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Síntese de nanofolhas de óxido de grafeno e titânia
decoradas com nanopartículas de ouro, paládio e
prata para aplicações catalíticas

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decorated with gold, palladium and silver nanoparticles
for catalytic applications

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"I am a great believer in luck, and I find the harder I work, the more I have of it."

Thomas Jefferson

To Felipe, my sun.

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Abstract

Papa, L. **Synthesis of hybrid nanosheets of graphene oxide, titania and gold and palladium nanoparticles for catalytic applications.** 2017. 72p. Master's Thesis – Graduate Program in Chemistry. Instituto de Química, Universidade de São Paulo, São Paulo.

Nanocatalysis has emerged in the last decades as an interface between homogeneous and heterogeneous catalysis, offering simple solutions to problems that conventional materials have not been able to solve. In fact, nanocatalyst design permits to obtain structures with high superficial area, reactivity and stability, and at the same time presenting good selectivity and facility of separation from reaction mixtures. In this work, we prepared hybrid structures comprising gold, palladium and silver nanoparticles (Au, Pd and Ag NPs), titanate nanosheets (Ti_xO_2), graphene oxide (GO), and partially reduced graphene oxide (prGO). We focused on bi- and tri-components hybrids, namely $\text{M}/\text{Ti}_x\text{O}_2$, $\text{M}/(\text{pr})\text{GO}$ and $\text{M}/\text{Ti}_x\text{O}_2/(\text{pr})\text{GO}$ ($\text{M} = \text{Au}, \text{Pd}$ or Ag) and developed facile, versatile and environment-friendly preparation methods with an emphasis on control over physicochemical features such as size, shape and composition. In order to exploit the catalytic applications, we employed the reduction of 4-nitrophenol as a model reaction, followed by visible-light assisted oxidation of p-aminothiophenol (PATP). With these tests, we unraveled metal-support interactions and cooperative effects that render hybrid structures superior to their individual counterparts.

Keywords: nanomaterials, catalysis, photocatalysis, plasmonic catalysis

Resumo

Papa, L. **Síntese de nanofolhas híbridas com óxido de grafeno, titânia e nanopartículas de ouro e paládio para aplicações catalíticas.** 2017. 72p. Dissertação de Mestrado – Programa de Pós-Graduação em Química. Instituto de Química, Universidade de São Paulo, São Paulo.

A nanocatálise surgiu nas últimas décadas como uma interface entre catálise homogênea e heterogênea, oferecendo soluções simples a problemas que os materiais convencionais não conseguiram resolver. De fato, o design de nanocatalisadores permite obter estruturas com grande área superficial, reatividade e estabilidade, e ao mesmo tempo apresentando boa seletividade e facilidade de separação de misturas reacionais. Neste trabalho apresentamos a preparação de estruturas híbridas compostas por nanopartículas de ouro, paládio e prata (Au, Pd e Ag NPs), nanofolhas de titanato (Ti_xO_2), óxido de grafeno (GO) e óxido de grafeno parcialmente reduzido (prGO). Focamos em híbridos do tipo $\text{M}/\text{Ti}_x\text{O}_2$, $\text{M}/(\text{pr})\text{GO}$ e $\text{M}/\text{Ti}_x\text{O}_2/(\text{pr})\text{GO}$ ($\text{M} = \text{Au}, \text{Pd}$ ou Ag) e desenvolvemos métodos de preparação simples, versáteis e ambientalmente amigáveis, com ênfase no controle sobre tamanho, forma e composição. Para explorar as potencialidades catalíticas utilizamos a redução do 4-nitrofenol como reação modelo, e em seguida a oxidação assistida por luz do p-aminotiofenol (PATP). Com esses testes, investigamos interações metal-suporte e efeitos cooperativos que tornam as estruturas híbridas superiores a cada um dos materiais que as compõem.

Palavras-chave: nanomateriais, catálise, fotocatálise, catálise plasmônica

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1. Introduction

1.1. Nanocatalysis

In many fields of great technological and economic interest, such as energy production and medicine, catalysis plays a central role; as a consequence, research towards developing cheap, efficient, and green catalysts has become increasingly important.¹⁻⁵ A catalyst is defined as a substance that increases the rate of a chemical reaction (catalytic activity) and/or favors the formation of specific products (catalytic selectivity) without being consumed in the process. Catalysis can be classified in homogeneous and heterogeneous: in homogeneous catalysis the catalyst, typically an organometallic compound, is dissolved in the same phase of the reactants, and presents high activity, selectivity and thermal stability. Heterogeneous catalysts are in a different phase than the reactants, and in this case catalysis takes place at the phase interface; heterogeneous catalysis offers the advantage of effortless catalyst removal after reaction, but displays inferior stability and activity.⁶

In this context, nanocatalysis surges as a third branch with similarities to both homogeneous and heterogeneous catalysis: the use of metal and metal oxide nanomaterials has recently gained attention due to the improved catalytic performance derived from a high surface-volume ratio, with advantages regarding costs and environmental impact; reactivity and selectivity of the catalysts can also be finely tuned through shape, size and composition control, broadening the range of possible applications and exceeding current performance limits.⁷⁻¹¹ Moreover, many

metal nanoparticles present surface plasmon resonance under UV, visible, and/or near-infrared radiation, becoming attractive in environmentally friendly, solar-light based applications.

Therefore, research over metal nanoparticles supported over graphene, graphene oxide (GO) and reduced graphene oxide (rGO) as well as semiconductor metal oxides, chalcogenides and sulfides has gained interest: electronic and mechanic properties of the supports, as well as the presence on their surface of defects and functional groups, not only allow for effective nanoparticle immobilization, but actively participate in the catalytic mechanism.^{12–19}

1.2. Surface Plasmon Resonance (SPR) and plasmonic catalysis

Surface plasmon resonance (SPR) is defined as the resonant oscillation of free electrons in a metal nanoparticle in response to the oscillating electric field component from an incoming electromagnetic radiation.²⁰ Even though the frequency of SPR excitation depends on parameters such as size, shape, structure and the dielectric constant of the environment, among others, it is usually observed in the visible range for silver (Ag) and gold (Au) nanomaterials.²¹ SPR excitation leads to absorption and scattering of the incoming electromagnetic wave at frequencies close to the SPR (in the far field), the generation of intense electric fields close to the nanomaterials surface (in the near field), the formation of hot electrons/holes, and the dissipation of local heating.^{20,22} Due to these features, plasmonic nanoparticles became of great interest in many fields including medicine (theranostics),^{23–25} sensing^{16,24,26} and energy-related applications.^{27,28}

Furthermore, it has been recently established that the SPR excitation of plasmonic nanoparticles can be put to work to enhance or mediate chemical transformations, and plasmonic catalysis emerged as a new, exciting field of heterogeneous catalysis;^{20,21,29} this new branch has drawn enormous attention due to the possibility, derived from the use of plasmonic nanoparticles as catalysts, of employing visible light as the main or even the only energy input to drive chemical transformations.^{20,21,29}

1.3. Hybrid nanostructures for catalysis

In the context of nanocatalysis, the optimization of electronic and optical properties of hybrid materials via controlled synthesis plays a pivotal role not only towards maximizing performances, but also to the understanding of how various fundamental chemical and physical features of a catalyst affect activities.^{30–33}

Improved catalytic performance can be attributed to the strong metal-support interactions (SMSI) observed between a metallic catalyst and the support employed for its immobilization.¹² In recent years, many studies reported on synergic and cooperative effects affecting the activity of a catalytically active metal that bring to an improvement of its performances. A support can influence parameters such as surface energy, Fermi level, size, exposed facets, and composition of nanoparticles, opening new possibilities in the field of controlled nanoparticles synthesis.^{8,11–13,18,34}

In the case of SPR-mediated catalytic processes, the modulation of charge transfer mechanisms taking place at the nanoscale represents a promising strategy towards the

optimization of activities and selectivities.³⁰ For instance, the combination of an electron donor or electron acceptor material with a plasmonic nanoparticle (forming a nanoparticle-based hybrid, for example) enables the tuning of charge states in a metal.^{14,15,19,35,36} This, in turn, affects the population and separation of SPR excited hot-electrons and holes that can drive reduction or oxidation processes. Therefore, the immobilization of plasmonic nanoparticles onto supports presenting electronic properties that enable the modulation of nanoscale charge transfer processes opens the possibility for the control of plasmonic catalytic properties in addition to providing a facile strategy to improve stability.^{8–11,27,26,29–31}

Despite these attractive features, the synthesis of well-defined and controlled hybrid nanostructures as well as the understanding of how the complex electronic mechanisms affect catalytic performances have remained limited. Nonetheless, these attributes are key to the design of catalytic systems with improved performances.

