

Electronic Supplementary Information

for

Ultrasensitive and Selective Sensing of Heavy Metal Ions with Modified Graphene

Chunmeng Yu^b, Yunlong Guo^a, Hongtao Liu^a, Ni Yan^b, Zhiyan Xu^b, Gui Yu^a, Yu Fang^{b*} and Yunqi Liu^{a*}

^aBeijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China

^bKey Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education), School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi'an 710062, P. R. China

1. Experimental section

Materials: 1,7-heptanediamine (99%) and D-glucono-1,5-lactone (99%) were purchased from Alfa Aesar and used as received. Pyrene (Acros, 96%) was re-crystallized from an ethanolic solution and then extracted with Soxhlet extractor by ethanol. All solvents and other chemicals used were of analytical grade and used after purification by standard literature methods. Graphite flakes (natural, Alfa Aesar, 325 mesh, 99.8%), NaNO₃ (Sinopharm Chemical Reagent, Co., Ltd, AR), KMnO₄ (Beijing Yili Fine Chemicals, Co., Ltd, AR), and concentrated H₂SO₄ (Beijing Chemical Works, AR) were all used as received.

Preparation of GO: GO was prepared by a modified Hummers method from the natural graphite,¹ and was then fully dissolved into water due to the strong hydrophilic properties of oxygenated groups. Stable GO sheets generated by sonication of the aqueous suspension of graphite oxide were directly reduced to obtain ERGO film with an electrochemical method.

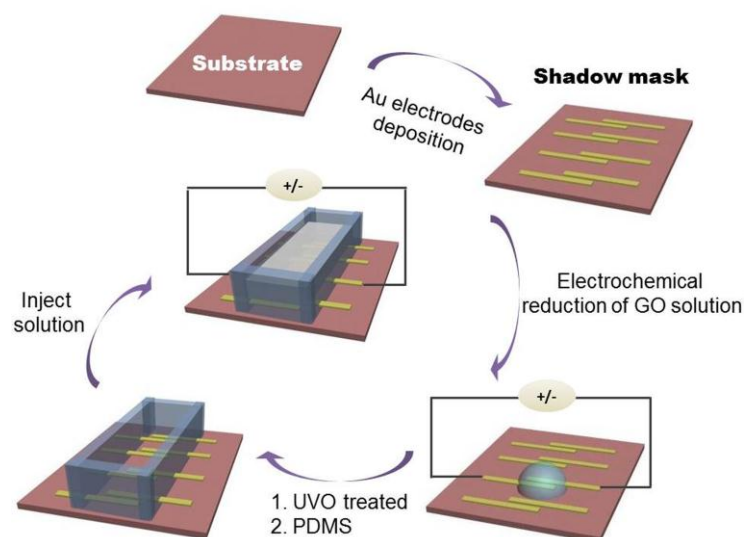
Preparation of the PG Compound: The PG was synthesized according to a method reported by some of the authors recently.²

Fabrication of Sensor Device: Au films as electrodes (100 μm width and 50 μm length) were deposited on glass substrate through vacuum evaporation with a shadow mask. A drop of the GO aqueous suspension was then dropped on the surfaces between the two electrodes and a certain voltage ($V = 0 - 4$ V) was applied in the electrodes with several cycles in order to carry out an electrochemical reduction process. The electrochemical reaction can be expressed as: $GO + H^+ + e^- = RGO + H_2O$, and eventually, ERGO sheets with sufficient conductivity were deposited between the electrodes. After that, the residue GO films were washed with deionized water (DI), and finally the immobilized ERGO films were obtained. The sensor measurements were performed in a flow cell made of flexible polydimethylsiloxane (PDMS) elastomer to confine the tested solution to the ERGO surface. It is noted that the contact areas between the glass substrate and the homebuilt PDMS cell, treated with UVO for 40 mins, were sealed through chemical bonding in vacuum oven at 100 °C for 1 h.

Non-covalent Modification of the Sensor Device: The ERGO sheets were fully covered with the PG/DI solution with 1 mM for 1 h at room temperature, in which process the PG was firmly adsorbed on the ERGO surface through π - π interaction. After that, the device was rinsed with DI to remove the extra-PG.

