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Square wave anodic stripping voltammetric determination of Cd²⁺ and Pb²⁺ at bismuth-film electrode modified with electroreduced graphene oxide-supported thiolated thionine

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ABSTRACT

Graphene oxide (GO)–thionine (TH) nanocomposite was prepared by π – π stacking. The nanocomposite was cast-coated on a glassy carbon electrode (GCE) to prepare an electroreduced GO (ERGO)–TH/GCE, then 2-mercaptoethanesulfonate (MES) was covalently tethered to ERGO–TH by potentiostatic anodization to form an ERGO–TH–MES/GCE. The thiolation reaction was monitored by electrochemical quartz crystal microbalance (EQCM). Square wave anodic stripping voltammetry (SWASV) was used to determine Cd²⁺ and Pb²⁺ at the ERGO–TH–MES/GCE further modified with Nafion and Bi. Under the optimal conditions, the linear calibration curves for Cd²⁺ and Pb²⁺ are from 1 to 40 $\mu\text{g L}^{-1}$, with limits of detection ($S/N=3$) of 0.1 $\mu\text{g L}^{-1}$ for Cd²⁺ and 0.05 $\mu\text{g L}^{-1}$ for Pb²⁺, respectively. The electrode was used for the simultaneous analysis of Cd²⁺ and Pb²⁺ in water samples with satisfactory recovery.

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1. Introduction

As it is well known, lead(II) and cadmium(II) are severe hazardous environmental pollutants with toxic effects on living organisms. Obviously, it is important to explore sensitive, rapid and simple analytical methods for dynamic monitoring of Pb²⁺ and Cd²⁺ [1–4]. Electrochemical techniques, especially anodic stripping voltammetry (ASV), have been well-established for determination of trace heavy metal ions including Pb²⁺ and Cd²⁺, owing to the advantages of low cost, high sensitivity, and great convenience in operation and proven capability of on-line environmental monitoring. Recently, various bismuth-based electrodes have been extensively studied for ASV instead of mercury-based electrodes [5–8], owing to the low toxicity, the ability to form alloys with many heavy metals, simple preparation, wide potential window, and insensitivity to dissolved oxygen at the bismuth-based electrodes. In addition, various chemically modified electrodes bearing surface functional groups with high affinity to heavy metals and their ions have been widely used for

ASV analysis of heavy metals with enhanced analytical performance [9–11].

Graphene is a two-dimensional honeycomb lattice packed by monolayer sp²-hybridized carbon atoms [12], which has attracted tremendous interest due to the large surface area, attractive thermal and mechanical properties, high electrical conductivity and great potential for chemical modification. On the other hand, thionine (TH) (also known as Lauth's violet) is a widely studied dye for biological staining. TH of conjugated π bonds can easily adsorb on graphene or graphene oxide (GO) through π – π stacking, and this nanocomposite has been widely used for chemo-/biosensing [13–15]. However, the thiolation of TH has not been examined for electroanalysis to date, though the thiolated functional materials and the thiol–ene chemistry have attracted great attentions recently [16–18].

Herein, we study the electrochemical thiolation of electroreduced GO (ERGO)-supported TH by reaction of 2-mercaptoethanesulfonate (MES) with TH at its oxidized state, and a new ERGO–TH–MES nanocomposite is thus prepared. Quartz crystal microbalance (QCM) is used for process monitoring and film characterization. A glassy carbon electrode (GCE) modified with ERGO–TH–MES, Nafion and Bi is applied to sensitively detect Cd²⁺ and Pb²⁺ by square wave anodic stripping voltammetry (SWASV).

