



# Development of an electrochemically reduced graphene oxide modified disposable bismuth film electrode and its application for stripping analysis of heavy metals in milk



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## ABSTRACT

A novel electrochemical sensing platform based on electrochemically reduced graphene oxide film modified screen-printed electrode was developed. This disposable electrode shows excellent conductivity and fast electron transfer kinetics. By in situ plating bismuth film, the developed electrode exhibited well-defined and separate stripping peaks for cadmium and lead. Several parameters, including electrolytes environment and electrodeposition conditions, were carefully optimized to achieve best stripping performance. The linear range for both metal ions at the disposable bismuth film electrode was from  $1.0 \mu\text{g L}^{-1}$  to  $60.0 \mu\text{g L}^{-1}$ . The detection limit was  $0.5 \mu\text{g L}^{-1}$  for cadmium ion and  $0.8 \mu\text{g L}^{-1}$  for lead ion. Milk sample analysis demonstrates that the developed electrode could be effectively used to detect low levels ( $\mu\text{g L}^{-1}$ ) of cadmium ion and lead ion. Graphene based disposable bismuth film electrode is a sensitive, stable, and reliable sensing platform for heavy metals determination.

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## 1. Introduction

Milk is an important food of animal origin and contains most of essential nutrients for a healthy diet. It is the only food consumed by newborn babies, but in general, human beings continue to drink milk during the entire life cycle. However, current studies have revealed that milk may contain varying amounts of different toxic heavy metals, such as Cd and Pb (Ataro, McCrindle, Botha, McCrindle, & Ndibewu, 2008). Especially in the developing countries, numerous milk safety incidents associated with heavy metals contamination have been reported recently (Rahimi, 2013; Xia, Chen, Liu, & Liu, 2011). Since the quick accumulation of heavy metals in human body and the toxicity towards the human organs, the determination of toxic heavy metals in milk is becoming increasingly important.

Current methods employed to detect toxic heavy metals, such as atomic absorption spectrometry (AAS) (Bagheri, Afkhami, Saber-Tehrani, & Khoshafar, 2012), inductively coupled plasma mass spectrometry (ICP-MS) (Ataro et al., 2008), and X-ray fluorescence spectrometry (XFS) (Sogut, Bali, Baltas, & Apaydin, 2013), are always labelled with expensive and time-consuming. Moreover, these detection techniques need to be operated in specialized laboratory that makes them unsuitable for 'application in the field' (Quintana et al., 2012). On the other hand, the complex emulsion

like matrices and low concentration levels of metal ions (commonly at  $\mu\text{g kg}^{-1}$  level) in milk samples make the determination a difficult task (Kazi et al., 2009). For these reasons, the development of sensitive, robust, and simple methods for quantifying trace metals is still highly desirable and challenging.

Electrochemical methods, particularly anodic stripping voltammetry (ASV), have been proven to be a powerful tool for fast access to metal ions information in complex samples due to their high sensitivity, easy operation, and low cost of analysis (Herzog & Beni, 2013). Furthermore, analytical instruments for ASV are relatively portable, compact and inexpensive compared with its spectroscopic counterparts, providing considerable feasibility for on-site measurements, e.g., biomedical, environmental and food monitoring (Ping, Wu et al., 2011; Wang, 2005). In most cases, mercury film electrodes (MFEs) are preferred due to their excellent stripping characters. However, the toxicity of mercury limits its wide applications, especially those involved in food contact. Recently, bismuth film electrodes (BiFEs) have been recognized as a promising substitute for MFEs in view of their low toxicity and comparable analytical performance to MFEs (Economou, 2005). Bismuth can normally be deposited on many electrode substrates, including glassy carbon electrode, carbon paste electrode, screen-printed electrode, boron doped diamond electrode, and some noble metal electrodes (Švancara, Prior, Hočevar, & Wang, 2010). Amongst them, screen-printed electrodes (SPEs) have been attracted extensive attention in stripping analysis of heavy metals due to the inherent superiority of their manufacturing process, which is

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inexpensive, rapid, simple and capable of mass production (Metters, Kadara, & Banks, 2013; Serrano, Alberich, Diaz-Cruz, Arino, & Esteban, 2013). There are several available methods for the preparation of BiF modified SPE (SPE/BiF), such as 'ex situ', 'in situ', and 'bulk' approaches (Hwang, Han, Park, & Kang, 2008; Khairy, Kadara, Kampouris, & Banks, 2010; Serrano, Diaz-Cruz, Arino, & Esteban, 2010). In the past years, these disposable sensors have been successfully used to determine heavy metals in various samples, such as soil, vegetable, seawater, and blood (Metters, Kadara, & Banks, 2011).

Graphene, an up-rising star of carbon-based nanomaterial, is a sheet of  $sp^2$  bonded carbon atoms that are arranged into a honeycomb structure, drawing tremendous interest from both the experimental and theoretical scientific communities since its discovery in 2004 (Novoselov et al., 2004). Like carbon nanotubes (CNTs), graphene provides an effective avenue for fabricating electrochemical sensing devices due to its large specific surface, high electron conductivity, and excellent biocompatibility (Liu, Dong, & Chen, 2012). Graphene-based MFEs (Li, Guo, Zhai, & Wang, 2009b) or BiFEs (Li, Guo, Zhai, & Wang, 2009a; Sahoo et al., 2013) have been developed for the determination of heavy metal ions with high sensitivity and good reproducibility. Until now, graphene film modified electrodes are mostly prepared by drop-casting graphene dispersion obtained from chemically reduced graphene oxide (CRGNO). However, such a preparation methodology suffers from some limitations. Firstly, the preparation of CRGNO always needs excessive toxic reducing agents (Li, Müller, Gilje, Kaner, & Wallace, 2008). Second, since the pure carbon materials are not soluble in most kinds of solvents, a suitable dispersion method must be used to obtain homogeneous carbon materials dispersion solution before the drop-casting process, particularly in the preparation of graphene films (Chen, Tang, Wang, Liu, & Luo, 2011). Group functionalization or the use of surfactants could obtain well-dispersed graphene solution (Georgakilas et al., 2012). However, the group functionalization can adversely influence the electronic properties of graphene nanosheets. Whilst the residual surfactants in graphene film may inhibit the stripping process in the determination of cadmium ion (Brownson & Bank, 2011; Brownson, Kampouris, & Banks, 2012). Therefore, the search for green and rapid method to build graphene film-based electrode are crucial to further expand the application of graphene in detection of heavy metals.

