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Selective detection toward Cd^{2+} using Fe_3O_4/RGO nanoparticle modified glassy carbon electrode

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ABSTRACT

This work reports the detailed study on the magnetite–reduced graphene oxide (Fe_3O_4–RGO) modified glassy carbon electrode, which could be used for the selective electrochemical detection of Cd^{2+}. The Fe_3O_4–RGO modified glassy carbon electrode (GCE) was characterized by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Square wave anodic stripping voltammetry (SWASV) was applied for the detection of Cd^{2+}. The limit of detection with the Fe_3O_4–RGO modified electrode toward Cd^{2+} was calculated as 0.056 μM (3σ method). The electrochemical parameters that exert influence on deposition and stripping of metal ions, such as supporting electrolytes, pH values, deposition potential and deposition time, were optimized. Besides, the interference and stability measurements were also evaluated under the optimized parameters. More importantly, selective detection toward Cd^{2+} was achieved. It is meaningful for electrochemical method to overcome the great challenge of improving the selectivity toward heavy metal ions.

1. Introduction

Heavy metal ions poses adverse toxic risks to human health at very low concentrations [1–4]. Over the past several decades, a variety of analytical methods have been used for heavy metal ions detection, such as solid phase spectrophotometry (SPS) [5], electrothermal atomic absorption spectrometry (ET-AAS) [6], cold vapor generation-atomic absorption spectrometry (CVG-AAS) [7], inductively coupled plasma atomic emission spectrometric (ICP-AES) [8], flame atomic absorption spectrometry (FASS) [9], inductively coupled plasma mass spectrometric (ICP-MS) [10]. However, these methods require high operating cost and expensive instruments, which are not suitable for the detection of a large number of samples. Therefore, it is extremely urgent to develop a simple and quick detection method towards heavy metal ions. The electrochemical method, as an alternative to these spectroscopic techniques, has been accepted as an efficient method to detect heavy metal ions, which offers advantages in terms of high sensitivity and fast analysis speed, simple instrument, low cost, favorable stability and easy to operate [11–14].

However, one of the great challenges is how to improve the selectivity of sensing heavy metal ions using electrochemical methods. To achieve the goal, much efforts have been devoted to modifying the electrode with the functional groups or DNA biomolecules. The good selectivity and sensitivity detection towards heavy metal ions were obtained after modifying some functional groups on electrode surface or sensor [15–19]. For instance, Alizadeh et al. have reported the selective determination of Cd^{2+} using a carbon paste electrode impregnated with Cd^{2+} imprinted polymer [20]. Complexing polymer film-coated electrodes realized the trace analysis of Cd^{2+} [21,22]. Huang et al. reported electrochemical determination of Cd^{2+} using carbon-based nanomaterials [3,23–25]. Luo et al. have reported a multi-walled carbon nanotubes-sodium dodecyl benzene sulfonate modified stannum film electrode to detect Zn^{2+} [26]. However, these methods suffer from complex modification processes and synthesis of modifiers [16,18,27,28]. Besides, bismuth-plated carbon microelectrodes, bimetallic Hg–Bi/single-walled carbon nanotubes, bismuth-modified multi-walled carbon nanotubes, etc., have also been reported for analysis of Cd^{2+} [29–31]. Therefore, it is important and necessary to develop novel and simple materials to improve the selective of electrochemical detection method.

Magnetite–reduced graphene oxide (Fe_3O_4/RGO) has provoked increasing research interest due to the large surface area and stability of the reduced graphene oxide (RGO) and strong magnetic of magnetite (Fe_3O_4), which has been applied in water treatment, lithium-ion batteries, drug delivery, magnetic-controlled switches, and microwave absorbing areas [32]. Bahadur et al. have reported the electrochemical detection of Cr^{3+} using Fe_3O_4–RGO modified

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electrodes [33]. Huang et Al. reported electrochemical detection of As(III) using Fe_3O_4–RTIL composite modified screen-printed carbon electrode for the first time [34]. In this work, we modify a glass carbon electrode (GCE) using Fe_3O_4–RGO composites for selective analysis of Cd^{2+} by square wave anodic stripping voltammetry (SWASV), and the selective detection toward Cd^{2+} was achieved. The optimizing of experimental conditions, such as supporting electrolytes, pH values, deposition potential, and deposition time were investigated. Other heavy Metal ions, such as Pb^{2+}, Hg^{2+}, Cu^{2+} and Zn^{2+}, were chosen as potential interfering ions for investigating the electrochemical selective behavior of Fe_3O_4–RGO composites toward Cd^{2+}. Furthermore, the stability of Fe_3O_4–RGO modified electrode was also studied.

2. Experimental

2.1. Chemical reagents

Graphite (325 mesh) was purchased from Alfa Aesar, and all other reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). All reagents and solvents were analytical grade and used as received without further purification. 0.1 M acetate buffer solutions (HAc–NaAc) with different pH values were prepared by mixing stock solutions of 0.1 M HAc and 0.1 M NaAc. The deionized water (18.2 MΩ cm) used to prepare all solutions was purified with the NANOpureDiamondTM UV water system.

