## Nanostructures

# Probing the Catalytic Activity of Reduced Graphene Oxide Decorated with Au Nanoparticles Triggered by Visible Light

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**Abstract:** Hybrid materials in which reduced graphene oxide (rGO) is decorated with Au nanoparticles (rGO–Au NPs) were obtained by the in situ reduction of GO and  $AuCl_4^{-}_{(aq)}$  by ascorbic acid. On laser excitation, rGO could be oxidized as a result of the surface plasmon resonance (SPR) excitation in the Au NPs, which generates activated O<sub>2</sub> through the transfer of SPR-excited hot electrons to O<sub>2</sub> molecules adsorbed from air. The SPR-mediated catalytic oxidation of *p*-aminothiophenol (PATP) to *p*,*p*'-dimercaptoazobenzene (DMAB) was then employed as a model reaction to probe the effect

## Introduction

Graphene-based materials have attracted considerable attention owing to their unique structure, in which the closely packed honeycomb of the sp<sup>2</sup>-hybridized carbon network leads to extraordinary electronic, thermal, and mechanical properties.<sup>[1-3]</sup> In addition to graphene, graphene oxide (GO) and reduced graphene oxide (rGO) have also attracted great interest for a variety of applications due to their facile solutionphase synthesis and hydrophilic properties.<sup>[4–8]</sup> GO and rGO are oxidized or partially oxidized forms of graphene, which are mainly functionalized with hydroxyl, carboxyl, and epoxy groups on the hexagonal network of carbon atoms.<sup>[9]</sup> Compared to pristine graphene, GO suffers from a significant loss of conductivity, which can be mitigated by a partial reduction of its functional groups.<sup>[10]</sup>

Gold nanoparticles (Au NPs) exhibit excellent catalytic activities and remarkable optical properties in the visible range as a result of their surface plasmon resonance (SPR) excitation.<sup>[11-13]</sup> Interestingly, it has been recently demonstrated that the SPR excitation in plasmonic nanoparticles can be put to

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of rGO as a support for Au NPs on their SPR-mediated catalytic activities. The increased conversion of PATP to DMAB relative to individual Au NPs indicated that charge-transfer processes from rGO to Au took place and contributed to improved SPR-mediated activity. Since the transfer of electrons from Au to adsorbed O<sub>2</sub> molecules is the crucial step for PATP oxidation, in addition to the SPR-excited hot electrons of Au NPs, the transfer of electrons from rGO to Au contributed to increasing the electron density of Au above the Fermi level and thus the Au-to-O<sub>2</sub> charge-transfer process.

work to enhance and/or mediate catalytic processes at the surface in so-called SPR-enhanced or SPR-mediated catalysis. This can occur through charge transfer of SPR-excited hot electrons at the metal/molecule interface, local heating, and as a result of the antenna effect.<sup>[14–16]</sup> However, in catalytic applications, nanoparticles frequently undergo aggregation and/or dissolution, which hampers their stability.<sup>[17]</sup> In this context, the utilization of supports is an interesting strategy to improve stability.<sup>[18]</sup> Graphene, GO, and rGO, for example, are promising support materials for catalytic applications owing to their mechanical properties and conductivity.<sup>[1,2,17,19]</sup> In the context of SPRenhanced or SPR-mediated catalysis, charge-transfer processes between the support and plasmonic nanoparticles may be a suitable strategy to improve the activity.<sup>[20,21]</sup>

Herein, we describe the synthesis of a hybrid material in which rGO is decorated with Au NPs (rGO-Au NPs) by an in situ strategy that employs ascorbic acid as both reducing agent and stabilizer. We investigated charge-transfer processes between rGO and Au NPs under visible-light excitation and their effect on the SPR-mediated catalytic activity. For instance, when the rGO-Au NPs were excited at 632.8 nm, rGO oxidation was detected as a result of the SPR excitation of the Au NPs, which increased with increasing laser power, in agreement with an SPR-mediated mechanism. We then employed the SPR-mediated catalytic oxidation of *p*-aminothiophenol (PATP) to p,p'-dimercaptoazobenzene (DMAB) as a model reaction to probe the effect of the rGO support on the activity of Au NPs. The increased conversion of PATP to DMAB relative to individual Au NPs indicated that charge-transfer processes from rGO to Au took place and contributed to improved SPR-mediated activity.

