

Supplementary Information for “Selective adsorption toward toxic metal ions results in selective response: electrochemical studies on polypyrrole/reduced graphene oxide nanocomposite”

Experimental Section

Chemical Reagents. Graphite (325 mesh) was from Alfa Aesar, all other reagents were commercially available from Sinopharm Chemical Reagent Co. Ltd. (China) with analytical grade and were used without further purification. The water used to prepare all solution was purified with from a Millipore water purification system (MilliQ, specific resistivity >18 MΩ cm, S.A., Molsheim, France) and used in all runs.

Apparatus. Electrochemical experiments were recorded using a CHI 660D computer-controlled potentiostat (ChenHua Instruments Co., Shanghai, China) with a standard three-electrode system. A bare glass carbon electrode (GCE, diameter of 2 mm) or modified GCE served as a working electrode; a platinum wire was used as a counter-electrode with a saturated Ag/AgCl electrode (ChenHua Instruments Co., Shanghai, China) completing the cell assembly. All experiments were performed at a temperature of 25±1°C.

Preparation of graphene oxide (GO), reduced graphene oxide (RGO), polypyrrole (PPy) and polypyrrole–reduced graphene oxide (PPy-RGO) nanocomposites. GO was synthesized from natural flake graphite (325 mesh) by Hummers method. Polypyrrole was synthesized by chemical polymerization using ammonium persulphate (APS) of freshly distilled pyrrole and chemical reduction of graphene oxide to reduced graphene oxide was done according to Kims' report.^[15] Briefly, Nanocomposites were synthesized by dilute polymerization in the presence of GO and pyrrole monomer. 45mg GO was dispersed in 45 mL H₂O under ultrasonication. Then pyrrole monomer (300 mg) was slowly added dropwise into the GO solution and continuously stirred at 0-5 °C for 30 min. Then 8.33 mL aqueous solution of APS (4g/25mL) was slowly added into the solution. The polymerization was carried out at 0-5 °C for 10 h with constant mechanical stirring.^[39,40] The formed product was washed with copious amount of water and dispersed in 50 mL distilled water. At 90 °C 450 μL hydrazine hydrate was added and reduced for 12 h which results in formation of PPy-RGO. The final product was dried in a vacuum oven at 40 °C.

Electrode Fabrication. The construction of PPy-RGO film on the surface of glassy carbon macroelectrodes were performed as follows: 50 mg of PPy-RGO nanocomposites were suspended in 1 mL of distilled water to form a suspension. The suspension was then briefly sonicated for 30 s in order to disperse the nanocomposites. A 5 μL aliquot of this suspension was then pipetted onto the surface of a freshly polished glassy carbon electrode. Similar procedure was used to prepare PPy modified electrode.

Electrochemical Experiments. The electrochemical characterization including cyclic voltammograms and EIS (electrochemical impedance spectra) were performed in a degassed solution with a high purity N₂ (Nanjing Special Gases Factory Co., Ltd.) containing 5 mM K₃Fe(CN)₆ and 0.1 M KCl. The frequency range is from 0.1 Hz to 10000 Hz with signal amplitude of 5 mV, and the scan rate is 0.1 V s⁻¹.

Hg²⁺ was chemically preconcentrated by immersing the PPy-RGO/GCE in the solution (pH 7.0) containing Hg²⁺ (varied from 10 to 100 nM) for 20 min in an open circuit potential conditions. The solution was stirred efficiently (below 250 rpm) during preconcentration. The electrode was taken out, and thoroughly washed with water and then kept in a cell containing 10 mL of supporting electrolyte solution (10 mM HNO₃ and 0.3 M KCl). A negative potential of -0.7V was applied to the electrode immediately for 60 s to reduce Hg²⁺ into Hg⁰. Subsequently, the square wave anodic stripping voltammetry (SWASV) measurements were performed in the potential range from -1.0 to +0.60 V with a frequency of 15 Hz, amplitude of 25 mV, and a potential step of 4 mV. After the measurements, the electrode was regenerated by immersing in a stirring solution containing 0.2 M HNO₃ at +0.8 V for 60 s. The renewed electrode then was checked in the supporting electrolyte before the next measurement to ensure that it did not show any peak within the potential range. All measurements were performed at room temperature.

