Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Tailoring multifunctional graphene-based thin films: from nanocalysts to SERS-based materials

Jéssica E. S. Fonsaca, Leandro Hostert, Elisa S. Orth, Aldo J. G. Zarbin*

Department of Chemistry, Federal University of Paraná (UFPR), CP 19032, CEP 81531-980, Curitiba, PR, Brazil.

. SUPPLEMENTARY INFORMATION

1. Experimental details

1.1 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 $KMNO_4$ 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 H_2O_2 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.

2. Mechanism for GO functionalization

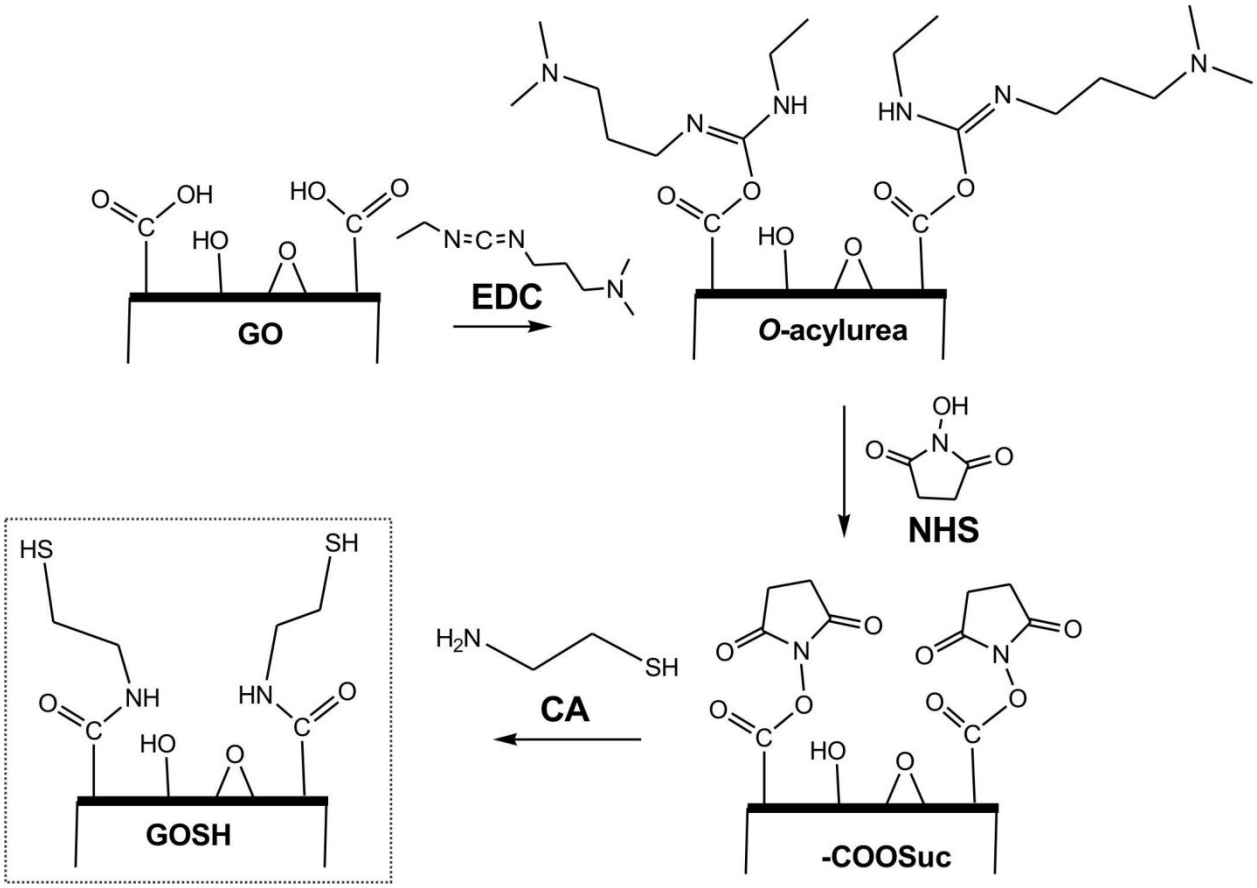

Figure S1. Schematic representation of the reactions involved in GO functionalization.

UV-Vis spectra of GO , GOSH1 and GOSH2

UV-Vis data mentioned in the synthesis and characterization session of functionalized thin films in the manuscript are given bellow.