1.4. Graphene, graphene oxide (GO), and reduced graphene oxide (rGO)

Graphene is an allotrope of elemental carbon, formed by a single layer of covalently bond sp^2 carbon atoms arranged in a honeycomb lattice. This material attracted the attention of the scientific community after it was isolated in 2004;⁴⁰ a variety of applications have since arose in sensing, electrodes, catalysis, photocatalysis, electronics, fuel and solar cells.^{41–46}

Graphene is defined as a zero-gap semiconductor, in which valence and conduction bands meet at the Dirac points: on its surface, electrons can move freely, as they behave as massless particles.⁴⁷ Thus, additionally to an exceptionally large specific area ($2,600 \text{ m}^2/\text{g}$) and outstanding

mechanical strength, graphene presents ultra-high electrical mobility as well as thermal and electrical conductivity, appearing as a material with exceptional technological potential.^{14,48,49}

Graphene-based nanosheets are commonly obtained through oxidation of graphite with concentrated sulphuric acid, nitric acid and potassium permanganate, followed by exfoliation, as was reported by Hummers in 1958 (**Figure 1**).^{50,51} The process allows to isolate graphene oxide (GO), which is heavily oxygenated if compared to pristine graphene. In GO, the carbon lattice comprises both sp^2 and sp^3 hybridized atoms, presenting hydroxyl and epoxide groups on its basal plane and carbonyl and carboxyl groups on its edges.^{45,52}

Figure 1. Scheme of graphite oxidation to graphene oxide and subsequent reduction to reduced graphene oxide.⁴⁵

Although functional groups on the surface of GO allow it to be easily suspended in water and permit the formation of strong bonds with metals, aiding in the immobilization of nanoparticles,

it must be noted that the process leads to the complete loss of the conductivity observed in graphene due to the widening of the band gap up to a value of 4 eV.^{52,53} The gap can be shrunk through chemical or thermal reduction,^{52,54–56} the products of this treatment, partially reduced graphene oxide (prGO) and, subsequently, reduced graphene oxide (rGO), have a lower density of functional groups and partially restored conductivity.

1.5. Titanium oxide nanosheets (Ti_xO_2)

One of the consequences of the progress in the study of graphene-based materials was the exponential growth of publications detailing properties and applications of 2D inorganic nanomaterials.^{11,57–60} Among those, titanate nanosheets (Ti_xO_2) stand out because of their low price, low toxicity, and high stability.^{59,61,62} These characteristics permitted the use of Ti_xO_2 in the fields of photocatalysis, sensing, and solar cells.^{59,62–66}

The most common approach employed in the preparation of Ti_xO_2 consists in the intercalation-exfoliation process of a lamellar titanate salt, depicted in **Figure 2**. Per this method, the original titanate ($\text{Cs}_{0.7}\text{Ti}_{1.83}\square_{0.18}\text{O}_4$ or $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$) is firstly submitted to an acid exchange that removes metallic Cs^+ , K^+ and Li^+ cations and introduces protons in the structure, yielding a protonic titanate. Subsequently a voluminous cation, typically tetrabutylammonium hydroxide (TBAOH), is introduced in an aqueous suspension of the titanate, causing it to exfoliate to single nanosheets.⁶⁷

Figure 2. Scheme of the intercalation-exfoliation process for the preparation of Ti_xO_2 nanosheets.⁶²

The interest in this technique is motivated by its simplicity and the use of inexpensive starting materials. Recently, alternative bottom-up methods have been proposed, both through vapor deposition⁶⁸ and in aqueous solution,^{69–71} but high cost, low product crystallinity and poor reproducibility of the results still limit their widespread application.

1.6. Controlled synthesis of metal nanoparticles

Many different properties can be responsible for high catalytic performances in metal nanoparticles. A demand for finely divided particles is generated from the abundance of active sites on structures with a high superficial area; at the same time, studies over facet control show that atomic arrangement over a nanocrystal surface is often more important than the surface area itself, as it strongly affects selectivity: nanoparticles with exposed facets and rough surfaces

prepared through controlled synthesis and oxidative etching can be tailored for specific applications, making for highly active catalysts.^{18,72–76}

Moreover, electron confinement by a nanocrystal gives place to size- and shape-dependent quantum size effects, with consequences on its electronic, optical and magnetic properties.^{77–79} For example, the number, position and intensity of SPR modes in gold and silver nanoparticles is reported to be strongly dependent on nanoparticle shape: sharp corners of cubic and triangular nanocrystals can constitute accumulation points for surface charges, enhancing charge separation and causing a marked red-shift in SPR peak position relative to round counterparts.^{33,80,81} Therefore, it becomes of key importance to finely control all structural parameters in the synthesis of metal nanoparticles when the objective is catalytic performance maximization.

Controlled nanoparticle synthesis can be achieved through wet chemistry methods that employ a metal salt as a precursor. Typical procedures involve the use of an organic reducing agent, often activated by heat, and a stabilizing agent that keeps newly formed nanoparticles in suspension by bonding on their surface, preventing aggregation into bulk solids.^{9,82} Alcohols, glycols or hydrazine can be employed as reducing agents, whereas polyethylene glycol (PEG) can act as both solvent and reducing agent, lowering the number of reactants and allowing higher temperatures than those achieved in aqueous solution (polyol method);^{82–84} on the other side, the use of an organic solvent results in a higher environmental impact, a factor that cannot be ignored in the context of industrial applications. Examples of common reagents that show effective in the stabilization of metal nanoparticles are sodium citrate, ascorbic acid,

polyvinylpyrrolidone (PVP), hydroquinone, cetyl trimethylammonium bromide (CTAB) and chloride (CTAC).

Regarding synthesis mechanism, two different steps, nucleation and growth, can be identified in the path leading from metallic precursor to nanocrystals (**Figure 3**). As metal atoms are introduced in the solution as a consequence of reduction, a supersaturation point is eventually reached which causes self-aggregation into metal clusters, the so-called nucleation, to occur. This process causes metal atoms concentration to drop under the supersaturation point, slowing down or arresting the formation of new clusters. Thus, the remaining metal atoms rapidly aggregate to the existing clusters, giving place to the growth step. It is essential for a narrow nanoparticle size distribution that the self-nucleation step be as short as possible (burst homogeneous nucleation), since different particle sizes are the consequence of different growth times (ongoing homogeneous nucleation).^{81,85}

Figure 3. The steps involved in nanoparticle synthesis, illustrated through a plot of atomic concentration vs reaction time.⁸¹

The strength and concentration of the reducing agent greatly influence the properties of the final nanoparticle: to a slow reduction corresponds the formation of kinetically controlled products (pyramids, plates), while the use of strong or concentrated reducing agents favors thermodynamically controlled shapes (Wulff polyhedrons).^{76,81,85}

As a nanocrystal's stability depends on surface energy of exposed facets, it is possible to study the correlation between its morphology and its stability to predict the most abundant products depending on experimental conditions. In this context, capping agents can be used to influence the shape and size of metal nanoparticles by interacting with specific facets and lowering their energy, as to promote faster growth in certain directions and shapes.^{80,82}

Although these and other principles can be applied to the synthesis of several metal nanoparticles, the peculiar properties and tendencies of each element cause ideal reaction conditions to vary considerably, calling for deeper knowledge over the behavior of each metal in order to develop effective synthetic routes.

1.6.1. Palladium

Palladium's most relevant characteristics are the ability to adsorb high volumes of H_2 and the catalytic activity in petroleum cracking and in hydrogenation, dehydrogenation and coupling reactions.^{86–88} It also finds several applications as an electrocatalyst for alcohol oxidation reactions.^{89,90} The synthesis of palladium nanoparticles is usually carried out under mild heating, employing Na_2PdCl_4 or K_2PdCl_4 as precursors and a variety of capping agents for shape control. Particle size can be increased through the addition of Fe^{3+} ions, whereas Br^- promotes the

formation of cubic nanoparticles as well as nanowires by stabilizing {100} facets. Decahedrons and icosahedrons, enclosed by {111} facets, can be obtained by reducing a palladium precursor in the presence of citric acid, and a kinetically controlled route can be induced by lowering reduction speed, yielding triangular and hexagonal nanoplates.^{75,81,91,92,88}

1.6.2. Gold

Research over gold nanoparticles led to the discovery of a unique catalytic potential, and this metal is extensively employed in selective oxidation, hydrogenation, C-H activation reactions.⁴ The great range of applications, biocompatibility, easy surface modification and SPR in the visible range made gold one of the most popular research topics over the last years.⁸¹

Synthesis of gold nanoparticles from reduction of HAuCl_4 was first reported by Michael Faraday in 1857,⁹³ and many experimental procedures were developed since. Among those, the Turkevich method stands out as an extremely simple and effective route for the preparation of monodisperse gold nanoparticles of tunable size.^{94,95} The method employs water as solvent, HAuCl_4 as precursor and sodium citrate or ascorbic acid as both reducing and stabilizing agent: a bright red suspension of spherical nanoparticles is obtained after as little as 30 minutes of reaction at temperatures close to 100°C.

Gold nanocubes and nanorods can be obtained by introducing Ag^+ and Br^- ions in the reaction mixture thanks to the stabilization of the {100} and {110} facets respectively.⁹⁶ As was already observed in the case of palladium, the strategy for the preparation of nanoplates once again relies on a slower reduction rate.⁹⁷

1.6.3. Silver

Silver nanoparticles are excellent catalysts for reaction such as oxidation and oxidative coupling, emerging as a cheaper, more abundant alternative to nobler metals.⁸¹ Moreover, they have been extensively researched for their optical properties, as the intense, highly tunable SPR peaks they present make them popular SERS substrates, and for their antibacterial properties, for which they are employed in medical products, dyes and water purification.^{80,98,99}

The Lee-Meisel method, only differing from the Turkevich method for the substitution of HAuCl_4 with AgNO_3 , was reported in 1982 to yield silver nanospheres;¹⁰⁰ however, the size dispersion is significantly larger than in the case of gold, and alternative procedures employing sodium borohydride are more often used.⁹⁸ Another effective route for the shape-controlled synthesis of silver nanoparticles is the polyol method, where a simple tuning of the EG:PVP ratio and of silver salt concentration can already lead to the growth of nanocubes, nanorods and nanowires.⁸⁰ In all mentioned methods, AgNO_3 is used as precursor, as it is highly soluble in both water and organic solvents, although the reagent easily decomposes under visible light, often preventing perfect control over nanoparticle properties.

