A sensitive electrochemical sensor using an iron oxide/graphene composite for the simultaneous detection of heavy metal ions

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ABSTRACT

We report an analytical assessment of an iron oxide (Fe_2O_3)/graphene (G) nanocomposite electrode used in combination with in situ plated bismuth (Bi) working as an electrochemical sensor for the determination of trace Zn^{2+}, Cd^{2+}, and Pb^{2+}. The as-synthesized nanocomposites were characterized by transmission electron microscopy, scanning electron microscopy, thermo-gravimetric analyzer, and X-ray diffraction. The electrochemical properties of the Fe_2O_3/G/Bi composite modified electrode were investigated. Differential pulse anodic stripping voltammetry was applied for the detection of metal ions. Due to the synergetic effect between graphene and the Fe_2O_3 nanoparticles, the modified electrode showed improved electrochemical catalytic activity high sensitivity toward trace heavy metal ions. Several parameters such as the preconcentration potential, bismuth concentration, preconcentration time, and pH were carefully optimized to determine the target metal ions. Under optimized conditions, the linear range of the electrode was 1–100 μg L^{-1} for Zn^{2+}, Cd^{2+}, and Pb^{2+}, and the detection limits were 0.11 μg L^{-1}, 0.08 μg L^{-1}, and 0.07 μg L^{-1}, respectively (S/N =3). Repeatability (% RSD) was found to be 1.68% for Zn^{2+}, 0.92% for Cd^{2+}, and 1.69% for Pb^{2+} for single sensor with 10 measurements and 0.89% for Zn^{2+}, 1.15% for Cd^{2+}, and 0.91% for Pb^{2+} for 5 different electrodes. The Fe_2O_3/G/Bi composite electrode was successfully applied to the analysis of trace metal ions in real samples. The solventless thermal decomposition method applied to the simple and easy synthesis of nanocomposite electrode materials can be extended to the synthesis of nanocomposites and promising electrode materials for the determination of heavy metal ions.

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1. Introduction

Certain heavy metals such as iron, copper, manganese, and zinc in small quantities are nutritionally essential for a healthy life. However, some heavy metals show a tendency to bind with ligands of biological matter containing nitrogen, sulfur, and oxygen. Accordingly, even low concentrations of some heavy metal ions can cause serious health problems such as those affecting the central nervous system (Hg^{2+}, Pb^{2+}, As^{3+}); the kidneys or liver (Cu^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}); or skin, bones, or teeth (Ni^{2+}, Cu^{2+}, Cd^{2+}, Cr^{2+}). The pollution caused by toxic heavy metals has drawn extensive attention worldwide. Although heavy metals can progressively accumulate through the food chain, they are readily excreted [1–5]. Therefore, it is necessary to develop highly sensitive, rapid, and simple methods for the detection of these

pollutants. At present, many analytical methods, such as inductively coupled plasma mass spectrometry (ICP-MS) [6], atomic absorption spectroscopy [7], and flame atomic absorption spectrometry (FAAS) [8], are used to detect trace heavy metal ions. These methods usually require analytical techniques performed by skilled personnel and require expensive instruments. Many efforts are ongoing to develop a simple and rapid technique for trace-heavy-metal detection. Electrochemical methods have attracted extensive attention as an alternative to spectroscopic techniques because they offer advantages of quick analysis speed, simple instrumentation, low cost, and high sensitivity [9,10]. Anodic stripping voltammetry (ASV) has been extensively used to analyze trace metal ions due to an effective preconcentration step prior to the stripping measurements [11]. Mercury-based electrodes are commonly used for AVS due to the unique ability of mercury to preconcentrate heavy metals [12]. However, because of its serious toxicity and difficult handling, new and more environmentally friendly mercury-free electrodes have replaced this electrode. Bismuth is a very attractive alternative material due to its

comparable performance to mercury for electrochemical analysis. Moreover, the advantageous properties of bismuth are attributed to its ability to form a "fused alloy" with heavy metals. Recently, there has been considerable interest in the study of bismuth-modified electrodes to improve the sensitivity of electrochemical detection methods [11,13–22]. A common approach is to incorporate carbon materials, including carbon nanotubes and graphene [23–27]. Moreover, graphene, a one-atom-thick planar sheet of sp^2-bonded carbon atoms, is a novel and fascinating carbon material due to its unique thermal, mechanical, and electrochemical properties. Graphene also has a larger specific surface area than other carbon-based materials, and this combination of physical properties enables graphene's application in a wide range of technological fields such as nanoelectronic devices, capacitors, and sensors [28–31]. The integration of nanoparticles and graphene has been reported by many researchers via various methods. Their enhanced properties provide wide applications, for example, in catalysis, biomedical fields, and energy storage [32–34].

Recently, the magnetic nanoparticle/graphene nanocomposite has attracted increasing interest because of its stability, large surface area, and catalytic activity. Thus, the magnetic nanoparticle/graphene composite is used in many applications such as a contrast agent for magnetic resonance imaging, magnetic separation, targeted drug delivery, wastewater treatments, and energy storage [35–39]. However, magnetic nanoparticle/graphene composites have not been widely investigated for application in electrochemical sensing [40–43].