Metal Ions Detection: All detection measurements were carried out with Keithley 4200 SCS semiconductor parameter analyzer at ambient temperature and pressure. In a typical measurement, 35 μ L of DI or a given metal ion solution was pipetted into the homemade PDMS cell and the two-terminal electrodes were biased at a constant voltage. The current of the sensor device was continuously recorded when a certain voltage was applied and a metal ion solution was added. It is to be noted that all the results shown in the Figures including those shown in the Supporting Information were obtained through several testes conducted in 2-3 sensor devices to make sure that the results can be repeated and the systems are stable.

2. Fabrication process of sensor device



Scheme S1. Schematic illustration of Fabrication process for electronic sensor device based on ERGO.

3. Raman spectra and SEM images

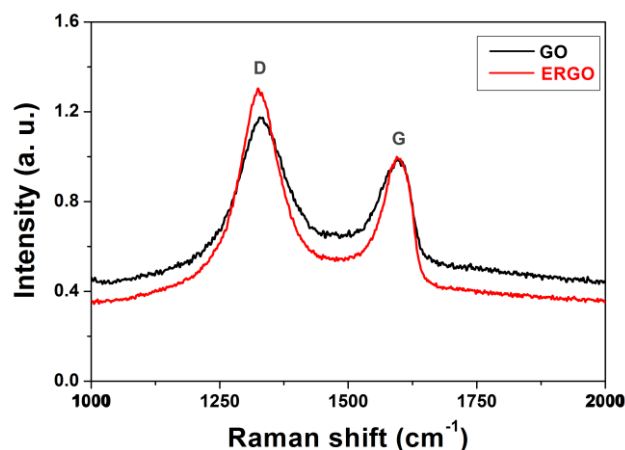


Figure S1. Raman spectra of the ERGO and GO sheet.

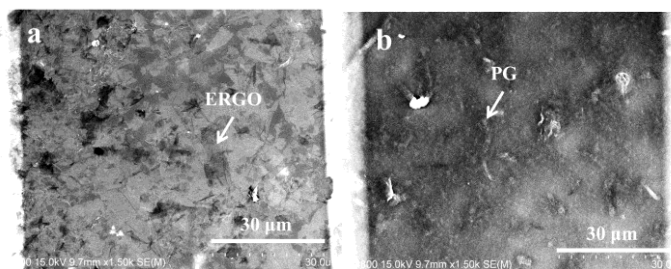
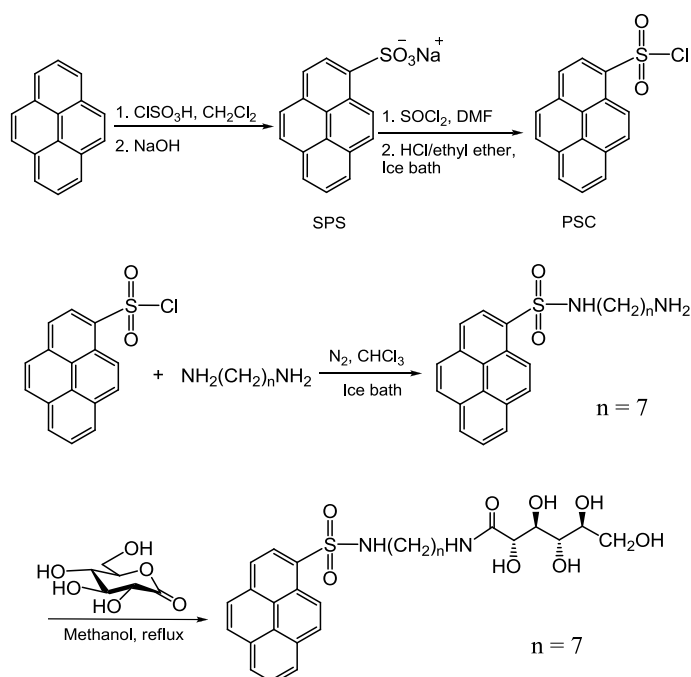


Figure S2. The SEM images of the ERGO surface (a) and ERGO surface decorated with PG (b).

4. Synthesis routes and characterization of glucose derivative of pyrene (PG)



Scheme S2. Synthesis route of N-[(1-pyrenyl-sulfonamido)-heptyl]-gluconamide (PG).