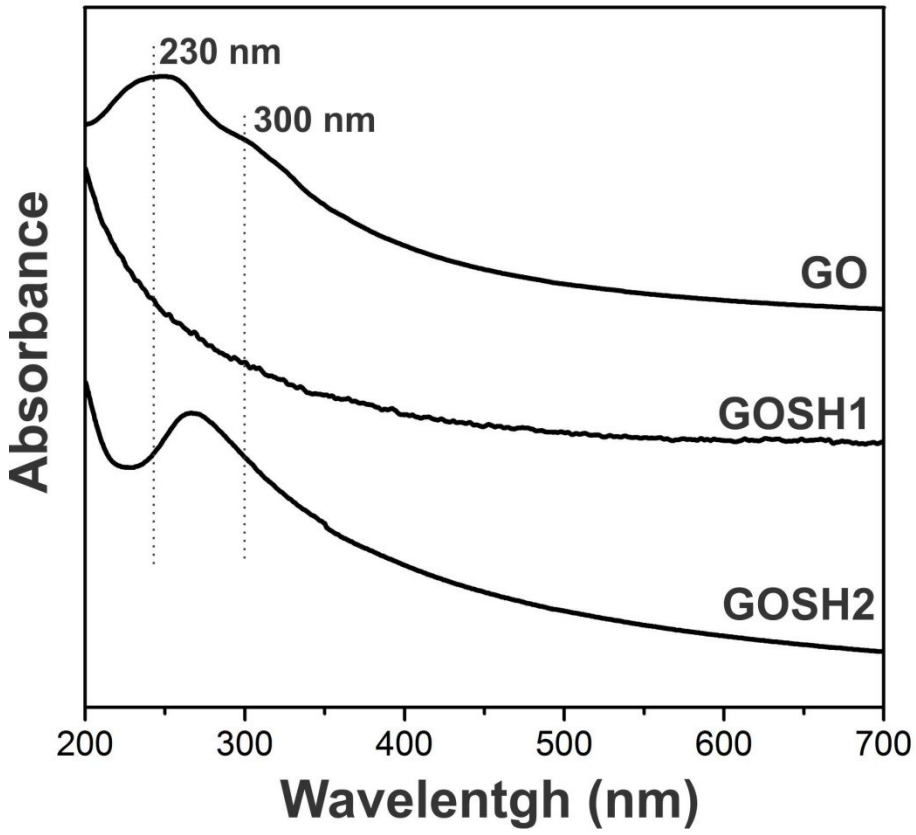

Figure S2. UV-Vis spectra of GO, GOSH1 and GOSH2 thin films.