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## **Results and Discussion**

Figure 1a shows an SEM image of the GO employed in our studies. The GO had smooth surfaces over large areas, and some regions displaying folded sheets could be clearly seen. The rGO decorated with Au NPs (rGO-Au NPs) was synthesized



Figure 1. SEM images of a) GO, b) rGO-Au, c) Au, and d) GO-Au NPs.

by in situ reduction of  $AuCl_4^{-}_{(aq)}$  and GO in the presence of ascorbic acid as both the reducing agent and stabilizer. The SEM image (Figure 1 b) showed that the Au NPs were spherical, relatively monodisperse, uniformly dispersed over both sides of the rGO material, and about 20 nm in diameter. To investigate the effect of Au NPs on the optical and catalytic properties rGO, we synthesized individual Au NPs by following a similar approach to that described for the rGO–Au material but in the absence of GO and GO–Au NPs hybrids by simply mixing GO and Au NPs. SEM images of individual Au NPs and the corresponding GO–Au NPs are shown in Figure 1c and d, respectively. The Au NPs in both of these samples had similar sizes to those depicted in Figure 1 b. Also, like the rGO–Au NPs (Figure 1 b), the Au NPs were uniformly dispersed over the GO in the GO-Au NPs (Figure 1 d).

Figure 2 shows the UV/Vis extinction spectra of GO, GO-Au, and rGO-Au NPs. The spectrum of GO showed a dominant peak with a maximum at 230 nm and a shoulder at 300 nm assigned to  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions of aromatic C=C and C=O



Figure 2. UV/Vis extinction spectra recorded from aqueous suspensions containing GO, GO-Au NPs, and rGO-Au NPs.

bonds, respectively.<sup>[22]</sup> No changes in the position of these bands were observed in the spectrum of GO-Au NPs, which also displayed a broad signal at 528 nm assigned to the dipole mode of the SPR of Au NPs. Interestingly, the simultaneous reduction of both GO and  $AuCl_4^-$  (aq) with ascorbic acid induced a redshift of the 230 nm band assigned to the  $\pi$ - $\pi$ \* transition in GO to 261 nm, whereas the peak at 300 nm due to the n- $\pi$ \* transition could not be clearly observed. Moreover, the intensity of the absorption tail in the visible region for the rGO-Au NPs increased significantly compared with those of GO and GO-Au NPs. These results are in agreement with reduction of GO to rGO, which leads to partial restoration of the aromatic network.<sup>[22]</sup> The formation of Au NPs on the rGO is also supported by the presence of the SPR band at 528 nm.<sup>[23]</sup>

Figure 3 a shows the Raman spectra of GO as a function of laser power at an excitation wavelength of 632.8 nm. The Raman parameters (G-band position, full width at half-maximum (FWHM), and intensity ratio  $I_G/I_D$ ) from these spectra are



**Figure 3.** a) Laser-power-dependent Raman spectra of GO recorded at 0.03, 0.12, 0.24, and 1.30 mW and an excitation wavelength of 632.8 nm. b) Schematic representation of the visible-light-driven reduction of GO to rGO.

depicted in Figure S1 in the Supporting Information. At a laser power of 0.03 mW, the spectrum showed the characteristic Raman bands of graphene-based materials: 1) the D band at approximately 1334 cm<sup>-1</sup> assigned to disorder in the graphitic material and/or a decrease in the average size of the sp<sup>2</sup>-hybridized domains and 2) the G band around 1601 cm<sup>-1</sup> attributed to the Raman-active  $E_{2g}$  phonon (in-plane optical mode).<sup>[22,24–28]</sup> The D' band, centered at about 1620 cm<sup>-1</sup>, should also be present, albeit not clearly visible in the spectra.<sup>[22,24–28]</sup> The Raman peak assigned to the G band shifted to lower wavenumbers with increasing laser power. More specifi-