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2. Experimental

2.1. Chemicals and apparatus

All electrochemical experiments were conducted on a CHI660C electrochemical workstation (CH Instrument Co.), and a conventional three-electrode electrolytic cell was used. A glassy carbon disk electrode (3 mm diameter) served as the working electrode, a KCl-saturated calomel electrode (SCE) as the reference electrode and a platinum sheet as the counter electrode. A computer-interfaced HP 4395A impedance analyzer equipped with an HP 43961A impedance test adapter and an HP 16092A impedance test fixture was employed in the QCM and electrochemical QCM (EQCM) experiments [19]. AT-cut 9-MHz gold-coated piezoelectric quartz crystals (PQCs, 12.5 mm diameter, Model JA5, Beijing Chenjing Electronics Co., Ltd., China) were used. The gold electrode of 6.0-mm diameter on one side of the PQC was exposed to the solution and connected to the ground terminal of the HP 16092A test fixture, while the other side of the PQC faced air and connected to the nonground terminal of the HP 16092A. Conductance (G) and susceptance (B) of the PQC resonance were measured synchronously on the HP 4395A during the frequency sweep centering at the PQC resonance frequency. A user program was written in Visual Basic (VB) 5.0 to control the HP 4395A and to acquire admittance data via an HP 82341C high-performance HPIB interface card for Windows 3.1/NT/95. A nonlinear least-squares fitting program based on the Gauss–Newton or Gauss–Newton–Marquardt algorithm was written in VB 5.0 for the simultaneous fits of G and B data during experiments [19]. UV–vis spectra were recorded on a UV2450 spectrophotometer (Shimadzu Co., Kyoto, Japan). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Nexus 670 FT-IR instrument (Nicolet Instrument Co., USA) in its transmission mode, and the films were carefully scraped off from the electrode surface for FT-IR analysis [18].

GO was purchased from XF NANO, Inc. (Nanjing, China). TH was purchased from Sinopharm Chemicals Co., Ltd. (Shanghai, China). MES was purchased from Aldrich (USA). Thioglycolic acid (TGA) and β -mercaptoethanol (ME) were purchased from Alfa Aesar. Nafion (5 wt%, in a mixture of water and lower aliphatic alcohols) was purchased from Aldrich (USA). The diluted 0.25 wt% Nafion solution was prepared with absolute ethanol. All other chemicals were of analytical grade, and all solutions were prepared using Milli-Q ultrapure water ($\geq 18 \text{ M}\Omega \text{ cm}$). National standard samples for water monitoring of Pb^{2+} and Cd^{2+} were commercially obtained from Shenzhen StarCare Technology Co., Ltd., China. Phosphate buffer solution (0.10 M, PBS, 0.039 M $\text{NaH}_2\text{PO}_4 + 0.061 \text{ M Na}_2\text{HPO}_4$, pH 7.0) and 0.10 M acetate buffer solution (0.049 M NaAc + 0.051 M HAc, pH 4.5) were used. All experiments were conducted at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$) in air atmosphere.

2.2. Procedures

The GO–TH nanocomposite was prepared as follows. The 0.500 mL of 0.50 mg mL^{-1} GO dispersion was obtained by ultrasonication for 30 min, which was then mixed with 0.500 mL of 1.00 mM TH solution at room temperature for at least 24 h. After centrifugation and rinse with water, the GO–TH nanocomposite was redispersed in 1.00 mL ultrapure water for subsequent experiments.

Prior to experiments, the GCE was in turn polished with 1.0 and 0.05 μm alumina powders, and it was then sequentially sonicated in ultrapure water and anhydrous ethanol. Afterwards, the GCE was subjected to potential cycling (-1.0 – 1.0 V , 0.1 V s^{-1}) in 0.50 mol L^{-1} aqueous H_2SO_4 until the cyclic voltammograms became reproducible. The Nafion/ERGO–TH–MES/GCE was prepared as follows. 1.0 μL of the