Characterization. The morphology of polypyrrole-reduced graphene oxide and Polypyrrole on the electrode surface was verified by field-emission scanning electron microscopy (FESEM, Quanta 200 FEG, FEI Company, USA). Transmission electron microscopy (TEM) was performed using a JEM-2010 microscope equipped with Oxford INCA EDS operated at 200 kV accelerating voltage (Quantitative method: Cliff Lorimer thin ratio section). Atomic force microscopy (AFM) images were carried out using Nanoscope III (Digital Instruments, Veeco Metrology). FT-IR spectroscopy was performed using an IFS 66v/S Vacuum FT-IR. X-Ray photoelectron spectroscopy (XPS) analyses of the samples were conducted on a VG ESCALAB MKII spectrometer using an Mg K α X-ray source (1253.6 eV, 120 W) at a constant analyzer. The energy scale was internally calibrated by referencing the binding energy (Eb) of the C 1s peak at 284.60 eV for contaminated carbon. The Raman measurements were carried out using a DXR Smart Raman spectrometer with 514 nm excitation laser lines (Thermal Fisher).

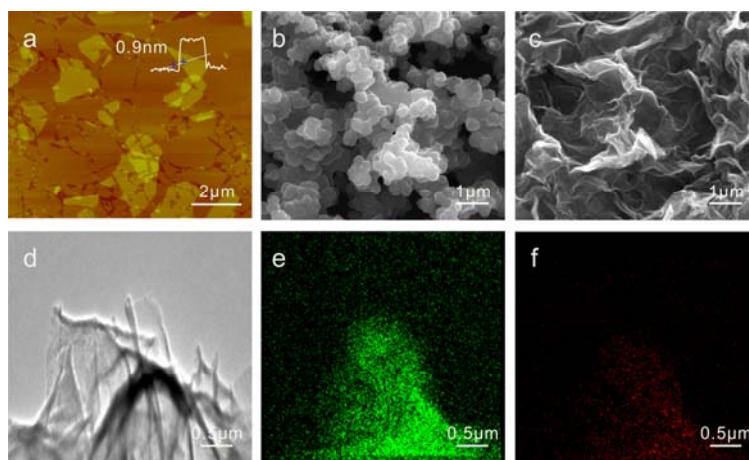


Figure S1 (a) A tapping mode AFM image of GO with height profile. (b) SEM image of PPy. (c) SEM image of the PPy-RGO nanocomposite. (d) TEM image of the PPy-RGO composite. (e-f) Carbon and nitrogen mapping images in the PPy-RGO nanocomposite.

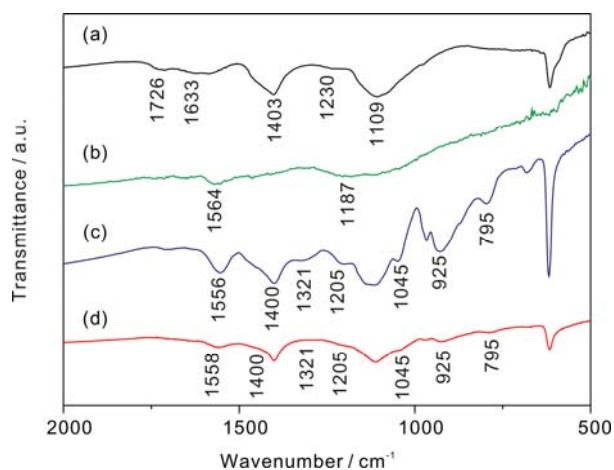


Figure S2 FT-IR spectra of (a) graphene oxide, (b) reduced graphene oxide, (c) polypyrrole, and (d) PPy-RGO nanocomposite