4. Raman spectra and XRD profiles of GO, GOSH1 and GOSH2

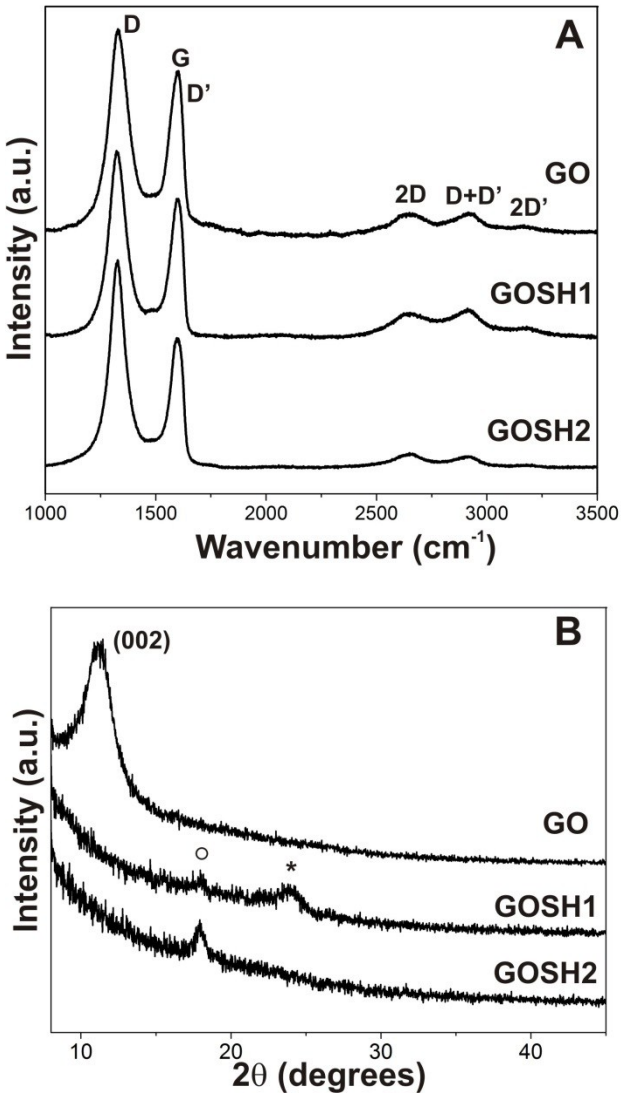

Figure S3. (A) Raman spectra (ʎ = 632.8 nm) and (B) XRD diffractograms of GO, GOSH1 and GOSH2 films (glancing angle mode).

5. Raman spectra of nanocomposites

Further RAMAN data mentioned in the synthesis and characterization session of nanocomposites in the manuscript are given bellow.

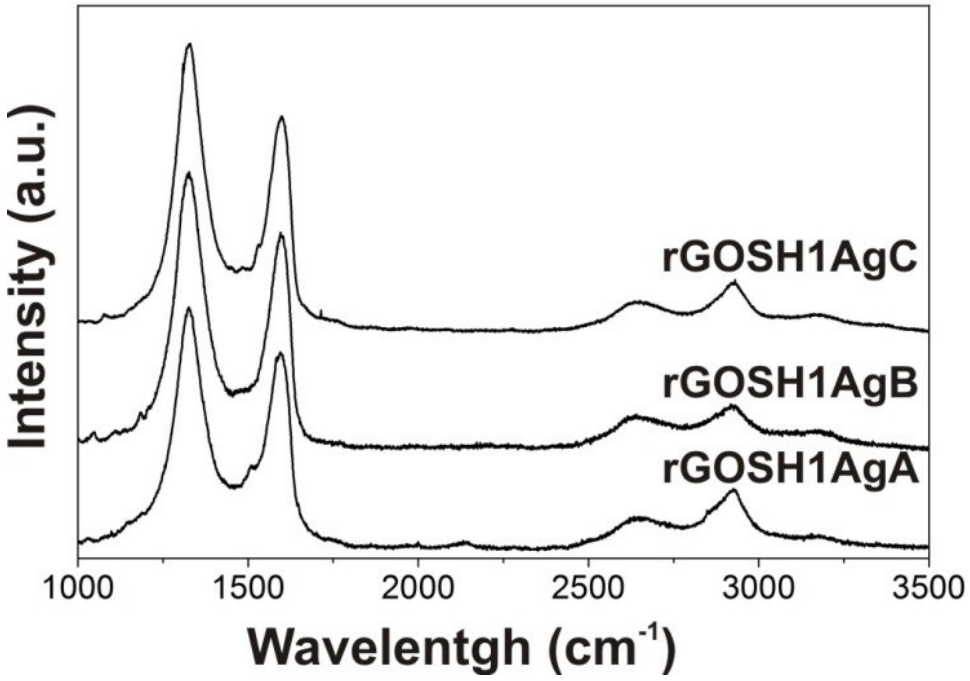

Figure S4 – RAMAN spectra (ʎ = 632.8 nm) for the nanocomposites obtained with GOSH1 thin film.

