



Simultaneous electrochemical sensing of thallium, lead and mercury using a novel ionic liquid/graphene modified electrode



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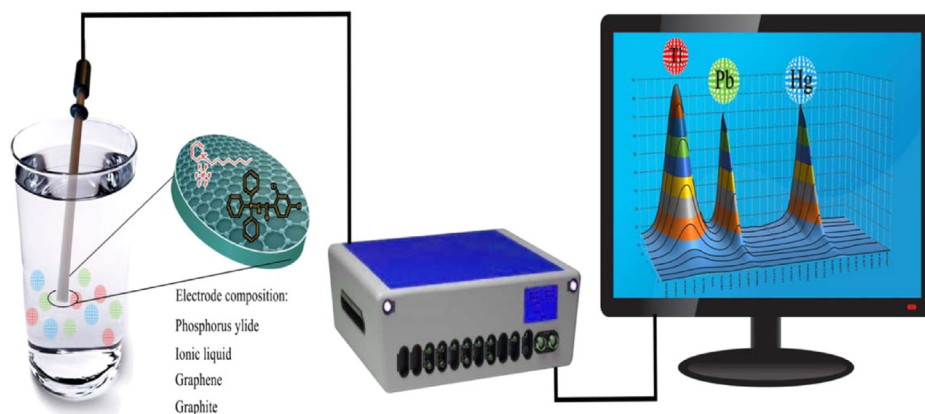
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HIGHLIGHTS

- A sensor using ionic liquid, graphene and phosphorus ylide was constructed.
- The surface morphology and properties of the electrode characterized.
- Simultaneous determination of Tl^+ , Pb^{2+} and Hg^{2+} in real samples was investigated.
- It is a useful method for determining of these analytes without overlapping problem.
- In comparison to previous methods, this method has wonderful figures of merit.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 6 November 2014
 Received in revised form 3 February 2015
 Accepted 1 March 2015
 Available online 3 March 2015

Keywords:

Electrochemical sensor
 Chemically modified carbon paste electrode
 Heavy metals
 Graphene
 Simultaneous determination of heavy metals

ABSTRACT

In the present manuscript, an electrochemical sensor for the sensitive detection of Tl^+ , Pb^{2+} and Hg^{2+} is described. A new composite electrode has been fabricated using graphene, 1-*n*-octylpyridinium hexafluorophosphate (OPFP), and [2,4- $Cl_2C_6H_3C(O)CHPh_3$] (L), as a new synthetic phosphorus ylide. The physicochemical and electrochemical characterizations of fabricated sensor were investigated in details. The advantages of the proposed composite electrode are its ability in simultaneous electrochemical detection of Tl^+ , Pb^{2+} and Hg^{2+} with good selectivity, stability and no need for separating of the three species from complex mixtures prior to electrochemical measurements. The analytical performance of the proposed electrode was examined using square wave voltammetry. Tl^+ , Pb^{2+} and Hg^{2+} can be determined in linear ranges from 1.25×10^{-9} to 2.00×10^{-7} mol L⁻¹. Low detection limits of 3.57×10^{-10} mol L⁻¹ for Tl^+ , 4.50×10^{-10} mol L⁻¹ for Pb^{2+} and 3.86×10^{-10} mol L⁻¹ for Hg^{2+} were achieved. Finally, the proposed electrochemical sensor was applied to detect trace analyte ions in various water and soil samples with satisfactory results.

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1. Introduction

Thallium, mercury and lead are well-known toxic contaminants in ecosystems and even their low-levels have carcinogenic, nervous, reproductive and teratogenic toxicity to human being

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[1–3]. Moreover, Tl^+ toxicity is even higher than that of Hg^{2+} and Pb^{2+} to the biosphere [2,3]. Therefore, knowledge of the quantity of these metal ions in real samples is important because their toxicological effects depend on their concentration and chemical form [4,5]. High sensitive spectroscopic methods allow determining metals at levels of $sub-\mu g L^{-1}$ [6,7]. However, the atomic spectrometric methods are expensive and not suitable for *in-situ* analysis of metals [6–8].

The electrochemical methods as an alternative of spectroscopic techniques have been accepted as one of the most efficient tools to determine heavy metal ions due to their excellent sensitivity, short analysis time, portability and low cost and maintenance [8,9]. Anodic stripping voltammetry (ASV) at the mercury electrode is a well-established technique for the determination of metal ions at low levels [9,10]. However, the usage of mercury is complicated in real samples due to the presence of other metal ions. Organics are also potential interfering species [10–13]. For example, interfering metal ions in thallium analysis are including lead, cadmium, copper, bismuth, indium, titanium and iron [14]. Therefore, various mercury-free electrodes have been developed over the past few decades [13–15]. A large variety of modified, composite, doped and thin film electrodes have been reviewed by Brainina et al. [8].

There are a great number of challenges for simultaneous electrochemical determination of Tl^+ , Pb^{2+} and Hg^{2+} ions in presence of other ions. One major difficulty is that voltammetric peaks corresponding to the oxidation/reduction of these ions are considerably overlapped in many cases. This makes the accurate measurement of peak heights complicated, so the concentration determinations remain unsatisfactory [15,16]. For example, on gold and mercury electrodes, the Tl^+ signal partially overlaps those of Pb^{2+} and Cd^{2+} , whereas on silver electrode, in non-complexing medium, the Tl^+ signal is only about 0.07 V more negative than that of Cd^{2+} [17,18]. Chemometric methods have been used to deconvolve overlapped current peaks [19,20]. They can be helpful, but unfortunately these approaches can result in low precision. On the other hand, the reduction and adsorption competition of metal ions at the electrode surface makes nonlinear the relationship between the response and their concentrations [15,16,19,20]. These causes the determinations complex, time-consuming or in some cases less precise [15,16].