2. Objectives

Our first objective in this project is to develop versatile and reliable procedures for the preparation of monodisperse Au, Pd and Ag NPs, as well as Ti_xO_2 , GO and rGO. After isolating these materials, we will employ them in the preparation of bi- and tri-component hybrids, comparing different immobilization approaches and focusing on homogeneous dispersion of all components in the structures.

Next, we will probe the SPR-mediated catalytic activity of Au and Ag NPs in the hybrids by employing the laser-assisted PATP oxidation to DMAB as a model reaction. Moreover, we will study the catalytic activity of supported Au and Pd NPs in the 4-nitrophenol reduction to 4-aminophenol.

In these applications, we will aim at investigating how catalytic properties depend on the morphological and electronic properties of all produced materials in order to achieve optimized performances.

3. Materials and methods

3.1. Reagents

Reagent	Formula	Purity (%)	Supplier
Chloroauric Acid	$\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$	99.9	Sigma-Aldrich
Potassium Tetrachloropalladate	K_2PdCl_4	99.9	Sigma-Aldrich
Silver Nitrate	AgNO_3	99.0	Sigma-Aldrich
Polyvinylpyrrolidone ($M_w=55,000 \text{ g mol}^{-1}$)	$((\text{C}_6\text{H}_9\text{NO})_n$	-	Sigma-Aldrich
Sodium Citrate	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 3\text{H}_2\text{O}$	99.0	Sigma-Aldrich
Potassium Carbonate	K_2CO_3	99.0	Vetec
Lithium Carbonate	Li_2CO_3	99.0	Sigma-Aldrich
Titanium Dioxide	TiO_2	-	Sigma-Aldrich
Titanium Dioxide (P25)	TiO_2	99.5	Degussa
Tetrabutylammonium Hydroxide	$((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2)_4\text{N}(\text{OH})$	40% in water	Sigma-Aldrich
p-aminothiophenol	$\text{H}_2\text{NC}_6\text{H}_4\text{SH}$	97.0	Sigma-Aldrich
Graphite Flakes (SP1)	C	-	Bay Carbon
Potassium Permanganate	KMnO_4	99.0	Sigma-Aldrich
Sulphuric Acid	H_2SO_4	95.0-99.0	Vetec
Hydrogen Peroxide	H_2O_2	30% in water	Sigma-Aldrich
Hydrochloric Acid	HCl	35.0-38.0 in water	Vetec
Ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	99.0	Vetec
Acetone	CH_3COCH_3	99.5	Sigma-Aldrich
Methylene Blue	$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$	-	

Table 1. List of used reagents

3.2. Nanomaterials Synthesis

3.2.1. Synthesis of Au NPs

2.5 mL of a 2.0 mM aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was mixed with 47.5 mL of water in a round bottom flask. The reaction mixture was then heated to boiling and 500 μL of sodium citrate (1% m/m) were added. After 30 minutes of reaction under stirring, the mixture was left to cool to room temperature.

3.2.2. Synthesis of Pd NPs

48 mL of water were heated to 89°C in a round bottom flask. 1 mL of sodium citrate (1% m/m) was then added to the reaction mixture, quickly followed by 2.5 mL of a 2.0 mM aqueous solution of K_2PdCl_4 . After 15 hours of reaction under stirring, the mixture was left to cool to room temperature.

3.2.3. Synthesis of Ag NPs

A polyol method was employed for the preparation of Ag NPs.³⁷ Typically, in 37.5 mL of ethylene glycol were dissolved 5 mg of PVP and 200 mg of AgNO_3 . The resulting solution was then heated to 125°C for 2.5 hours. After cooling down to room temperature, the suspension was diluted with water to the volume of 125 mL. The product was collected by centrifugation at

the speed of 28,000 g, brought to a concentration of 2.2 mM by resuspension in 1/40th of the initial solvent volume, washed with ethanol and water through several cycles of centrifugation and supernatant removal, and finally resuspended in water.

3.2.4. Synthesis of GO, prGO and rGO

GO was prepared by a modified Hummers method.^{51,101} In a typical experiment, 1 g of pristine graphite was added to 60 mL of sulfuric acid in a round-bottom flask placed in an ice bath. 3.5 g of potassium permanganate were then gradually added over a period of 15 minutes. After 2 hours of stirring at room temperature, the round-bottom flask was again cooled to 0°C. 200 mL of deionized water were slowly added, followed by 2.5 mL of hydrogen peroxide (30% w/v). The formed material was filtered and washed several times with deionized water, hydrochloric acid (10% w/w), ethanol and acetone before being vacuum-dried to yield a black powder, named graphite oxide (Gr-O). An aqueous dispersion of GO was prepared by sonicating dried Gr-O in deionized water (1.5 g/L) for 1 hour. In order to prepare prGO, 5 mL of the GO suspension were diluted with water, under stirring, to 20 mL. The solution was heated to 100°C and 4.3 mL of sodium citrate (1% w/w) were added. After 2 hours (prGO) or 24 hours (rGO) the reaction mixture was left to cool to room temperature.

3.2.5. Synthesis of Ti_xO_2

Ti_xO_2 nanosheets were prepared by exfoliation of a lithium-potassium layered titanate.^{40,41,42} In a typical procedure, 84 mg of K_2CO_3 , 15 mg of Li_2CO_3 , and 200 mg of TiO_2 were mixed with an agate mortar and pestle for 30 minutes and calcined in air at 800°C for 2 hours. The powder was then again mixed for 30 minutes and calcined in air at 800°C for another 24 hours. $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ was suspended in water and washed through several cycles of centrifugation at the speed of 7,000 g and supernatant removal. 0.1 g of $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ were then suspended in 25 mL of a 1 M HCl aqueous solution and left under stirring at room temperature for 24 hours. This procedure was repeated two more times, and the product collected by centrifugation and resuspended in fresh 1M HCl solutions. $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$ was collected by centrifugation at the speed of 7,000 g and washed through successive cycles of centrifugation and removal of the supernatant. Finally, this product was suspended in 25 mL of a 0.3 M aqueous tetrabutylammonium hydroxide solution and the mixture was left under stirring for two weeks to yield $\text{Ti}_{0.87}\text{O}_2^{0.52-}$ nanosheets, that were collected by centrifugation at the speed of 28,000 g, washed by successive cycles of centrifugation and supernatant removal, and re-suspended in water for further use.

3.3. Preparation of Hybrid Materials

3.3.1. Ex-situ Approach for the synthesis of M/Ti_xO₂, M/(pr)GO and M/Ti_xO₂/(ppr)GO

A suspension containing 2 or 4 μmol of metal nanoparticles, depending on the desired mass ratio, was thoroughly washed with ethanol and water. After resuspension in water, the metal was mixed with 1 mg of Ti_xO₂ or P25 and/or with 0.35 mg of GO or prGO. The final volume was brought to 1.5 mL and the obtained suspension was left under stirring at room temperature for 24 hours. Metal and Ti_xO₂ contents were determined by FAAS and TG analyses, respectively, of the starting suspensions.

3.3.2. In-situ approach for the synthesis of Au/Ti_xO₂, Au/(pr)GO and Au/Ti_xO₂/(pr)GO

2.5 mL of a 2.0 mM aqueous solution of H₂AuCl₄·3H₂O were mixed with 47.5 mL of water in a round bottom flask. The reaction mixture was heated to a boiling. 2.5 mg of Ti_xO₂, and/or 0.875 mg of GO or prGO were added to the boiling solution. After one minute, 500 μL of sodium citrate (1% m/m) were added. After 30 minutes of reaction under stirring the mixture was left to cool to room temperature.

3.3.3. In-situ approach for the synthesis of Pd/Ti_xO₂

48 mL of water were heated to 89°C in a round bottom flask. 1 mL of sodium citrate (1% m/m) was added to the reaction mixture, together with 2.5 mg of Ti_xO₂. After one minute, 2.5 mL of a 2.0 mM aqueous solution of K₂PdCl₄ were also added. After 15 hours of reaction under stirring the mixture was left to cool to room temperature.

3.4. Material Characterization

Scanning electron microscopy (SEM) images were obtained with a Jeol FEG-SEM JSM 6330F microscope operated at 5 kV. The samples for SEM were prepared by drop-casting an aqueous suspension of the nanostructures over a Si wafer, followed by drying in air. Size of the nanoparticles was determined by individually measuring the diameter of ~200 nanoparticles from SEM images. Transmission electron microscopy (TEM) images were obtained with a Jeol 1010 microscope operated at 80 kV. The samples for TEM were prepared by drop-casting an aqueous suspension of the nanostructure over a carbon-coated copper grid, followed by drying in air.

UV-VIS spectra were obtained from aqueous suspensions of the nanostructures with a Shimadzu UV-2600 spectrophotometer. Raman and SERS spectra were acquired on a Renishaw Raman System 3000 equipped with a CCD detector and coupled to a microscope. The laser beam was focused on the sample by using a 50x lens. The experiments were performed under ambient conditions in a back-scattering geometry. The samples were irradiated with a (He-Ne) 632.8 nm

line with controlled laser power outputs. All Raman spectra were acquired in a single scan with 10-second accumulation time.

Concentration of Au, Pd and Ag in all nanocatalyst suspensions was determined by FAAS using a Shimadzu AA-6300 atomic absorption spectrophotometer.

X-ray diffractograms were obtained using a Bruker D2 Phaser equipment with a standard Cr/Co/Cu ceramic sealed tube ($\lambda = 0.154060$ nm). Integration time was set to 0.75 s and step to 0.03° . XRD samples were prepared by drop-casting 100 μL of nanostructure suspension over a microscopy cover slip followed by drying in air

TGA analyses were performed using a thermal analysis Shimadzu DTG 60 equipment. 5 mg of dried sample were heated in an open platinum crucible under a $50 \text{ mL}\cdot\text{min}^{-1}$ air flow from room temperature up to 600°C with a heating rate of $10^\circ\text{C}/\text{min}$.

