NOTE

Picomolar detection of mercury (II) using a three-dimensional porous graphene/polypyrrole composite electrode

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Abstract A polypyrrole (PPy)-functionalized three-dimensional (3D) porous electrode of electrochemically reduced graphene oxide (ErGO) has been prepared by electrochemical deposition. This PPy-modified 3D-ErGO electrode was used for the electrochemical detection of Hg^{2+} ions, and it exhibited high sensitivity and selectivity. Furthermore, the limit of detection (LOD) was measured to be as low as 0.03 nM (30 ppt), and this value is much lower than the guideline value of 2 ppb for drinking water given by the World Health Organization.

Keywords Polypyrrole · Reduced graphene oxide · Hg^{2+} ions · Porous electrode

Introduction

Mercury and its compounds are highly toxic. To control the quality of drinking water, the limit of its Hg^{2+} ion content has been set to be as low as 2 ppb [1]; thus, the development of selective and sensitive techniques to detect mercury in water is important. Atomic absorption spectroscopy, inductively coupled plasma atomic emission spectrometry, and X-ray fluorescence have been successfully used for this purpose. However, these methods are limited in practical applications because of the requirements of expensive instruments and the complicate procedures of pretreating samples. Electrochemical approaches can address these issues, while their performances need to be optimized by rationally choosing

electrolytes and/or functionalization of electrodes [2, 3]. Recently, PPy/rGO composite-modified glassy carbon (GC) electrode has been used to selectively detect Hg^{2+} ions [3]. The mechanism of this sensing process is believed to be that Hg^{2+} ions can selectively coordinate with the nitrogen atoms of the pyrrole units of PPy in a 1:4 complexation mode [3]. However, in this case, the electrode surface has a nearly compact morphology with a limited surface area for accumulating the target ions. Recently, we developed a one-step electrochemical deposition technique to fabricate electrochemically reduced graphene oxide (ErGO) electrode with interconnected three-dimensional (3D) microstructures [4]. This unique structure and the excellent electrical and electrochemical properties of ErGO make the 3D-ErGO electrode attractive for electrochemical sensing. Here, we report a PPy-modified 3D-ErGO composite electrode (3D-ErGO/PPy) for the sensitive and selective electrochemical sensing of Hg^{2+} ions with an extremely low limit of detection.

Materials and methods

GO was prepared by the oxidation of natural graphite powder (325 mesh, Qingdao Huatai Lubricant Sealing S&T Co. Ltd., Qingdao, China) according to a modified Hummers' method [4]. It was purified by dialysis for 1 week using a dialysis membrane with a molar mass cutoff of 8,000 to 14,000 g mol^{-1} to remove the remaining metal species.

3D-ErGO electrodes were fabricated by electrochemical deposition of rGO sheets on the surfaces of gold (Au) disk electrodes. The Au electrode was chosen because it had been tested to be the best substrate for growing 3D-ErGO [4]. Prior to use, Au electrodes (3 mm in diameter) were carefully polished with 0.5- and 0.05-μm alumina powder slurries and then washed by sonication successively in water and ethanol for a few minutes. A clean Au electrode was used as the

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working electrode, a platinum (Pt) foil was applied as the counter electrode, and all the potentials were referred to an Ag/AgCl electrode. A 3-mg mL^{-1} GO dispersion containing 0.1 M LiClO$_4$ was used as the electrolyte. The electrochemical deposition was carried out at a constant potential of -1.2 V by using a CHI 660D potentiostat-galvanostat (CH Instruments Inc.). During this process, GO sheets were reduced into conductive 3D-ErGO as reported in the literature [4]. Finally, the electrodes were washed with deionized water and successively immersed in deionized water for 1 h to remove the residual GO absorbed on the electrodes. For comparison, flat ErGO electrodes have also been fabricated by electrochemical reduction, and the procedures are described as follows. Five microliters of 3 mg mL^{-1} GO dispersion was pipetted onto the

surface of a freshly polished gold disk electrode. After drying in air, the GO coating on the electrode was reduced at a constant potential of -1.2 V under the same condition as that used for fabricating 3D-ErGO electrodes.

