



Glassy carbon electrode modified by graphene–gold nanocomposite coating for detection of trace lead ions in acetate buffer solution



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ABSTRACT

Reduced graphene oxide (RGO) decorated with gold nanoparticles (AuNPs) was electrodeposited on glassy carbon electrode (GCE) using cyclic voltammetric method. The results of Raman spectroscopy confirmed the simultaneous formation of AuNPs and reduction of graphene oxide through the electrodeposition process. Scanning electron microscopic measurements showed a uniform distribution of the AuNPs on the RGO sheets. The RGO–AuNP nanocomposite coated GCE (G–Au/GCE) was used to detect lead ions (Pb^{2+}) contained in a 0.1 M acetate buffer solution (pH 5.3) using square wave anodic stripping voltammetry (SWASV). The G–Au/GCE demonstrated higher detection sensitivity and stronger SWASV signals than the bare GCE, with the limit of detection of about 0.8 nM.

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1. Introduction

Industrialization activities have released certain amounts of toxic metals into the environment [1]. Toxic metals such as lead (Pb), cadmium (Cd) and copper cause water contamination and bring negative effects to human, plants and animals. Excessive consumption of Pb leads to malfunction of the central nervous system [2] and kidney damage [3]. Prolonged consumption of Cd leads to hypocalcaemia [3–5]. As a result, demand for detection of trace heavy metals is ever-increasing. Square wave anodic stripping voltammetry (SWASV) is widely used for trace heavy metal detection due to its high sensitivity and cost effectiveness [6–8].

In the past, platinum and gold electrodes have been widely used in electrochemical analyses due to their excellent electron transfer kinetics. However, they suffer from low hydrogen overvoltage that reduces their cathodic potential window. Furthermore, formation of surface oxides on their surfaces leads to high background noises [9].

Graphene is a two-dimensional sp^2 -hybridized carbon and arrayed in a honeycomb pattern [10,11]. Graphene possesses several exceptional properties, such as high electrical conductivity, tensile strength, thermal conductivity and chemical inertness [12,13]. With these properties, graphene forms useful electronic and sensing materials. Graphene-modified electrode has been widely developed in trace heavy metal

sensing. For example, graphene ultrathin film electrode is able to detect lead ion (Pb^{2+}) as low as 7 nM in aqueous solutions [14].

Recently, graphene nanocomposite electrode has been applied in detection of trace heavy metals. This is because graphene or reduced graphene oxide (RGO) is highly electrically conductive, while nanoparticles can selectively react with the trace heavy metal ions [10]. For example, RGO/bismuth (Bi) nanocomposite electrode can detect as low as 2.65 nM of Pb^{2+} [15].

In this manuscript, a mixture of gold nanoparticles (AuNPs) and RGO was electrodeposited on glassy carbon electrode (GCE) through cyclic voltammetry (CV) deposition. The AuNPs were used due to their high electrical conductivity, while the RGO helped disperse the AuNPs. The RGO–AuNP nanocomposite coated GCE (G–Au/GCE) was used to study the detection of Pb^{2+} through SWASV.

2. Experimental details

2.1. Reagents and chemicals

All chemicals employed in this work were purchased from Sigma-Aldrich with analytical grade and were used without further purification. 0.1 M acetate buffer solution (ABS) (pH 5.3) and 0.4 M ABS (pH 5) were prepared by acetic acid (Fluka) and sodium acetate (Fluka). Stock solutions of lead (II) nitrate with 0.1 mM and 0.05 M of gold (III) chloride (HAuCl_4) were prepared and stored at room temperature (23 °C). All the chemicals used were of analytical grade.

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2.2. Apparatus

Electrochemical experiments were performed by using CHI 900 electrochemical workstation (CHI Instruments Inc., USA). The image of scanning electron microscopy (SEM) was obtained with JEOL SEM, JSM 5600-LV, with 15 kV. Raman spectroscopy (RS) analysis was performed by using Renishaw Raman spectroscopy (RS) with 633 nm wavelength.

2.3. Preparation of electrodes

Graphite oxide was synthesized from natural flake graphite by using Hummers method [16]. The prepared graphite oxide powder was exfoliated in a 0.4 M ABS, pH 5 to form 0.1 mg ml⁻¹ of graphene oxide (GO) colloidal dispersion. The GO colloidal dispersion was mixed with 100 μM of HAuCl₄, followed by bubbling with N₂ gas for 1 h to exfoliate the stacked GO and to deoxygenate the solution. The CV reduction was performed in the mixture of the dispersed GO and the AuNPs by using CHI 900 electrochemical workstation with a three-electrode system where Ag/AgCl electrode was used as the reference electrode, platinum mesh as the counter electrode and GCE as the working electrode. The mixture of GO and AuNPs was stirred by a magnetic stirrer at a rotational speed of 400 rpm during the CV reduction. The CV scanning was performed at a potential range of -1.5 V to 0.6 V and a scan rate of 0.2 V s⁻¹. After the CV electrodeposition, the fabricated samples were washed twice with DI water and dried with air gun, followed by characterization.