6. Kinetic analysis

6.1 Kinetic profile of GO with DEDNPP

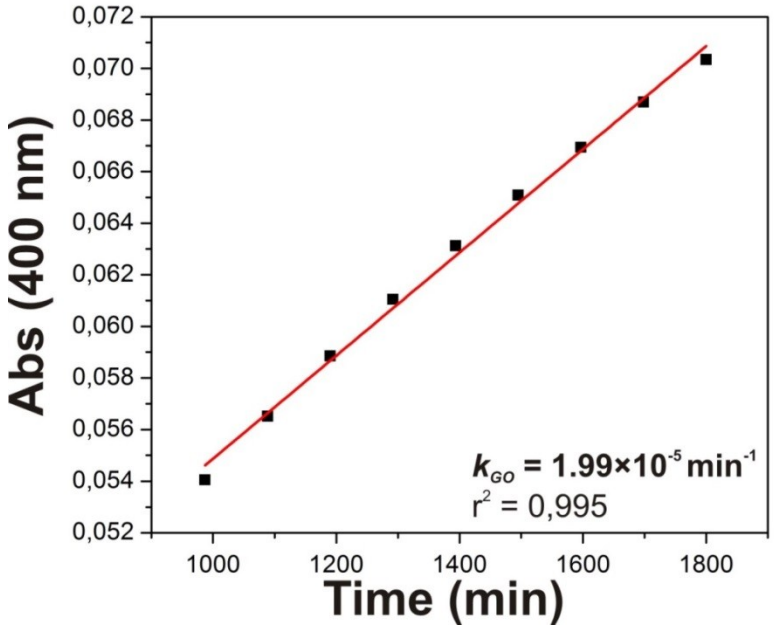

Figure S5. Profile obtained from UV-Vis spectra at different times of the reaction of GO and DEDNPP. Initial rate method applied.

6.2. Recycling of nanocatalyst

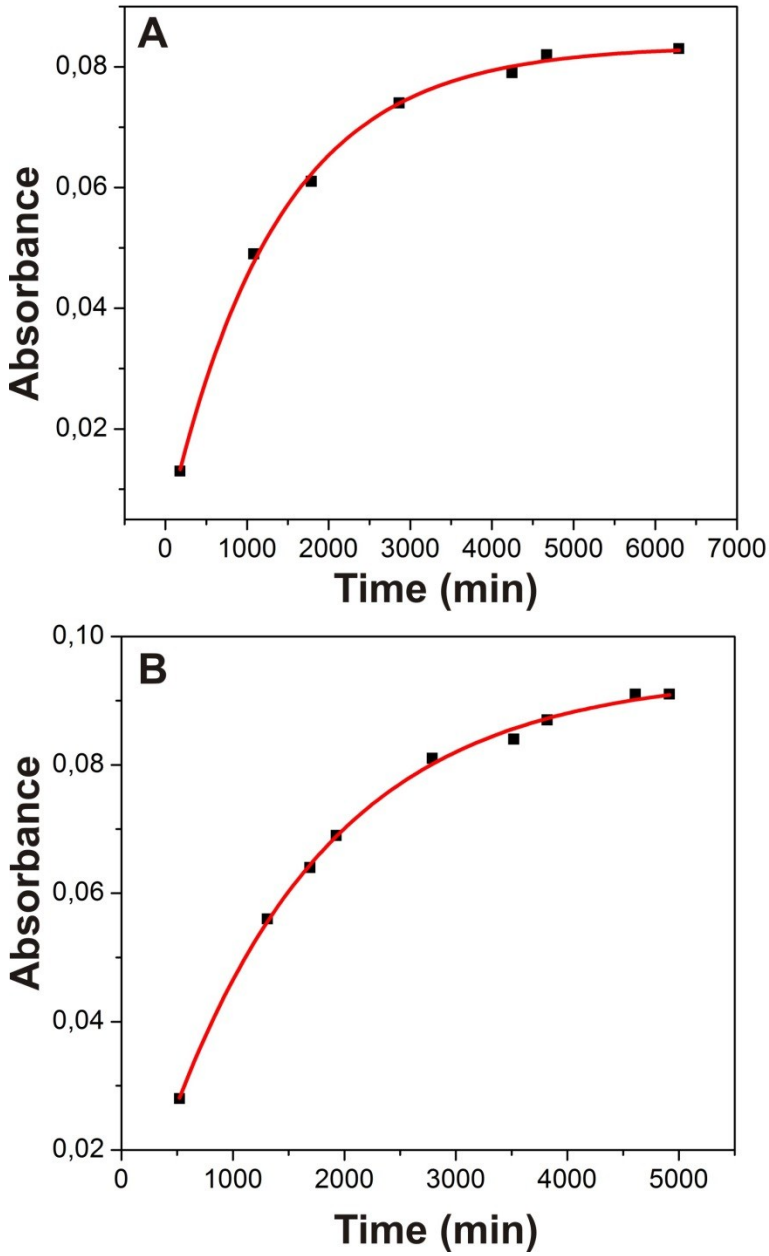

Figure S6. Profile obtained from UV-Vis spectra at different times of the reaction of used GOSH2 and DEDNPP. Initial rate method applied.