The 3D-ErGO/PPy electrodes were prepared by electrochemical deposition of a thin PPy layer on the surface of 3D-ErGO electrode. An aqueous solution of 0.1 M pyrrole and 0.1 M sodium dodecyl benzene sulfonate (SDBS) was used as the electrolyte, and PPy was deposited at a potential of 0.7 V for 2 s. Finally, the electrodes were soaked in deionized water to remove electrolyte and residual monomer molecules. The PPy-modified Au disk electrode (PPy electrode) and PPy-modified ErGO electrodes (ErGO/PPy electrodes) were also prepared for comparison. An Au or ErGO electrode was used

Fig. 1 Side (**a**, **c**, **e**) and top (**b**, **d**, **f**) view SEM images of 3D-ErGO (**a**, **b**), 3D-ErGO/PPy (**c**, **d**), and flat ErGO/PPy (**e**, **f**) electrodes
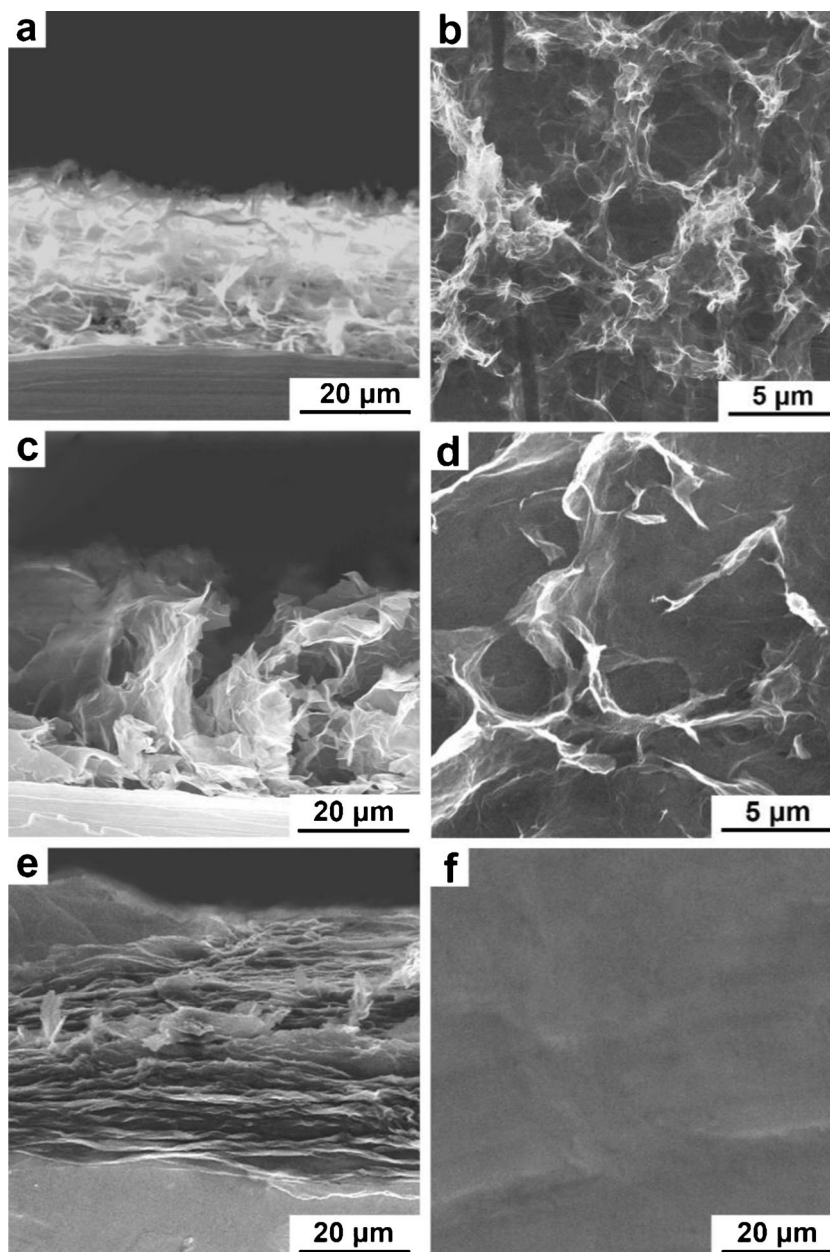
as the working electrode, and the PPy layer was deposited under the same condition as that used for fabricating 3D-ErGO/PPy electrodes.