Atomic force microscopy (AFM) images were obtained with a PicoSPM microscope coupled to PicoScan 2100 and MACMode™ controllers (Agilent Technologies). Mac Levers – Type II tips were used in intermittent contact mode, with a resonance frequency of ~ 70 kHz and a force constant of $\sim 2,8$ N/m. AFM samples were prepared by deposition of 2 μL of nanostructure suspension on a freshly cleaved mica surface (Ted Pella Inc) followed by drying in air.

3.5. Catalytic Tests

3.5.1. Reduction of 4-nitrophenol

In a 4 ml quartz cuvette, 500 μl of a $1.4 \cdot 10^{-4}$ M solution of 4-nitrophenol and 1 ml of a $4.2 \cdot 10^{-2}$ M solution of NaBH_4 were mixed with a few microliters of a washed catalyst suspension. UV-VIS absorption spectra in the range from 250 to 500 nm are collected at intervals of 15 or 30 seconds. The relative concentration of 4-nitrophenol C/C_0 was obtained from the relative intensity of the absorption peak at 400 nm.

3.5.2. SPR-mediated Oxidation of PATP

In a typical procedure, 1.5 mL of catalyst suspension was centrifuged at the speed of 28,000 g and, after supernatant removal, the solid was re-suspended in 15 μL of water, drop-cast onto a 1x1 cm Si(001) surface and dried in air. 40 μL of a 1.0 mM PATP ethanolic solution was then drop-cast on the substrate, followed by drying under ambient conditions. All samples were used for SERS measurements immediately after preparation.

4. Results and discussion

4.1. Synthesis of Ti_xO_2

Titanium oxide nanosheets (Ti_xO_2) with titanate crystal structure were successfully prepared by following a procedure firstly reported by Sasaki et Al. in 1996.⁶⁷ Following this method, we synthesized the layered titanate of formula $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ by two cycles of crushing and calcination at 800°C and submitted it to ion exchange in an acidic solution to produce $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$. During these steps, purity and crystalline structures of the intermediate materials were confirmed by X-Ray diffraction (**Figure 4**).

Figure 4. X-Ray diffractograms of $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ (A) and $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$ (B).

The resulting protonic titanate was then exfoliated by treatment with tetrabutylammonium hydroxide (TBAOH) in aqueous solution. In this step, intercalation of the bulky TBA^+ ion in the interlayer space of $\text{H}_{1.07}\text{Ti}_{1.73}\text{O}_4 \cdot \text{H}_2\text{O}$ leads to separation of the lamellar titanate into single nanosheets.¹⁰² After removal by centrifugation of excess TBAOH, we obtained a stable suspension of Ti_xO_2 .

Microscopic characterization of Ti_xO_2 revealed a lateral size of 1-5 μm and confirmed the complete exfoliation of the material, with a nanosheet thickness of 0.8 nm (**Figure 5A-C**). UV-VIS spectroscopy indicated an absorption maximum at 270 nm (**Figure 5D**): in fact, due to the extreme thinness of Ti_xO_2 , quantum confinement effects cause its optical gap to reach 3.8 eV,¹⁰³ a much higher value than the 3.2 eV commonly observed in TiO_2 nanoparticles. The absorption of electromagnetic radiation by Ti_xO_2 is thus only possible with $\lambda < 320$ nm.

These Ti_xO_2 nanosheets present Ti vacancies that give them a 0.87:2 Ti:O ratio, and thus a partial negative charge. This is a direct consequence of the top-down preparation method, since $\text{K}_{0.8}\text{Ti}_{1.73}\text{Li}_{0.27}\text{O}_4$ contains Li^+ cations embedded in the Ti-O lattice that are removed during the exfoliation process, leaving vacancies in the structure.⁶⁷ Raman spectrum and X-ray diffraction patterns (Error! Reference source not found.**E-F**) confirmed the formation of Ti_xO_2 in the titanate structure without the presence of any crystalline impurities.^{67,104}

Figure 5. SEM image (A), AFM image (B), AFM line profile (C), UV-VIS spectrum (D), Raman spectrum (E), and X-Ray diffractogram (F) of the Ti_xO_2 nanosheets.

4.2. Synthesis and controlled reduction of GO

Graphene oxide was produced by a modified Hummers method.^{51,101} We approached its controlled reduction using sodium citrate: after being treated at the temperature of 100°C for different periods of time spanning from 10 minutes to 24 hours, several samples of aqueous GO were submitted to UV-VIS absorption spectroscopy in order to investigate their levels of reduction. By using Tauc's expression it is in fact possible to extract information regarding the band gap of the materials from the absorption band situated in the near-UV region.^{52,105,106} The wide band at 225-235 nm that arises from π - π^* transitions that can be observed in GO, corresponding to a gap energy of 3.5-4 eV, is known to undergo a red-shift when reduction occurs, up to a maximum wavelength of 270 nm, corresponding to a gap energy under 1 eV, in completely reduced GO.⁵²

The results of gradual reduction of the material are shown in **Table 2** and in **Error! Reference source not found..**

Sample	Reduction time (minutes)	Absorption peak position (nm)	Gap energy (eV)
GO	0	231	3.5
prGO-1	10	233	2.4
prGO-2	30	235	2.3
prGO-3	60	243	1.4
prGO-4	120	248	1.2
rGO	1440	268	1.0

Table 2. Comparison of absorption peak maximum wavelengths and band gap energy values of GO samples submitted to reduction for different periods of time.

Although treatment for up to one hour (prGO-1, 2, 3) achieved little or no modification of the GO, after two hours of reaction (prGO-4) a small but noticeable red-shift of the absorption band can be observed. Whereas the magnitude of the peak shift is moderate, the change in band gap energy is considerable, indicating a material with much different electronic properties. We defined this material as partially reduced graphene oxide (prGO). In the case of GO submitted to the 24-hour treatment, complete reduction was achieved and a suspension of strongly hydrophobic reduced graphene oxide (rGO) was obtained.

Figure 6. UV-VIS absorption spectra (A) and appearance (B) of aqueous solutions of GO, prGO and rGO.

Our attention was thus focused on as-synthesized GO, prGO-4 (2 hours of reduction) and rGO (24 hours of reduction) for the preparation of the hybrid materials. However, we soon realized as we begun the preparation of hybrids that the hydrophobic nature of rGO led to a substantial loss of the material whenever transfer from a vessel to another occurred, an inevitable event in the preparation and application of nanocatalysts. As a consequence, control over the metal:support ratio was possible in hybrids containing GO and prGO, but not in those comprising rGO. We decided to focus our efforts on the two former materials, and thus to work with M/GO, M/prGO, M/Ti_xO₂/GO and M/Ti_xO₂/prGO materials. As a convention, we use M/(pr)GO when

discussing phenomena and procedures common to M/GO and M/prGO, and M/Ti_xO₂/(pr)GO for M/Ti_xO₂/GO and M/Ti_xO₂/prGO.

Characterization of GO and prGO was completed through Raman spectroscopy, confirming different physical-chemical properties for the two supports (**Figure 7**). As can be seen in **Figure 7A**, we detected two distinct bands in the Raman spectrum of GO: the D band, at approximately 1334 cm⁻¹, arises from a breathing mode of A_{1g} symmetry, and its intensity is inversely proportional to the size of sp² domains in the graphitic lattice; the G band, at approximately 1600 cm⁻¹, results from an in-plane bond-stretching mode of E_{2g} symmetry, and does not require the presence of aromatic rings (**Figure 7B**).

Figure 7. Raman spectra for GO and prGO (A) and vibrational modes of the graphitic lattice responsible for the observed D and G bands (B).

These same peaks are present in the Raman spectrum of prGO, although their relative intensity I_G/I_D shows a marked decrease. As the reduction of GO to prGO causes smaller, more numerous sp² domains to form, the intensity of the D band increases, and by showing that $I_G/I_D(\text{prGO}) < I_G/I_D(\text{GO})$ we further confirm that a reduced material, abundant in sp² domains, is obtained by treatment of GO.^{107–109}

4.3. Au-based hybrid materials

We synthesized spherical gold nanoparticles (Au NPs) according to the Turkevich method,⁹⁴ adding sodium citrate to a hot aqueous chloroauric acid solution. A temperature of 100°C, a molar ratio of 3.5:1 (citrate:gold) and a reaction time of 30 minutes were optimal for the synthesis of monodisperse Au NPs of the desired size. SEM images confirm that the nanoparticles present a spherical shape (Figure 8A) with a diameter $d = 15.5 \text{ nm} \pm 1.5 \text{ nm}$ (Figure 8B). Aqueous suspensions of Au NPs display a bright red color (Figure 8C), coherently with the narrow absorption band observed in their UV-VIS spectrum, peaking at 521 nm, that can be attributed to surface plasmon resonance excitation of their LSPR dipole mode (Figure 8D).⁹⁵

We then approached the synthesis of hybrid materials by comparing three different procedures. We used Au/GO and Au/Ti_xO₂ as model systems to identify the best approach to produce all hybrids, as well as to determine the optimal ratios between the components.

We first employed an *ex-situ* approach, by which aqueous suspensions of the components were mixed and left under stirring for 24 hours. Au NPs were washed by centrifugation before GO and Ti_xO₂ were added, however, we observed that the washing step caused a considerable loss of material as well as aggregation of the spheres.

We then tried mixing Au NPs with GO or Ti_xO₂ suspensions without removing the excess stabilizing agent. This method yielded better results, with a satisfactorily homogeneous distribution of Au NPs over the support surface.

