This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier’s archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/authorsrights
Graphene ultrathin film electrodes modified with bismuth nanoparticles and polyaniline porous layers for detection of lead and cadmium ions in acetate buffer solutions

Zhaomeng Wang, Lin Li, Erjia Liu *

School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

ARTICLE INFO
Available online 5 March 2013

Keywords:
Graphene
Solid-state carbon diffusion
Bismuth nanoparticle
Polyaniline porous layer
Square wave anodic stripping voltammetry
Trace lead and cadmium

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 (Pb²⁺ and Cd²⁺) 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) (Pb²⁺) 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) (Cd²⁺) 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
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 Bi³⁺ 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. Bi³⁺ + 3e⁻ → Bi⁰ and M⁰ + n e⁻ → Mⁿ⁺, 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 Pb²⁺ and Cd²⁺ 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 (CH 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 H₂SO₄ 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 KNO₃ and predetermined concentrations of target Pb²⁺ (and Cd²⁺ if necessary) ions without or with Bi³⁺. To obtain the best SWASV performance, the Bi³⁺ concentrations in the buffer solutions were varied from 0 to 2.25 μM with the Pb²⁺ and Cd²⁺ 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 recleneed 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 Bi³⁺ 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 Tafel Plot method in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO₃ 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 50 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 Cd²⁺ and Pb²⁺ ions both increase with a higher Bi³⁺ concentration, indicating that the electrode sensitivity is obviously improved by introducing the Bi³⁺ ions into the electrolyte. It was reported that for a too high Bi³⁺ concentration, the electrode surface could be saturated with the Bi based alloys, which was not preferred [24]. Thus for the following discussion, an optimized Bi³⁺ concentration of about 1.25 μM is used to avoid the electrode surface saturation with higher Pb²⁺ or Cd²⁺ concentrations. As shown in Fig. 1b, the voltammogram measured with the graphene electrode in the electrolyte without Bi²⁺ shows only 2 peaks located at about −0.83 V for Cd²⁺ and about −0.62 V for Pb²⁺. When 1.25 μM of Bi³⁺ ions is added in the electrolyte, both the Pb²⁺ and Cd²⁺ stripping peaks in the voltammogram are significantly enhanced compared to those measured in the electrolyte without Bi³⁺, with an additional stripping peak observed at around −0.1 V for Bi²⁺.

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
Tefel plots shown in Fig. 3, the corrosion current measured by the PANI/graphene electrode (about 54.6 nA) is much smaller than that of the bare graphene electrode without a PANI layer (about 59.2%). This indicates the occurrence of the passivation of the electrodes. The Bi/PANI/graphene electrode has consistent higher \( i_{p}/i_{\text{max}} \) ratios than the Bi/graphene electrode, implying that the electrode modified with the PANI layer is more tolerant to the surface-active compounds (SDS), which can be explained with the branch-structured PANI molecules that can prevent the surface active species from reaching the electrode surface [24]. For comparison, the \( i_{p}/i_{\text{max}} \) ratios of glassy carbon electrodes modified with PANI and Bi are about 71% and 48% [24] measured in electrolyte solutions containing 3 and 8 mg/L SDS, respectively, which are much lower than those (about 98.3% and 59.2%, respectively) measured with the Bi/PANI/graphene electrode in the similar solutions used in this study, indicating that the PANI film electrode has a better passivation resistance than the commonly used glassy carbon electrodes.

The repeatability of the Bi/PANI/graphene electrode is tested for 32 cycles in a 0.1 M acetate buffer solution (pH 5.3) containing 3 and 8 mg/L SDS, which can be explained with the branch-structured PANI molecules that can prevent the surface active species from reaching the electrode surface [24]. For comparison, the \( i_{p}/i_{\text{max}} \) ratios of glassy carbon electrodes modified with PANI and Bi are about 71% and 48% [24] measured in electrolyte solutions containing 3 and 8 mg/L SDS, respectively, which are much lower than those (about 98.3% and 59.2%, respectively) measured with the Bi/PANI/graphene electrode in the similar solutions used in this study, indicating that the PANI film electrode has a better passivation resistance than the commonly used glassy carbon electrodes.

