

SUPPLEMENTARY INFORMATION

SERS DETECTION AND COMPREHENSIVE STUDY OF P-NITROPHENOL: TOWARDS PESTICIDE SENSING

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SYNTHESIS OF GRAPHENE OXIDE

The graphitic oxide (Gr-O) was prepared according to the modified Hummers method,¹ by stirring 2.0 g of powdered flake graphite and 1.0 g of sodium nitrate into 46 mL of sulfuric acid contained in a 500 mL round-flask. The mixture was maintained under ice-bath and strong magnetic stirring for 15 min, followed by the slowly addition of 6.0 g of KMNO₄ to the system. The reaction mixture was kept under strong magnetic stirring for 75 min and further diluted by the slowly addition of 92 mL of distilled water and 280 mL of warm distilled water (~ 100 °C). At the end of 30 minutes, 10 mL of an aqueous solution of H₂O₂ 30 % v/v was added and the system was maintained under stirring for 30 min. After that, the aqueous part was replaced for 250 mL of 1.0 M HCl, process repeated 4 times, and distilled water for several times until neutral pH. The resulting solid Gr-O was separated by filtration and dried at 60 °C for 24 h. An aqueous dispersion of graphene oxide (GO) was obtained by the mechanical exfoliation of Gr-O. The procedure was performed in an amber bottle of 250 mL by the addition of 90 mg of Gr-O and 90 mL of deionized water. The mixture was sonicated for 90 min in ultrasonic bath (Unique, 37 KHz) leading to a stable dispersion of brown color characteristic of this type of material.

GO FUNCTIONALIZATION

The material's synthesis used in this work was described in a previous work,² where GO is first functionalized with cysteamine (CA) through the liquid-liquid (L/L) interfacial reaction (toluene and water), named GOSH. For this, 20 mL of GO dispersion (1 mg mL^{-1}) is mixed with 10 mL of toluene and is kept stirring at 1000 rpm for 12h. After this time it is possible to check the presence of a film at the L/L interface that contains the GO. To perform the functionalization we used the coupling reagents N-hydroxysuccinimide (NHS - $5.91 \times 10^{-3} \text{ mol L}^{-1}$) and 1-ethyl -3-(3-dimethylaminopropyl) carbodiimide (EDC - $5.95 \times 10^{-3} \text{ mol L}^{-1}$) which are added to the flask containing the interfacial film and the system is stirred for 1 h in an ice bath. The flask is then removed from the ice bath and kept for 1h at room temperature under magnetic stirring. Then CA ($4.4 \times 10^{-3} \text{ mol L}^{-1}$) is added to the system and stirred for 12h. After this period, the stirring is stopped and it is possible to observe the film at the liquid-liquid interface formed like an emulsion. Cleaning and removal of excess reagents is performed with the aid of a pipette. The aqueous phase is removed and replaced with milli-Q water. This procedure is repeated 5 times. After GOSH synthesis the material is deposited on the substrate of interest (glass, Si/SiO₂ or quartz). The deposition occurs after transferring the two-phase system to a 25 mL beaker containing the substrate of interest at the bottom. The functionalized film self-assembles at the liquid-liquid interface of the beaker and the substrate is pulled towards the L/L interface where the deposition occurs. The deposited material is then dried for 1 h at 70 °C.

