Journal of Electroanalytical Chemistry 801 (2017) 146–152

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Voltammetric sensing of Pb(II) using a glassy carbon electrode modified with composites consisting of Co_3O_4 nanoparticles, reduced graphene oxide and chitosan

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ARTICLE INFO

Keywords:
Differential pulse anodic stripping voltammetry
Co_3O_4
Reduced graphene oxide
Pb(II)
Electrochemical detection

ABSTRACT

A sensitive Pb(II) sensor was fabricated based on Co_3O_4/reduced graphene oxide/chitosan (Co_3O_4/rGO/chitosan) nanocomposite modified glassy carbon electrode (GCE). The Co_3O_4/rGO material was synthesized through in situ growth of Co_3O_4 nanoparticles (NPs) on GO and subsequent hydrazine reduction process. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that Co_3O_4 NPs with a diameter of around 100 nm are attached on rGO sheets. The structures and compositions of Co_3O_4/rGO were further characterized by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Many experimental parameters, such as pH value, deposition time and deposition potential were optimized. Under optimal conditions, the calibration plot for Pb(II), with data acquired at -0.556 V (*vs.* SCE) is linear in the concentration range from 1.0 to 200.0 nM. Combining the good conductivity and high surface area of rGO, strong Pb(II) adsorption ability of Co_3O_4 NPs, and excellent Pb(II) complex-forming ability of chitosan, the nanocompsite provides a sensitive Pb(II) senor with a detection limit of 0.35 nM. Moreover, the positively charged chitosan can interact with the negatively charged rGO to increase the stability of Co_3O_4/rGO nanocomposite. The hybrid nanocomposite Pb(II) senor provides new opportunity for vegetable analysis.

1. Introduction

Interests in sensitive detection of heavy metal ions have increased enormously over past two decades due to their toxicity to organism and environment even in low concentrations [1–5]. Lead (Pb(II)), as one of the most toxic elements, is attracting fast growing research enthusiasm in analysis because of its toxicity on central nervous system [6]. Many techniques, including surface-enhanced Raman scattering [7], X-ray fluorescence spectrometry [8] and inductively coupled plasma atomic emission spectroscopy [9] have been employed for precise analysis of Pb(II). Although these strategies are effective for the detection of Pb(II), some defects such as reagent and time consumption, high cost and operating complexity hampered its large-scale applications. In contrast, electrochemical stripping voltammetry has been considered as a reliable and sensitive method for trace Pb(II) analysis. The property of selected materials is a key factor in electrochemical determination because it can control the analytical parameters such as sensitivity, selectivity and stability.

In the past, gold [10], platinum [11] and silver [12] were widely used in electrochemical analysis, which exhibited excellent catalytic ability and conductivity among various electrode materials. However, the high cost of noble metals restricted their use. To overcome this shortage, many kinds of metal oxides, such as Bi_2O_3 [13] MnO_2 [14] and Co_3O_4 [15] were synthesized to electrochemical determination Pb (II) due to their low cost, non-toxic and simple preparation. For example, based on the strong affinity of Co_3O_4 to Pb(II), Huang et al. reported a novel electrochemical platform for the detection of Pb(II) using porous Co_3O_4 microsheets [15]. However, as is well-known, Co_3O_4 is one p-type semiconductor. Pure Co_3O_4 shows low electronic conductivity and inferior stability during cycling [16], which inhibits its electrochemical activity. Many strategies have been proposed to tackle these problems. Among them, incorporation of Co_3O_4 into conducting matrix is a simple and effective one [17]. Conductive carbon materials, such as graphene and CNTs are usually deemed as suitable candidates because they are not only cushion the internal stress induced by volume change, but also make the composites more conductive.

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http://dx.doi.org/10.1016/j.jelechem.2017.07.046
Received 18 May 2017; Received in revised form 22 July 2017; Accepted 26 July 2017

Graphene, a two-dimensional (2D) honeycomb sp^2 carbon lattice, has triggered worldwide research interest for various applications because of its high surface area, good electrical conductivity and strong mechanical stability [18]. Combining the advantages of Co_3O_4 (high adsorption ability and large active site) [19,20] together with the unique features of graphene (high electrical conductivity and large surface area) [21], the Co_3O_4/rGO nanocomposite is expected to provide a sensitive and stable platform for electroanalysis. Up to now, Co_3O_4/rGO nanocomposite as sensing material has been utilized for the determination of L-tryptophan [22], glucose [23] and *Staphylococcus aureus* nuc gene sequence [24]. However, to the best of our knowledge, Co_3O_4/rGO nanocomposite has never been found in detecting heavy metal ion. In general, Co_3O_4/rGO nanocomposite can be prepared through various approaches, such as microwave-assisted method [25], hydrothermal method [26] or replication and deposition processes [27]. These synthetic routes usually involve template, surfactants and tedious multistep procedure that severely restrict their wide applications. Therefore, it is necessary to develop a simple and effective method for the preparation of Co_3O_4/rGO nanocomposite. In addition, chitosan was derived from incomplete deacetylation of chitin, which has the merits of metal binding ability, biodegradability and biocompatibility [28–30]. According to previous reported literature [31], the functional groups (hydroxyl and amine) in chitosan can easily coordinate with Pb(II). Moreover, the positively charged chitosan can interact with the negatively charged rGO to increase the stability of Co_3O_4/rGO nanocomposite, and the sticky chitosan can adhere well on the electrode surface [32].