Figure 8. SEM image (A), size distribution (B), appearance (C) and UV-VIS absorption spectrum (D) of Au NPs.

Lastly, we evaluated the *in-situ* approach: the synthesis of Au NPs was conducted as usual, but concentrated GO or Ti_xO_2 suspensions were also added to the hot chloroauric acid solution shortly before the sodium citrate. In this case, the distribution of Au NPs over the support surface was found to be homogeneous and their shape and size were not affected by the presence of the support. However, *in-situ* reduction of chloroauric acid has some disadvantages: it eliminates the possibility of fine-tuning the reduction state of GO, as the support is inevitably affected by the presence of the sodium citrate needed to produce Au NPs; moreover, it calls for convoluted methods to assess the actual mass ratio between components. In fact, it is no longer possible to determine the mass of each material before mixing, but various analyses are required to

ascertain the composition of the hybrid structure. After the evaluation of all available methods for the preparation of hybrids, we selected the *ex-situ* immobilization of unwashed Au NPs over the supports for most applications.

The relative composition of the hybrids was tuned through qualitative observation of SEM images. We aimed at the synthesis of a structure where all three starting materials were present in comparable quantities: with the overabundance of any one structure in the hybrids, their properties could be mainly influenced by its presence, with little or no contribution from the other materials. Thus, we picked a 2.3:2.9:1 Au:Ti_xO₂:GO mass ratio as a starting point to be further optimized for each application (**Figure 9A-C**). Formation of the hybrids was further confirmed by UV-VIS spectra of the materials, where the different components' peaks were identified (**Figure 9D-F**).

It has been recently established that the LSPR excitation in Au NPs can lead to the formation of hot electrons (electrons that transiently occupy levels above the Fermi level during plasmon oscillation) and holes.¹¹⁰ Under proper conditions, these species can trigger charge transfer processes at the metal-molecule interface and mediate oxidation or reduction transformations.²⁰

Figure 9. SEM images of Au/TiO₂ (A), Au/GO (B) and Au/TiO₂/GO (C) and normalized UV-VIS extinction spectra recorded from aqueous suspensions containing the hybrid materials and their individual components (D, E, F).

Thus, we employed the selective SPR-mediated oxidation of p-aminothiophenol (PATP) to p'-dimercaptobenzene (DMAB) as a model transformation in order to investigate the hybrids' plasmonic catalytic activities. In this system, it has been shown that SPR-excited hot electrons can be transferred to adsorbed oxygen species, which in turn contribute to the PATP oxidation to DMAB, as shown in the mechanism in **Figure 10**.^{111–113} As this transformation is very sensitive to charge transfer processes, it represents an excellent probe to monitor how the modulation of charge transfer processes at the nanoscale among different materials can affect the SPR-mediated performances.²⁹ Another attractive feature is that this reaction can be studied in a Raman spectrophotometer, in which the incident laser can work both as the SPR excitation source and to probe the PATP conversion by the SERS effect.^{114,115}

We employed pure Au NPs as well as Au/GO, Au/prGO, Au/Ti_xO₂, Au/Ti_xO₂/GO and Au/Ti_xO₂/prGO *ex-situ* hybrids for the catalytic tests. In all cases, the previously mentioned 2.3:2.9:1 mass ratio between components was maintained.

Figure 10. Scheme of SPR-mediated oxidation of PATP to DMAB under laser exposure.

Our results are summarized in Error! Reference source not found.. The spectra contain two sets of bands: the signals at 1081, 1142, 1390, 1433 and 1575 cm⁻¹ can be assigned to the A_g modes of DMAB while the signals at 1081, 1489 and 1593 cm⁻¹ can be assigned to the A₁ modes of PATP.¹¹¹ PATP conversion can be inferred by the 1433:1081 cm⁻¹ DMAB:(PATP+DMAB) intensity ratios.^{114,116} DMAB:(PATP+DMAB) ratios followed the order: Au/prGO > Au/GO > Au/Ti_xO₂/prGO > Au/Ti_xO₂/GO > Au NPs = Au/Ti_xO₂, corresponding respectively to 0.251 ± 0.056, 0.148 ± 0.035, 0.074 ± 0.020, 0.065 ± 0.024, 0.049 ± 0.022 and 0.052 ± 0.022. Coherently with the SPR-mediated mechanism for DMAB formation, PATP conversion increases with laser power, as can be observed in **Figure 12**.^{114,116}

Figure 11. SERS spectra (A) and 1433:1081 cm⁻¹ DMAB:(PATP+DMAB) intensity ratios (B) for Au NPs, Au/Ti_xO₂, Au/GO, Au/prGO, Au/Ti_xO₂/GO and Au/Ti_xO₂/prGO materials that had been functionalized with PATP (red, green, blue, light blue, purple and yellow traces, respectively). These spectra were acquired by using 0.13 mW as the laser irradiation power. All spectra were normalized employing the 1081 cm⁻¹ signal as reference.

Our proposed mechanisms are illustrated in **Figure 13**. The addition of GO and prGO to Au NPs produced a positive effect over the catalytic performance of the material (**Figure 13A**). As supported by previous studies,¹⁰⁹ visible light triggers electron excitation above the Fermi level in GO and prGO, and electron density promptly reaches the already resonant Au NPs, where DMAB production is boosted. Between the two supports, prGO shows the greatest enhancement in catalytic activity, coherently with its higher electrical conductivity and visible light response. On the contrary, addition of Ti_xO₂ to pure Au NPs did not affect the rate of PATP oxidation, suggesting that no electron transfer is taking place in Au/Ti_xO₂ (**Figure 13B**).

Figure 12. Laser-power-dependent SERS spectra for Au NPs (A), Au/GO (B), Au/prGO (C), Au/Ti_xO₂ (D), Au/Ti_xO₂/GO (E) and Au/Ti_xO₂/prGO (F) that had been functionalized with PATP. All spectra were normalized with respect to the band located at 1081 cm⁻¹.

The tri-component hybrids Au/Ti_xO₂/GO and Au/Ti_xO₂/prGO both show a PATP oxidation rate slightly higher than that of Au NPs. In this case, PATP oxidation is mainly a consequence of Au NPs excitation, and no Au $\leftrightarrow$ Ti_xO₂ interaction takes place. At the same time, (pr)GO $\rightarrow$ Au electron transfer is almost completely disrupted, as the conduction band of Ti_xO₂ traps excited (pr)GO electrons and prevents most of them from reaching Au NPs (**Figure 13C**). As expected, PATP conversion is higher for Au/Ti_xO₂/prGO than for Au/Ti_xO₂/GO, reflecting what was already observed in the comparison between Au/GO and Au/prGO.

Figure 13. Proposed charge transfer mechanisms and energy level diagrams for Au/(pr)GO (A), Au/ Ti_xO_2 (B) and Au/ Ti_xO_2 /(pr)GO (C) materials that had been excited at 633 nm. In (A), electrons can be transferred from GO and prGO to Au NPs, increasing the populations of hot electrons that can be transferred to adsorbed O_2 producing O_2^- and contributing to the PATP oxidation. In (B), excited Au NPs electrons alone are responsible for the production of O_2^- ions, whereas Ti_xO_2 does not participate in the reaction. In (C), excited GO and prGO electrons are trapped in the conduction band of Ti_xO_2 and do not contribute to the formation of O_2^- over the surface of Au NPs.

Next, we investigated the effect of Ti_xO_2 , GO and prGO over the catalytic activity of Au NPs in the reduction of 4-nitrophenol to 4-aminophenol. The model reaction is illustrated in **Figure 14**. In this catalytic test, a few microliters of a diluted 4-nitrophenol solution are dissolved in water in the presence of an excess of reducing agent ($NaBH_4$). 4-nitrophenol readily deprotonates due to the alkaline environment, forming 4-nitrophenolate, whose yellow color gives place, in the UV-VIS spectra, to an intense peak at 400 nm. When a catalyst is added, complete reduction to 4-aminophenol is quickly achieved. The starting yellow solution becomes completely clear as reduction occurs: during this step, the UV-VIS peak of 4-nitrophenolate disappears and a weaker

signal rises at 300 nm, originating from 4-aminophenol. Due to the large excess of NaBH_4 , the reaction can be considered pseudo-first order with respect to 4-nitrophenol concentration.

Figure 14. Mechanism and typical time-dependent UV-VIS spectra for the reduction of 4-nitrophenol to 4-aminophenol.

Most supported nanocatalysts described in the literature owe their shape, size and stability – and thus their high catalytic activity – to synthesis methods that promote nanoparticle growth over a support surface. As a consequence, in these studies it is often hard to distinguish between performance enhancements originating from nanoparticle morphology and from metal-support interactions. For our catalytic tests, on the other hand, we employed Au NPs, Au/ Ti_xO_2 , Au/GO, Au/prGO, Au/ Ti_xO_2 /GO and Au/ Ti_xO_2 /prGO prepared by *ex-situ* impregnation of unwashed Au NPs suspensions: with this method, properties of Au NPs were the same in all samples, allowing us to observe fluctuations in catalytic performance that arose directly from the participation of

Ti_xO₂, GO and prGO in the catalytic mechanism. The employed catalyst suspension volumes were chosen as to provide 0.9 µg of Au loading in all cases.

Our results are summarized in **Table 2** and in **Figure 15**. We could observe that reduction took place in all cases, with Au NPs showing an intermediate rate between its supported forms. Au/Ti_xO₂ and Au/GO display a catalytic performance that is slightly lower than that of Au NPs: this can be attributed to the reduction of available Au surface in the hybrids, as a portion of the nanoparticle area is now in direct contact with a support. We believe that no strong interactions are affecting the catalytic process in the presence of these two hybrids: both Ti_xO₂ and GO surfaces present a partial negative charge, the former due to Ti vacancies in the crystalline lattice, and the latter due to hydroxyl and carboxyl functional groups that deprotonate in the alkaline environment. As a consequence, significant adsorption of 4-nitrophenolate cannot take place.