GO–TH suspension was dropped on a pretreated GCE and the electrode was kept in air until the solvent evaporated. An ERGO–TH/GCE was prepared by scanning the GO–TH/GCE between -1.3 and 1.1 V at 50 mV s^{-1} in 0.10 M PBS (pH 7.0). Afterwards, the ERGO–TH film interacted with MES at a constant potential (1.1 V) in 0.10 M PBS (pH 7.0) containing 5.00 mM MES to form an ERGO–TH–MES/GCE. Then, 1.0 μL of Nafion ethanol solution (0.25 wt%) was cast on the electrode surface and dried in air. Nafion acted here as a binder to stabilize the modified species on electrodes and as a permselective film to alleviate the interferences of anions [20]. In QCM studies, the ERGO–TH film was also prepared similarly on a QCM Au electrode to study its interaction with MES. Control experiments were conducted similarly in the absence of TH.

SWASV measurements were performed in 0.10 M acetate buffer (pH 4.5) containing $400 \mu\text{g L}^{-1} \text{ Bi}^{3+}$. A preconcentration potential of -1.1 V and a preconcentration time of 300 s were applied to the working electrode under stirring conditions. After an equilibration period of 10 s, the square wave anodic stripping voltammogram was then recorded from -1.1 to 0.1 V , and the solution was not stirred in these two steps. The electrode was cleaned for 30 s at 0.3 V to remove the residual metals and bismuth film under solution-stirred conditions. After recording the background voltammograms in 0.10 M acetate buffer (pH 4.5) containing $400 \mu\text{g L}^{-1}$ of bismuth, cadmium and lead standard solutions were added into the electrolytic cell as required and the measurements were repeated five times for each experiment. All experiments were performed at room temperature ($25 \pm 2 \text{ }^\circ\text{C}$).

3. Results and discussion

3.1. Electrosynthesis and characterization of the ERGO–TH–MES film

The EQCM using a PQC as its central sensing element is a powerful method to monitor many electrodeposition processes with a mass-detection sensitivity down to (sub)monolayer discrimination [19,21–25]. Generally, the EQCM frequency response (Δf_0) can reflect information both on the electrode-mass change and on the change in viscous loading on the electrode, but the simultaneously recorded EQCM response of the motional resistance (ΔR_1) only reflects information on the change in viscous loading on the electrode. Hence, a pure mass-effect should theoretically not change the R_1 value (i.e. $\Delta R_1 = 0$), namely, a pure mass effect should have a very large $-\Delta f_0/\Delta R_1$ value (theoretically $\rightarrow \infty$). In contrast, a pure density–viscosity effect on the 9-MHz PQC resonance possesses a characteristic value of $-\Delta f_0/\Delta R_1 = 10 \text{ Hz } \Omega^{-1}$ [19]. Accordingly, the characteristic $-\Delta f_0/\Delta R_1$ value can be used for data interpretation in EQCM studies. Here, the EQCM technique was used to monitor the electrode reactions of interest. At first, the ERGO and ERGO–TH coated QCM Au electrodes prepared as in the Experimental section were used to tether MES by cyclic voltammetry, as shown in Fig. 1. Note here that TH in the ERGO–TH/QCM Au electrode may mainly exist as poly(TH) (PTH) and/or TH oligomers after its preparation by scanning the electrode cast-coated with GO–TH between -1.3 and 1.1 V at 50 mV s^{-1} in 0.10 M PBS (pH 7.0). When an ERGO–TH/QCM Au electrode was swept in MES-free 0.10 M PBS (pH 7.0, Fig. 1A), the frequency decrease due to oxidation of uncovered Au and the frequency increase due to reduction of Au oxides were observed in the potential range of Au redox chemistry (ca. 10-Hz within each cycle) [23]. After 3-cycle CV, the net frequency change in total was within ca. 3 Hz. When an ERGO/QCM Au electrode was swept in 0.10 M PBS (pH 7.0) containing 5.00 mM MES (Fig. 1B), a large thiol-oxidation peak was observed at 1.0 V, accompanying with a frequency decrease. After 3-cycle CV, and the net frequency change in total reached at ca. -36 Hz .

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