Sensors and Actuators B 178 (2013) 379–384

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Square wave anodic stripping voltammetry determination of lead based on the Hg(II) immobilized graphene oxide composite film as an enhanced sensing platform

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ARTICLE INFO

Article history:
Received 13 September 2012
Received in revised form
21 December 2012
Accepted 30 December 2012
Available online 4 January 2013

Keywords:
Square wave anodic stripping voltammetry
Lead
Graphene oxide
Hg nanodroplets

ABSTRACT

In present paper, Hg(II) modified graphene oxide (Hg(II)/GO) was firstly prepared by reaction of graphene oxide (GO) with Hg(II). The Hg(II)/GO dispersed in a Nafion solution was coated on the polished glassy carbon electrode (GCE) for fabricating the enhanced electrochemical sensing platform. And then Hg(II)/GO modified GCE was held at a negative potential (−1.0 V) to reduce the coordinated Hg(II) to Hg forming Hg nanodroplets, which was been used as the sensing platform to determine Pb^{2+} by square wave anodic stripping voltammetry (SWASV). In comparison with the Hg(II) immobilized MWCNT graphite electrode, the response signal of our electrode was obviously increased owing to the unique structure of GO. The linear calibration curves ranged from 5 ng L^{-1} to 70 ng L^{-1} and 0.1 μg L^{-1} to 10 μg L^{-1} for Pb^{2+}. The detection limit (S/N = 3) was estimated to be around 0.13 ng L^{-1} for Pb^{2+}. The practical application of Hg(II)/GO modified GCE was also evaluated by the detection of Pb^{2+} in different water samples, the results suggest that the sensor is very promising for practical applications.

1. Introduction

At present, the importance of controlling the level of heavy metals in natural waterways, potable water and soils has generated increasing interest in the development of novel sensors for the detection of them. Lead as a heavy metal has serious toxic effect to human health, such as anemia, gastrointestinal diseases, hypoevolutismus and brain tissue damage [1,2]. Thus, its serious effect on human health make it necessary to develop a rapid and simple analytical method for precise monitoring of Pb^{2+}. Although atomic absorption spectrometry (AAS) [3–5] and ion coupled plasma mass spectrometry (ICPMS) [6,7] are widely used in lead detection, the characteristics of these methods make them inconvenient for onsite analysis. Anodic stripping voltammetry (ASV) as a classical electrochemical technique shows the same high sensitivity compared with the above methods, at the same time, ASV is also attractive due to its portability and low cost [8–10]. The traditional mercury film electrode and hanging drop mercury electrode have good reproducibility and high sensitivity, but their toxicity is always an inevitable problem. So how to reduce the toxicity of these electrodes is worth researching.

Nowadays, nanomaterials are widely used in many research fields, including ASV. For example, Au nanoparticles [11–13], carbon nanotubes [14–16], graphene [17–19], etc. Owing to the special physicochemical properties of nanomaterials, they can obviously improve the sensitivity and selectivity of ASV. For example, Hg carbon screen printed electrodes for detection of Pb^{2+} have been widely studied in which the nanomaterials come from nano carbon materials and Hg could be successfully applied to ASV analysis [20–22]. Moreover, the thought that the introduction of nanomaterials could reduce the toxicity of mercury based electrodes gradually comes into prominence [23]. So Hg(II) immobilized MWCNT graphite electrode has been developed in ASV analysis [24], this novel method can obviously eliminate the fear of Hg leaching. So this kind of material has an important research value, but the related research is scarce. Graphene was a kind of novel and fascinating carbon material since experimentally produced in 2004 [25–28], the excellent electrical and mechanical properties of graphene have attracted a great deal of attention and provide the potential application in highly sensitive and selective detection [29–32]. So it can be used as an excellent electrochemical platform for ASV analysis such as Hg^{2+} [33], Pb^{2+} [17], Cd^{2+} [18], etc. Considering the features of the graphene, GO could be used as the excellent support materials for fabricating Hg(II) immobilized electrodes. On the one hand, the properties of GO are similar to graphene which have a single atomic plane of graphite structure, this unique structure could help to adsorb more target ions

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http://dx.doi.org/10.1016/j.snb.2012.12.114