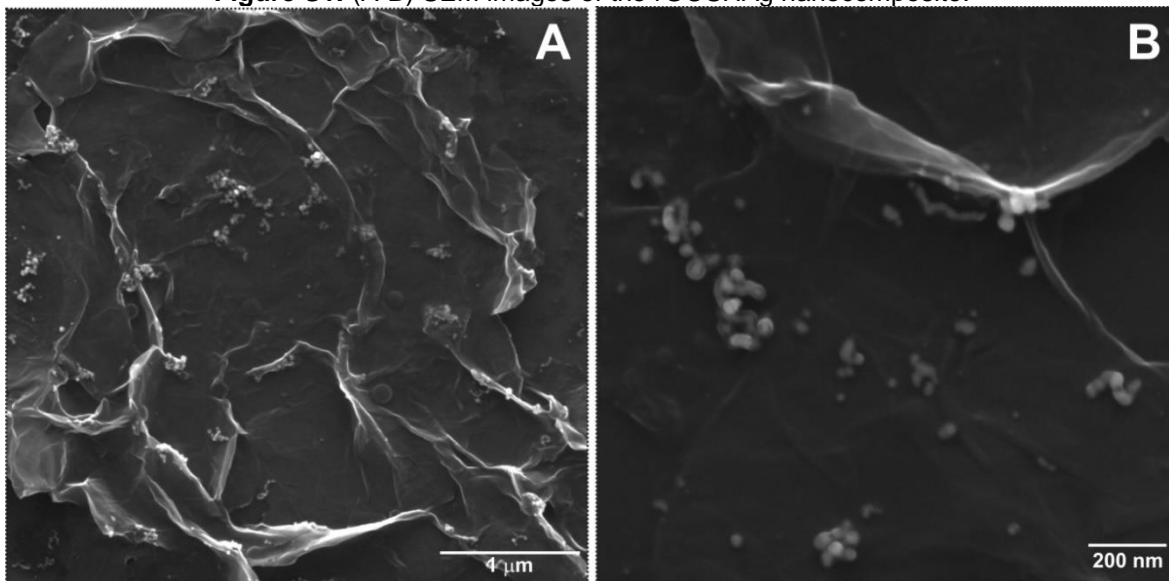
NANOCOMPOSITE SYNTHESIS

GOSH was used for the nanocomposite synthesis by depositing two layers of the material on a glass substrate (7.5 cm² area) followed its immersion the film in a closed compartment containing 40 mL of milli-Q water and Ag⁺ at a concentration of $4.86 \times 10^{-3} \text{ mol L}^{-1}$.² The system was kept under stirring for 6 h and after that NaBH₄ reducer (0.043 mol L^{-1}) was rapidly added with a syringe. The system was maintained under stirring for 2 h and after which time the film (rGOSHAg) was removed from the milli-Q water washing solution and dried for 1 h at 70 °C.

NANOCOMPOSITE CHARACTERIZATION

Typical SEM images of rGOSHAg are shown in Fig S1. More information about the nanocomposite is available in previous work.²

Figure S1: (A-B) SEM images of the rGOSHAg nanocomposite.



RAMAN MEASUREMENTS

The PNP were also measured on a raw Si substrate (Fig S2) and in powder form (Fig S3), as reference samples to study the main bands of the compound.

Figure S2: PNP Raman spectra (1 mM) dropped on Si and substrate at different exciting laser lines. Measurement conditions 0.5% laser intensity with 1s accumulation time.

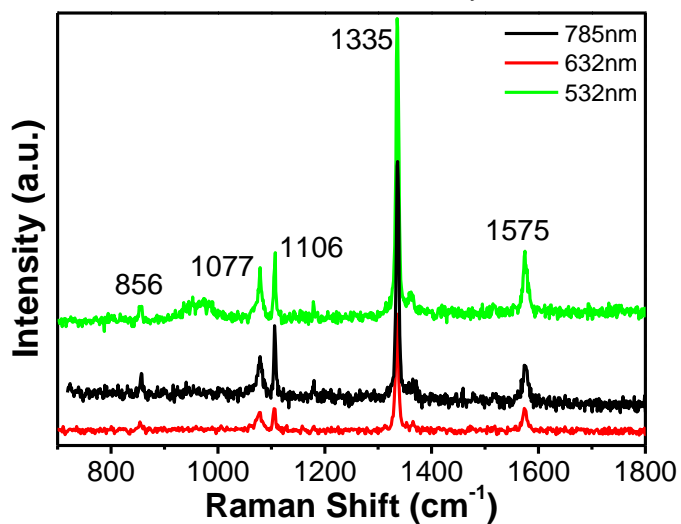
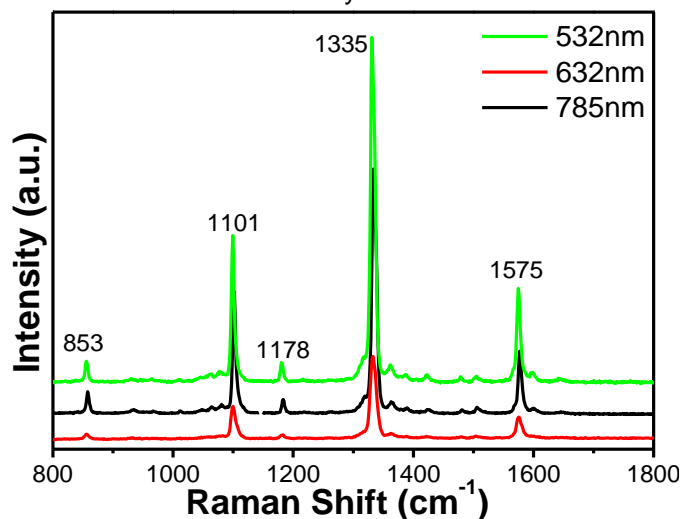


Figure S3: PNP Raman spectra in powder at different exciting lasers lines. Measurement conditions 0.5% laser intensity with 1s accumulation time.



