



# Voltammetric determination of trace heavy metals using an electrochemically deposited graphene/bismuth nanocomposite film-modified glassy carbon electrode



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## ABSTRACT

A novel electrochemically deposited graphene (EG)/bismuth (Bi) nanocomposite film-modified glassy carbon electrode (GCE) was prepared through successive electrodeposition of exfoliated graphene oxide (GO) and in situ plating bismuth film. Experimental variables, including deposition potential and bismuth concentration, were carefully optimized to determine trace zinc, cadmium, and lead ions by using the EG/Bi electrode as an electrochemical-sensing platform. The linear calibration curves ranged from 1 to 100  $\mu\text{g L}^{-1}$  for  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$ . The detection limits were 1.80  $\mu\text{g L}^{-1}$  for  $\text{Zn}^{2+}$ , 0.18  $\mu\text{g L}^{-1}$  for  $\text{Cd}^{2+}$ , and 0.11  $\mu\text{g L}^{-1}$  for  $\text{Pb}^{2+}$  ( $S/N = 3$ ). The EG/Bi nanocomposite film electrode was successfully applied to the analysis of trace metals in real environments.

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## 1. Introduction

Heavy metals such as lead, cadmium, and zinc are well-known undesirable constituents in groundwater, drinking water, and soil. Especially they can be accumulated in the human body through the food chain to induce a severe threat to human health [1–3]. The increase in concentration of heavy metals, resulting from anthropogenic activities such as mining and industrial processing, has become a global concern [4]. Accordingly, it is increasingly necessary to develop sensitive, rapid, and simple analytical methods required for continuous monitoring of these pollutants. Analytical methods, such as electrothermal atomic absorption spectrometry, flame atomic absorption spectrometry [5], inductively coupled plasma mass spectrometry (ICP-MS) [6], and electrochemical techniques, have been developed for trace metal determination. However, spectrometric methods are unsuitable for in situ measurements owing to the complex instrumentation required. In addition, they are expensive, cumbersome mode of administration, and time consuming, requiring analysis to be performed by skilled personnel in a specialized manner. In contrast, electrochemical methods, especially electrochemical stripping analysis, have been widely recognized as convenient techniques for measuring heavy metal ions owing to good selectivity, low cost, portability and the ability to accurately determine multiple elements at trace

level [7,8]. Until now, mercury and mercury film electrodes have been commonly used as materials in stripping voltammetric analysis for heavy metal determination, due to good reproducibility and high sensitivity [9]. Mercury is, however, a very hazardous material, its use raising serious health and environmental concerns. Numerous attempts have been made to replace it with new, more environmentally friendly mercury-free electrodes. Bismuth electrodes have recently been developed in the field of the stripping technique as a possible replacement for mercury electrodes. Bismuth electrodes have shown results comparable to mercury electrodes, which can form fused alloys with trace heavy metals. Moreover, bismuth electrodes have many beneficial properties such as low toxicity, high sensitivity, good stripping signal, and simple preparation [8,10–12]. However, new materials with bismuth film for working electrodes are still needed for developing a high-sensitivity heavy metal-sensing platform [13–19].

Graphene, a one atom-thick planar sheet of  $\text{sp}^2$ -bonded carbon atoms, is attracting tremendous attention due to its large specific surface area, high thermal conductivity, and good electrical conductivity. Moreover, graphene exhibits remarkable electrochemical properties, such as a large potential window, low charge-transfer resistance, excellent electrochemical activity, and fast electron transfer rate [20,21]. The extraordinary properties of graphene enhance its application to electrochemical sensing [22–24]. Mechanical cleavage of graphite led to the discovery of graphene, but the low productivity of this approach makes it impractical for large-scale preparations [25]. Later, graphene sheets were grown on a single crystal of silicon carbide

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by vacuum graphitization [26], or produced continuously in microwave plasma reactors [27]. Furthermore, graphene has been made from rapid thermal expansion of graphite or chemical reduction of exfoliated graphite oxide (GO), a soft chemical synthesis route [28,29]. All these methods suffer from limitations of high temperature, expensive special equipment, use of toxic chemicals or conditions, and tedious procedures. Therefore, a “green synthesis” of graphene under mild conditions is needed. Recently, electrochemical deposition has been reported as a simple method and green strategy for graphene synthesis [30–34]. For sensing applications, the modification of electrodes for depositing graphene is crucial. Graphene-modified electrodes are normally fabricated by drop-casting solution-based graphene obtained from chemical reduction of graphene oxide. However, this method has intrinsic limitations such as weak adhesion to substrate electrode, lack of control of film thickness, and agglomeration of the reduced graphene suspension through strong interactions and  $\pi$ - $\pi$  stacking. Thus, a method for the direct electrochemical reduction of GO was proposed [35–38].

In this study, we carried out direct electrochemical reduction of GO on a glassy carbon electrode (GCE) from GO dispersion to determine trace heavy metal ions by differential pulse anodic stripping voltammetry (DPASV). This method can be used to control film thickness quantitatively and form a stable film on the electrode surface without any further treatment.