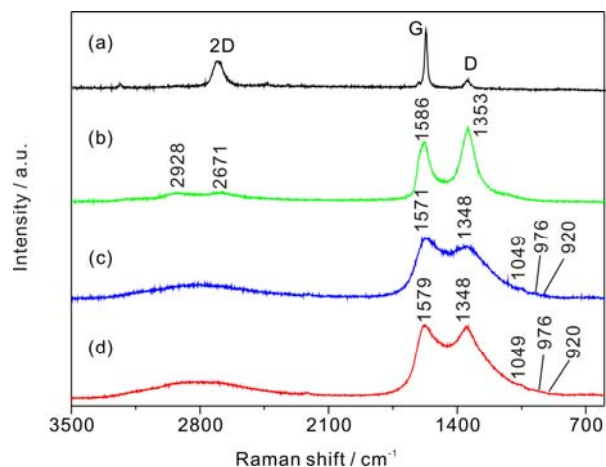


Figure S3 Raman spectra (514 nm) of (a) graphite, (b) RGO, (c) polypyrrole, and (d) PPy-RGO composite.

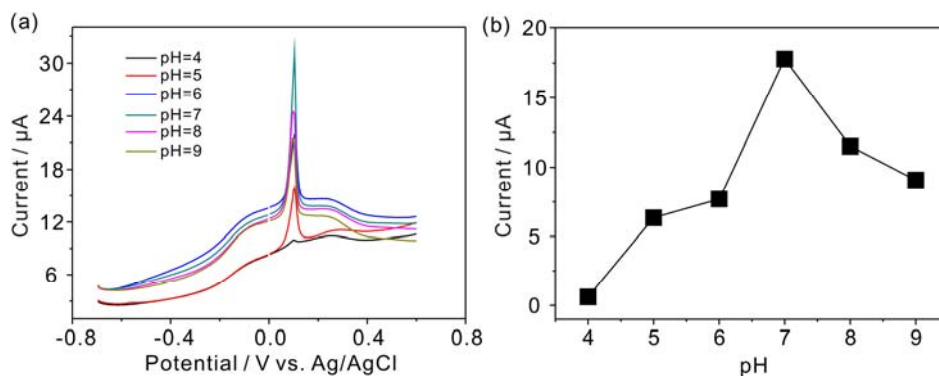


Figure S4 Effect of pH of the solution containing 100nM Hg(II) on the SWASV response using PPy-RGO/GCE. (preconcentration time: 30 min)

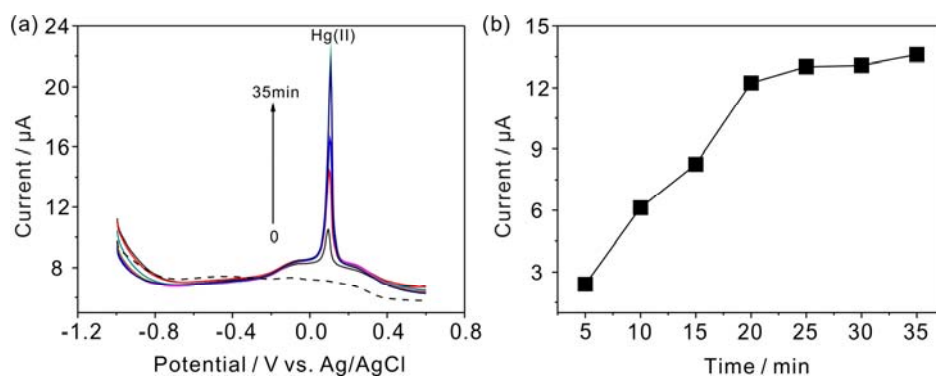


Figure S5 Effect of preconcentration time of the solution containing 100 nM Hg(II) on the SWASV response using PPy-RGO/GCE.