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cally, although no significant changes in the G-band position were observed when the laser power was increased to 0.12 mW, a shift to 1592 and 1589 cm<sup>-1</sup> could be detected when the laser power was increased to 0.24 and 1.30 mW, respectively. These shifts are in agreement with the reported reduction of GO by laser excitation, because its reduction should lead to recovery of the hexagonal network of carbon atoms and thus the graphite structure, the G band of which is located at about 1583 cm<sup>-1</sup>.<sup>[25,29]</sup>

The intensity ratio of the G and D bands in the Raman spectrum of carbon-based materials can be used to evaluate the density of defects and the size of sp<sup>2</sup>-hybridized domains. The  $I_{G}/I_{D}$  ratios for the Raman spectra of GO depicted in Figure 3 were 1.18, 1.14, 1.03, and 0.94 at laser powers of 0.03, 0.12, 0.24, and 1.30 mW, respectively. The decrease in the  $I_{\rm G}/I_{\rm D}$  ratios suggests a decrease in the average size of the sp<sup>2</sup>-hybridized domains and can be explained if the graphitic domains created by the reduction of GO are smaller in size than those present in GO before reduction, albeit more numerous.  $^{\left[ 26,27\right] }$  Therefore, the decrease of both G-band wavenumber and the  $I_{\rm G}/I_{\rm D}$  ratio with increasing laser power are in agreement with previously reported results and can be attributed to a transition from more disordered graphitic structures (stage II) to more ordered ones (stage I) as a result of partial reduction of GO to rGO (Supporting Information, Figure S1).<sup>[30-33]</sup> When the GO sheet is deoxygenated by the reduction process, the distortion of the six-membered rings is removed, and the carbon lattice returns to an essentially graphitic one.<sup>[34]</sup> This process is depicted schematically in Figure 3b.

Figure 4a shows Raman spectra of rGO–Au as a function of laser power. The Raman parameters (G-band position, FWHM, and  $I_G/I_D$  ratio) from these spectra are depicted in Figure S1 in the Supporting Information. The variations in the G-band posi-



**Figure 4.** Laser power-dependent Raman spectra of a) rGO–Au NPs and b) GO-Au NPs. The spectra were registered at 0.03, 0.12, 0.24, and 1.30 mW and an excitation wavelength of 632.8 nm.

tion and  $I_G/I_D$  ratios as a function of laser power were remarkably different from those observed for pure GO. Specifically, an increase in the wavenumber as a function of laser power was observed. For instance, the G band gradually shifted from 1563 to 1567 cm<sup>-1</sup> as the laser power increased from 0.03 to 0.12 mW and then to 1578 and 1588  $\rm cm^{-1}$  for 0.24 and 1.30 mW, respectively. Meanwhile, a steady decrease in  $I_{\rm G}/I_{\rm D}$ ratio with increasing laser power was observed: 1.55, 1.46, 1.04, and 0.90 for 0.03, 0.12, 0.24, and 1.30 mW, respectively. The decrease in the  $I_G/I_D$  ratio is in agreement with the proposed decrease in the average size of the sp<sup>2</sup>-hybridized domains in rGO-Au under laser exposure at higher powers.<sup>[22, 26, 27]</sup> This observation indicates oxidation of rGO in rGO-Au under laser excitation at higher laser powers. Therefore, whereas 632.8 nm excitation led to reduction of the GO material, oxidation was detected for rGO-Au NPs.