The objective of this work was to improve analytical performance and fabricate a sensitive, mercury-free, electrochemical platform combining the advantages of EG with the in situ plating bismuth nanocomposite film-coated GCE. Associated with an enlarged active surface area, high electronic conductivity, and strong absorptive ability of graphene, the modified composite electrode showed enhanced electron transfer properties and excellent stripping performance for the analysis of trace heavy metal ions. The experimental results indicated that this electrode exhibited excellent voltammetric response to heavy metal ions. This simple, fast, highly sensitive, reducing-agent-free, low-cost sensor was fabricated to determine the traces of lead, cadmium, and zinc in real samples.

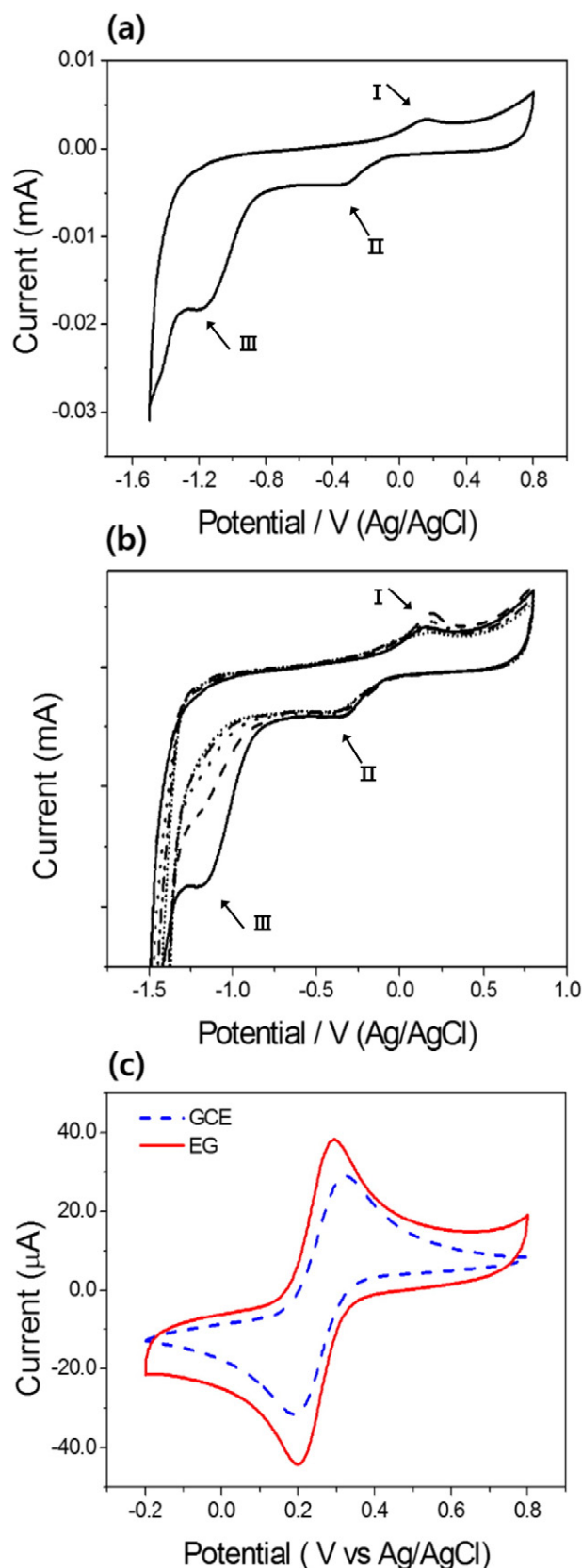
## 2. Experimental

### 2.1. Reagents

All chemicals were of analytical grade and used without further purification. Standard solutions of  $\text{Bi}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Pb}^{2+}$  ( $1000 \text{ mg L}^{-1}$ ) were obtained from Sigma-Aldrich and diluted as required. Graphite powder ( $<20 \mu\text{m}$ ), sodium acetate, and acetic acid were purchased from Aldrich (USA). Sodium phosphate buffer (PBS) was used as supporting electrolyte to prepare the EG film. A 0.1 M acetate buffer (pH 4.5), prepared by mixing appropriate amounts of acetic acid and sodium acetate, was used to prepare solutions of the supporting electrolyte. All solutions were prepared with double-distilled water.

### 2.2. Apparatus

Electrochemical measurements were performed on an Autolab potentiostat (Metrohm, USA) with a conventional three-electrode system. A modified GCE (3 mm in diameter, Bioanalytical Systems, Inc.) served as the working electrode, while a Ag/AgCl electrode (Bioanalytical Systems, Inc.) and platinum wire were used as the reference and counter electrodes, respectively. A transmission electron microscope (TEM; JEM-3010, JEOL) and field-emission scanning electron microscope (FE-SEM; JSM-6700F, JEOL) were used to check the morphologies of the GO, EG and EG/Bi composite. Raman analysis was performed using a Raman spectrometer (Dongwoo DM 500i) employing a 15 mW Argon laser at 514.5 nm.



**Fig. 1.** A cyclic voltammogram of GCE in  $5 \text{ mg ml}^{-1}$  GO dispersion solution containing 0.1 M PBS (pH 7) at scanning rate of  $50 \text{ mV s}^{-1}$  (a). CVs for electrochemical reduction of GO on GCE in PBS solution (0.1 M) at a scan rate of  $50 \text{ mV s}^{-1}$  for five cycles (b). CVs obtained at a bare GCE and EG electrode in 0.1 M KCl solution containing 5 mM  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  at a scan rate of  $50 \text{ mV s}^{-1}$  (c).

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