For electrochemical sensing, PPy, ErGO, 3D-ErGO, or 3D-ErGO/PPy electrode was immersed into the sensing solution containing Hg^{2+} ions for 20 min under stirring to preconcentrate the target ions onto its surface. Successively, the electrode was washed with deionized water and kept in an aqueous electrolyte containing 10 mM HNO_3 and 0.3 M KCl. A −0.7 V was applied for 60 s to reduce Hg^{2+} into Hg^0. Successively, square wave anodic stripping voltammetry (SWASV) measurements were carried out in the potential range of −0.6 to +0.6 V at a frequency of 15 Hz with an amplitude of 25 mV and a 4-mV potential step. After the SWASV measurement, the electrode was regenerated by anodizing in 0.2 M HNO_3 at +0.8 V for 60 s. Before the next measurement, the renewed electrode was checked by SWASV to show no detectable signal of residual Hg. All the measurements were performed at room temperature with an Ag/AgCl electrode as the reference electrode.

The 3D-ErGO/PPy electrode has also been used to detect the Hg^{2+} ions in an industrial wastewater. For this purpose, the wastewater was firstly filtered with cotton to remove any solid particles. The filtrate was further treated with concentrated nitric acid to form a solution containing 1 M nitric acid and then boiled for 20 min.

Scanning electron micrographs (SEM) were taken out by using a Sirion 200 field-emission scanning electron microscope. The atomic absorption spectroscopic (AAS) analysis was performed on an Agilent 280Z external PC-controlled atomic absorption spectrometer.

Results and discussion

The typical 3D-ErGO electrode was prepared by electrochemical reduction of a 3-mg mL^{-1} dispersion at −1.2 V for 20 s. It has a porous ErGO layer with a thickness of about 10 μm (Fig. 1a). This porous structure was formed by assembling ErGO sheets under electrical field, and the ErGO sheets are nearly vertical to the substrate Au electrode (Fig. 1b). After modification of a PPy layer by electrochemical polymerization of 0.1 M pyrrole at 0.7 V for 2 s, this porous structure was mainly kept, while part of the pores were collapsed and the thicknesses of pore walls were increased (Fig. 1c, d). On the contrary, the ErGO/PPy electrode has a compact flat morphology, and its thickness is about 25 μm (Fig. 1e, f).

The comparison of different electrodes toward 0.1 μM Hg^{2+} is shown in Fig. 2. The SWASV curve of the PPy electrode showed only a weak peak at around 0.12 V, and this curve is similar to the baseline (Fig. 2a). The 3D-ErGO electrodes exhibited an apparent current peak of 3.49 μA; however, its response is about ten times weaker than that of 3D-ErGO/PPy electrode (Fig. 2b). The introduction of ErGO or 3D-ErGO strongly increased the response of Hg^{2+} ions. However, the peak current at 3D-ErGO/PPy electrode is about 50 times that at a flat ErGO/PPy electrode (Fig. 2b). On the basis of these observations, it is reasonable to conclude that the synergistic effect of PPy and 3D-ErGO layers led 3D-ErGO/PPy electrode to be the most sensitive toward Hg^{2+} ions. Either a PPy or 3D-ErGO layer can accumulate Hg^{2+} ions. However, the porous microstructure of 3D-ErGO/PPy increased the specific surface area of loading Hg^{2+} ions, and

Fig. 2 **a** SWASV curve of PPy electrode in a 0.1-μM Hg^{2+} aqueous solution or blank solution. **b** SWASV curves of 3D-ErGO, ErGO/PPy or 3D-ErGO/PPy in a 0.1-μM Hg^{2+} aqueous solution. **c** The calibration plot of the SWASV peak current (background current was subtracted) vs. C_{Hg2+}. **d** The SWASV peak current (background current was subtracted) of the typical ErGO/PPy and 3D-ErGO/PPy electrodes toward 0.1 μM Hg^{2+} ions or 1 μM Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{2+}, or Cu^{2+} ions
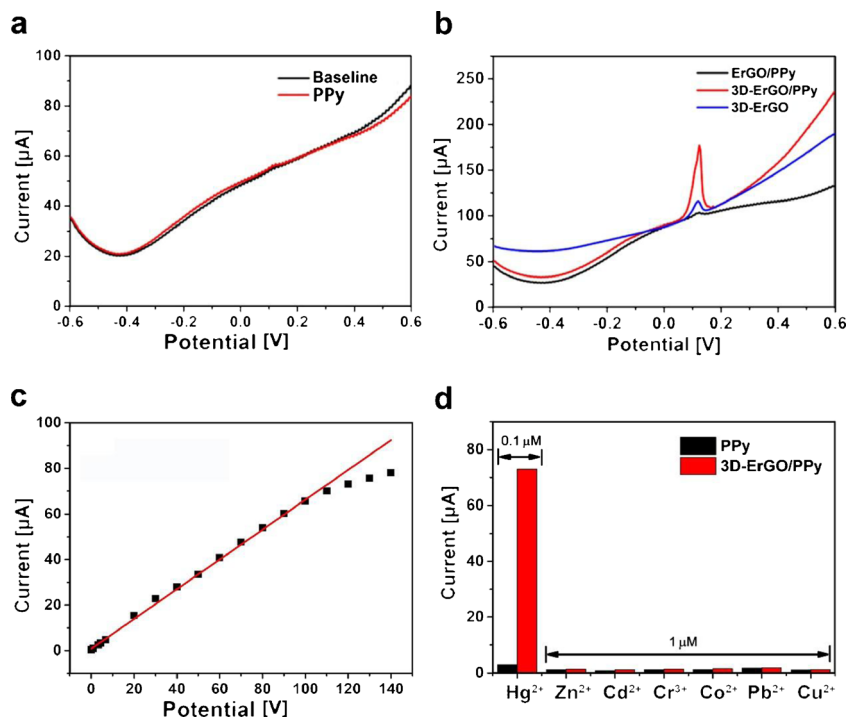
the vertical orientation of ErGO sheets improved the electroactivity of the electrode [5].

