formation of an extended chain that is connected to each other by the coordination of the OH^- to the $\text{Cu}^{2+} d_z^2$ orbital.^{22,24,26} Finally, these 2D layers stack together by weak H-bond interactions to become a 3D crystal.^{22,24,26} It is important to note that orthorhombic $\text{Cu}(\text{OH})_2$ presents a layered structure, which induces anisotropic growth and acts as the driving force for the formation of the nanowires.

Scheme 13.3. Proposed mechanism for the formation of $\text{Cu}(\text{OH})_2$ nanowires, which is based on the formation of square-planar $[\text{Cu}(\text{OH})_4]^{2-}$ units which undergo a coordination assembly growth via the formation of Cu-OH-Cu bridging bonds. These extended chain can then be connected to each other and stack to become an anisotropic 3D crystal.

The monoclinic CuO nanowires are then produced by the loss of H₂O from Cu(OH)₂ during heat treatment as depicted in Scheme 13.4 according to the following reaction:

In this case, the loss of water takes place by an oxolation mechanism,²² which involves a dehydration process accompanied by the formation of O–Cu–O bridges, and therefore does not lead to any morphological change. The topotatic or pseudomorphic conversion of Cu(OH)₂ to CuO via the loss of water can also be discussed in terms of the crystal structures as depicted in Scheme 13.4.^{25,27} The orthorhombic crystal structure of Cu(OH)₂ is drawn in Scheme 13.4 A.

Scheme 13.4. Representation of the crystal structure of the Cu(OH)₂ nanowires (A and B, orthorhombic) and the mechanism of oxolation involving water loss (C and D) that lead to the formation of CuO nanowires (D and E, monoclinic structure) during the heat treatment, favoring the retention of the nanowire morphology.

When the temperature is raised to 50-60 °C, the longer Cu–O bond is broken leading to the formation of square planar $\text{Cu}(\text{OH})_4$ entities linked together by two opposite edges (Scheme 13.4 B-C). Thus, the stability of the structure is only due to the network of hydrogen bonds, so that this structural conformation allows easy shifts of CuO_4 groups or Cu atoms, which in turn enables the evolution towards crystallized CuO. As the temperature is increased to > 150 °C, dehydration of $\text{Cu}(\text{OH})_2$ starts to take place in the b,c plane of $\text{Cu}(\text{OH})_2$, in which the loss of water occurs via an oxolation mechanism is illustrated in Scheme 13.4 D and E. Bridges (Scheme 13.4 F) are obtained after the loss of water molecules followed by a big contraction of the structure along the [010] direction (contraction value near of $b/2$). In the course of the oxolation in the b,c plane, the Cu–O bonds are established, leading to the formation of a CuO nanowires (Scheme 13.4 G, orthorhombic structure). Meanwhile, owing to the ability of coordination of the Cu–O bond, the crossing bonds of CuO_4 are finally obtained. Because of the topotactic transformation existing during the dehydration process, the morphology can be maintained during the $\text{Cu}(\text{OH})_2$ transformation to CuO.

After the electron microscopy and X-ray diffraction characterizations, we turned our attention to the study of $\text{Cu}(\text{OH})_2$ and CuO nanowires by vibrational spectroscopy. Both Infrared and Raman spectroscopies represent powerful tools to elucidate the vibrational structure in solids and molecules as the selection rules of IR and Raman transitions are complementary for structures with an inversion center. Here, it is noteworthy that while $\text{Cu}(\text{OH})_2$ does not display an inversion center, CuO does.²⁸ In fact, as shown in Figure 13.3, $\text{Cu}(\text{OH})_2$ and CuO displayed distinct FTIR and Raman signatures. The FTIR spectra of the $\text{Cu}(\text{OH})_2$ and CuO nanowires are shown in Figure 13.4 A.

Figure 13.4. FTIR (A) and Raman (B) spectra registered from Cu(OH)₂ and CuO nanowires. The FTIR spectra were obtained from diluted in KBr pellets and recorded in the 4000-400 cm⁻¹ range. The Raman spectra measurements were performed using a 532 nm laser wavelength with 5 mW/cm² output power and 10 s exposure time.

The spectrum for the Cu(OH)₂ nanowires displayed an absorption band at 3574 cm⁻¹ assigned to the vibrational stretching modes of hydroxyls groups in copper hydroxide structure and another band at 418 cm⁻¹ that can be assigned to the Cu-O stretching mode, in agreement with the formation of Cu(OH)₂.^{26,29,30} Three bands at 3312, 1627, and 1383 cm⁻¹ that can be assigned to the stretching and bending modes of the hydroxyls groups from adsorbed H₂O were also observed.^{26,29,30} Interestingly, the band at 3574 cm⁻¹ corresponding to the OH⁻ stretching modes in

$\text{Cu}(\text{OH})_2$ disappeared after the heat treatment step in agreement with the formation of CuO nanowires.^{26,29,30} The FTIR spectrum for the CuO nanowires also displayed a band at 500 cm^{-1} assigned to the Cu-O stretching mode in CuO structure.^{26,29,30} The absorption bands at 3429 , 1626 , and 1381 cm^{-1} were assigned to the stretching and bending modes of the hydroxyl groups of adsorbed H_2O molecules.²⁹

The Raman spectra for the $\text{Cu}(\text{OH})_2$ and CuO nanowires (Figure 13.4B) are in agreement with FTIR results and support the conversion of $\text{Cu}(\text{OH})_2$ to CuO. While three bands centered at 283 , 449 and 486 cm^{-1} could be observed in the Raman spectrum of $\text{Cu}(\text{OH})_2$ due to stretching vibrations of Cu-OH bonds,^{31,32} the Raman spectrum for the CuO nanowires presented a signal at 273 cm^{-1} assigned to the A_g mode (stretching along b-axis of Cu-O bonds), and two peaks at 319 and 610 cm^{-1} corresponded to the B_g mode (stretching vibrations in the x^2-y^2 plane of Cu-O-Cu bonds).^{33,34} The Raman spectra collected from the samples produced by the 16 groups of students during the laboratory experiment are shown in Figure 13.5.

