

Electronic Supporting Information

Sensitive and Selective Voltammetric Measurement of Hg²⁺ by Rational Covalent Functionalization of Graphene Oxide with Cysteamine

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Experimental Section

Chemicals. Cysteamine was purchased from Acros Organics without further purification. Solutions of metal ions were prepared daily with 0.10 M HCl solution. All chemicals used were of analytical grade. (*Caution! Hg²⁺ is highly toxic; proper care must be taken in handling and waste disposal.*) All the solutions were prepared using Milli-Q water (18.2 MΩ cm). Electrochemical experiments were conducted at room temperature.

Synthesis of cysteamine-functionalized graphene. Graphite oxide was firstly synthesized from graphite by a modified Hummers method,¹ which was suspended into water. The suspension was then subject to dialysis to remove residual salts and acids. After that, the suspension was again dispersed into water to form 0.05 wt % dispersion of graphene oxide. The resulting dispersion was then subject to 30 min of centrifugation at 3,000 r.p.m to remove any unexfoliated graphite oxide. The obtained dispersion of exfoliated graphene oxide (10.0 mL) was mixed with 10 mg cysteamine and 10 mg KOH into a vial and the resulting mixture was then subject to ultrasonication for 30 minutes until formation of a homogeneous and transparent dispersion. The homogeneous dispersion was then vigorously stirred at 80 °C for 24 h. Finally, the resulting product was centrifuged, washed with ethanol and water, and dried. The final product was dispersed in water to give a 0.50 mg/mL dispersion by ultrasonication.

Apparatus and electrochemical measurements. All electrochemical measurements were performed with a computer-controlled electrochemical analyzer (BAS 100B/W, BAS) with a conventional three-electrode cell. For metal ion detection, the cysteamine-functionalized graphene modified Au electrodes were used as working electrode, platinum spiral wire as counter electrode, and Ag/AgCl (KCl-saturated) electrode as reference electrode. For preparation of the cysteamine-functionalized graphene modified Au electrodes, bare Au electrodes were firstly polished with alumina powder (0.05 and 0.3 μm) and sonicated in Milli-Q water and ethanol, each for 3 min. The electrodes were then electrochemically cleaned by consecutively cycling the potential between -0.20 and +1.60 V at 0.5 V/s in 0.50 M H₂SO₄ solution until a cyclic voltammogram characteristic of a clean Au electrode was obtained. Cysteamine-functionalized graphene modified Au electrodes were prepared by immersing the clean bare Au electrodes into 0.50 mg/mL solution of cysteamine-functionalized graphene for 12 h. The electrodes were then washed with Milli-Q water and air-dried. For detection of metal ions, the cysteamine-functionalized graphene modified Au electrodes were first immersed into 0.10 M HCl solution containing different

metal ions for 2 h. The electrodes were then taken out of the solutions and rinsed with water. After that, the electrodes were immersed into 0.10 M HCl solution containing no metal ions and were polarized at -0.10 V for 10 s prior to the electrochemical measurements. For control experiments, graphene oxide modified Au electrodes were prepared by first dip-coating of 3 μ L graphene oxide dispersion (0.05 wt%) onto Au electrodes and then allowing the electrodes to be dried under room temperature. For electrochemical measurements, square wave anodic stripping voltammetry (SWASV) was used. The conditions for SWASV were: scan rate, 4 mV/s; reduction time, 10 s; frequency, 14 Hz; and amplitude, 25 mV.

Fourier Transform Infrared (FT-IR) spectra were recorded on Tensor-27 FT-IR spectrometer (Bruker) with KBr pellet. X-ray photoelectron spectroscopy (XPS) used for characterization of functionalized graphene was performed on an ESCALab220i-XL electron spectrometer from VG Scientific under the condition of using 300W AlK α radiation, the base pressure was about 3×10^{-9} mbar and the binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

Reference

1. W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.