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Graphene ultrathin film electrodes modified with bismuth nanoparticles and polyaniline porous layers for detection of lead and cadmium ions in acetate buffer solutions

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ABSTRACT

Graphene ultrathin films were synthesized by means of solid-state carbon diffusion from amorphous carbon (a-C) thin layers deposited on silicon substrates, which was catalyzed by nickel layers coated on the top of the a-C layers. The graphene films were used as working electrodes that were modified by a polyaniline (PANI) porous layer together with in-situ deposited bismuth (Bi) nanoparticles for the detection of trace heavy metal ions (Pb^{2+} and Cd^{2+}) in acetate buffer solutions (pH 5.3) with square wave anodic stripping voltammetry. The graphene electrodes modified with PANI porous layers and Bi nanoparticles had excellent repeatability, ultrahigh sensitivity (as low as 0.33 nM) and good resistance to passivation caused by the surface active species adsorbed on the electrode surfaces.

1. Introduction

Heavy metal ions in an aquatic system can enter a bloodstream through a food chain with a toxic effect on living organisms and pose severe impacts on human health [1]. For example, lead (II) (Pb^{2+}) in blood can occupy the calcium binding sites on numerous calcium-dependent proteins in cells (e.g. calmodulin), causing the corresponding damages to physiological functions [2]. Exposure to a small amount of cadmium (II) (Cd^{2+}) can cause renal dysfunction, bone degeneration, lung insufficiency, liver damage and hypertension in humans with both acute and chronic toxicity [3]. Even trace amounts of heavy metal ions can pose detrimental risks to human health, so the sensitive, rapid, simple and reliable analysis of heavy metal ions is urgently needed [4].

Among the electroanalytical methods reported so far, square wave anodic stripping voltammetry (SWASV) provides a powerful tool for the determination of heavy metal ions, which possesses simplicity in both instrumentation and experimental procedures [5], portability, low cost, and high-sensitivity, and can analyze several trace heavy metals at the same time.

Graphene, a single atomic sheet of graphite, has been developed as an advanced nanoelectrocatalyst for constructing electrochemical sensors, owing to its extraordinary electronic transport properties, large surface area, and high electrocatalytic activities [6]. Most of graphene used in electrochemistry is produced by a chemical exfoliation method from the reduction of graphene oxide that is formed by using a Hummers' method [7]. However, because of van der Waals and π–π stacking interactions among individual graphene sheets, the as-reduced graphene sheets from graphene oxide tend to form irreversible agglomerates and even restack to form graphite when graphene dispersion solutions are dried [8–10].

Recently, an approach of metal-catalyzed fabrication of graphene based on solid-state carbon diffusion was introduced [11,12], with an embedded solid carbon material (e.g., a nickel/amorphous carbon (Ni/a-C) bilayer deposited on a silicon (Si) substrate by sputtering deposition [11,12]) as the C source, instead of a hydrocarbon gas used in chemical vapor deposition. During the post thermal processing, the C atoms first dissolve into the Ni layer by diffusion during heating at a high temperature (800–1100 °C), and then are expelled from the Ni layer during cooling due to a sharp fall of the solubility of C in the Ni layer. Compared to chemical vapor deposition, this method could have a better control of graphene film thickness due to a fixed and finite C supply and may be less sensitive to fabrication parameters. The agglomeration of graphene sheets [8–10], which usually occurs for the graphene films fabricated by chemical exfoliation method, can be effectively eliminated by this method.

Graphene species can be mixed with polymers, e.g. amine [13], cysteamine [14] and nafion [15–18] to form polymer-graphene composites that are used as sensors for detection of heavy metal ions. A main disadvantage of this kind of composites is the poor conductivity of the polymers used. Therefore, electrically conductive polymers, such as polyaniline (PANI) [19,20] and polypyrrole [21], are more favorable materials for modification of composite electrodes.