Material	k (s ⁻¹)
Au NPs	6.71 · 10 ⁻³
Au/Ti _x O ₂	5.03 · 10 ⁻³
Au/GO	6.21 · 10 ⁻³
Au/prGO	1.2 · 10 ⁻²
Au/Ti _x O ₂ /GO	6.99 · 10 ⁻³
Au/Ti _x O ₂ /prGO	1.45 · 10 ⁻⁴

Table 2. Pseudo-first order kinetic constants for the catalytic reduction of 4-nitrophenol carried out in the presence of gold-based hybrids.

Interestingly, prGO-based and tri-component materials displayed a different behavior: catalytic performance of Au/prGO is significantly superior to that of Au NPs, Au/Ti_xO₂/GO shows the same conversion rate as pure Au NPs and Au/Ti_xO₂/prGO appears to be a very poor catalyst.

Figure 15. Plots of 4-nitrophenol % concentration as a function of time for catalytic reduction tests with Au NPs, Au/Ti_xO₂, Au/GO, Au/prGO, Au/Ti_xO₂/GO and Au/Ti_xO₂/prGO as catalysts obtained by UV-VIS spectroscopy measurements at 400 nm (A), and % conversion of 4-nitrophenol to 4-aminophenol after 5 minutes of reaction in the presence of each of the catalysts (B).

In Au/prGO, we believe that π - π stacking takes place between prGO and 4-nitrophenol, enhancing substrate adsorption onto the catalyst surface and boosting reduction rate. π - π interactions are reported to take place between graphene-based materials and aromatic compounds, with their force being proportional to the support's hydrophobicity.^{117,118} The removal from the surface of GO of hydrophilic functional groups that takes place during reduction to prGO permits the latter to establish π - π interactions that were impossible in pristine GO, and adsorption of 4-nitrophenol on prGO facilitates reduction over the close Au NPs, also immobilized on the support's surface. Reduction of GO is thus responsible for the substantial difference in performance of Au/GO and Au/prGO, and this treatment proves to be crucial in the preparation of hybrid nanomaterials to be employed as catalysts in the presence of aromatic substrates.

In Au/Ti_xO₂/GO and Au/Ti_xO₂/prGO, a new support-support interaction must be taken into account. In fact, graphene-based materials and Ti_xO₂ nanosheets are known to undergo self-assembly, with the formation of uniform, stacked GO-Ti_xO₂ and prGO-Ti_xO₂ composites.¹¹⁹ This

phenomenon can cause segregation of Au NPs from the nanosheets, leading the metal to behave in the same manner as when no support is introduced into the system. However, consequences are remarkably different for the two hybrids.

In Au/Ti_xO₂/GO, exclusion of Au NPs from the support surface simply allows its catalytic sites to be fully exposed, and thus conversion rate can reach the same level that was observed in pure Au NPs. In Au/Ti_xO₂/prGO, Au NPs surface is also exposed, but π - π stacking between prGO and 4-nitrophenol causes the substrate to be retained within the prGO-Ti_xO₂ composite, subtracted from interaction with Au NPs. As a result, conversion rate sharply drops.

Having identified Au/prGO as the most efficient catalyst for 4-nitrophenol reduction, we probed its stability by submitting the material to 10 cycles of reaction: during the catalytic test, we introduced fresh 4-nitrophenol into the reaction mixture as soon as UV-VIS measurements revealed that the substrate had been completely consumed. Our results are summarized in **Table 3** and in **Figure 16**. The initial 5-minute 4-nitrophenol conversion of 93.8% steadily declines in the first 6 cycles, after which it stabilizes around 70%. Conversion efficiency thus suffers a 25% drop after 10 cycles.

Cycle	k (s ⁻¹)	Cycle	k (s ⁻¹)
1	1.2 · 10 ⁻²	6	5.5 · 10 ⁻³
2	1.2 · 10 ⁻²	7	4.8 · 10 ⁻³
3	7.0 · 10 ⁻³	8	4.8 · 10 ⁻³
4	7.0 · 10 ⁻³	9	4.5 · 10 ⁻³
5	6.3 · 10 ⁻³	10	4.5 · 10 ⁻³

Table 3. Pseudo-first order kinetic constants for 10 successive cycles of catalytic reduction of 4-nitrophenol carried out in the presence of Au/prGO.

This data reveals that the catalyst is still largely active in the reduction after prolonged use, although only in the first 4 cycles performance is superior to that of fresh, pure Au NPs. Performance loss can be attributed to stacking of the prGO nanosheets, which reduces the surface area available for 4-nitrophenol adsorption.

Figure 16. Plots of 4-nitrophenol % concentration as a function of time for 10 successive cycles of catalytic reduction tests with Au/prGO, obtained by UV-VIS spectroscopy measurements at 400 nm (A), and % conversion of 4-nitrophenol to 4-aminophenol after 5 minutes of reaction in each cycle (B).

4.4. Palladium-based hybrid materials

We synthesized spherical palladium nanoparticles (Pd NPs) through an adaptation of the Turkevich method, with the parameters we employed for Au NPs as a starting point. Potassium tetrachloropalladate (K_2PdCl_4) was used in this case as a metal precursor. We employed a citrate:palladium molar ratio of 7:1, a reaction temperature of 89°C and a reaction time of 15 hours. We observed that tetrachloropalladate does not present the same thermal stability as tetrachloroaurate: uncontrolled nucleation results from heating aqueous K_2PdCl_4 in the absence of reducing agents, precluding controlled nanoparticle synthesis. As a consequence, the addition

order of the reagents was switched, and K_2PdCl_4 was added to a boiling citrate solution, which led to monodisperse Pd NPs. SEM images confirm that the nanoparticles display a spherical shape (**Figure 17A**) and a diameter $d = 40.9 \text{ nm} \pm 4.5 \text{ nm}$ (**Figure 17B**).

Figure 17. SEM image (A) and size distribution (B) of Pd NPs.

In this case, no notable optical properties were detected for the metal nanoparticles, as surface plasmon resonance in the case of palladium falls out of the visible range of the electromagnetic spectrum, more specifically in the UV region. As a consequence, suspensions of Pd NPs only present a faint yellow color originating from unconsumed K_2PdCl_4 .

We then began the preparation of supported Pd NPs by the *in-situ* approach, with the reduction of tetrachloropalladate over Ti_xO_2 and prGO through the same procedure described for gold-based materials. We obtained Pd/ Ti_xO_2 and Pd/prGO hybrids with metal:support mass ratios of 1:1 and 2.8:1, respectively. As shown by the SEM and TEM images in **Figure 18A-C** and by the size distribution histogram in **Figure 18D**, in both Pd/ Ti_xO_2 and Pd/prGO mean particle size displays a severe drop if compared to pure Pd NPs. In fact, the presence of a 2D support in the reaction mixture played a crucial role in the path that lead to the formation of Pd NPs.

Figure 18. SEM image of Pd/prGO (A). SEM (B) and HRTEM (C) images and size distribution histogram (D) of Pd/Ti_xO₂ prepared by the *in-situ* approach. Inset scale: 2 nm.

We believe adsorption of metallic precursor and of newly formed metal clusters over support surface promoted nanoparticle nucleation in close proximity to Ti_xO₂ and prGO. At this point, the stabilizing effect exerted by the supports further directed the nanoparticle growth, which led to the formation of nanoparticles at the surface of the supports.

We were able to achieve a narrow nanoparticle size distribution in Pd/Ti_xO₂, where monodisperse Pd NPs with a diameter $d = 2.4 \text{ nm} \pm 0.4 \text{ nm}$ were deposited over the nanosheets. On the other hand, we observed a weaker adsorption/stabilizing effect in prGO, that could only

partially direct the formation of smaller Pd NPs. In this case, larger nanoparticles ($d \approx 40$ nm) were still detected at the surface of the prGO.

Consequently, we probed the catalytic performance of Pd/Ti_xO₂ employing the reduction of 4-nitrophenol to 4-aminophenol as a model reaction aiming to determine if the ultrasmall nanoparticles that can be obtained in the presence of Ti_xO₂ actually present a superior performance in catalytic applications as compared to the commercial Pd/C catalyst.

The results of our catalytic tests are summarized in **Figure 19A**. We used palladium on carbon (Pd/C) with a 10% weight loading as a reference. This material is commonly employed in an industrial context for hydrogenation and coupling reactions, and comprises irregular palladium micro- and nanoparticles immobilized over activated carbon. As can be seen from SEM images in **Figure 19B-C**, palladium distribution is radically different in the two materials.

Figure 19. Plots of 4-nitrophenol % concentration as a function of time for catalytic reduction tests with Pd/Ti_xO₂ and Pd/C obtained by UV-VIS spectroscopy (A), and SEM images of Pd/Ti_xO₂ (B) and Pd/C (C).

The Pd loading corresponded to 0.5 μg in all cases. As can be seen from the kinetic plot, at this loading, Pd/Ti_xO₂ completely reduces 4-nitrophenol in less than 15 minutes, whereas Pd/C is barely active. The difference can be undoubtedly attributed to the high number of catalytic sites presented by the finely divided palladium nanoparticles in Pd/Ti_xO₂, making this material very attractive for catalytic applications.