6.3 Characterization of GOSH1 before and after catalysis

6.3.1. FTIR data

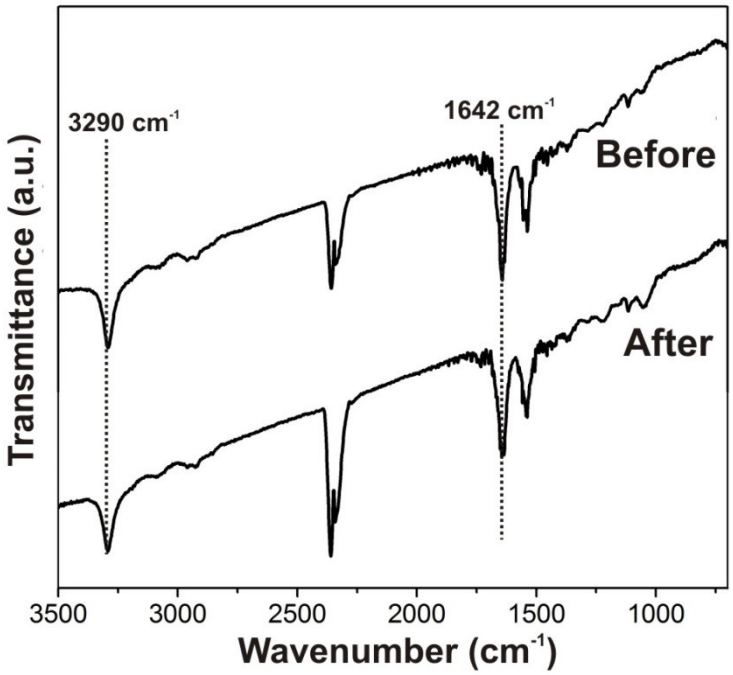

Figure S7. FTIR spectra of the nanocatalyst before and after reaction with DEDNPP.

6.3.2. Raman data

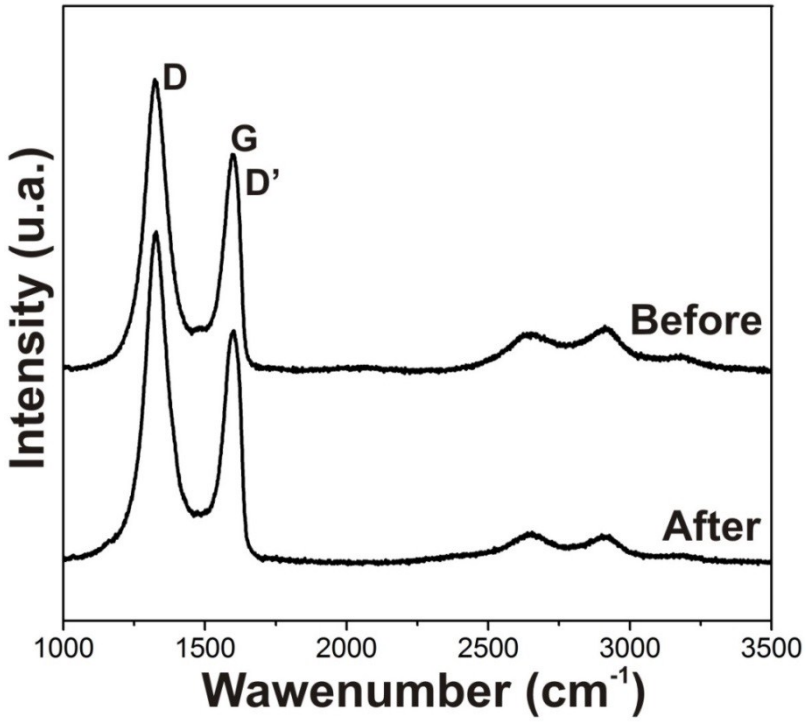

Figure S8. Raman spectra (ʎ = 632.8 nm) obtained before and after GOSH1 employment in DEDNPP dephosphorylation reaction.

