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Differential pulse anodic stripping voltammetric determination of Pb ion at a montmorillonites/polyaniline nanocomposite modified glassy carbon electrode

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ABSTRACT

In this paper, Na^{+}–montmorillonites/polyaniline nanocomposite modified glassy carbon electrode (PANI/MMT/GCE) was prepared and characterized by scanning electron microscopy and electrochemical techniques. It was found that when PANI/MMT film was modified on the electrode, electrochemical responses could be improved significantly. The modified electrode could be applied in sensitive detection of Pb^{2+} by differential pulse anodic stripping voltammetry (DPASV). The 50 wt% feeding ratio of MMT to aniline of the nanocomposite exhibited the best electrochemical response to Pb^{2+}. In 0.2 mol L^{-1} acetate buffer solution (pH 3.5), the stripping peak currents after enrichment at −1.20 V for 120 s showed good linear relationships with Pb^{2+} at concentration ranges of 4–100 nM with the correlation coefficient of 0.998, and the detection limit is 1 nM. The proposed method is applicable in the determination of trace Pb^{2+} in real water samples with the relative standard deviations less than 5.2% and the recovery rates of 94–103%.

1. Introduction

Lead is one of the most serious environmental contaminants which are highly toxic to nervous, immune, reproductive and gastrointestinal systems of both humans and animals [1–3]. Additionally, the accumulation of Pb^{2+} in the human body exhibits severe deleterious effects on neurobehavioral development in children, increases blood pressure, and causes kidney injury and anemia. Therefore, the development of a highly sensitive method for the determination of trace amounts of lead has received a considerable attention. Over the past decades, many techniques such as spectrophotometry, inductively coupled plasma optical emission spectrometry, atomic absorption spectrometry, atomic fluorescence spectrometry, and neutron activation analysis have been employed for the determination of heavy metals [4–9]. However, most of the above methods require several time consuming manipulation steps, sophisticated instruments and special training. Electrochemical stripping voltammetry has been widely recognized as a powerful technique for the determination of trace metal ions due to its unique ability to preconcentrate target metal ions during the accumulation step [10]. The mercury electrodes including hanging drop mercury electrode, dropping mercury electrode and thin mercury film electrode have been widely used as the working electrode in stripping voltammetry. However, the toxicity of mercury restricts its use. Ordinary electrochemical solid electrodes, such as glassy carbon, platinum, gold, and graphite electrodes are also not suitable for the determination of metal ions because of their poor sensitivity [11]. Thus, it is very important to develop a sensitive, selective, and non-toxic electrode for the determination of heavy metals by stripping methods. Chemically modified electrode (CME) might be the most suitable substitute for the traditional electrodes in the stripping voltammetry. Various CMEs have been exploited for anodic stripping voltammetric determination of trace metals, such as functionalized mesoporous silica electrode, carbon nanotubes modified electrode, ordered mesoporous carbon, nanocrystalline diamond thin-film electrode, graphene modified electrode, and graphite nanofiber–Nafion modified bismuth film electrode [12–19]. Though CMEs have been widely used in the detection of metal ions, new materials still needed to improve the detection sensitivity and reproducibility in analysis of trace metals.

Recently, organic–inorganic nanocomposites have received considerable attention and many hybrid composite materials have been synthesized and studied [20]. Conducting polymers and clay

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are two frequently-used organic and inorganic materials which are widely used in the electrode modification. Among the conducting polymers, polyaniline (PANI) is most famous and often used in the electrode modification due to its simple synthesis, high conductivity, and excellent environment stability [21]. When a PANI coating modified glassy carbon electrode is immersed in a solution containing trace heavy metal ions, interactions occur between electron-rich sites and positively charged metal species and thus the metal ions are adsorbed onto the electrode surface and further separated from the bulk solution [22,23]. However, the poor thermal stability and difficult processability of PANI should be overcome for the application of this electrically conducting polymer. Many reports have focused on the preparation and new property studies of novel nanocomposites consisting of PANI with various layered materials [24–29]. Montmorillonite (MMT) is a layered silicate known for good swelling and ion-exchange properties [30]. MMT is also very popular inorganic matrix because of its layered nanostructure, natural origin, and availability at low cost. MMT has already been employed in electrochemical analysis because of its low cost and remarkable improvement in sensitivity, which attained attention for voltammetric determination of organic compounds and traces of heavy metal ions [31–36]. In the last decade, the growth of the interest in PANI composites with montmorillonite has been observed. The composites of PANI and MMT were synthesized by mechanochemical reaction [37], in emulsion polymerization [38], in situ deposition of PANI on MMT [39–41]. The composite of MMT and conducting polymer has been applied in gas sensor and corrosion protection [42,43]. However, to the best of our knowledge, PANI/MMT nanocomposite has not been reported in the detection of trace heavy metals. Therefore, in the present paper, PANI/MMT nanocomposite was synthesized and used to modify glassy carbon electrode (GCE). The modified electrode was used to detect Pb^{2+} in water samples by differential pulse anodic stripping voltammetry.