The characterization data of N-[(1-pyrenyl-sulfonamido)-heptyl]-gluconamide (PG) are provided below:

^1H NMR ($\text{DMSO}-d_6/\text{Me}_4\text{Si}$, 300 MHz) δ (ppm): 9.00-9.03 (d, J = 9 Hz, 1H), 8.59-8.61 (d, J = 6 Hz, 1H), 8.20-8.48 (m, 7H), 8.10 (s, 1H), 7.46 (s, 1H), 5.35 (s, 1H), 4.35-4.58 (m, 4H), 3.90-3.97 (m, 2H), 3.38-3.60 (m, 4H), 2.80-2.82 (b, 4H), 0.85-1.24 (m, 10H). ^{13}C NMR ($\text{DMSO}-d_6/\text{Me}_4\text{Si}$, 100 MHz): δ 172.53 (1C, CO), 134.32, 133.17, 130.96, 130.30, 130.13, 129.80, 127.55, 127.39, 127.21, 127.15, 127.06, 124.73, 124.59, 124.32, 123.93, 123.63 (16C, ArC), 74.02, 72.85, 71.91, 70.51, 63.80 (5C, COH), 42.66, 38.47, 29.29, 29.26, 28.48, 26.48, 26.16 (7C, CH₂). FTIR (KBr) ν_{max} (cm^{-1}): 3419 (NH), 3590-3050 (OH); 3375 (HNSO₂); 2929 (CH); 1625 (C=O); 1544 (NH); 1430 (CN); 1308, 1141 (S=O). EA (%) calcd for $\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}_8\text{S}\cdot\frac{1}{2}\text{H}_2\text{O}$: C, 59.88; H, 6.41; N, 4.82. Found: C, 59.71; H, 6.27; N, 4.94. mp: 139.9-142.4 °C.

5. Sensor performances for metal ions

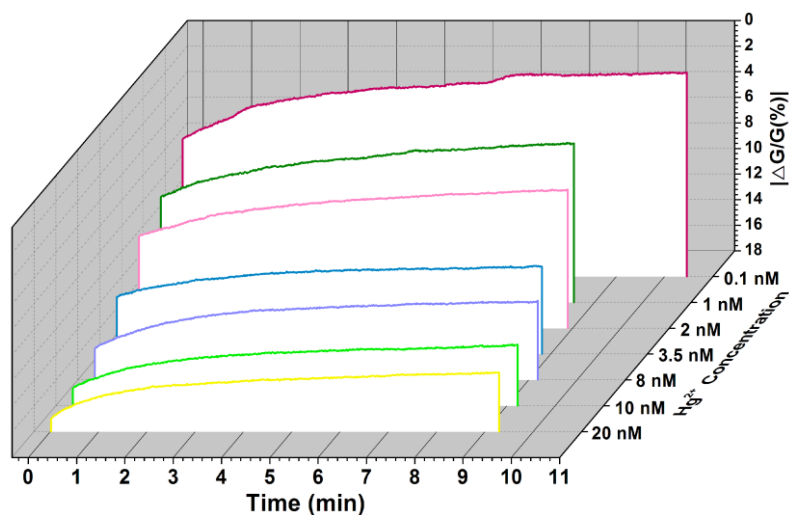


Figure S3. The conductivity changes versus time upon addition of Hg^{2+} solutions of different concentration.

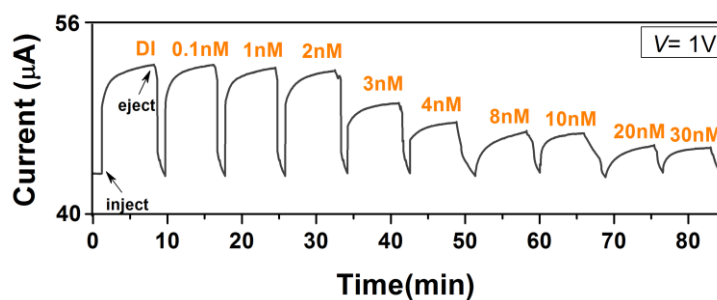


Figure S4. The real-time current recording of the modified ERGO sensor upon addition of Cd^{2+} solutions of different concentration.

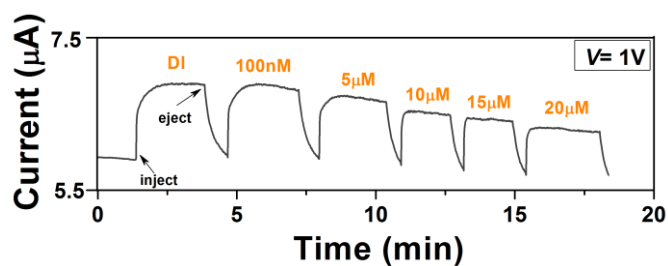


Figure S5. The real-time current recording of the modified ERGO sensor upon addition of Cu^{2+} solutions of different concentration.