We recently reported a solventless thermal decomposition method to prepare iron oxide/graphene nanocomposites for application as lithium-ion battery anodes [44]. This method was simple, cheap, and scalable for mass production. It can be easily prepared by a simple heat treatment using a mixture of an iron–oleate precursor and graphene. After characterizing the as-prepared nanocomposite and confirming the stable formation of iron oxide nanoparticles on graphene, we modified a glassy carbon electrode (GCE) as an electrochemical sensing platform for sensitive and selective analysis of heavy metal ions. The experimental results indicated that this electrode exhibited a better electrochemical performance and higher electrocatalytic behavior response to heavy metal ions. Finally, this simple, low-cost, and highly sensitive sensor was used to determine the amounts of Pb, Cd, and Zn in real samples.

2. Experimental

2.1. Chemicals

All reagents were analytical grade and used as received without further purification. Graphite powder ($< 20\ \mu m$), sodium acetate, acetic acid, iron(III) acetylacetonate ($Fe(acac)_3$) and oleic acid were purchased from Sigma-Aldrich (USA). Standard solutions of Bi^{3+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ($1000\ mg\ L^{-1}$) were obtained from Sigma-Aldrich and diluted as required. Acetate (Ac) buffer solutions (HAc-NaAc, 0.1 M) with different pH values were prepared by mixing stock solutions of 0.1 M HAc and 0.1 M NaAc. All solutions were prepared with doubly-distilled water.

2.2. Apparatus

Electrochemical experiments were performed with an Autolab potentiostat (Metrohm, USA). A modified GCE (3 mm in diameter, Bioanalytical Systems, Inc.) served as the working electrode, with the Ag/AgCl electrode (Bioanalytical Systems, Inc.) and platinum wire acting as a reference and a counter electrode, respectively. Transmission electron microscopy (TEM; JEM-3010, JEOL) and field-emission scanning electron microscopy (FE-SEM; JSM-6700F, JEOL) were used to examine the morphologies of the graphene and iron oxide/graphene (Fe_2O_3/G) composite. X-ray diffraction (XRD) analysis was performed using a Rigaku Dmax 2500 diffractometer. The carbon content was revealed by thermos-gravimetric analysis (TGA) measurements, with a TA Instruments Q-5000 IR model at 20–700 °C and a heating rate of 10 °C min^{-1} in air flux.

2.3. Synthesis of Fe_2O_3/graphene composites

Graphene oxide (GO) was prepared from graphite powder by an improved Hummers' method. The as-prepared GO was thermally expanded to synthesize reduced GO by rapid heating to 250 °C in a tube furnace (heating rate: 13 °C min^{-1}) and the final product was washed several times with ethanol. Fe_2O_3/G composites were prepared by a solventless method according to a previous report. Briefly, $Fe(acac)_3$ (2 mmol) was mixed with oleic acid (6 mmol). These iron–oleate precursors were mixed in a mortar with 0.2 g of the as-prepared graphene without any solvent. The mixture was heated to 600 °C (heating rate: 10 °C min^{-1}) and maintained at that temperature for 3 h under a N_2 atmosphere.

2.4. Preparation of the modified electrode

Prior to the modification, the GCE was polished with 1.0, 0.3, and 0.05 μm alumina slurries and then rinsed with doubly distilled water. The cleaned electrode was dried. Fe_2O_3/G (1 mg) was sonicated in a solution containing H_2O (1 mL) and ethanol (3.4 mL) for 10 min to form a homogenous solution. Then, 8 μL of the Fe_2O_3/G solution was added onto the GCE and dried for 5 min under an infrared heat lamp. For comparison, an RGO-modified electrode was fabricated using the same process.

2.5. Procedure of DPASV analysis

The $Fe_2O_3/G/GCE$ modified with bismuth was plated in situ using the following procedure: the composite modified electrode, Ag/AgCl (3 M KCl), and Pt wire electrodes were immersed in an electrochemical cell containing 0.1 M acetate buffer (pH 4.5) and 0.2 mg L^{-1} of bismuth and the appropriate target metal ions. Differential pulse anodic stripping voltammetry (DPASV) was used for the detection of trace heavy metals with a deposition potential of -1.4 V for 300 s with stirring. Anodic stripping of the electrodeposited metal was performed in the potential range varying from -1.4 V to -0.3 V under the following conditions: amplitude, 50 mV; pulse width, 50 ms; potential step, 4 mV; and pulse period, 0.2 s. Prior to the next cycle, the electrode was cleaned for 60 s at 0.1 V in a fresh supporting electrolyte with stirring to remove the target metals and bismuth.

3. Results and discussion

3.1. Characterization of Fe_2O_3/G composites

SEM, TEM, TGA, and XRD were used to characterize the morphology and structure of the as-prepared Fe_2O_3/G composite. Fig. 1 shows the TEM images of RGO and the Fe_2O_3/G composite. Fig. 1 (a) shows the typical wrinkled and sheet-like character of RGO. Fig. 1(b) and (c) show the TEM and SEM images of the Fe_2O_3/G composite, respectively. The images of the Fe_2O_3/G composite shows well-dispersed Fe_2O_3 nanoparticles that uniformly decorated the graphene sheets (average particle size=30 nm); the folding nature of the graphene sheets is clearly visible. The crystal structures of RGO and the Fe_2O_3/G composite were further characterized by XRD in Fig. 2(a). The broad peak corresponds to the