Figure 13.5. Raman spectra registered from CuO nanowires prepared by the student groups (1 through 16) during the laboratory experiment. The Raman spectra measurements were performed using a 532 nm excitation wavelength with a 5 mW/cm^2 output power and 10 s exposure time.

As CuO presents an inversion center, it may serve an excellent model system to further demonstrate which vibrational modes are expected, which are expected to be Raman and IR active, and how IR and Raman modes can be complementary. In solids, the vibrational properties are described in terms of phonon vibrations. CuO has 12 phonon branches because there are four atoms in the primitive cell. A factor-group analysis gives the following zone-center modes:²⁸

$$\Gamma_{\text{vib}} = A_g + 2B_g + 4A_u + 5B_u$$

The three acoustic modes are of $A_u + 2B_u$ symmetry. Among the nine optical modes, three ($A_g + 2B_g$) are Raman-active, and the remaining six ($3A_u + 3B_u$) are IR-active.³⁵ In the A_g and B_g Raman modes, only the oxygen atoms move, with displacements in the b -direction for A_g and perpendicular to the b -axis for B_g modes. The infrared active modes involve the motion of both the O and the Cu atoms. The induced dipole moment is along the b -axis for the A_u modes and perpendicular to it for the B_u modes.²⁸ Ref. 28 depicts the images corresponding to each some of these vibrations in the crystal structure. Table 13.1 depicts the assignments of these modes that are Raman and IR-active, which agree with the experimental spectra recorded in Figure 13.4.

Table 13.1. Symmetries, activity and calculated and experimental frequencies for the vibrational modes for CuO described in the Raman and FTIR spectra.

Symmetry	Activity	Calculated frequencies (cm ⁻¹) ²⁸	Experimental frequencies (cm ⁻¹)
B_u	IR	141	not applicable
A_u	IR	164	not applicable
A_g	Raman	319	273
A_u	IR	327	not applicable
B_g	Raman	382	319
A_u	IR	457	439
B_u	IR	503	501
B_u	IR	568	581
B_g	Raman	639	610

Figure 13.5 A shows digital photographs from the starting $\text{Cu}^{2+}_{(\text{aq})}$ solution and aqueous suspensions containing $\text{Cu}(\text{OH})_2$ and CuO nanowires (from left to right, respectively).

Figure 13.5. (A) Digital photographs for the $\text{Cu}^{2+}_{(\text{aq})}$ solution (left) and aqueous suspensions containing $\text{Cu}(\text{OH})_2$ (middle) and CuO (right) nanowires. (B) UV-VIS extinction spectra recorded for the $\text{Cu}^{2+}_{(\text{aq})}$ solution (red trace) and aqueous suspensions containing $\text{Cu}(\text{OH})_2$ (blue trace) and CuO (black traces) nanowires.

While the $\text{Cu}^{2+}_{(\text{aq})}$ precursor solution had a light blue color, the $\text{Cu}(\text{OH})_2$ and CuO nanowires presented dark blue and brown colors, respectively. Therefore, the variation in optical properties was due to the formation of the nanowires and also the conversion of $\text{Cu}(\text{OH})_2$ to CuO can be qualitatively visualized by the naked eye. More quantitatively, the UV-VIS spectra (Figure 13.5B) for the starting $\text{Cu}^{2+}_{(\text{aq})}$ solution (red trace) displayed two bands peaks centered at 300 and 808 nm. While the band at 300 nm can be assigned to the ligand to metal charge transfer (LMCT) from the σ (sp^3) orbitals of NH_3 ligands to the $d_{x^2-y^2}$ orbitals of the Cu^{2+} ions, the broad band at 808 nm corresponded to the d–d transitions of Cu^{2+} ions in the square planar coordination sphere of $[\text{Cu}(\text{NH}_3)_4]^{2+}$.³⁶ It is well established that the UV-VIS absorption spectrum for various nanostructures are strongly dependent on size and shape.^{6,37,38} The UV-VIS spectrum for the CuO nanowires displayed a band centered at 265 nm corresponding to the excitation of electron across the band gap in this semiconductor.³⁹ The wavelength of this absorption band, for a given material, is strongly dependent on size due to quantum confinement effects.³⁰ For $\text{Cu}(\text{OH})_2$, a broad signal centered at 326 nm also due to the excitation of electrons across the band gap was detected. The broad absorption band may be assigned due to the presence of surface-related defects that give rise to intra-gap states.³⁰

After demonstrating the synthesis of $\text{Cu}(\text{OH})_2$ and CuO nanowires displaying uniform sizes and shapes (first laboratory session) and their characterization by a variety of techniques (second laboratory session), two important questions remain that should be discussed in the third part of this experiment: *i*) the growth mechanism that leads to the formation of $\text{Cu}(\text{OH})_2$ nanowires having uniform sizes without the need of any stabilizing agents; and *ii*) why does the nanowire structure remain unaffected after the heat treatment that leads to the formation of CuO .