2.2. Apparatus

All electrochemical experiments were recorded using a CHI 660D computer-controlled potentiostat. Measurements were carried out in a conventional three-electrode cell using the modified or bare glassy carbon electrode (GCE, 3 mm in diameter) as a working electrode, Ag/AgCl as a reference electrode and Pt wire as a counter electrode. The scanning electron microscopy (SEM) images were obtained by a field-emission scanning electron microscope (FESEM, Quanta 200 FEG, FEI Company, USA). X-ray diffraction (XRD) patterns were gained with a Philips X'Pert Pro X-ray diffractometer with Cu Kα radiation (1.5418 Å).

2.3. Preparation of Fe_3O_4–RGO composites

Graphene oxide (GO) was prepared from natural graphite based on Hummers' method [35]. Fe_3O_4–RGO composites were prepared via a hydrothermal method according to previous report [36]. Briefly, 0.036 g GO was first dispersed in 40 mL deionized water. At the same time, 0.270 g $FeCl_3 \cdot 6H_2O$ and 0.528 g ascorbic acid were added into the beaker, forming a homogenous solution by ultrasonication. 10 mL hydrazine hydrate was added to the above solution under stirring. Then, the black solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 8 h. After cooling to room temperature, solid precipitate was collected by centrifugation and washed three times with ultrapure water and alcohol, respectively. Finally, the Fe_3O_4–RGO composites were obtained by drying at 60 °C under vacuum for 12 h.

2.4. Fabrication of modified electrode

Prior to modification, bare GCE was polished with 1.0, 0.3 and 0.05 μm of alumina power, respectively, and rinsed with ultrapure water, followed by sonication in 1:1 HNO_3, alcohol and ultrapure water successively and dried under nitrogen. Then 5 mg Fe_3O_4–RGO composites were dissolved in 10 mL of the alcohol solution and sonicated for 10 min to get a homogenous suspension. A 4 μL aliquot of this suspension was then dropped onto the surface of GCE. The electrode was then allowed to air-dry at room temperature. For comparison, Fe_3O_4 modified electrode was fabricated using the same process. Note that RGO as a modifier could adsorb metal ions and produce a strong stripping current, but suffer from desorption, leading to that pure RGO modified electrode could not be regenerated [24]. Thus, the electroanalysis on the pure RGO modified electrode was not included in this work.

2.5. Electrochemical detection

Square wave anodic stripping voltammetry (SWASV) was used for the observation of electrochemical behavior under optimized conditions. Cd, Pb, Cu, Hg, and Zn were deposited at the potential of −1.0 V for 120 s by the reduction of Cd^{2+}, Pb^{2+}, Cu^{2+}, Hg^{2+} and Zn^{2+} in 0.1 M HAc–NaAc (pH 5.0). The anodic stripping (reoxidation of metal to metal ions) of electrodeposited metal was performed in the potential range of −1.0 to −0.2 V at the following optimized condition: frequency, 15 Hz; amplitude, 25 mV; increment potential, 4 mV; vs Ag/AgCl. A desorption potential of 0.1 V for 150 s was performed to remove the residual metals under stirring condition. The same experiment conditions were applied in the interference, stability and selective studies. Cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) were performed in mixing solution of 5 mM $Fe(CN)_6^{3-/4-}$ with 0.1 M KCl and the scanning rate was 100 mV s^{-1}.

3. Result and discussion

3.1. Characterization of Fe_3O_4–RGO composites

The morphology and structure of the as-prepared Fe_3O_4–RGO composites were characterized by SEM and XRD, respectively. Fig. 1 shows the SEM images of RGO, Fe_3O_4 and Fe_3O_4–RGO. As shown in Fig. 1a, the morphology of RGO was full of wrinkles. The wrinkles formed a curled morphology, which was represented the intrinsical characterization of the RGO [37]. It can be found in Fig. 1b that the size distribution of Fe_3O_4 was non-uniform due to the agglomerates to large particles [36,37]. From the SEM image shown in Fig. 1c, the obtained Fe_3O_4–RGO shows a layer-by-layer assembled structure. In addition, the presence of RGO can prevent the aggregation of Fe_3O_4 nanoparticles, which was consistent with the previous reports [36–39].

Fig. 2 shows the XRD pattern of RGO, Fe_3O_4 and Fe_3O_4–RGO composites. Curve a shows a weak and broad diffraction peak at $2\theta = 23.5°$ (002). The broad peak corresponded to the reflection peak of the RGO [36,40]. As seen in curves *b* and *c*, the peaks represented the Bragg reflections of (220), (311), (440), (422), (511) and (440), which matched well with that of Fe_3O_4 nanoparticles (JCPDS Card No. 19-0629) [36,41,42]. However, for the Fe_3O_4–RGO composites, all peaks in the XRD pattern of Fe_3O_4 nanoparticles can also be observed. While no obvious peak diffraction of RGO was observed, which indicated that the stacking of graphene sheets in the Fe_3O_4–RGO nanocomposite was disordered. The distribution of RGO sheet can be confirmed by the SEM images [37]. The result demonstrated that Fe_3O_4–RGO composites were successfully prepared by the hydrothermal method.

3.2. CV and EIS characterization of Fe_3O_4–RGO composites

The cyclic voltammetric responses of bare, Fe_3O_4 and Fe_3O_4–RGO composite modified GCE have been characterized using the solution of 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.1 M KCl (Fig. 3). Fig. 3a displays the CV responses of bare GCE, Fe_3O_4 and Fe_3O_4–RGO modified electrodes. As compared with the bare GCE, the anodic and cathodic peak currents were decreased at Fe_3O_4 modified