4.5. Silver-based hybrid materials

We prepared spherical silver nanoparticles (Ag NPs) using AgNO₃ as a metal precursor. Due to the high reactivity of this reagent, the first attempts to produce Ag NPs with the use of sodium citrate in aqueous solution (Lee-Meisel method) did not yield satisfactory results, and the more robust polyol method had to be employed instead. We carried out the reaction at a temperature of 125°C, with ethylene glycol as a solvent and source of reducing agents and polyvinylpyrrolidone (PVP) as a stabilizing agent.

As seen from SEM images (**Figure 20A**), the obtained Ag NPs displayed spherical shape and monodisperse size, with a diameter of 37 nm $\pm$ 5 nm (**Figure 20B**). Aqueous suspensions of Ag NPs display a yellow-green color (**Figure 20C**), and their UV-VIS spectrum show an intense peak at 429 nm (**Figure 20D**), originating once again from surface plasmon resonance.

Figure 20. SEM image (A), size distribution (B), appearance (C) and UV-VIS absorption spectrum (D) of Ag NPs.

We employed the *ex-situ* approach to assemble Ag/Ti_xO₂, Ag/prGO and Ag/Ti_xO₂/prGO, mixing aqueous suspensions of the components with an Ag:Ti_xO₂:prGO mass ratio of 1:2.4:1.3. Due to the stronger nature of the interaction of the metal surface with PVP if compared with sodium citrate, washing of Ag NPs before impregnation was necessary. Nonetheless, we obtained uniform dispersions of Ag NPs over the surface of the 2D supports, as can be observed in the SEM images in **Figure 21A-C**. Formation of the hybrids was also confirmed by UV-VIS extinction spectra, as can be seen in **Figure 20D-F**.

Figure 21. SEM images of Ag/TiO₂ (A), Ag/prGO (B) and Ag/TiO₂/prGO (C) materials and normalized UV-VIS extinction spectra recorded from aqueous suspensions containing the hybrid materials and their individual components (D, E, F).

In order to investigate the hybrids' plasmonic catalytic activities, we once again employed the selective SPR-mediated oxidation of PATP to DMAB. The same electron-mediated mechanism responsible for DMAB formation in Au NPs (**Figure 10**) can take place over the surface of PATP-functionalized Ag NPs. In the case of silver-based hybrids, however, many reports suggest that the holes produced during SPR excitation can also participate and drive the PATP oxidation to DMAB, giving place to a different electronic mechanism, illustrated in **Figure 22** (hole pathway).^{120–123}

Figure 22. Scheme of SPR-mediated oxidation of PATP to DMAB under laser exposure by the hole pathway.

The SERS spectra for Ag NPs, Ag/Ti_xO₂, Ag/prGO, and Ag/Ti_xO₂/prGO materials that had been functionalized with PATP are shown in **Figure 23A** (red, green, orange, and blue traces, respectively) while DMAB:(PATP+DMAB) intensity ratios are depicted in **Figure 23B**.

Figure 23. SERS spectra (A) and 1433:1081 cm⁻¹ DMAB:(PATP+DMAB) intensity ratios (B) for Ag NPs, Ag/Ti_xO₂, Ag/prGO, and Ag/Ti_xO₂/prGO materials that had been functionalized with PATP (red, green, orange, and blue traces, respectively). These spectra were acquired by using 0.13 mW as the laser irradiation power. All spectra were normalized employing the 1081 cm⁻¹ signal as reference.

Our results indicate that PATP oxidation took place on the surface of all Ag-based materials, albeit the conversion was strongly dependent on the nature of the hybrid material employed as plasmonic catalyst. The DMAB:(PATP+DMAB) ratios followed the order: Ag/Ti_xO₂/prGO =

Ag/prGO > Ag/Ti_xO₂ > Ag NPs, corresponding to 0.55 ± 0.07 , 0.55 ± 0.07 , 0.40 ± 0.08 and 0.20 ± 0.03 for Ag/Ti_xO₂/prGO, Ag/prGO, Ag/Ti_xO₂, and Ag NPs, respectively. Here, it is important to note that all hybrids displayed higher PATP conversions as compared to pure Ag NPs. Moreover, as shown in **Figure 24**, an increase in PATP conversion as a function of the laser-irradiation power was observed for all Ag-based materials, which is in agreement with the SPR-mediated mechanism for DMAB formation.^{114,116}

Figure 24. Laser-power-dependent SERS spectra for Ag NPs (A), Ag/Ti_xO₂ (B), Ag/prGO (C), and Ag/Ti_xO₂/prGO that had been functionalized with PATP. All spectra were normalized with respect to the band located at 1081 cm⁻¹.

The proposed mechanism for explaining the observed differences in PATP conversion is illustrated in **Figure 25** and **Figure 26**. In prGO, electrons can be excited across the band gap under 633 nm excitation. These excited electrons can, in turn, be transferred to Ag NPs as depicted in **Figure 25A**. As Ag NPs also present SPR-excited hot electrons under 633 nm illumination, charge

transfer from prGO to Ag NPs leads to an increase in the population of hot electrons in Ag NPs that can be transferred to adsorbed O₂ molecules, contributing to an increase in the PATP conversion in the Ag/prGO hybrid as compared to pure Ag NPs (**Figure 25A**). On the other hand, electrons cannot be excited across the band gap in the Ti_xO₂ nanosheets under 633 nm illumination. Therefore, Ti_xO₂ behaves as an acceptor of SPR excited hot electrons from Ag in the Ag/Ti_xO₂ hybrid (**Figure 25B**).¹⁰³ As the work function of Ag is estimated to be smaller than that of Ti_xO₂ (4.8 vs 5.0),^{103,124,125} AgNPs→Ti_xO₂ electron transfer should readily occur upon contact and intensify under laser radiation. This leads to the accumulation of positive charges (holes) in the Ag NPs that can also act as a direct oxidizing agents, subtracting electrons from PATP molecules and driving its oxidation to DMAB (**Figure 25B**).^{110,45–47} Whereas a mechanism in which Ag acts as a reducing agent towards O₂ or other oxidizing species is often reported and supported by experimental evidence,^{112,111,113} a direct oxidation path for DMAB production involving holes as a direct oxidizing agent has been recently reported in in Ag/TiO₂ materials under N₂ atmosphere.³² Surprisingly, the higher PATP conversion for Ag/Ti_xO₂ relative to Ag NPs through this mechanism hints at a more efficient electron-hole separation upon SPR excitation, which in turn leads to improved performances. However, the activity for Ag/Ti_xO₂ was lower as compared to Ag/prGO, indicating that the PATP oxidation by the adsorbed O₂ pathway (involving transfer of SPR-excited hot electrons) presented a higher contribution relative to the role of holes as oxidizing agents towards the formation of DMAB.

Figure 25. Proposed charge transfer mechanisms and energy level diagrams for Ag/prGO (A) and Ag/Ti_xO₂ (B) materials that had been excited at 633 nm. Φ indicates work function values and E_c indicates conduction band energy.^{103,125–128} In (A), electrons can be transferred from prGO to Ag NPs, increasing the populations of hot electrons that can be transferred to adsorbed O₂ producing O₂^{•−} and contributing to the PATP oxidation (hot electron pathway). In (B), charge transfer from Ag to Ti_xO₂ takes place, and the PATP is oxidized by the SPR-generated holes in Ag NPs (hole pathway).

When the Ag/Ti_xO₂/prGO hybrid was employed as catalysts, the PATP conversion exceeded that of Ag/Ti_xO₂ and was similar to what was reported for Ag/prGO. In this case, under light excitation, Ti_xO₂ can subtract electrons from both Ag NPs and prGO, and prGO can donate electrons to both Ag NPs and Ti_xO₂ as depicted in **Figure 26A**. This leads to the accumulation of negative charges in Ti_xO₂ as described for the Ag/Ti_xO₂ hybrid. As the addition of prGO cannot enhance electron-acceptor properties of Ti_xO₂ towards Ag NPs, we can assume that the observed PATP conversion does not follow the direct, hole-mediated oxidation mechanism proposed for Ag/Ti_xO₂. Therefore, it is plausible that the formation of DMAB occurs from reaction with O₂^{•−} (hot electron pathway). Thus, the proposed mechanism for the detected PATP conversion to DMAB in the Ag/Ti_xO₂/prGO hybrid comprises, firstly, the transfer of excited electrons from Ag NPs and prGO to Ti_xO₂. Then, as the energy level of negatively charged Ti_xO₂ quickly approaches the Fermi level of Ag NPs, Ti_xO₂ will continue to receive excited electrons from prGO, but not from Ag NPs (**Figure 26B**), leading to a performance which is similar to what was observed for the Ag/prGO

material. At this point, laser-excited prGO electrons will be directed to both Ti_xO_2 and Ag NPs, as the Fermi level of Ag NPs (coinciding with the energy level of negatively charged Ti_xO_2) is still located at a lower energy level than prGO conduction band. Consequently, electrons that reach Ag NPs will be employed in the production of O_2^- , and those that reach the CB of Ti_xO_2 will be accumulated and then transferred to Ag NPs (**Figure 26B**). This will lead to enhanced electron density at Ag NPs due to plasmon resonance and to $\text{prGO} \rightarrow \text{AgNPs}$ and $\text{Ti}_x\text{O}_2 \rightarrow \text{AgNPs}$ charge transfer processes.

Figure 26. Proposed charge transfer mechanisms and energy level for Ag/ Ti_xO_2 /prGO that had been excited at 633 nm. Φ indicates work function values and E_c indicates conduction band energy.^{103,125–128} Ti_xO_2 can subtract electrons from both Ag NPs and prGO, and prGO can donate electrons to both Ag NPs and Ti_xO_2 (A). As the conduction band of Ti_xO_2 fills up and its energy level rises, Ti_xO_2 will continue to receive excited electrons from prGO, but not from Ag NPs (B). In this case, both prGO and Ti_xO_2 transfer electrons to Ag NPs and production of O_2^- takes place.