This experiment was designed in order to introduce the synthesis of nanomaterials to undergraduate students (Chemistry major). We believe this laboratory experiment is ideal for upper-level inorganic chemistry courses. However, we also strongly encourage the use of a simplified version of this laboratory experiment for introducing nanotechnology General Chemistry courses (first and second year undergraduate students) as a demonstration of the synthesis of nanomaterials, which we consider to be very interesting and motivating for undergraduate chemistry students. The fundamental concepts related to nanoparticle synthesis and characterization were presented to students previously to the experiment, in which the definitions, importance, and motivations for the controlled synthesis of nanomaterials as well as their structural elucidation were discussed. A week before the experiment, students received a pre-lab material containing theoretical support that focused on the characterizations techniques (theory and useful videos are available in the Instructor Notes). For that reason, students were expected to understand this laboratory. Students found the procedure easy enough to be completed without significant aid from the instructor. They collected experimental data and were asked to complete a laboratory report (see the Instructor Notes for details), from which the comprehension level achieved could be estimated. In general, students expressed a great appreciation and were excited about nanoscience learning. The laboratory report showed that the students understood successfully the theoretical concepts related to the preparation and characterization of the nanomaterials, in which students averaged a grade of 77.8 % to the questions proposed in the Student Guide (Figure 13.6). Upon the completion of this laboratory experiment, students are required to write a report using a scientific style, which allows instructors to assess the students' understanding of the entire activity and their scientific writing skills.

Figure 13.6. Student grades obtained from their answers to the questions proposed in the Student Guide.

13.4. Conclusions

We described herein an undergraduate level laboratory experiment involving the facile synthesis of $\text{Cu}(\text{OH})_2$ and CuO crystalline nanowires having well defined sizes and shapes. These nanowires could be employed as model materials to introduce and teach students a variety of characterization techniques that included SEM, XRD, and FTIR, Raman, and UV-VIS spectroscopies. We believe that the reported activity enables students to learn about different concepts that include the synthesis of nanomaterials having controlled shapes and uniform sizes, investigate transformation at the nanoscale, have hands-on experience with a variety of characterization techniques that are important in the context of inorganic and solid state chemistry, materials and nanoscience, learn how these techniques work and how they complement each other, and proposed mechanistic explanations for the formation of nanomaterials and their

transformations. This experiment can be further adapted by using other or fewer characterization techniques depending on their availability or by providing students with the obtained results for discussion. This laboratory experiment provides students the opportunity to integrate multidisciplinary concepts in a single activity as well as getting introduced/familiarized with a currently active research field (nanoscience) and its associated literature. Moreover, it provides the students understanding in nanoscience to better prepare them for their scientific and professional careers.

13.5. References

- (1) Zaera, F. Nanostructured Materials for Applications in Heterogeneous Catalysis. *Chem. Soc. Rev.* **2013**, 42 (7), 2746–2762.
- (2) Abdelmohsen, L. K. E. A.; Peng, F.; Tu, Y.; Wilson, D. A. Micro- and Nano-Motors for Biomedical Applications. *J. Mater. Chem. B* **2014**, 2 (17), 2395–2408.
- (3) Izumi, Y. Recent Advances in the Photocatalytic Conversion of Carbon Dioxide to Fuels with Water And/or Hydrogen Using Solar Energy and beyond. *Coord. Chem. Rev.* **2013**, 257 (1), 171–186.
- (4) Baffou, G.; Quidant, R. Nanoplasmonics for Chemistry. *Chem. Soc. Rev.* **2014**, 43 (11), 3898–3907.
- (5) da Silva, A. G. M.; Rodrigues, T. S.; Slater, T. J. A.; Lewis, E. A.; Alves, R. S.; Fajardo, H. V; Balzer, R.; da Silva, A. H. M.; de Freitas, I.; Oliveira, D. C. de; et al. Controlling Size, Morphology, and Surface Composition of AgAu Nanodendrites in 15 S for Improved Environmental Catalysis under Low Metal Loadings. *ACS Appl. Mater. Interfaces* **2015**, 7 (46), 25624–25632
- (6) da Silva, A. G. M.; Rodrigues, T. S.; Wang, J.; Yamada, L. K.; Alves, T. V; Ornellas, F. R.; Ando, R. A.; Camargo, P. H. C. The Fault in Their Shapes: Investigating the Surface-Plasmon-Resonance-Mediated Catalytic Activities of Silver Quasi-Spheres, Cubes, Triangular Prisms, and Wires. *Langmuir* **2015**, 31 (37), 10272–10278.
- (7) Wang, Q.; CUI, X.; Guan, W.; Zhang, L.; Fan, X.; Shi, Z.; Zheng, W. Shape-Dependent Catalytic Activity of Oxygen Reduction Reaction (ORR) on Silver Nanodecahedra and Nanocubes. *J. Power Sources* **2014**, 269, 152–157.
- (8) Rodrigues, T.; da Silva, A. M.; Macedo, A.; Farini, B.; Alves, R.; Camargo, P. C. Probing the Catalytic Activity of Bimetallic versus Trimetallic Nanoshells. *J. Mater. Sci.* **2015**, 50