6.3.3. SEM analysis

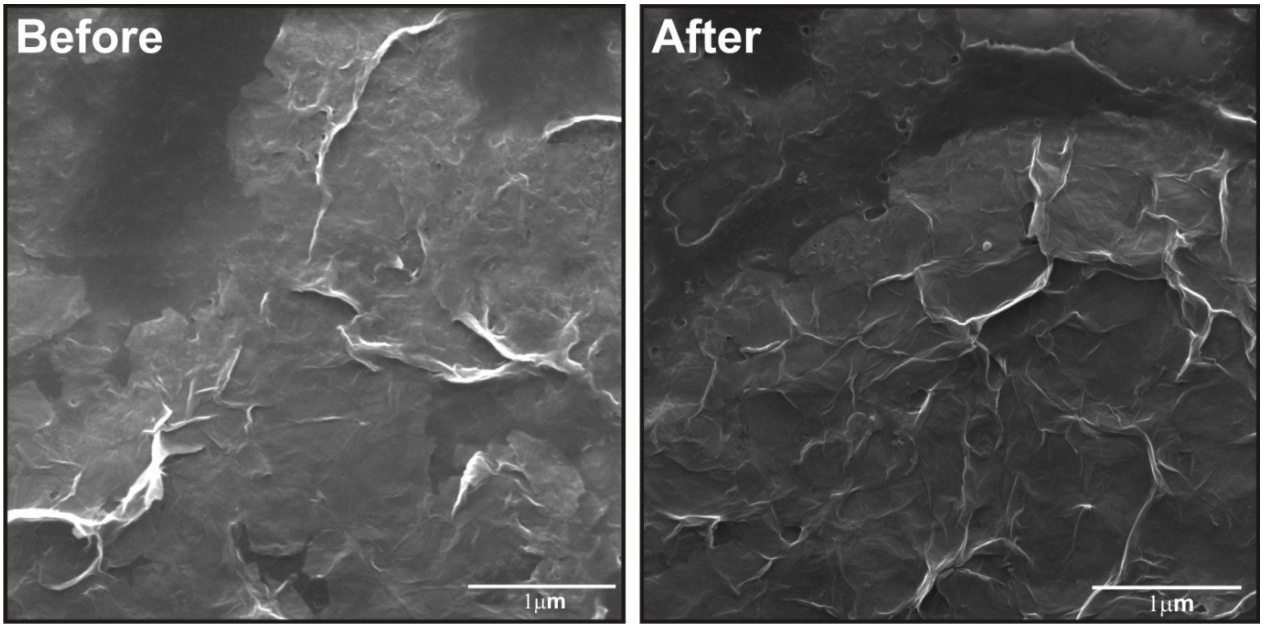

Figure S9. SEM images obtained before and after GOSH1 employment in DEDNPP dephosphorylation reaction.

6.4. Kinetic profile of GOSH1 and Paraoxon

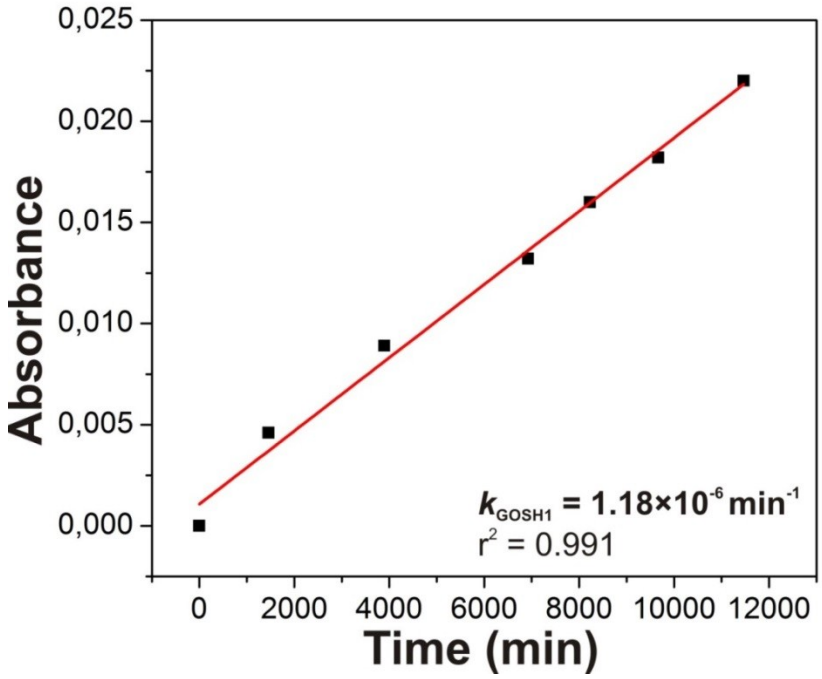

Figure S10. Profile obtained from UV-Vis spectra at different times of the reaction of GOSH1 and Paraoxon. Initial rate method applied, $k_{GOSH1} = 5.92\times10^{-4}$ s^{-1} g^{-1}.