To gain further insight into the role of Au NPs in the properties of rGO and GO under laser irradiation, we also studied the Raman properties of GO-Au NPs materials prepared by mixing GO and Au NPs as a function of laser power (Figure 4 b). The Raman parameters (G-band position, FWHM, and  $l_G/l_D$  ratios) from these spectra are depicted in Figure S1 in the Supporting Information. The variations in the G-band positions, FWHM, and  $l_G/l_D$  ratios as a function of laser power were very similar to those described for the pure GO sample (Figure 3 a), and this suggests that the presence of Au NPs did not change the Raman properties of GO under our employed conditions.<sup>[35]</sup> For instance, the  $l_G/l_D$  ratios were 1.16, 1.10, 0.98, and 0.92 for laser powers of 0.03, 0.12, 0.24, and 1.30 mW, respectively.

The oxidation of rGO in the presence of Au NPs can be explained as follows. Theoretical calculations and experimental evidence for rGO suggest a bandgap smaller than 1 eV, the exact value of which depends on the ratio of carbon to oxidized functional groups and their different arrangements (Figure 5 a).<sup>[5,36-38]</sup> Under visible-light exposure, electrons can be excited from the valence band (VB) to the conduction band (CB). Because the Fermi level of Au is lower than the rGO conduction band, excited electrons from rGO can be transferred to Au NPs, as illustrated in Figure 5 b, Thus, electrons accumulate in the Au NPs and occupy energy levels above the Fermi level. At



**Figure 5.** Schematic energy-level diagrams for a) the rGO–Au NPs without excitation and b) under visible-light (632.8 nm) excitation. Under light excitation, both SPR-excited hot electrons and electrons transferred from rGO to Au occupy energy levels above the Fermi level that can participate in the activation of adsorbed  $O_2$  molecules.

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the same time, the SPR excitation in Au NPs also generates hot electrons that occupy energy levels above the Fermi level. In this case, both hot electrons from SPR-excited Au NPs and electrons transferred from rGO to Au can be transferred to adsorbed  $O_2$  molecules (from air) to generate activated  $O_2$  ( $^2O_2^{-}$ ), which subsequently contributes to rGO oxidation to GO.<sup>[23,39]</sup>

To confirm this mechanism, the rGO–Au NPs were functionalized with PATP, and the SPR-mediated oxidation of PATP to DMAB was employed a model reaction to probe the chargetransfer processes taking place between rGO and Au NPs. In this process, the transfer of hot electrons from SPR-excited Au NPs to adsorbed  $O_2$  molecules is the crucial step for  $O_2$  activation, which in turn contributes to the PATP oxidation.<sup>[39]</sup> Figure 6a shows the surface-enhanced Raman scattering (SERS)



**Figure 6.** a) Laser-power-dependent SERS spectra of PATP-functionalized rGO-Au NPs at 0.03, 0.12, 0.24, and 1.30 mW. b) SERS spectra of PATP-functionalized rGO-Au (solid line) and Au NPs (dashed line) at 0.12 mW laser power. All spectra were recorded at 632.8 nm excitation wavelength and were normalized with respect to the 1081 cm<sup>-1</sup> band.

spectra for PATP-functionalized rGO-Au NPs as a function of laser power. At laser powers of 0.03 and 0.12 mW, the SPRmediated oxidation of PATP to DMAB was clearly revealed by the appearance of bands at 1081, 1142, 1390, 1433, and 1575 cm<sup>-1</sup> assigned to the A<sub>g</sub> mode of DMAB.<sup>[40,41]</sup> The bands at 1081, 1188, 1489, and 1593 cm<sup>-1</sup> are assigned to the A<sub>1</sub> mode of PATP.<sup>[40,41]</sup> This result indicated that the formation of activated  ${}^{3}O_{2}$  due to the transfer of electrons from Au to adsorbed O<sub>2</sub> takes place in the rGO-Au NPs. However, as the laser power was further increased, many PATP and DMAB peaks overlapped with the strong signals arising from the graphitic material (D and G bands).