The FE-SEM image of the bare graphene electrode shown in Fig. 6a shows that the graphene film has a rough surface, which is due to the thermal expansion and shrinkage of the sample caused by the thermal processing. The PANI coated graphene electrode (Fig. 6b) has a similar surface morphology as the bare graphene electrode (Fig. 6a), which may be due to that the PANI layer is too thin to be viewed with SEM. The FTIR spectra will be used to confirm the formation of the PANI films on the graphene electrodes later. The FE-SEM image of the Bi/graphene electrode surface shows a lot of nano-sized bright dots (about 3 nm diameter) as seen in Fig. 6c, which are attributed to the as-deposited Bi nanoparticles. With the modifications by both PANI and Bi, the Bi nanoparticles on the Bi/PANI/graphene electrode surface (Fig. 6d) are slightly bigger (about 10 nm diameter) than those on the Bi/graphene electrode surface (Fig. 6c). A possible reason is the adsorption and preconcentration effects of a porous PANI coating on metal ions [30,31], which lead to a relatively higher Bi\(^{3+}\)

---

**Fig. 1.** (a) SWASV peak currents of Cd\(^{2+}\) and Pb\(^{2+}\) with respect to varied Bi\(^{3+}\) concentrations and (b) SWASV voltammograms without Bi\(^{3+}\) and with 1.25 mM Bi\(^{3+}\) dissolved in electrolyte, measured by a graphene electrode in 0.1 M acetate buffer solutions (pH 5.3) containing 12 mM Cd\(^{2+}\) and 0.5 mM Pb\(^{2+}\).

**Fig. 2.** CV curves recorded during PANI deposition on a graphene electrode for 30 cycles in a 0.25 M H\(_2\)SO\(_4\) electrolyte containing 7.3 \( \mu \)M aniline with a scan rate of 50 mV/s and a potential range of −0.2 to 0.9 V.

**Fig. 3.** Tafel plots measured by graphene electrodes without/with PANI modification in a 0.1 M acetate buffer solution (pH 5.3) containing 0.1 M KNO\(_3\).
concentration around the electrode surface, and thus, the larger as-deposited Bi nanoparticles on the Bi/PANI/graphene electrode surface as shown in Fig. 6d.

Fig. 7 shows the FTIR spectra of the graphene and PANI/graphene electrodes. Compared to the graphene electrode (Fig. 7a), the PANI/graphene electrode depicts two main absorption bands of PANI (Fig. 7b), which locate at about 1585 and 1497 cm$^{-1}$ corresponding to the stretching mode of C$\equiv$C double bonds in the quinonoid and benzene rings, respectively [32]. The peak at about 1302 cm$^{-1}$ is typical of a standard PANI base and assigned to the C$\equiv$N stretching in the neighborhood of the aromatic rings [33]. The diketone rings have a characteristic vibration peak at about 1152 cm$^{-1}$, indicating that the generated PANI is in a form of emeraldine base (EB) that is a neutral state [34,35]. The absorption band at about 1445 cm$^{-1}$ is attributed to the $\pi$-coupled aniline [36]. The above confirms the formation of the PANI layer on the graphene electrode.

The SWASV curves of Pb$^{2+}$ (1 $\mu$M) measured with the graphene electrodes without/with PANI and/or Bi modifications are compared in Fig. 8. The bare graphene electrode has a stripping peak current of about 380.2 $\mu$A, which is relatively small. The PANI/graphene electrode has a slightly higher response compared to the bare graphene electrode, which may be due to the higher specific surface area of the branch-structured PANI layer [20]. With 1.25 $\mu$M Bi$^{3+}$ introduced in the electrolyte, the Bi/graphene electrode has a greatly increased SWASV peak than the PANI/graphene and bare graphene electrodes, which is due to the in-situ deposited Bi-Pb alloys that can promote the reduction of Pb$^{2+}$ to form Pb$^0$. The Bi/PANI/graphene electrode has the highest anodic stripping peaks among the four, due to the higher specific surface area [24] and the preconcentration effect of the branch structured porous PANI layer on the deposition of the metal ions [30,31], combined with the enhancement effect of the Bi based nanoparticles.

As shown in Fig. 9a, the voltammogram measured with the PANI/graphene electrode in the solution without Bi$^{3+}$ and Pb$^{2+}$ is smooth and has no obvious stripping peak. With 1.25 $\mu$M of Bi$^{3+}$ ions added in the electrolyte, an obvious Bi$^{3+}$ stripping peak current (about 112.9 $\mu$A) is observed at around $-0.08$ V. With the Pb$^{2+}$ ions added to the electrolyte, the stripping peak current of Bi$^{3+}$ (about 91.9 $\mu$A), which is deposited together with Pb$^{2+}$ to form the Bi–Pb alloys on the PANI/graphene electrode surface, is slightly smaller compared to the one measured in the electrolyte having no Pb$^{2+}$. As shown in Fig. 9a, with Pb$^{2+}$ concentrations increased from 0.1 to 1.1 $\mu$M, the stripping peak currents of Pb$^{2+}$ almost linearly increase, and their respective peak positions shift from about $-0.65$ to $-0.59$ V. The shift of the stripping peak positions toward less negative potentials at higher target metal concentrations can be explained by the Nerst potential.