- (16), 5620–5629.
- (9) da Silva, A. G. M.; Rodrigues, T. S.; Correia, V. G.; Alves, T. V.; Alves, R. S.; Ando, R. A.; Ornellas, F. R.; Wang, J.; Andrade, L. H.; Camargo, P. H. C. Plasmonic Nanorattles as Next-Generation Catalysts for Surface Plasmon Resonance-Mediated Oxidations Promoted by Activated Oxygen. *Angew. Chemie Int. Ed.* **2016**, *55* (25), 7111–7115.
 - (10) Jenkins, S. V.; Gohman, T. D.; Miller, E. K.; Chen, J. Synthesis of Hollow Gold–Silver Alloyed Nanoparticles: A “Galvanic Replacement” Experiment for Chemistry and Engineering Students. *J. Chem. Educ.* **2015**, *92* (6), 1056–1060.
 - (11) Silva, A. G. M. da; Rodrigues, T. S.; Macedo, A.; Silva, R. T. P. da; Camargo, P. H. C. An Undergraduate Level Experiment on the Synthesis of Au Nanoparticles and Their Size-Dependent Optical and Catalytic Properties. *Quím. Nova* **2014**, *37* (10), 1716–1720.
 - (12) Guedens, W. J.; Reynders, M.; Van den Rul, H.; Elen, K.; Hardy, A.; Van Bael, M. K. ZnO-Based Sunscreen: The Perfect Example To Introduce Nanoparticles in an Undergraduate or High School Chemistry Lab. *J. Chem. Educ.* **2014**, *91* (2), 259–263.
 - (13) Orbaek, A. W.; McHale, M. M.; Barron, A. R. Synthesis and Characterization of Silver Nanoparticles for an Undergraduate Laboratory. *J. Chem. Educ.* **2015**, *92* (2), 339–344.
 - (14) Frank, A. J.; Cathcart, N.; Maly, K. E.; Kitaev, V. Synthesis of Silver Nanoprisms with Variable Size and Investigation of Their Optical Properties: A First-Year Undergraduate Experiment Exploring Plasmonic Nanoparticles. *J. Chem. Educ.* **2010**, *87* (10), 1098–1101.
 - (15) McFarland, A. D.; Haynes, C. L.; Mirkin, C. A.; Van Duyne, R. P.; Godwin, H. A. Color My Nanoworld. *J. Chem. Educ.* **2004**, *81* (4), 544A.
 - (16) Zemke, J. M.; Franz, J. A Biphasic Ligand Exchange Reaction on CdSe Nanoparticles: Introducing Undergraduates to Functionalizing Nanoparticles for Solar Cells. *J. Chem. Educ.* **2016**, *93* (4), 747–752.
 - (17) Williams, G. L.; Vohs, J. K.; Brege, J. J.; Fahlman, B. D. Supercritical Fluid Facilitated Growth of Copper and Aluminum Oxide Nanoparticles. *J. Chem. Educ.* **2005**, *82* (5), 771.
 - (18) Campbell, D. J.; Andrews, M. J.; Stevenson, K. J. New Nanotech from an Ancient Material: Chemistry Demonstrations Involving Carbon-Based Soot. *J. Chem. Educ.* **2012**, *89* (10), 1280–1287.
 - (19) Lee, C.-F.; You, P.-Y.; Lin, Y.-C.; Hsu, T.-L.; Cheng, P.-Y.; Wu, Y.-X.; Tseng, C.-S.; Chen, S.-W.; Chang, H.-P.; Lin, Y.-W. Exploring the Stability of Gold Nanoparticles by Experimenting with Adsorption Interactions of Nanomaterials in an Undergraduate Lab. *J. Chem. Educ.* **2015**, *92* (6), 1066–1070.
 - (20) Panzarasa, G. Just What Is It That Makes Silver Nanoprisms so Different, so Appealing? *J. Chem. Educ.* **2015**, *92* (11), 1918–1923.
 - (21) Silvert, P.-Y.; Herrera-Urbina, R.; Duvauchelle, N.; Vijayakrishnan, V.; Elhsissen, K. T. Preparation of Colloidal Silver Dispersions by the Polyol Process. Part 1-Synthesis and Characterization. *J. Mater. Chem.* **1996**, *6* (4), 573–577.
 - (22) Du, G. H.; Van Tendeloo, G. Cu(OH)₂ Nanowires, CuO Nanowires and CuO Nanobelts. *Chem. Phys. Lett.* **2004**, *393* (1–3), 64–69.