Control experiments employing Degussa P25 TiO_2 instead of Ti_xO_2 (Ag/P25/prGO) show that cooperation between the three components can lead to an even higher DMAB production (**Figure 27**), in which the Ag/P25/prGO material displayed the highest DMAB:(PATP + DMAB) ratio among all the studied materials. This observation suggests that, whereas the catalytic performance of Ag/ Ti_xO_2 /prGO did not exceed that of Ag/prGO, further optimization of the tri-component hybrid can allow even higher DMAB production than both its bi-component counterparts, Ag/ Ti_xO_2 and Ag/prGO. Here, DMAB production will suffer from an initial barrier constituted by the tendency

of Ti_xO_2 to accept excited electrons in its conduction band, but will then be greatly enhanced by the possibility for prGO to transfer electrons to Ag NPs at an increased rate through Ti_xO_2 mediation. The weight of each contribution will depend on the nature of the components: the morphology-dependent electron-exchange properties of Ti_xO_2 , which preferentially oxidizes substrates on the nanosheets surface and reduces them at the borders,¹²⁹ hint at a faster electron transfer rate from prGO to Ti_xO_2 than from Ti_xO_2 to Ag NPs. In P25, the absence of the anisotropy of nanosheets leads to a greater tendency to promptly transfer excited electrons to Ag NPs, explaining the improved DMAB production.

Figure 27. PATP conversion as expressed by the $1433:1081\text{ cm}^{-1}$ DMAB:(DMAB+PATP) intensity ratios for Ag NPs supported over Ti_xO_2 nanosheets and Degussa P25 titanium oxide with and without prGO. The hybrid materials correspond to Ag/ Ti_xO_2 , Ag/P25, Ag/ Ti_xO_2 /prGO, and Ag/P25/prGO from left to right.

It is important to note that the proposed mechanism for the enhanced catalytic performance of Ag/ Ti_xO_2 /prGO is in contrast with previous reports on the high photocatalytic activity of Ag/ TiO_2 /GO systems,^{130,131} which suggested GO as an electron acceptor responsible for charge-recombination inhibition. In order to better understand the nature of the electronic exchange among components and assess whether the charge-transfer process actually relies on the

enhancement of electron-donor properties of prGO in the presence of Ti_xO_2 , we analyzed the behavior of prGO under laser radiation.

The Raman spectra of Ag/prGO and Ag/ Ti_xO_2 /prGO as a function of laser irradiation power are shown in **Figure 28**. The D and G bands, located at approximately 1334 and 1600 cm^{-1} , respectively, can give valuable information about the oxidation state of prGO. The G band of pristine graphene, at 1583 cm^{-1} , surges when reduction occurs, provoking the shift of the G band of prGO to lower Raman shift values, and the intensity ratio between G and D bands (I_G/I_D) increases with reduction as a consequence of a decrease in the average size of the sp^2 -hybridized domains. However, oxidation to GO is also accompanied by the same increase in I_G/I_D ratio.^{107–109} In the case of Ag/prGO, the position of the G band shifts to lower Raman shift values, whereas the I_G/I_D ratio steadily increases, indicating that the reduction of prGO to rGO takes place under laser radiation. In Ag/ Ti_xO_2 /prGO, the I_G/I_D ratio shows an increase, but the G band does not present any significant shift, suggesting that reduction of the material was not detected. Thus, the observed light-induced redox behavior of prGO in Ag/prGO and Ag/ Ti_xO_2 /prGO demonstrates that the photoexcited electrons are being transferred to a greater extent when Ti_xO_2 is present in the hybrids, in agreement with our proposed mechanism.

Figure 28. Irradiation-power dependent Raman spectra of Ag/prGO (A) and Ag/TiO₂/prGO (B). It can be observed that the intensity ratio between the G and D bands of prGO increases in both cases, but only in Ag/prGO the position of the G band shifts to a lower Raman shift values, indicating that prGO was only reduced by irradiation in the absence of TiO₂.

5. Conclusions

We developed facile and water-based procedures for the preparation of spherical and monodisperse Au, Pd and Ag nanoparticles. Next, we focused on titanate nanosheets of formula $\text{Ti}_{0.87}\text{O}_2^{0.52-}$ from exfoliation of a lamellar lithium-potassium titanate and graphene oxide by the Hummers method as support materials. Moreover, we submitted GO to controlled chemical reduction, yielding prGO. We proceeded to characterize all obtained materials, elucidating their structure, morphology and optical properties, and employed them in the preparation of bi- and tri-component hybrids (2D supports and metal nanoparticles). We evaluated different approaches for the immobilization of nanoparticles, finally identifying the *ex-situ* mixing of unwashed nanoparticle suspensions with support suspensions as the best option. This led to advantages regarding both uniformity of the hybrids and control over components' properties. In the case of palladium, *in-situ* reduction of metal precursor over the surface of Ti_xO_2 and prGO also proved interesting, as the presence of the support, especially in the case of Ti_xO_2 , directed nanoparticle growth towards the formation of ultra-small crystals ($d \approx 2.4$ nm).

We employed two different model reactions to probe catalytic performance of Au NPs and its hybrids, namely Au/ Ti_xO_2 , Au/GO, Au/prGO, Au/ Ti_xO_2 /GO and Au/ Ti_xO_2 /prGO. First, we investigated the hybrids' plasmonic catalytic activities with SPR-mediated oxidation of PATP to DMAB: our results revealed that GO can improve the catalytic efficiency of Au NPs, as visible light triggers electron excitation above the support's Fermi level, causing hot electrons to reach the already resonant Au NPs and DMAB production to increase. Moreover, GO reduction to prGO enhances the support's electron-donor properties, leading to the highly active Au/prGO material.

On the other hand, we could not detect any metal-support interaction in Au/Ti_xO₂, where the nanosheets did not influence the PATP conversion rate, and we observed that the addition of Ti_xO₂ to Au/GO and Au/prGO led to a considerable loss of performance. We believe that in the tri-component hybrids, Au/Ti_xO₂/GO and Au/Ti_xO₂/prGO, Ti_xO₂ can trap excited GO and prGO electrons, preventing them from reaching Au NPs and participating in PATP conversion to DMAB.

Next, we investigated the effect of Ti_xO₂, GO and prGO over the catalytic activity of Au NPs in the reduction of 4-nitrophenol to 4-aminophenol. Among bi-component materials, only Au/prGO displayed a higher catalytic activity than Au NPs, whereas Au/Ti_xO₂ and Au/GO showed a slightly lower conversion rate than unsupported nanoparticles. For Au/prGO, π - π stacking between prGO and 4-nitrophenol causes the substrate to be more readily available to the Au NPs, explaining the increase in catalytic activity. For Au/Ti_xO₂ and Au/GO, electrostatic repulsion prevents significant 4-nitrophenol adsorption, and a smaller available Au surface alone can justify the loss of performance: a portion of the nanoparticle area is now in direct contact with a support, and the number of catalytic sites is reduced. In Au/Ti_xO₂/GO, the catalytic activity of pure Au NPs is restored, as we believe that strong GO-Ti_xO₂ interactions lead to the segregation of Au NPs from the nanosheets. In Au/Ti_xO₂/prGO, catalytic performance sharply drops: 4-nitrophenol adsorption over prGO and separation of prGO-Ti_xO₂ composites from Au NPs take place at the same time, subtracting the substrate from reaction with the metal nanoparticles. We demonstrated the recyclability of the high-performing Au/prGO material, that after 10 reduction cycles retains 75% of its initial 4-nitrophenol conversion.

For Pd/Ti_xO₂, we employed the model reduction of 4-nitrophenol to 4-aminophenol to compare the hybrid to a commercial catalyst (Pd/C). We detected a fast conversion in the

presence of a minimal quantity of our hybrid which was not registered when Pd/C was used, and thus confirmed the high activity of Pd/Ti_xO₂, which shows a good potential for catalytic applications.

Finally, we probed the SPR-mediated catalytic activities of Ag NPs, Ag/Ti_xO₂, Ag/prGO and Ag/Ti_xO₂/prGO through the oxidation of PATP to DMAB. All hybrids presented higher SPR-mediated activities as compared to Ag NPs. In the Ag/prGO material, under light excitation, PATP oxidation takes place by a hot-electron pathway, in which electrons are transferred from prGO to Ag NPs, increasing the population of SPR-excited hot electrons that can be transferred to adsorbed O₂ and subsequently participate in the PATP oxidation. Conversely, in Ag/Ti_xO₂, PATP oxidation takes place by a hole-based pathway, in which charge transfer from Ag NPs to Ti_xO₂ takes place, leaving holes in Ag NPs that can also drive the PATP oxidation. Our results demonstrated that the SPR excited hot electron pathway contributed to a larger extent to the PATP oxidation, leading to higher conversions relative to the oxidation by the SPR-excited holes. In order to further investigate the relative effects of charge-transfer over SPR mediated activities, we prepared the tri-component hybrid material comprising Ag NPs, prGO and Ti_xO₂ nanosheets (Ag/Ti_xO₂/prGO). Interestingly, the detected performance of Ag/Ti_xO₂/prGO was similar to that of Ag/prGO. The proposed mechanism was based on the cooperative effect of the two supports, in which charge transfer from prGO to Ag NPs is intensified by the presence of Ti_xO₂ nanosheets.

We believe the results described in this thesis shed new light on the effect of nanoscale charge-transfer processes and metal-support strategies over catalytic and plasmonic catalytic activities. This may have important implications for the design of novel catalysts with improved performances comprised of metal NPs and 2D supports.

6. References

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Résumé

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Conferences

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