6.5. Kinetic profile of GOSH2 and Paraoxon

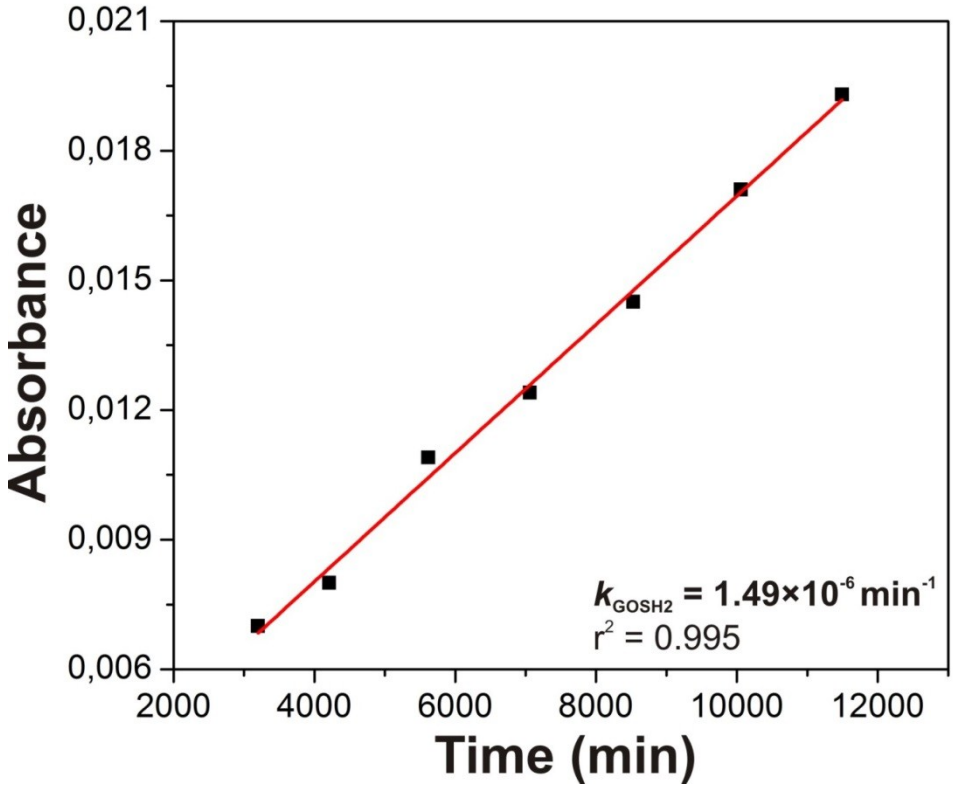

Figure S11. Profile obtained from UV-Vis spectra at different times of the reaction of GOSH2 and Paraoxon. Initial rate method applied, $k_{GOSH2} = 4.86\times10^{-4}$ s^{-1} g^{-1}.