Passivation, which is usually caused by various surface active species (e.g. sodium dodecyl sulfate (SDS)) in an electrolyte, is one of the major problems faced by electrochemical electrodes, especially carbon (e.g. glassy carbon, diamond-like carbon, graphene) electrodes. The surface

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active species in an electrolyte can be easily adsorbed onto electrode surfaces and cause the reduction of the surface activities of the electrodes, resulting in lower sensitivities and poorer repeatability of the electrodes [22].

Metal nanoparticles, such as bismuth (Bi) [23,24] and tin [25,26], can be used to modify electrodes to enhance the sensitivities of the electrodes by forming alloys with target metals. During the deposition period of SWASV with a low potential (e.g. −1 V) applied to the working electrode, the introduced Bi^{3+} ions in the electrolyte can be deposited together with target trace heavy metals (e.g. Pb, Cd, copper, titanium, antimony, indium, or gallium) on the working electrode surface via electrochemical reduction reactions (e.g. $Bi^{3+} + 3e^- \rightarrow Bi^0$ and $M^{n+} + ne^- \rightarrow M^0$, where M is the heavy metal) to form binary- or multi-component alloys of low-temperature melting (fusible) [22]. Such Bi based alloys exhibit a strong adsorptive ability towards the metal ions and thus can facilitate the nucleation of those heavy metals during the deposition period of SWASV, leading to higher responses and sensitivities of electrodes. It was also reported that Bi-film electrodes are less susceptible to oxygen background interference than mercury ones [27], making the removal of the dissolved oxygen in the electrolyte unnecessary.

In this paper, graphene film electrodes fabricated using solid-state carbon diffusion were modified with both conductive PANI layers and Bi nanoparticles, which were used to detect Pb^{2+} and Cd^{2+} ions in 0.1 M acetate buffer solutions (pH 5.3) by means of SWASV. It was found that the in-situ deposited Bi nanoparticles could enhance the sensitivity of the graphene film electrodes, while the PANI layer could eliminate the passivation of the electrodes.

2. Experimental details

2.1. Sample preparation

P–Si (111) wafers (boron doped, resistivity ≈ 0.01–0.02 Ω-cm, and thickness ≈ 525 μm) were used as substrates and designated as Si substrates. Before transferred into the sputtering chamber, they were cut into square pieces of 1.2 cm × 1.2 cm, which were ultrasonically cleaned with acetone, ethanol, NaOH (0.1 M) and deionized water successively, and finally dried with compressed air. Inside the deposition chamber and before the deposition, the substrate surfaces were further etched using Ar^+ plasma with a RF power of 50 W for 10 min. During the Ar^+ plasma etching and sputtering deposition processes, an Ar gas flow rate of 10 sccm and a vacuum pressure of about 0.667 Pa in the deposition chamber were maintained. A-C layers of about 50 nm in thickness were deposited via DC magnetron sputtering deposition using a pure graphite target (≥99.99% C) as the C source with a DC sputtering power of 200 W (a deposition rate of about 1.2 nm/min) applied for 40 min. A Ni layer of about 100 nm thick was deposited on the top of the a-C layers also via DC magnetron sputtering process. The DC sputtering power applied to the Ni target (≥99.99% Ni) and time for the deposition of the Ni layers were 50 W (a deposition rate of about 2.9 nm/min) and 30 min, respectively.

The coated samples were thermally treated at 1000 °C via rapid thermal processing with both heating and cooling rates of 20 °C/s, a dwell time of 3 min, and a continuous Ar gas flow of 200 sccm to prevent oxidation. All the parameters for the a-C and Ni deposition and thermal processing were optimized in order to achieve the optimum electrochemical performance. The thermally treated Ni/a-C bilayer coated samples, which were used as the film electrodes for electrochemical detection of trace heavy metals, were designated as graphene electrodes.