The SWASV responses of 3D-ErGO/PPy electrode toward the solutions with different concentrations of Hg^{2+} ions (C_{Hg2+}) are shown in Fig. 2c. The peak current increases linearly with C_{Hg2+} in the range of 0.1 to 110 nM. The sensitivity of the electrode was calculated to be 20.8 nA nM^{-1} cm^{-2}. The limit of detection (LOD) was tested to be about 0.03 nM (30 ppt, signal to noise ratio ≥3), and this LOD is much lower than the guideline value of 2 ppb for drinking water given by the World Health Organization [1]. More importantly, in addition to the excellent sensing performance, the 3D-ErGO/PPy electrode can be regenerated by treating in 0.2 M HNO_3 at +0.8 V for 60 s for repeated applications.

The selectivity of 3D-ErGO/PPy electrode toward Hg^{2+} ions was evaluated by separately testing their SWASV stripping responses of several possible interfering metal ions (e.g., Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{2+}, Cu^{2+}). The response of 100 nM Hg^{2+} ions has not been changed in the medium containing other metal ions with a much higher concentrations (1 μM). The stripping current toward Hg^{2+} ions is 80–100 times stronger than that toward Zn^{2+}, Cd^{2+}, Pb^{2+}, Cr^{2+}, or Cu^{2+} ions with the same concentration (Fig. 2d). This is possibly due to the excellent uptake of Hg^{2+} and slight/negligible adsorption of other ions by the 3D-ErGO/PPy electrode [3]. On the contrary, the stripping current toward Hg^{2+} ions at the PPy-modified electrode is only two to nine times higher than those toward other ions, indicating that the 3D-ErGO component in the nanocomposite plays an important role in the highly selective detection.

The 3D-ErGO/PPy electrode is also applicable for detecting Hg^{2+} ions in wastewater. The C_{Hg2+} in a sample of wastewater was measured to be 1.20±0.02 nM according to its SWASV current response (1.67±0.04 μA), and this value is in a good agreement with that measured by atomic absorption spectroscopy (1.3 nM). In order to validate the obtained calibration curve, the recovery rates for wastewater samples were determined. For the samples of wastewater with C_{Hg2+} in the range of 10.1 and 59.6 nM, the recovery rates were measured (three 3D-ErGO/PPy electrodes for each sample) to be in the range of 90.79±1.7 to 112.3±2.2 %. This range is much narrower than that (80 to 115 %) suggested by the Association of Official Analytical Chemists (AOAC) International (http://www.eoma.aoac.org/smpr/info.asp?id=8). These results indicate that the 3D-ErGO/PPy electrode is reliable and reproducible for practical detection of Hg^{2+} ions in wastewater.

Conclusion

The 3D-ErGO/PPy electrode can be used to sensitively and selectively detect Hg^{2+} ions in aqueous media. The LOD of sensing Hg^{2+} ions at this electrode was measured to be 0.03 nM for lab samples. The superior sensing performance of this electrode is attributed to its oriented porous microstructure and strong and selective adsorption of the target ions. The 3D-ErGO/PPy electrode can be readily fabricated and regenerated, making it attractive for practical applications.

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