2.4. Electroanalysis

SWASV measurements were applied to study the performance of the electrodes. The same three electrodes were dipped into a 0.1 M ABS (pH 5.3) containing predetermined concentrations of target Pb²⁺ ions. In the SWASV measurement, a preconcentration potential ranging from -1.3 to -0.8 V was applied to the working electrode for 60 s to 300 s with continuous magnetic stirring. After that, a 30 s quiet time was performed to stabilize the solution. Then, SWASV scanning was performed from -1 V to 0.2 V. The optimum preconcentration potential and time were selected for the subsequent SWASV measurements. In the interference study, copper ions (Cu²⁺) with the concentrations ranging from 10 nM to 100 nM were added into the 0.1 M ABS (pH 5.3) containing Pb²⁺. In the study on the application of the G-Au/GCEs in real samples, tap water samples were initially adjusted to pH 5.3 using acetic acid and sodium acetate, followed by SWASV measurements using the G-Au/GCEs as the working electrode. Then, the recovery tests were conducted by adding Pb²⁺ and Cu²⁺ ions into the tap water samples.

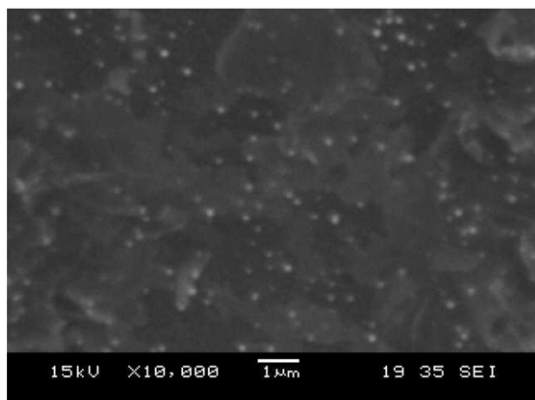


Fig. 1. SEM micrograph of G-Au/GCE.

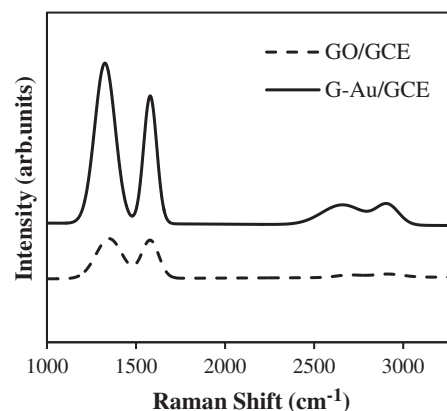


Fig. 2. Raman spectra of GO/GCE and G-Au/GCE.

3. Results and discussion

There are several factors that affect the current response in SWASV, such as the composition of bulk solution, structure of G-Au nanocomposite, surface condition of GCE, condition of Pb²⁺ accumulation and parameters of square wave voltammetry (SWV) mode.

3.1. Characterization of electrodes

3.1.1. Morphology study of G-Au/GCE by SEM

The SEM micrograph in Fig. 1 illustrates the surface morphology of the G-Au/GCE electrode, where a wrinkled paper-like microstructure with spread white dots is observed. This indicates the formation of G-Au on the GCE electrode surface. The average size of AuNPs is about 10 nm in diameter. In this structure, the crumpled nature of RGO enhances the electrode surface area for effective detection of Pb²⁺ [17]. It also helps to uniformly disperse the AuNPs [10] to avoid agglomeration of the AuNPs.

3.1.2. RS study on GO/GCE and G-Au/GCE

The electrochemical reduction of GO/GCE is verified by RS as shown in Fig. 2, where two distinct peaks can be observed at 1335 cm⁻¹ and 1580 cm⁻¹, which are attributed to the D band and G band, respectively. The D band commonly indicates structural defects, while the G band represents sp² hybridized carbon-based materials [18], characteristic of graphite-like materials [19]. The D/G peak intensity ratio (I_D/I_G) provides the information of the degree of structural defects [20]. Fig. 2 shows a relatively increased I_D/I_G of 1.25 in the G-Au/GCE relative to 1.05 in the GO, which may be due to the incorporation of Au nanoparticles. The G-Au/GCE shows two more relatively weak Raman peaks at ~2700 cm⁻¹ and 2900 cm⁻¹, which are attributed to the 2D band and D + G band, respectively. The 2D band is usually induced by crystalline

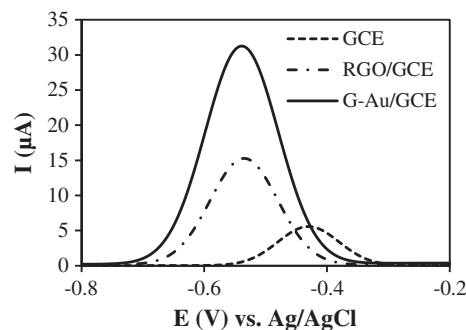


Fig. 3. SWASVs of 75 nM Pb²⁺ in 0.1 M acetate buffer solution (pH 5.3) measured with bare GCE, RGO/GCE and G-Au/GCE.

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