2.2. Characterization

All electrochemical experiments were performed using an electrochemical workstation (CHI 660C) having a conventional three-electrode cell configuration comprising a graphene coated sample of 7.5 mm in diameter as the working electrode, a platinum mesh as the counter electrode and an Ag/AgCl (saturated KCl) as the reference electrode. A magnetic stirrer (Heidolph MR3001K) was used to stir the testing solutions (400 rpm) when necessary. All the electrochemical experiments were carried out at room temperature (RT, ~22 °C).

With 7.3 μM aniline dissolved in a 0.25 M H_2SO_4 electrolytic solution, a PANI layer was electrochemically coated on the graphene electrodes via a cyclic voltammetry (CV) method with a scan rate of 50 mV/s within a potential range of −0.2 to 0.9 V for 30 scan cycles under continuous stirring. The deposition parameters for the PANI layers were reported elsewhere [24]. The PANI layer modified graphene electrodes were designated as PANI/graphene electrodes.

In SWASV tests, the electrodes were dipped into 0.1 M acetate buffer solutions (pH 5.3 [20]) containing 0.1 M KNO_3 and predetermined concentrations of target Pb^{2+} (and Cd^{2+} if necessary) ions without or with Bi^{3+}. To obtain the best SWASV performance, the Bi^{3+} concentrations in the buffer solutions were varied from 0 to 2.25 μM with the Pb^{2+} and Cd^{2+} concentrations maintained at 0.5 and 1.2 μM, respectively. In a SWASV measurement, a preconcentration potential of −1 V was first applied to the working electrode for 180 s with continuous stirring. Next, a quiet time of 30 s was taken to stabilize the solution. Finally, the anodic stripping was performed from −1.1 to 0.2 V with a frequency of 50 Hz, increment of 5 mV/s and amplitude of 50 mV, with voltammograms recorded for analysis. For repetitive measurements, the electrode surfaces were recleaned after each test at 0.2 V for 180 s with continuous stirring to remove the residual metals on the electrodes for the preparation of next measurement. For the SWASV test with Bi^{3+} dissolved in the electrolyte, the graphene and PANI/graphene electrodes were designated as Bi/graphene and Bi/PANI/graphene electrodes, respectively.

The corrosion performance of the electrodes was evaluated using a Tefel Plot method in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO_3 with potentials applied from −0.8 to 0.4 V, a scan rate of 1 mV/s and a sensitivity of 0.1 mA/V.

The surface morphology of the samples was measured using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F, operating voltage of 5.0 kV). The PANI layers were characterized by Fourier Transform infrared spectroscopy (FTIR, Thermo Scientific Nicolet 6700, IR mode).

3. Results and discussion

As shown in Fig. 1a, the SWASV peak currents measured by a graphene electrode for detection of Cd^{2+} and Pb^{2+} ions both increase with a higher Bi^{3+} concentration, indicating that the electrode sensitivity is obviously improved by introducing the Bi^{3+} ions into the electrolyte. It was reported that for a too high Bi^{3+} concentration, the electrode surface could be saturated with the Bi based alloys, which was not preferred [24]. Thus for the following discussion, an optimized Bi^{3+} concentration of about 1.25 μM is used to avoid the electrode surface saturation with higher Pb^{2+} or Cd^{2+} concentrations. As shown in Fig. 1b, the voltammogram measured with the graphene electrode in the electrolyte without Bi^{3+} shows only 2 peaks located at about −0.83 V for Cd^{2+} and about −0.62 V for Pb^{2+}. When 1.25 μM of Bi^{3+} ions is added in the electrolyte, both the Pb^{2+} and Cd^{2+} stripping peaks in the voltammogram are significantly enhanced compared to those measured in the electrolyte without Bi^{3+}, with an additional stripping peak observed at around −0.1 V for Bi^{3+}.

As reported elsewhere [20], the deposition of the PANI layers on the graphene electrodes can be confirmed with the three pairs of peaks in the CV curves as shown in Fig. 2, which are labeled as 1, 2 and 3.

It was reported that the corrosion protection of metal surfaces can be achieved by modification with a PANI coating [28,29]. From the