The performance of ASV using a chemically modified electrode (CME) is strongly affected by the electrode materials [21]. Chemically modified matrices are usually utilized to increase the surface area, conductivity and sensitivity of electrochemical sensors and to improve selective interactions between sensing layer and analytes [22–24]. Since the first use of carbon paste electrode (CPE) by Adams [25], it has been widely applied in the electroanalytical community due to its low cost, ease of fabrication, flexible substrate for modification, high sensitivity, renewable surface, etc. [26]. Generally, the concept of a paste made up with carbon material and a non-conductive and inert binder. By substituting non-conductive organic binders (e.g., oil) with suitable conductive binder (e.g., ionic liquids), low cost and easy-to-fabricate electrodes have been produced, with the advantages of high conductivity and sensitivity, fast electron transfer and good antifouling ability for electroanalysis compared to traditional oil-based electrodes. Ionic liquids (ILs) can be used as not only the pasting binders of CPE but also the extractant of metal ions [27–29].

Also, the recent emergence of nanomaterials has opened new horizons in designing electrochemical sensors based on CMEs [30,31]. Graphene (Gr), as a next generation electronic material, which is also the basic structure of all graphitic materials, is a one-atom-thick planar sheet of sp^2 bonded carbon atoms in a honeycomb crystal lattice. Gr exhibits excellent electron transfer promoting ability for some species and excellent catalytic behavior

toward small bio/molecules, which makes Gr extremely attractive for electrochemical sensors [32,33]. CMEs based on Gr take advantages of the increased electrode surface area, mass-transport rate and fast electron transfer compared to electrodes based on bulk materials between other factors [34,35].

However, the main challenge of how to improve the selectivity of the electrochemical sensors to Tl^+ , Pb^{2+} and Hg^{2+} ions remains. In order to meet this requirement, the inducing of metal ions-specific functional groups onto the electrode with the desired properties is particularly attractive [3,9,21,22,29]. For this purpose, L as a new synthesized ylide is introduced into the matrix of IL/Gr paste composite (Fig. 1a) [36]. Moreover, the combination of Gr and OPFP with L can provide excellent electrochemical platforms for target heavy metals sensing due to the combination of enlarged active surface area, strong adsorptive capability and the specific complexing ability of the L in analysis of environmental samples.

2. Experimental

The details of some experimental Sections (2.1–2.6) [36–40] are given in Supporting information.

2.1. Analytical procedure

Square wave voltammetry (SWV) and cyclic voltammetry (CV) were carried out in a 20 mL electrochemical cell containing acetate buffer (0.2 mol L^{-1} , pH 4.0) as supporting electrolyte medium. SWASV was used for the detection under optimized conditions. Tl^+ , Pb^{2+} and Hg^{2+} were deposited at the potential of -1.1 V for 90 s by the reduction of Tl^+ , Pb^{2+} and Hg^{2+} . The anodic stripping (reoxidation of metals to metal ions) of the electrodeposited metals was performed in the potential range of -1.0 to 0.4 V . Before each measurement to ensure dissolution of the remaining deposits on the surface of the modified electrode, pre-conditioning step was performed at the potential of $0.9 \text{ V vs. Ag/AgCl}$ for 45 s. During the preconcentration and cleaning steps, the solution in the electrochemical cell was stirred. The peak currents at potentials about -0.76 , -0.41 and $0.18 \text{ V vs. Ag/AgCl}$ for Tl^+ , Pb^{2+} and Hg^{2+} were measured, respectively.

3. Results and discussion

3.1. Morphologies of the different electrodes

The SEM of CPE, Gr/CPE and IL/Gr/CPE are shown in Fig. 1. The surface of the CPE was predominated by isolated and irregularly shaped graphite flakes and separated layers were seen (Fig. 1b). Therefore, the charges could not be transferred along the vertical direction of planes because of the block of non-conductive binder. On the surface of Gr modified CPE (Fig. 1c), homogeneous, flexible and typical crumpled and wrinkled sheets were observed, suggesting excellent water dispersion ability. Water dispersible property of Gr possesses many fascinating properties such as large specific surface area, numerous functional groups, strong adsorption ability and high carrier mobility [41]. The SEM image of IL/Gr/CPE showed more uniform surface. As a liquid with good conductivity and high viscosity, OPFP is capable of better dispersing the Gr in the paste than the conditional paraffin, thus, could better bridge the Gr sheets together [41,42]. Thus, the conductive performance of the IL/Gr/CPE was notably improved due to a mixed electronic (carbon)–ionic (IL) contribution.

In FT-IR spectrum of Gr (Fig. 1e), the absence of band of $C=O$ stretch at 1700 cm^{-1} is related to reduction of the carboxyl groups ($Gr-COOH$) to hydroxymethyl ($Gr-CH_2OH$) by hydrazine as indicated by the appearance of bands at 2913 and 2828 cm^{-1} corresponding to the $C-H$ stretch vibrations of the methylene

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