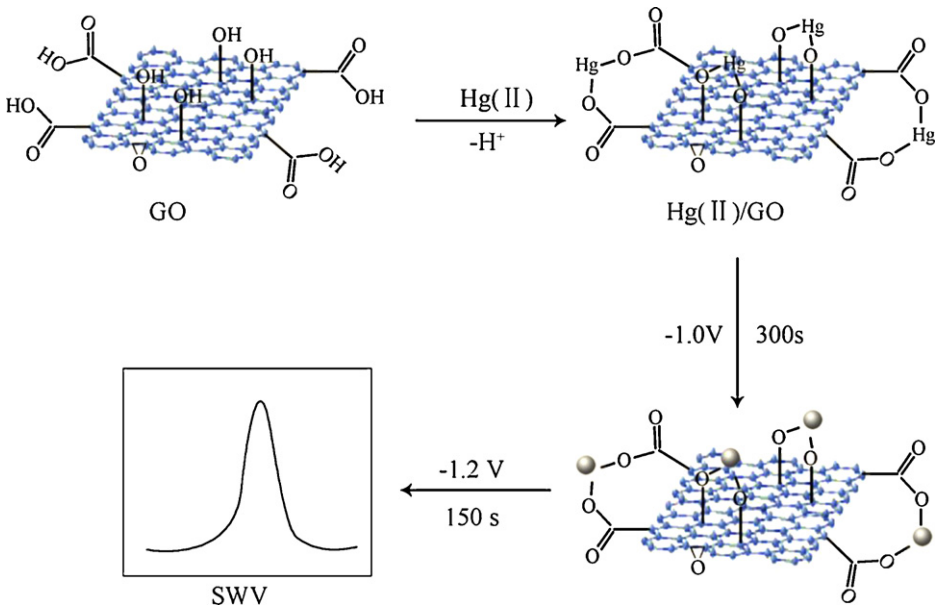

Fig. 1. Schematic representation of the Hg(II) binding to GO and the detection of Pb^{2+}.

and obtain stronger current signal [34,35], on the other hand, GO has a lot of oxygen-containing functional groups (—OH, —COOH, C—O—C), and Hg(II) could covalently attach to the GO surface by the effective groups (—OH, —COOH). The Hg(II) immobilized electrodes could greatly reduce the toxicity of mercury compared with the traditional mercury electrodes.

In this work, Hg(II)/GO was prepared and dispersed into a Nafion solution, then this sensitive material was coated on GCE for fabricating the enhanced electrochemical sensing platform. And then Hg(II)/GO modified GCE was held at a negative potential (−1.0 V) to reduce the coordinated Hg(II) to Hg, the prepared Hg-film electrodes were been used as the sensing platform to determine Pb^{2+}. The performance of this novel platform for detection of Pb^{2+} is investigated in detail. Encouragingly, these results suggest that the sensitivity and selectivity of our sensor are remarkably improved, and it was successfully applied in the determination of Pb^{2+} ion concentration in practical water samples.

2. Experimental

2.1. Reagents

Graphene oxide was purchased from Nanjing Xianfeng Nano Co. (Nanjing, China). Nafion (5 wt.% in low aliphatic alcohols), was purchased from J&K Chemical Ltd., and then diluted to 0.5 wt.% Nafion with anhydrous ethanol. Pb(II) and Hg(II) working solutions were obtained by diluting the corresponding standard stock solutions. All of the chemicals used were analytical-regent grade and twice-distilled water was used in all experiments.

2.2. Apparatus

Square wave anodic stripping voltammetry (SWASV) was performed in a conventional three-electrode cell with a CHI 660 A electrochemical workstation (Shanghai Chenhua Instrument Co., China). The conventional three-electrode system included a modified GCE as the working electrode, a saturated calomel reference electrode (SCE) and a platinum wire were used as the reference electrode and auxiliary electrode, respectively. Scanning electron micrographs were studied with a scanning electron microscope (SEM, Hitachi, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed with a VG Scientific ESCALAB 250 spectrometer, using Al KR X-ray (1486.6 eV) as the light source. The AC impedance was recorded with an impedance measurement unit (IM6e, ZAHNER Elektrick Co., Germany) and the frequency range used was 10^{-2}–10^{6} Hz. The analysis of different water samples were accomplished by a Model TAS-986 atomic absorption spectrophotometer (AAS, Purkinje, Beijing, China). All electrochemical measurements were carried out in a static cell after magnetic stirring at room temperature.

2.3. Synthesis of Hg(II)/GO complexes

The preparation of Hg(II)/GO complexes was carried out by the previous report [36] (Fig. 1). The GO (2 mg) was mixed with 3 mL of 0.35 M $Hg(NO_3)_2$ aqueous solution, and stirred at room temperature for 5 h. The Hg(II)/GO complexes was washed repeatedly with twice-distilled water, and Hg(II)/GO complexes were obtained after drying under vacuum.

2.4. Fabrication of the Hg(II)/GO modified GCE

Glassy carbon electrode (GCE, diameter 4.0 mm) was respectively polished with 0.3 and 0.05 μm alumina slurry, and then rinsed ultrasonically with ethanol and water for several minutes, successively. Hg(II)/GO complexes obtained from Section 2.3 were dispersed in 1 mL of 0.5% Nafion and sonicated to get a homogenous suspension. Then, an aliquot of 5 μL of the mixture was coated on the electrode and allowed to dry at room temperature for 2 h to obtain the Hg(II)/GO modified GCE.

2.5. Procedure for the SWASV analysis

The Hg(II)/GO modified GCE was characterized by SWASV. The modified electrode was held at a negative potential of −1.0 V in 0.1 M perchloric acid for 300 s for the reduction of Hg(II) bound to the GO. The obtained Hg/GO modified GCE, reference electrode and the auxiliary electrode were soaked in the 10 mL electrochemical cell containing appropriate amounts of Pb^{2+}, and 0.1 M acetate buffer solution was used as the supporting electrolytes. The deposition potential of −1.20 V and the deposition time of 150 s were applied to electrochemically deposit Pb^{2+}. And then the modified