Recently, a promising strategy in graphene synthesis based on electrochemical method to produce electrochemically reduced graphene oxide (ERGNO) has been introduced (Zhou et al., 2009). This method offers several advantages over other graphene preparation methods, including green, efficient, inexpensive, and rapid (Ping, Wang, Fan, Wu, & Ying, 2011). Moreover, due to the insolubility of graphene in common solvents, the obtained ERGNO could remain and further form a stable film on the electrode surface that significantly reduces the fabrication time in graphene film-based electrodes (Chen et al., 2011; Ping, Wang, Ying, & Wu, 2012). Despite such remarkable advantages of the synthesis as well as the excellent physicochemical properties of ERGNO film, its electrochemical sensing applications in determination of heavy metals yet have not been explored so far.

In this work, a novel disposable sensing platform based on ERGNO film modified SPE (SPE/ERGNO) was present. The ERGNO film was prepared by on-step electrodeposition of the exfoliated graphene oxide (GNO) onto the SPE surface. For heavy metals sensing, the developed SPE/ERGNO was plated with BiF by 'in situ' approach. Results shows that BiF modified SPE/ERGNO (SPE/ERGNO/BiF) exhibited excellent stripping performance for simultaneous analysis of cadmium ion ( $Cd^{2+}$ ) and lead ion ( $Pb^{2+}$ ) via square wave anodic stripping voltammetry (SWASV). Furthermore, the developed disposable electrode was applied to determine  $Cd^{2+}$  and  $Pb^{2+}$  in milk sample extracts.

## 2. Experimental

### 2.1. Reagents

All chemicals were of analytical grade and used without any further purification. Graphite powder (320 mesh, spectral pure) and *N,N'*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Graphite oxide (GO) was synthesized from graphite powder by using a modified Hummers method (Hummers & Offeman, 1958; Kovtyukhova et al., 1999). Exfoliation of GO to graphene oxide (GNO) was achieved by ultrasonication of GO dispersion (0.5 wt%) using a supersonic cleaner (SK3300HP, 180W, Shanghai, China). Chemically reduced graphene oxide (CRGNO) was synthesized by the chemical reduction of GNO with hydrazine (Li et al., 2008) and then dispersed in DMF solvents. The commercially available silver ink (Electrodag 427SS), conductive graphite ink (Electrodag 423SS), and insulating ink (Electrodag 452SS) were obtained from Acheson Co., Ltd. (USA). Standard solutions of  $Cd^{2+}$  and  $Pb^{2+}$  (1000 mg L<sup>-1</sup>) were prepared and diluted as required. Except note, acetate buffer solution (NaAc-HAc, 0.1 mol L<sup>-1</sup>, pH 4.5) was used as the supporting electrolyte. Millipore-Q (18.2 MΩ cm) water was used for all experiments.

### 2.2. Apparatus

Tapping-mode atomic force microscopy (AFM) measurements were made on the mica with a Dimension Icon AFM equipped with a ScanAsyst (Bruker AXS, Germany). Scanning electron microscopy (SEM) images were collected on a Zeiss Ultra-55 field emission scanning electron microscope (Carl Zeiss Microscopy, Germany). Raman spectra were conducted using a micro-Raman spectrometer (Jobin Yvon LabRam HRUV, France, excited by 514 nm laser excitation). Electrochemical impedance spectroscopy (EIS) experiments were carried out using a Solartron Analytical model 1260 Impedance-Gain-Phase Analyzer in combination with a model 1287 Electrochemical Interface (Solartron Analytical, UK). Voltammetric measurements were carried out with using a PalmSens (Palm Instrument BV, Houten) that consists of a portable potentiostat interfaced with a palmtop PC. The electrochemical cell was assembled with a conventional three-electrode system: a saturated Ag/AgCl reference electrode, a Pt wire auxiliary electrode, and the prepared disposable electrode. The electrochemical experiments were carried out in a one-compartment electrochemical cell. All the experiments were performed at room temperature.

### 2.3. Electrode preparation

The fabrication of SPE was performed on a semi-automatic screen printer (Z-C3050A, Zheng Ting Screen Printing Material Co. Ltd., Shanghai, China). The size of screen mesh was about 150 μm. Prior to the printing process, the ceramic substrate (5 mm thickness) was cleaned with ethanol and distilled water, and then dried at room temperature. The first layer on the ceramic substrate is made from silver ink which was used to act as the connections and reference electrode. The drying process of silver layer was performed by putting the ceramic substrate in an oven for 15 min at 93 °C. Then, the conductive graphite ink was used to print the counter electrode and working electrode. The evaporation of solvents was performed by heating the substrate in an oven for 5 min at 121 °C. Finally, an insulating ink was printed to cover the connections and define the working electrode area. After irradiating with 254 nm ultraviolet, the home-made SPEs were obtained. The working area of these prepared SPEs was calculated as 0.08

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