The anodic stripping peak currents of Pb$^{2+}$ with increased concentrations from 0.33 nM to 1.1 $\mu$M are recorded with the corresponding calibration curve shown in Fig. 9b. The Pb$^{2+}$ peak currents are almost linearly proportional to the Pb$^{2+}$ concentrations in the range of 0.1–1.1 $\mu$M Pb$^{2+}$, which can be represented by the following equation:

$$I(\mu A) = -45.05 + 490.12 \times \left[\text{Pb}^{2+}\right](\mu M)$$

where $I$ is the peak current in $\mu$A and $[\text{Pb}^{2+}]$ is the Pb$^{2+}$ concentration in $\mu$M in the 0.1 M acetate buffer solution (pH 5.3). The regression coefficient of the above equation is about 0.995, indicating a good linear relationship between Pb$^{2+}$ anodic stripping peak currents and Pb$^{2+}$ concentrations.

The range for the ultralow Pb$^{2+}$ concentrations (0.33–5 nM) in Fig. 9b is magnified in Fig. 9c, from which a near linear relationship between the stripping peak currents and the Pb$^{2+}$ concentrations is also observed, which can be described by the following equation:

$$I(\mu A) = 0.42 + 0.67 \times \left[\text{Pb}^{2+}\right](nM)$$

where $I$ is the peak current in $\mu$A and $[\text{Pb}^{2+}]$ is the Pb$^{2+}$ concentration in nM. The regression coefficient of the equation is about 0.996. The Pb$^{2+}$ detection limit of the Bi/PANI/graphene electrodes is about 0.33 nM, which is much lower than that of the bare graphene electrode (about 7 nM, figure not shown). The high regression coefficient and low detection limit indicate the excellent performance of the Bi/PANI/graphene electrodes.

The SWASV peak currents of Pb$^{2+}$ with respect to ultralow Pb$^{2+}$ concentrations can be measured with an under-potential deposition (UPD) condition [37], which is related to a phenomenon wherein a metal monolayer is deposited onto the electrode surface of a foreign material. With a higher metal ion concentration and a sufficient deposition duration a multilayer metal can be deposited onto the pre-deposited monolayer, which is called bulk deposition (BD) [37]. As reported in the literature [37], UPD is usually used for the surface modification with metal catalysts. In this study, UPD is employed for anodic stripping voltammetry. As shown in Fig. 9d, the voltammogram has no stripping peak if no Pb$^{2+}$ ions are added in the electrolyte solution. With the electrolyte containing 4 nM Pb$^{2+}$, a single Pb$^{2+}$ peak is observed at around $-0.58$ V in the voltammogram, which is due to the UPD condition, while with a higher Pb$^{2+}$ concentration (120 nM) in the electrolyte, two peaks can be found at around $-0.645$ V (BD) and $-0.55$ V (UPD) in the voltammogram. This is because for the
electrochemical detection of trace heavy metals by means of SWASV, the anodic stripping peak positions of BD are mainly controlled by the Nernst potential and would increase with higher Pb$^{2+}$ concentrations as confirmed by Fig. 9a. Due to the strong bonding between metal deposits and electrode surface, the potentials corresponding to the anodic stripping peaks of UPD are more positive than those of BD.

4. Conclusions

In this paper, graphene ultrathin film electrodes were fabricated using a solid-state carbon diffusion method. The graphene electrodes were further modified with both conductive PANI porous layers and Bi nanoparticles to form Bi/PANI/graphene electrodes. During the electrochemical detection of Pb$^{2+}$ and Cd$^{2+}$ ions in acetate buffer solutions using the graphene electrodes developed in this study, it was observed that the Bi nanoparticles could significantly enhance the
sensitivity of the graphene electrodes, while the PANI porous layer could efficiently suppress the passivation of the electrodes. The anodic stripping peak currents measured with the Bi/PANI/graphene electrodes showed a perfect linear proportionality to the Pb$^{2+}$ concentrations. With the UPD condition, the Bi/PANI/graphene electrodes showed an ultralow detection limit of about 0.33 nM Pb$^{2+}$.

Acknowledgment

Z.M. Wang was grateful for the PhD scholarship from the Nanyang Technological University (NTU), Singapore.

References