- (23) Kwiat, M.; Cohen, S.; Pevzner, A.; Patolsky, F. Large-Scale Ordered 1D-Nanomaterials Arrays: Assembly or Not? *Nano Today* **2013**, 8 (6), 677–694.
- (24) Song, X.; Sun, S.; Zhang, W.; Yu, H.; Fan, W. Synthesis of Cu(OH)₂ Nanowires at Aqueous–Organic Interfaces. *J. Phys. Chem. B* **2004**, 108 (17), 5200–5205.
- (25) Cudennec, Y.; Lecerf, A. The Transformation of Cu(OH)₂ into CuO, Revisited. *Solid State Sci.* **2003**, 5 (11–12), 1471–1474.
- (26) Li, C.; Yin, Y.; Hou, H.; Fan, N.; Yuan, F.; Shi, Y.; Meng, Q. Preparation and Characterization of Cu(OH)₂ and CuO Nanowires by the Coupling Route of Microemulsion with Homogenous Precipitation. *Solid State Commun.* **2010**, 150 (13–14), 585–589.
- (27) Huang, H.; Yu, Q.; Ye, Y.; Wang, P.; Zhang, L.; Gao, M.; Peng, X.; Ye, Z. Thin Copper Oxide Nanowires/carbon Nanotubes Interpenetrating Networks for Lithium Ion Batteries. *CrystEngComm* **2012**, 14 (21), 7294–7300.
- (28) Debbichi, L.; Marco de Lucas, M. C.; Pierson, J. F.; Krüger, P. Vibrational Properties of CuO and Cu₄O₃ from First-Principles Calculations, and Raman and Infrared Spectroscopy. *J. Phys. Chem. C* **2012**, 116 (18), 10232–10237.
- (29) Zhang, L.; Lu, W.; Feng, Y.; Ni, J.; Lü, Y.; Shang, X. Facile Synthesis of Leaf-like Cu(OH)₂ and Its Conversion into CuO with Nanopores. *Acta Physico-Chimica Sin.* **2008**, 24 (12), 2257–2262.
- (30) El-Trass, A.; ElShamy, H.; El-Mehasseb, I.; El-Kemary, M. CuO Nanoparticles: Synthesis, Characterization, Optical Properties and Interaction with Amino Acids. *Appl. Surf. Sci.* **2012**, 258 (7), 2997–3001.
- (31) Chan, H. Y. H.; Takoudis, C. G.; Weaver, M. J. Oxide Film Formation and Oxygen Adsorption on Copper in Aqueous Media As Probed by Surface-Enhanced Raman Spectroscopy. *J. Phys. Chem. B* **1999**, 103 (2), 357–365.
- (32) Niaura, G. Surface-Enhanced Raman Spectroscopic Observation of Two Kinds of Adsorbed OH[–] Ions at Copper Electrode. *Electrochim. Acta* **2000**, 45 (21), 3507–3519.
- (33) Yu, T.; Zhao, X.; Shen, Z. X.; Wu, Y. H.; Su, W. H. Investigation of Individual CuO Nanorods by Polarized Micro-Raman Scattering. *J. Cryst. Growth* **2004**, 268 (3–4), 590–595.
- (34) Wang, W.; Zhou, Q.; Fei, X.; He, Y.; Zhang, P.; Zhang, G.; Peng, L.; Xie, W. Synthesis of CuO Nano- and Micro-Structures and Their Raman Spectroscopic Studies. *CrystEngComm* **2010**, 12 (7), 2232–2237.
- (35) Kliche, G.; Popovic, Z. V. Far-Infrared Spectroscopic Investigations on CuO. *Phys. Rev. B* **1990**, 42 (16), 10060–10066.
- (36) Anufrienko, V. F.; Shutilov, R. A.; Zenkovets, G. A.; Gavrilov, V. Y.; Vasenin, N. T.; Shubin, A. A.; Larina, T. V.; Zhuzhgov, A. V.; Ismagilov, Z. R.; Parmon, V. N. The State of Cu²⁺ Ions in Concentrated Aqueous Ammonia Solutions of Copper Nitrate. *Russ. J. Inorg. Chem.* **2012**, 57 (9), 1285–1290.
- (37) Bastús, N. G.; Merkoçi, F.; Piella, J.; Puentes, V. Synthesis of Highly Monodisperse Citrate-Stabilized Silver Nanoparticles of up to 200 Nm: Kinetic Control and Catalytic Properties.

- Chem. Mater.* **2014**, 26 (9), 2836–2846.
- (38) Wang, Y.; Wan, D.; Xie, S.; Xia, X.; Huang, C. Z.; Xia, Y. Synthesis of Silver Octahedra with Controlled Sizes and Optical Properties via Seed-Mediated Growth. *ACS Nano* **2013**, 7 (5), 4586–4594.
- (39) Dhineshababu, N. R.; Rajendran, V.; Nithyavathy, N.; Vetumperumal, R. Study of Structural and Optical Properties of Cupric Oxide Nanoparticles. *Appl. Nanosci.* **2016**, 6 (6), 933–939.

Concluding Remarks and Perspectives

In this dissertation, we have demonstrated through a consistent number of examples, the understanding of fundamental mechanisms involving the synthesis of a variety of controlled nanomaterials based on noble-metals (Ag, Au, and Pd) and metal oxide (MnO_2 and CuO) nanostructures. This led to progresses and strategies on the use of galvanic replacement for generating noble-metal hollow nanomaterials with sophisticated surface architectures and compositions. We also put their controlled synthesis to work towards the optimization of catalytic and plasmonic catalytic activities, in which their performances as a function of the various physical and chemical parameters that define the materials were unraveled. We also focused our attention on the use of these developed controlled nanomaterials for applications in green catalytic transformations (heterogeneous catalysis and plasmonic catalysis), and compare their performance relative to conventional nanomaterials usually employed in these applications. Finally, we discussed and proposed two experiments that were implemented in the undergraduate education in order to show to undergraduate students how controlled synthesis, characterization, catalysis, and optical properties are important. We believe this knowledge that was presented herein enabled us the development of next generation nanomaterials by design displaying tailored activity, selectivity, recyclability, and distribution of active sites towards different classes of transformations, providing a strong foundation for inspiring future work in both nanotechnology and catalysis fields.

Academic Curriculum Vitae

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Education

Georgia Institute of Technology, Atlanta, GA, United States

Visiting PhD. student in Chemistry, 2016-2017

Advisor: Professor Younan Xia

University of São Paulo, SP, Brazil

PhD. student in Chemistry, 2013-2016

Advisor: Professor Pedro H. C. Camargo

Federal University of Ouro Preto, Ouro Preto, MG, Brazil

M.S. in Materials Engineering, Chemistry, February 2011-2013

Thesis: Synthesis of transition metals-containing matrices: study of catalytic activity in fine chemistry reactions

Advisor: Professor Patricia A. Robles-Dutenhefner

Federal University of Ouro Preto, Ouro Preto, MG (Brazil)

B.S. in Industrial Chemistry, April 2007-2010.

Research Experience

2016-2017: Georgia Institute of Technology

Visiting PhD. Graduate Research Fellow

(Advisor: Younan Xia)

- Worked on the controlled synthesis of noble-metal (gold, palladium, platinum) nanostructures, investigation of nucleation and growth mechanisms for metal nanoparticles, and their use as catalysts in the oxygen reduction reaction (ORR) for energy generation.