7. Raman data of 4-ATP

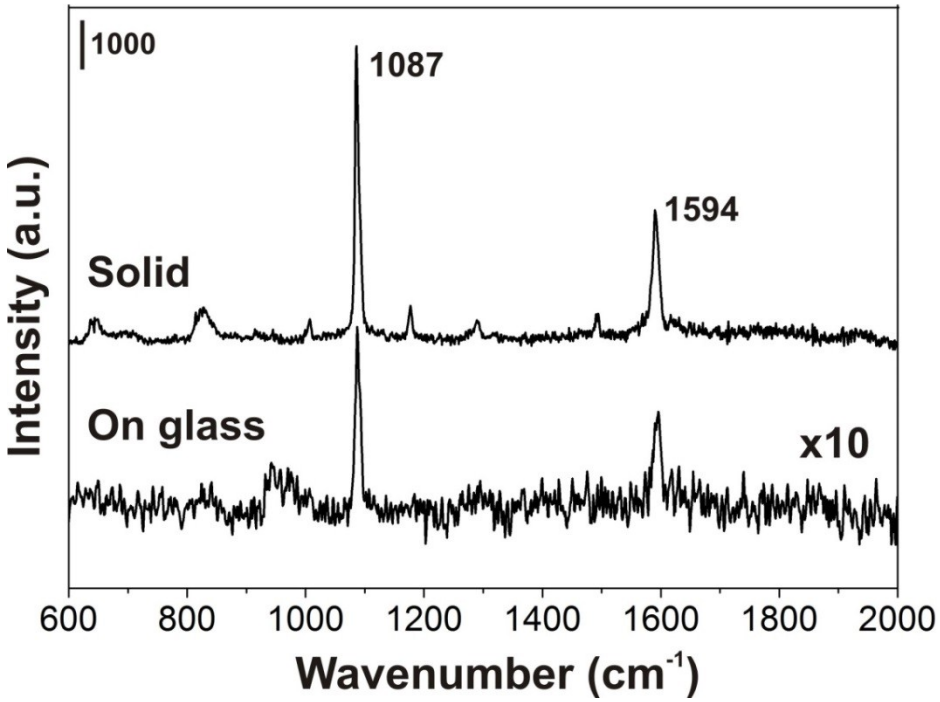

Figure S12. Raman spectra (ʎ = 632.8 nm) of solid 4-ATP and 4-ATP (1×10^{-3} mol L^{-1}) over glass.

8. SERS: Detailed description of EF equation

The band centered at 1087 cm^{-1} was used to calculate the values, avoiding conflict with graphene bands. N_{normal} and N_{sers} are the number of molecules adsorbed within the laser spot in a normal Raman and in SERS setting, respectively. N was obtained considering the drop diameter of 4-ATP as 0.75 cm, from where we can obtain an area ($A = \pi \times r^2$) related to an amount of molecules (30 μL at 1×10^{-10} mol L^{-1}). Then, the same relation is done considering the laser spot of 1 μm^2. So, we consider only the amount of molecules illuminated by the laser. All spectra were normalized accordingly to laser power.[1]

REFERENCES

1. S. Zhang, X. Tian, J. Yin, Y. Liu, Z. Dong, J.-L. Sun and W. Ma, *Scientific Reports*, 2016, **6**, 24503.

.**Raman data of DNP and DEDNPP solutions**

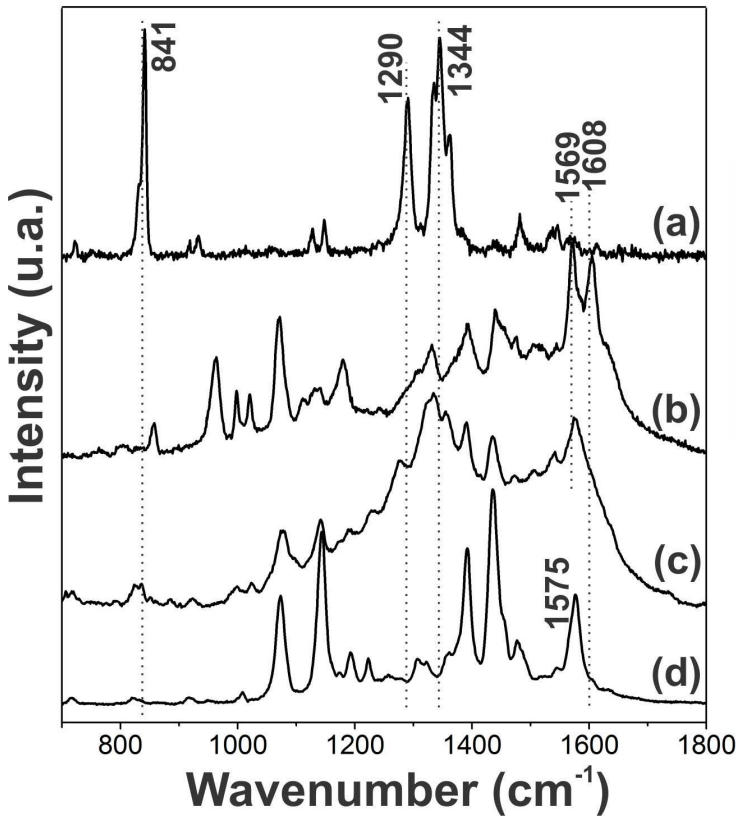

Figure S13. Raman spectra (ʎ = 632.8 nm) of control samples dropped over different substrates: (a) DNP on rGOSH1AgC film, (b) DNP on glass (c) DEDNPP on rGOSH1AgC film and (d) DEDNPP on glass.

REFERENCES

(1) Domingues, S. H.; Salvatierra, R. V.; Oliveira, M. M.; Zarbin, A. J. G. *Chemical Communications* **2011**, *47*, 2592.