## **Support Information**

## Photoinduced Electron Transfer Dynamics on AuNP and Au@PdNP Supported on Graphene Oxide Probed by Dark-field Hyperspectral Miscroscopy

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## Experimental

## Materials

HPLC grade solvents for spectroscopy and synthesis were supplied by Sigma-Aldrich. Graphene oxide (GO), 4 mg/mL, water dispersion, tetrachloroauric (III) acid trihydrated and sodium citrate were purchased from Aldrich. Ultrapure (type 1) water from Direct- $Q^{$ ®5UV, Millipore, was used throughout the work.

**Synthesis of AuNP.** All the glassware was previous washed with aqua regia (HCI:HNO<sub>3</sub> (3:1)). For the AuNP, 50 mL of 5 x  $10^{-4}$  M HAuCl<sub>4</sub> aqueous solution was heated under reflux and high stirring rate in a three neck round bottom flask, during 30 minutes. Then, 1 mL of 1% citrate aqueous solution was added. After 5 min, the solution was cooled down to room temperature.

Synthesis of RGO@AuNP hybrids For the RGO@AuNP hybrids, the procedure was slightly modified from the literature.<sup>1</sup> 1 mL of GO (1 mg.mL<sup>-1</sup>), aqueous dispersion was added to 20 mL of HAuCl<sub>4</sub>(0.01 wt%), aqueous solution and then were sonicated for 30 min. When the mixture reach 80°C (water bath), it was added 1 mL of sodium citrate (1 wt%), aqueous solution. After 1 hour, the system was cooled down to room temperature

with continuous stirring. To remove the free suspended gold nanoparticles the sample was centrifuged for 10 min at 5,000 rpm, resuspended in ultrapure water and then, centrifuged 3 times at 10,000 rpm for 60 min, and resuspended in 15 mL of ultrapure water.

Synthesis of the GO/Au@Pd Core-shell Nanostructures. A total of 5  $\mu$ L of Na<sub>2</sub>PdCl<sub>6</sub> (0.05, 0.1, 0.2 and 1% w/v) was added to 100  $\mu$ L of RGO/AuNP, followed by the addition of 20  $\mu$ L of 12.5 mmol/L fresh ascorbic acid aqueous solution. The mixture was vigorous stirred for 1 min. The reaction was aged for 2 h at room temperature, protected from light and without agitation. Finally, the washing step (centrifugation) was carried out to interrupt the reduction reaction. The resulting material (<u>GO/Au@PdNP</u>) was resuspended in 500  $\mu$ L of water.

**Dark-field hyperspectral microscopy:** A CytoViva ultra-resolution imaging system, composed by a dark-field hyperspectral arrangement mounted on an Olympus BX51 microscope, was used for recording the single particles Rayleigh scattering spectra<sup>3</sup>. The sample was prepared by drop casting 2uL of the nanomaterials suspension, on a NEXTERION® ultra-clean glass B (Schott). An ultra-clean NEXTERION® glass cover slip (Schott) was put over the drop, and sealed with adhesive tape to avoid oil penetration in the sample.<sup>4</sup> The dark-field optical images and the Rayleigh scattering spectra were recorded with the sample wet, in order to keep the same refraction index.

Atomic force microscopy (AFM) images was recorded on a Bruker ICON system in taping mode using a RTESPA-300 tip. For the GO film, a silicon wafer was kept under the corresponding 1 mg mL<sup>-1</sup> water dispersion for 12 h, washed with Milli-Q water, and dried under a N<sub>2</sub> stream. In the case of the RGO/AuNP and RG/Au@PdNP films, 1  $\mu$ L of the suspension from the synthesis was dropcasted onto a NEXTERION ultraclean glass, from Schott. **Raman Spectroscopy:** A WITec confocal Raman microscope, equipped with a He–Ne laser, was used to obtain the Raman spectra at  $\lambda$  exc of 633 nm. **XRD:** A Bruker D2 Phaser diffractometer equipped with a Cu K $\alpha$  source ( $\lambda = 1.5418$ Å, 30 kV, 15 mA, step = 0.05°), in the 2 $\theta$  range from 8 to 80. **SEM:** JEOL field emission electron microscope, model 7200, operating at 7kV and working distance of 8mm using a backscattering electron detector. **TEM:** Transmission electron microscopy (TEM) measurements were performed using a probe-corrected FEI Titan operated at 300 kV. Scanning transmission electron microscopy (STEM) images were acquired using a high-angle annular dark field (HAADF) detector under camera length of 100 mm. Particles size distribution were calculated using Image J software.

Electrochemical impedance spectroscopy. EIS experiments were conducted with a PGSTAT128N potentiostat (Metrohm Autolab, Utrecht, Netherlands) with a FRA32M module with built-in data acquisition software (NOVA v.2.1.4). An integrated disposable sensor was used as electrodes and its construction is described here. To prepare the photolith, the layout electrode was drawn using a free graphic software (Inkscape 0.92.3 (2405546, 2018-03-11)), then the negative was printed in a transparency film using an inkjet printer (Epson EcoTank L 3150, sistema Bulk Ink) with an UV block ink (Stampset para Epson L 3150). A copper-boardd printed circuit board was cleaned with water and isopropanol. A Dry Film was cut and the protective side was removed and placed onto the board. To ensure the Dry Film was correctly fixed to the board, the set was passed through a hot laminator (Mazzilli ModeloMZ-320) three times. The photolith was then placed over the Dry Film and this new set was exposed to black light (2 lamps of 20 W) for 20 seconds. The Dry Film not exposed to black light (which was protected by the photolith) was then removed using a  $Na_2CO_3$ solution (1 g / 100 ml). The carbonate excess was removed with water and the board was corroded in FeCl<sub>3</sub> solution. After the corrosion the board was washed and placed in NaOH solution (3g / 100 ml) to remove the other protective layer from Dry Film. The board was washed again and the sensor was cut to fit in the cuvette. A transparent nail varnish was manually added to the body of the electrode to isolate the electric contact. A small amount of silver epoxy (Joint Metal Comércio LTDA, São Paulo, Brazil) was manually deposited onto the copper surface, to obtain a pseudo-reference electrode; no modification was done to the counter electrode. A picture of the electrodes can be seen on Figure S 6 The working electrode was modified with the nanomaterials, i.e. 20 µl of each nanomaterial suspension was added to the electrode surface and let to dry naturally for 24h.

Each electrode was inserted in a glass cuvette filled with phosphate buffer 0,1 mol  $L^{-1}$  (pH = 7,1) and connected to the potentiostat with a homemade connector. The open

circuit potential (OCP) was measured for 150 s and the potential used for the experiments was the average potential from the last five seconds of the OCP measurement. The frequency scan was performed from 100kHz to 100 mHz in a distribution of 10 points per decade with an amplitude of 10 mV RMS. Experiments were conducted in the absence and presence of a green LED (thre leds of 3W each). The led emission spectra is shown on Figure S 7.



Figure S 1: Size distribution of gold nanoparticles on RGO/AuNP



Figure S 2: AFM images of RGO@AuNP hybrids



Figure S 3: Size distribution of the Au core on the <u>RGO/Au@PdNP</u> hybrids for the different Pd concentration used.



Figure S 4: RGO/AuNP hyperspectral dark-field image (right) and its respective scattering spectra (left)



Figure S 5: SEM image (A) and size distribution (B) of pristine AuNP



Figure S 6: Esquemactic drawing of the Cu electrode (right), images of the modified electrodes (left)



Figure S 7: Emission spectra of Green LED used on the electrochemical impedance spectroscopy experiments