To confirm that electrons can be transferred from rGO to Au NPs on light excitation, we compared the SPR-mediated catalytic oxidation of PATP to DMAB of rGO-Au NPs with that of individual Au NPs. Figure 6b shows the SERS spectra of PATPfunctionalized rGO-Au and Au NPs at 0.12 mW laser irradiation power. The intensities of DMAB A<sub>g</sub> modes at 1390 and 1433 cm<sup>-1</sup> were almost the same in both cases, with a slight increase in intensity for the rGO-Au NPs. However, the DMAB  $A_{a}$  band for rGO-Au at 1575 cm<sup>-1</sup> was clearly more intense relative to Au NPs, which indicates higher PATP to DMAB conversion for rGO-Au NPs relative to Au NPs. This observation confirms that light irradiation leads to the excitation of electrons across the rGO bandgap, which are subsequently transferred to Au NPs and can also participate in O<sub>2</sub> activation, the crucial step for oxidation of both PATP and rGO. In this case, it is plausible that a higher population of electrons at the Au NPs (electrons from SPR-activated Au and electrons transferred from rGO to Au) led to higher PATP to DMAB conversion. Control experiments on the catalytic conversion of PATP to DMAB on GO, a simple mixture of GO and Au NPs, and Au NPs are shown in Figure S2 of the Supporting Information. No catalytic conversion was observed for GO alone, while the conversions for GO-Au and Au NPs were comparable.

## Conclusion

Hybrid materials in which rGO is decorated with Au NPs (rGO-Au NPs) were obtained by an eco-friendly approach based on the in situ reduction of both GO and  $AuCl_{4\ (aq)}^{-}$  by ascorbic acid. On laser excitation, rGO could be oxidized as a result of SPR excitation of the Au NPs, which generates activated O<sub>2</sub> from the transfer of SPR-excited hot electrons to adsorbed O<sub>2</sub> molecules from the air. The rGO oxidation increased as a function of laser power, in agreement with an SPR-mediated mechanism. These observations were the opposite of what was observed for GO, for which reduction to rGO was detected as a function of laser power. Furthermore, by comparing the SPRmediated catalytic activities for oxidation of PATP to DMAB on both rGO-Au and Au NPs samples, we confirmed that photogenerated electrons from rGO excitation could be transferred to Au NPs and contribute to a higher SPR-mediated catalytic activity of the rGO-Au NPs relative to individual Au NPs. Since the transfer of electrons from Au to adsorbed O<sub>2</sub> molecules to produce activated O<sub>2</sub> is the crucial step for PATP oxidation, the transfer of electrons from rGO to Au contributed to increasing the electron density of Au above the Fermi level and thus PATP oxidation relative to individual Au NPs. We believe the results described herein have important implications and may inspire the design of hybrid materials containing rGO and metal nanoparticles with improved and/or desired catalytic properties.

## **Experimental Section**

#### Materials and instrumentation

HAuCl<sub>4</sub>·3H<sub>2</sub>O (48% Au, Sigma-Aldrich), polyvinylpyrrolidone (PVP, Sigma-Aldrich,  $M = 55000 \text{ g mol}^{-1}$ ), ascorbic acid ( $\geq 99.0$ %, BioXtra, Sigma-Aldrich), *p*-aminothiophenol (> 97.0%, Sigma-Aldrich), graphite flakes (SP1, Bay Carbon), KMnO<sub>4</sub> (Sigma-Aldrich), H<sub>2</sub>O<sub>2</sub>,



(30 vol% in water, Sigma-Aldrich), HCl (Vetec), ethanol (Vetec), and acetone (Sigma-Aldrich) were analytical-grade reagents and used without further purification. Deionized water (18.2 M $\Omega$  cm) was used throughout the experiments.