2013-2016: University of São Paulo, SP, Brazil

PhD. Graduate Research Fellow

(Advisor: Pedro H. C. Camargo)

- Worked on the synthesis of noble-metal (gold, palladium, platinum) and metal oxide (manganese, cerium, titanium, copper, zinc, Nickel) nanostructures displaying uniform structures (size, shape, composition, architectures) for applications in heterogeneous catalysis (liquid- and gas-phase transformations).

2011-2013: Federal University of Ouro Preto, Ouro Preto, MG, Brazil

M.S. Graduate Research Fellow

(Advisor: Patricia A. Robles-Dutenhefner)

- Worked on the synthesis of ordered mesoporous silica (MCM-41 and SBA-15) containing palladium, gold, cerium for application as heterogeneous catalysts in the oxidation of alcohols, alkenes, and monoterpenes.

2009-2011: Federal University of Ouro Preto, Ouro Preto, MG (Brazil)

Undergraduate Research Fellow, Department of Chemistry

(Advisor: Patricia A. Robles-Dutenhefner)

- Worked on the synthesis of silica prepared by sol-gel method containing nickel, cobalt, palladium, and gold for application as heterogeneous catalyst.

Teaching Experience

2013-2015: University of São Paulo, São Paulo, SP (Brazil)

Graduate monitor, Institute of Chemistry

- General Chemistry
- Inorganic Chemistry

Activities included: preparing, teaching and coordinating lab sections as well as correcting exams/homework. Received excellent teaching evaluations from students and from the professors.

Complementary Experience

Electron Microscopy: Experience in the operation (Zeiss Ultra60, and JEOL JSM-7401F) and TEM (Hitachi HT7700) microscopes, including sample preparation and analyses of results.

Catalysis: Experience in the operation of different characterization techniques widely employed in catalysis field such as surface area and chemisorption measurements (Quantachrome Autosorb IQ BET), Temperature programmed reduction (TPR Quantachrome ChemBET-300) X-ray diffraction (Rigaku Geigerflex-3034 diffractometer), UV-VIS spectroscopy (Shimadzu UV-1700 spectrophotometer), and gas chromatography (GC-2014, and GC-2010AF). Experience in analyzing results by BET, gas chemisorption, TPR, XRD, XPS, UV-VIS, Raman, and gas chromatography.

Honors and Awards

- Quality in Publication award within the Chemistry Institute at University of São Paulo, **2016**.
- Best poster award within the 39th Brazilian Chemical Society meeting, **2016**.
- Paper featured as Back Cover by the ChemNanoMat Journal, Wiley, **2016**.
- Best poster award within the 20th Brazilian Eletrochemistry and Electroanalytical Symposium, **2015**.
- Best poster award within the 18th Brazilian Catalysis Congress, Brazilian Catalysis Society, **2015**.
- Paper featured as Frontispiece and Hot Paper by the Chemistry: an European Journal, Wiley, **2015**.
- Brazilian Fair of Sciences and Engineering award (Shared First Place), **2015**.
- Best student pôster (Shared First Place) and Best poster nominee award within the Materials Research Society Meeting, MRS Fall, **2014**, Boston, US.
- Paper featured as Hot Paper by the Chemistry: an European Journal, Wiley, **2014**.
- Awarded Idea to Product Latin America, Center for Entrepreneurship and New Business of the Getulio Vargas Foundation FGVcenn in **2012**.
- Awarded Best Outstanding Presentation - Idea to Product Latin America, Center for Entrepreneurship and New Business of the Getulio Vargas Foundation FGVcenn in **2012**.
- Awarded Santander Entrepreneurship - Biotechnology and Health category, Santander Bank in **2011**.

Publications as the First Author (2013-2017)

1. **da Silva, A.G.M.**, Rodrigues, T.S., Correia, Alves, T.V, Alves, R.S.; Ando, R.A., Ornellas, F.O. Wang, J., Andrade, L.H., Camargo, P.H.C. Plasmonic Nanorattles as Next-Generation Catalysts for Surface Plasmon Resonance-Mediated Oxidations Promoted by Activated Oxygen *Angewandte Chemie International Edition*, **2016**, 55, 7111-7115.
2. **da Silva, A.G.M.**, Kisukuri, C.M., Rodrigues, T.S.,Candido, E.G., de Freitas, I.C., da Silva, A.H.M, Assaf, J.M., Oliveira, D.C, Andrade, L.H.; Camargo, P.H.C., MnO₂ Nanowires Decorated with Au Ultrasmall Nanoparticles for the Green Oxidation of Silanes and Hydrogen Production under Ultralow Loadings, *Applied Catalysis B: environmental*, **2016**, 184, 35-43.
3. **da Silva, A.G.M.**, Fajardo, H.V., Balzer, R., Probst, L.F.D., Camargo, P.H.C., Robles-Dutenhefner, P.A., Efficient Oxygen Storage of Ceria-Silica Catalysts: Improving the catalytic performance of ceria-based materials with ordered structure, *Chemical Engineering Journal*, **2016**, 286, 369-376.