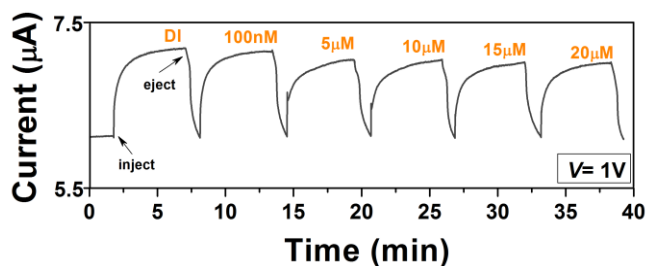


Figure S6. The real-time current recording of the modified ERGO sensor upon addition of Fe^{3+} solutions of different concentration.

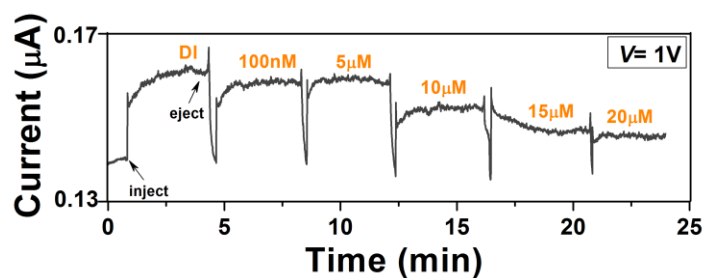


Figure S7. The real-time current recording of the modified ERGO sensor upon addition of K^+ solutions of different concentration.

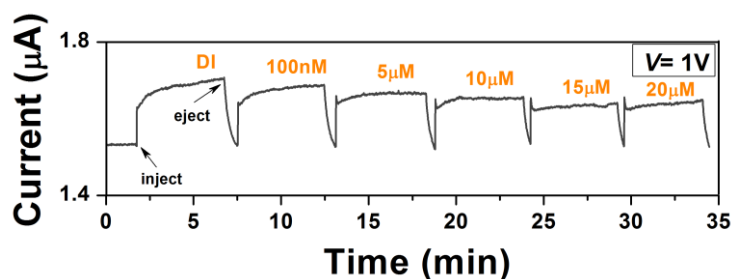


Figure S8. The real-time current recording of the modified ERGO sensor upon addition of Na^+ solutions of different concentration.

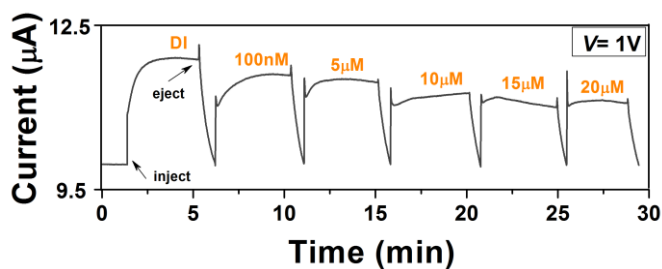


Figure S9. The real-time current recording of the modified ERGO sensor upon addition of Zn^{2+} solutions of different concentration.

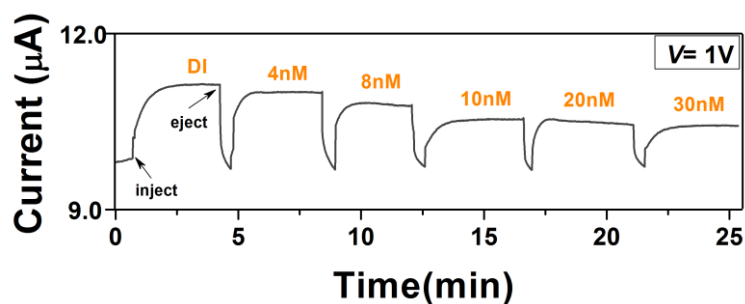


Figure S10. The real-time current recording of the modified ERGO sensor upon addition of Hg^{2+} solutions of different concentration.

References

- 1 M. Hirata, T. Gotou, S. Horiuchi, M. Fujiwara and M. Ohba, *Carbon*, 2004, **42**, 2929.
- 2 N. Yan, Z. Xu, K. K. Diehn, S. R. Raghavan, Y. Fang and R. G. Weiss, *Langmuir*, 2012, **29**, 793.