2. Experimental

2.1. Apparatus and reagents

All electrochemical experiments were performed with a model 760D CHI electrochemical workstation (Chenhua Instruments Co., Shanghai, China). A conventional three-electrode cell configuration was employed for the voltammetric measurements. A PANI/MMT/GCE (3-mm diameter disk) was used as the working electrode, with a saturated calomel reference electrode (SCE) and a platinum wire electrode for the reference and the counter electrode, respectively. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 scanning electron microscope.

All chemicals employed in this work were of analytical-reagent grade and used without further purification and solutions were prepared with doubly distilled water. Stock solutions of 0.1 mol L^{-1} Pb^{2+} was prepared by dissolving $Pb(NO_3)_2$ (Shanghai Reagent Corporation, China) into redistilled water, and then diluted to working solution at desired concentration with redistilled water. Aniline (99%), ammonium peroxydisulfate (APS), glycidyl methacrylate (GMA), diethanol amine (DEA) and 2-Acrylamido-2-Methyl Propane Sulfonic Acid (AMPS) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium montmorillonite (Na^+-MMT) was obtained from Kunipia-F (Kunimine Co.).

2.2. Synthesis of PANI–MMT composites

The organic modification of Na^+–MMT clay with GMA–DEA is carried out according to the Ref. [44]. The typical process is as follows: 15 g of Na^+–MMT clay were fully dispersed in 450 mL redistilled water by stirring overnight at room temperature. An excess of GMA–DEA (6.45 g) was dissolved in 50 mL of redistilled water, then continuously and drop-wisely added to the clay dispersion. The pH value of the mixture was adjusted to 3 by using hydrochloric acid. The mixture was stirred for 6 h. Afterward, the modified MMT clay (hereinafter referred to as GMA–DEA–MMT) were filtrated and washed several times to remove excess GMA–DEA and hydrochloric acid. Then, put 150 mL of 2 wt% GMA–DEA–MMT dispersion into a 250 mL round-bottom flask equipped with a mechanical stirrer, a condenser, and nitrogen inlet. 3.0 g AMPS was then added and stirred under a nitrogen atmosphere by purging for 30 min. The initiator, 0.03 g APS (dissolved in 5 mL of redistilled water), was finally introduced in the reactor and the polymerization allowed to proceed at 70 °C for 4 h under a slow stream of nitrogen. The resulted dispersion was centrifuged and washed repeatedly with redistilled water to remove the ungrafted poly (AMPS). The obtained modified MMT clay was dried at 50 °C in an oven.

The PANI/MMT is prepared by the chemical oxidation method as follows [44]: the certain amount of the PAMPS-g-MMT was well-dispersed in 80 mL of 0.5 mol L^{-1} hydrochloric acid. Then, 0.8 g aniline monomer was added and stirred for 30 min. The polymerization started by introduction of APS solution (1.96 g APS in 20 mL of 0.5 mol L^{-1} hydrochloric acid) drop-wisely. An overnight reaction was allowed to ensure completion of polymerization. The resultant precipitate was filtered and sequentially washed with copious amounts of 0.1 mol L^{-1} hydrochloric acid and industrial alcohol until the filtrate was clear. Finally, the product was dried at 50 °C in an oven.

According to the aforementioned approach, numerous samples of the PANI/MMT nanocomposites with different MMT/aniline feeding ratio are obtained. The feeding ratio of MMT/aniline is defined using following equation:

$$\text{MMT/Aniline feeding ration} = \frac{W_{\text{MMT}}}{W_{\text{Aniline}}} \times 100\ \text{wt\%}$$

2.3. Preparation of the modified GCE

Before modification, the bare glassy carbon electrode was carefully polished to a mirror with 1.0 μm, 0.30 μm and 0.05 μm alumina slurry on a polishing cloth, respectively. Then, rinsed thoroughly with doubly distilled water between each polishing step and washed successively with doubly distilled water, 1:1 (v/v) HNO_3 aqueous solution and doubly distilled water in an ultrasonic bath and dried in air, and used for the following experiments. The modifier suspension was prepared by dispersing 25 mg of PANI/MMT in 5.0 mL of water under sonication for 30 min, giving a quite stable black suspension. The PANI/MMT modified GCE (denoted as PANI/MMT/GCE was prepared by casting 10 μL of the suspension on GCE surface using a micropipette and letting water evaporate in air.

2.4. Electrochemical detection of Pb(II)

DPASV was used for the observation of electrochemical behavior under optimized conditions. Pb were deposited at the potential of −1.2 V for 120 s by the reduction of Pb(II) in 0.1 M NaAc-HAc (pH 3.5). The Solid-phase extraction (SPE) procedures were performed by stirring the solution with a magnetic stirrer, which is included in the electrodeposition step. Following the preconcentration step, the stirring was stopped. After 10 s, DPASV was performed by potential scan from −1.0 V to −0.1 V with amplitude of 50 mV, pulse width of 50 ms and potential step of 4 mV vs SCE. Aliquots of the $Pb(NO_3)_2$ standard solution were introduced after the background signal was recorded. Prior to the next cycle,