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 on a Si wafer, followed by drying under ambient conditions. The size of the nanoparticles was determined by individually measuring the size of about 100 nanoparticles from SEM images. UV/Vis spectra were obtained from aqueous suspensions containing the nanostructures with a Shimadzu UV-2600 spectrophotometer. Raman and SERS spectra were acquired on a Renishaw Raman InVia equipped with a CCD detector and coupled to a Leica microscope that allows rapid accumulation of Raman spectra with a spatial resolution of about 1 µm (micro-Raman technique). The laser beam was focused on the sample by using a  $50 \times$  lens. The experiments were performed under ambient conditions in a back-scattering geometry. The samples were irradiated with the 632.8 nm line of a He-Ne laser (Renishaw RL633 laser) with controlled laser power outputs. All Raman spectra were acquired in a single scan with 30 s accumulation time.

#### Synthesis of GO

GO was produced by a modified version of the Hummers method.<sup>[27,42]</sup> Pristine graphite (1 g) was added to sulfuric acid (60 mL) in a round-bottom flask held around 0 °C with an ice bath, followed by addition of potassium permanganate (3.5 g) gradually over 15 min. After 2 h of stirring at room temperature, the round-bottom flask was returned to an ice bath. Deionized water (200 mL) was slowly added, followed by 2.5 mL of hydrogen peroxide (30 vol%). The product was filtered, washed several times with 500 mL of deionized water, 250 mL of hydrochloric acid (10%), 500 mL of ethanol, 250 mL of acetone, 100 mL of deionized water, and dried in vacuo to yield a black powder of graphite oxide (Gr-O). Aqueous dispersions of GO were prepared by sonicating dried solid Gr-O in deionized water (0.5 mg mL<sup>-1</sup>) for 1 h.

#### Synthesis of rGO decorated with Au NPs (rGO-Au NPs)

The rGO-Au NPs material was obtained by an in situ approach. Typically, 4 mL of an aqueous solution containing 35 mg of PVP and 60 mg of ascorbic acid was added to 2 mL of an aqueous GO dispersion (0.5 mg mL<sup>-1</sup>). This mixture was heated to 90 °C for 10 min under magnetic stirring. Then, 1 mL of 3 mM  $AuCl_{4(ac)}$  was added dropwise with magnetic stirring, and the reaction allowed to proceed for 3 h. The final product was collected by centrifugation, washed several times with 1.5 mL of ethanol by successive cycles of centrifugation and removal of the supernatant, and resuspended in water for further use.

#### Preparation of Au NPs

In a typical synthesis, 6 mL of an aqueous solution containing 35 mg of PVP and 60 mg of ascorbic acid was prepared. This mixture was heated to 90 °C for 10 min with magnetic stirring. Then, 1 mL of 3 mm  $AuCl_{4^{-}(aq)}$  was added dropwise with magnetic stirring and the reaction allowed to proceed for 3 h. The obtained Au NPs were washed several times with 1.5 mL of water by successive cycles of centrifugation and removal of the supernatant and resuspended in water for further use.

#### Synthesis of GO decorated with Au NPs (GO-Au NPs)

GO-Au NPs were obtained by an ex situ approach at room temperature. Briefly, 2 mL of GO suspension (0.5 mg mL<sup>-1</sup>) was mixed with 1 mL of the obtained Au NPs with vigorous magnetic stirring for 22 h. The product was collected by centrifugation and washed several times with 1.5 mL of water by successive cycles of centrifugation and removal of the supernatant and resuspended in water for further use.

#### **Preparation of Raman substrates**

An 1.5 mL aliquot from the as-obtained aqueous suspension containing of GO, rGO–Au NPs, GO-Au NPs, or Au NPs were centrifuged, the supernatant decanted, and the corresponding solid resuspended in 10  $\mu$ L of H<sub>2</sub>O. The 10  $\mu$ L of suspension was then drop-cast onto a 1×1 cm Si(001) surface and dried in air. The sample was then immediately used for the Raman measurements. For SERS measurements, 40  $\mu$ L of an 1.0 mM ethanolic solution of *p*-aminothiophenol was drop-cast on the corresponding Raman substrates and dried under ambient conditions. All samples were used immediately for SERS measurements after preparation.

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