4. **da Silva, A.G.M.**, Rodrigues, T.S., Taguchi, L.S.D., Fajardo, H.V., Balzer, R., Probst, L.F.D., Camargo, P.H.C., Pd-based nanoflowers catalysts: controlling size, composition, and structures for the 4-nitrophenol reduction and BTX oxidation reactions. *Journal of Materials Science*, **2016**, *51*, 603-614 (**Awarded Best Student Poster within the Materials Research Society Meeting**).
5. **da Silva, A.G.M.**, Rodrigues, T.S., Slater, T.J.A Lewis, E., Alves, R.S., Fajardo, H.V., Balzer, R., da Silva, A.H.M, de Freitas, I.C., Oliveira, D.C., Assaf, J.M., Probst, L.F.D., Haigh, S.J., Camargo, P.H.C., Controlling Size, Morphology, and Surface Composition of AgAu Nanodendrites in 15 s for Improved Environmental Catalysis under Low Metal Loadings, *ACS applied materials & interfaces*, **2015**, *7*, 25624-25632 (**Awarded Best Poster within the 39th Brazilian Chemical Society meeting**).
6. **da Silva, A.G.M.**, Rodrigues, T.S., Lewis, E., Slater, T.J.A., Alves, R.S., Haigh, S.J., Camargo, P.H.C., Surface Segregated AgAu Tadpole-Shaped Nanoparticles Synthesized Via a Single Step Combined Galvanic and Citrate Reduction Reaction. *Chemistry-A European Journal*, **2015**, *21*, 12314-12320 (**Featured as frontispiece, hot paper, and awarded Best Poster within the 39th Brazilian Chemical Society meeting**).
7. **da Silva, A.G.M.**, Fajardo, H.V., Balzer, R., Probst, L.F.D., Lovón, A.S.P. Lovón-Quintana, J.J., Valença, G.P., Schreiner, W.H., Robles-Dutenhefner, P.A., Mesoporous silica containing Au, Pd and Au-Pd: versatile and efficient catalysts for energy and environmental processes, *Journal of Power Sources*, **2015**, *285*, 460-468.
8. **da Silva, A.G.M.**, Rodrigues, T.S., Wang, J., Yamada, L.K., Ando, R.A., Camargo, P.H.C., The Fault in Their Shapes: Investigating the Surface Plasmon Resonance-Mediated Catalytic Activities of Silver Quasi-Spheres, Cubes, Triangular Prisms and Wires. *Langmuir*, **2015**, *31*, 10272-10278 (**Awarded Best Poster within the 18th Brazilian Catalysis Congress**).
9. **da Silva, A.G.M.**, de Souza, M., Rodrigues, T.S., Alves, R.S., Temperini, M.L.A., Camargo, P.H.C. Rapid Synthesis of Hollow Ag-Au Nanodendrites in 15 Seconds by Combining Galvanic Replacement and Precursor Reduction Reactions. *Chemistry- A European Journal*, **2014**, *20*, 15040-15046 (**Featured as hot paper**).
10. **da Silva, A.G.M.**, Rodrigues, T.S., Dias, A., Fajardo, H.V., Gonçalves, R.F., Godinho, M., Robles-Dutenhefner, P.A., $\text{Ce}_{1-x}\text{Sm}_x\text{O}_{1.9-\delta}$ nanoparticles obtained by microwave-assisted hydrothermal processing: an efficient application for catalytic oxidation of α -bisabolol. *Catalysis Science & Technology*, **2014**, *4*, 814.

11. **da Silva, A.G.M.**, Rodrigues, T.S., Macedo, A., Silva, R.T.P., Camargo, P.H.C. An Undergraduate Level Experiment on the Synthesis of Au Nanoparticles and their Size-Dependent Optical and Catalytic Properties, *Química Nova*, **2014**, 37, 1716-1720.
12. **da Silva, A.G.M.**, Rodrigues, T.S., Gurgel, L.V.A., de Assis, P.A., Gil, L.F., Robles-Dutenhefner, P.A., A new use for modified sugarcane bagasse containing adsorbed Co^{2+} and Cr^{3+} : Catalytic oxidation of terpenes. *Industrial Crops and Products*, **2013**, 50, 288-296.
13. **da Silva, A.G.M.**, Robles-Dutenhefner, P.A., Dias, A., Fajardo, H.V., Lovón, A.S.P., Lovón-Quintana, J.J., Valença, G.P., Gold, palladium and gold-palladium supported on silica catalysts prepared by sol-gel method: synthesis, characterization and catalytic behavior in the ethanol steam reforming, *Journal of Sol-Gel Science*, **2013**, 67, 273.
14. **da Silva, A.G.M.**, Speziali, M.G., Miranda, D.M.V., Monteiro, A.L., Robles-Dutenhefner, P.A., Air stable ligandless heterogeneous catalyst systems based on Pd and Au supported in SiO_2 and MCM-41 for Suzuki-Miyaura cross-coupling in aqueous medium, *Applied Catalysis A: General*, **2013**, 462-463, 39.

Submitted Papers

15. **da Silva, A.G.M.**, Rodrigues, T.S, Gilroy, K.D., Vara, M., Camargo, P.H.C., Xia, Y. One-pot synthesis of size-controlled porous Pd nanospheres by a non-classical growth mechanism combining the LaMer and DLVO theories, **2017**.
16. **da Silva, A.G.M.**, Rodrigues, T.S, Gilroy, K.D., Vara, M., Camargo, P.H.C., Xia, Y. Rapid Single-step Synthesis of Monodisperse Sub-10 nm Pd Nanocubes and Their Evolution into Concave and Assembled Cubic Nanostructures, **2017**.
17. **da Silva, A.G.M.**, Rodrigues, T.S, Camargo, P.H.C. New Frontiers for the Galvanic Replacement Reaction: Maneuvering Surface Chemistry to Optimize Catalytic Activities, **2017**.
18. **da Silva, A.G.M.**, Rodrigues, T.S, Gilroy, K.D., Camargo, P.H.C., Xia, Y. Toward the Physics and Chemistry of Metal Nanowires: Synthesis, Applications, and Perspectives, **2017**.
19. **da Silva, A.G.M.**, Rodrigues, T.S, Candido, E.G., Fajardo, H.V., Balzer, R., Probst, L.F.D., Oliveira, D.C., Assaf, J.M., Wojcieszak, R. Camargo, P.H.C. Boosting Catalysts by the Concerted Design of the Support and Active Phase: Achieving High Activities for MnO_2 -Au Nanoflowers Towards Green Oxidations, **2017**.