Besides the PNP Raman main bands as described, we also carried out measurements of PNP deposited on raw Au NPs as presented in Fig S4 and on rGOSHAg (Fig S5). Fig. S5 illustrates the influence of the laser lines (Fig S5(A)) and laser powers at 532 nm (Fig S5(B)), in the dimerization of PNP.

Figure S4: PNP Raman spectra (1 mM) dropped on Au substrate at exciting lasers lines. Measurement conditions 0.5% laser intensity with 1s accumulation time.

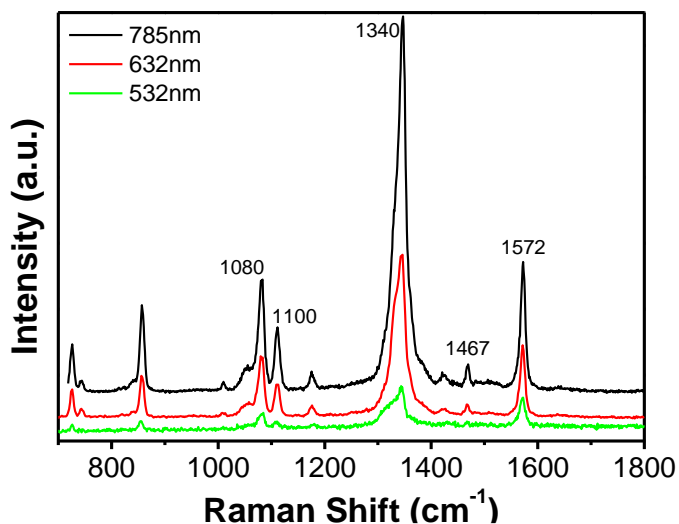


Figure S5: PNP Raman spectra (1 mM) dropped on rGOSHAg substrate measured with (A) different exciting lasers lines and (B) different laser powers at 532 nm.

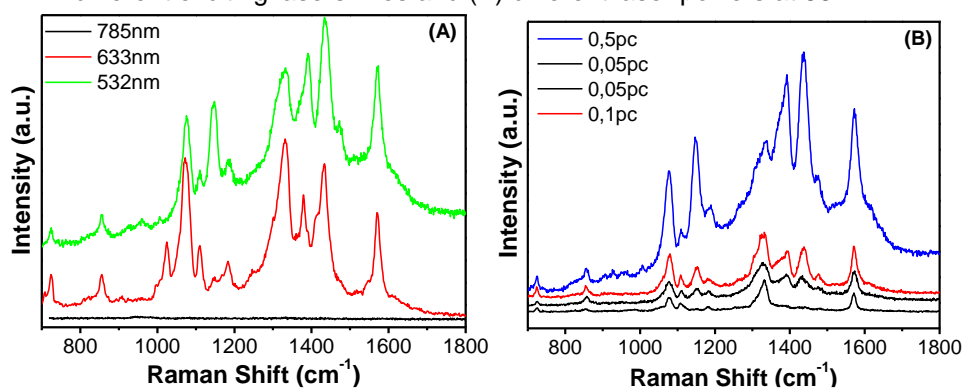


Table S1 compares the laser powers for the three different lasers excitation lines. The values correspond to the Raman measurements on a Renishaw Invia spectrometer with two gratings (2400 l/mm at 532 nm and 1200 l/mm at 633 and 785 nm).

Table S1: Intensities of different lasers on the 100x objective.

Filter (% - pc)	633 nm	532 nm	785 nm
100	4.5mW	16.8mW	7.6mW
50	1.9mW	9mW	3.9mW
10	430 μ W	2.7mW	1.3mW
5	183 μ W	1.5mW	615 μ W
1	42 μ W	219 μ W	297 μ W
0,5	30,7 μ W	122 μ W	150 μ W
0,1	4 μ W	21 μ W	47.6 μ W
0,05	2 μ W	12 μ W	24.2 μ W
0,0001	5nm	16.8mW	622nW

REFERENCES

- (1) Domingues, S. H.; Salvatierra, R. V.; Oliveira, M. M.; Zarbin, A. J. *Chem. Commun.* **2011**, 47, 2592.
- (2) Fonsaca, J. E. S.; Hostert, L.; Orth, E. S.; Zarbin, A. J. G. *Journal of Materials Chemistry A* **2017**, 5, 9591.