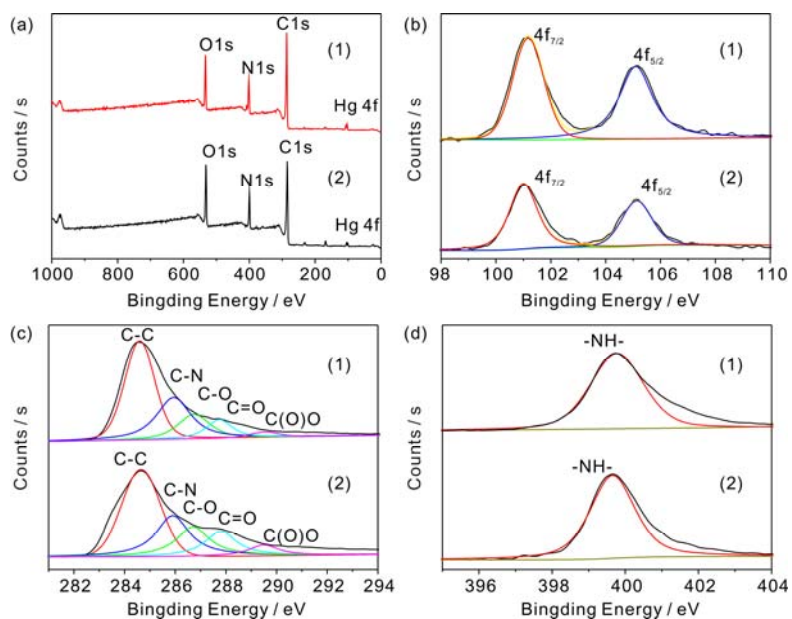


Figure S6 X-ray photoelectron spectrum after Hg^{2+} adsorption on PPY-RGO composite (1) and PPY (2). (a) full spectrum, (b) Hg 4f spectrum, (c) C1s spectrum, and (d) N1s spectrum.

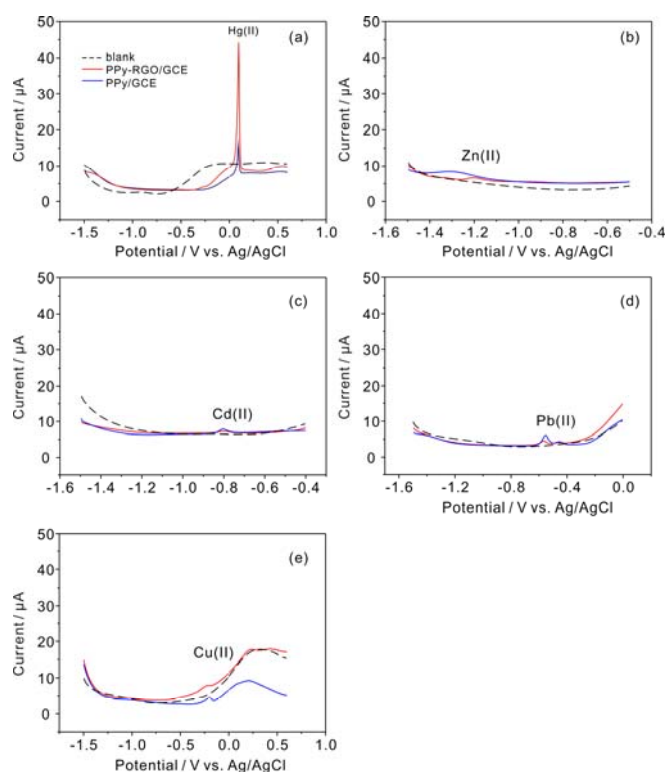


Figure S7 Typical SWASV stripping signals of (a) Hg^{2+} , (b) Zn^{2+} , (c) Cd^{2+} , (d) Pb^{2+} , and (e) Cu^{2+} on the PPY/GCE (blue) and PPY-RGO/GCE (red). The dotted line is baseline.