20. da Silva, A.G.M., Rodrigues, T.S, Parussulo, A.L.A., Candido, E.G., Geonmonond, R.S., Brito, H.F., Toma, H.E. Controlled Synthesis of Nanomaterials at the Undergraduate Laboratory: Cu(OH)₂ and CuO Nanowires, **2017**.

21. da Silva, A.G.M., Hood, Z., Rodrigues, T.S, Candido, E.G., Fernandes, C.G. Camargo, P.H.C. Simple One-Step Deposition of Monodisperse Ultrasmall Pd, Pt, and PdPt NPs over TiO₂ nanowires: Improved Catalytic Activities Towards the Water Splitting Reaction, **2017**.

Other Publications

22. Rodrigues, T.S, da Silva, A.G.M., de Oliveira, L.C., da Silva, A.M., Teixeira, R.R., Camargo, P.H.C. Cu₂O Spheres as an Efficient Source of Catalytic Cu (I) Species for Performing Azide-Alkyne Click Reactions. *Tetrahedron Letters*, **2017**, 58, 590-595.

23. Rodrigues, T.S, da Silva, A.G.M, de Moura, A.B.L., Geonmonond, R.S., Camargo, P.H.C. AgAu Nanotubes: Investigating the Effect of Surface Morphologies and Optical Properties over Applications in Catalysis and Photocatalysis. *Journal of the Brazilian Chemical Society*, **2017**, impress.

24. Rodrigues, T.S, da Silva, A.G.M., de Moura, A.B.L., Freitas, I.G., Camargo, P.H.C. Rational design of plasmonic catalysts: matching the surface plasmon resonance with lamp emission spectra for improved performance in AgAu nanorings. *RCS Advances*, **2016**, 6, 62286-62290.

25. Yamada, L.K., da Silva, A.G.M., Rodrigues, T.S., Haigh, S.J., Camargo, P.H.C. Bimetallic Au@ Pd-Au Tadpole-Shaped Asymmetric Nanostructures by a Combination of Precursor Reduction and Ostwald Ripening, *Chemnanomat*, **2016**, 2, 509-514. (featured as Back Cover).

26. Rodrigues, T.S, da Silva, A.G.M, Gonçalves, M.C., Fajardo, H.V., Balzer, R., Probst, L.F.D., da Silva, A.H.M, Assaf, J.M., Camargo, P.H.C. On the Catalytic Properties of AgPt Nanoshells as a Function of Size: Larger Outer Diameters Lead to Improved Performances. *Langmuir*, **2016**, 32, 9371-9379.

27. Rodrigues, T.S., da Silva, A.H.M., da Silva, A.G.M., Ceara, D.G., Gomes, J.F. Hollow AgPt/SiO₂ nanomaterials with controlled surface morphologies: is the number of Pt surface atoms imperative to optimize catalytic performances? *Catalysis Science and Technology*, **2016**, 6, 2162-2170

28. Rodrigues, T.S., **da Silva, A.G.M.** Gonçalves, M.C., Fajardo, H.V. Balzer, R., Probst, L.F.D., da Silva, A.H.M, Assaf, J.M., Camargo, P.H.C., On the Catalytic Properties of AgPt Nanoshells as a Function of Size: Larger Outer Diameters Lead to Improved Performances, *Langmuir*, **2016**, 32, 9371-9379.

29. Rodrigues, TS **da Silva, AGM** de Moura, A. Geonmonond, R. RAFAEL, Camargo, P.H.C. AgAu Nanotubes: Investigating the Effect of Surface Morphologies and Optical Properties over Applications in Catalysis and Photocatalysis. *J. Brazilian Chem. Soc.* **2016**, impress.

30. Rodrigues, T.S., **da Silva, A.G.M.**, Gonçalves, M.C., Fajardo, H.V., Balzer, R., Probst, L.F.D., Camargo, P.H.C., AgPt Hollow Nanodendrites: Synthesis and Uniform Dispersion over SiO₂ Support for Catalytic Applications. *ChemNanoMat*, **2015**, 1, 46-51.

31. Rodrigues, T.S., **da Silva, A.G.M.**, Macedo, A., Fariuni, B.W., Alves, R.S., Camargo, P. H.C., Probing the Catalytic Activity of Bimetallic versus Trimetallic Nanoshells, *Journal of Materials Science*, **2015**, 50, 5620-5629.

32. Rodrigues, T.S., **da Silva, A.G.M.**, Macedo, A., Fariuni, B.W., Alves, R.S., Camargo, P. H.C., Probing the Catalytic Activity of Bimetallic versus Trimetallic Nanoshells, *Journal of Materials Science*, **2015**, 50, 5620-5629.

Patent

- Patent application, Robles-Dutenhefner, P.A., Silva, A.G.M., Rodrigues, T.S., Synthesis of bisabolol oxides by catalytic oxidation of alpha-bisabolol using solid metallic oxides, INPI 221105495250, **2011**.

Book Chapter

- Camargo, P. H.C., Rodrigues, T.S., **da Silva, A.G.M.**, Wang, J. Controlled Synthesis: Nucleation and Growth in Solution, *Metallic Nanostructures*, Springer, **2015**, 1, 49-74.