In this paper, Co_3O_4 NPs were firstly in situ growth onto graphene oxide (GO) sheet via the decomposition of cobalt nitrate, followed by reduction of GO to rGO with hydrazine hydrate solution. The Co_3O_4/rGO/chitosan nanocomposite was employed as electrode material for detecting Pb(II). Benefiting from the excellent Pb(II) adsorption ability of Co_3O_4 and chitosan, high conductivity of rGO, good film-forming and metal absorbing ability of chitosan, the modified electrode provided a sensitive electrochemical platform for Pb(II) determination.

2. Experimental

2.1. Chemical reagents

Graphene oxide was commercially available from Nanjing Xianfeng Nanomaterials Technology Co. Ltd. (Nanjing, China.). Cobalt nitrate hexahydrate, n-hexanol, CH_3COOH (HAc), hydrazine monohydrate and chitosan were obtained from Aladdin (Shanghai, China.). CH_3COONa (NaAc) was provided by chemical reagent factory in Tianjin (Tianjin, China.). Acetate buffer solutions with different pH values (HAc-NaAc, 0.1 M) were prepared by mixing appropriate amount of 0.1 M HAc and 0.1 M NaAc. Stock solutions of Pb(II) were prepared by dissolving lead nitrate salts in the distilled water. All these reagents were analytical grade and doubly distilled water was used throughout the experiments.

2.2. Apparatus

The morphology and structure were characterized by SEM (Hitachi SU 8020), TEM (FEI Tecnai G2 20), XRD (miniflex 600) and XPS (XPS, K-Alpha). Electrochemical measurements were operated with CHI 660E electrochemical workstation (ChenHua Instruments Co., Shanghai, China.) with conventional three-electrode system, which includes a bare GCE ($\Phi = 3$ mm) or modified GCE as the working electrode, a platinum foil electrode as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode.

2.3. Preparation of the Co_3O_4/rGO nanocomposite

The nanocomposite was obtained using the previously reported procedure with minor modification [33]. Briefly, 50 mg GO was dissolved in 50 mL n-hexanol. Subsequently, 1.5 mmol cobalt nitrate hexahydrate was added into the above suspension. The mixture was sonicated for 30 min. Then the slurry was magnetically stirred for 30 min and heated at 140 °C for 8 h. After cooling to room temperature, the resulting composite (Co_3O_4/GO) was centrifuged and washed with ethanol to move any impurities.

The obtained Co_3O_4/GO (35 mg) was then dispersed in water by ultrasonication. 0.1 mL of hydrazine monohydrate was subsequently added to the suspension. The mixture was heated to reflux at 80 °C for 12 h to prepare Co_3O_4/rGO nanocomposite. After cooling to room temperature, the powder (Co_3O_4/rGO) was centrifuged and washed with deionized water. Following the same procedure above, Co_3O_4 NPs were obtained but without the addition of GO. rGO was prepared but with no cobalt nitrate hexahydrate.

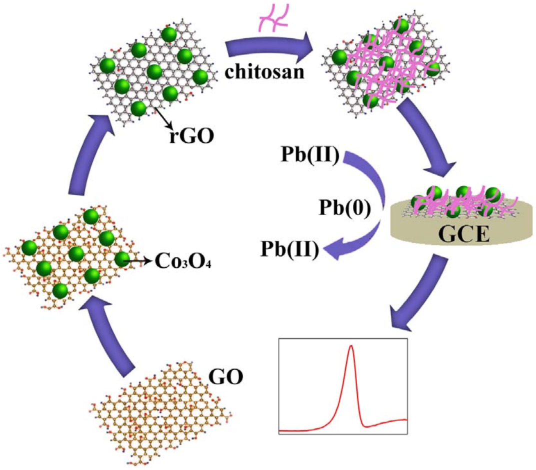
2.4. Preparation of the modified electrodes

A solution of chitosan (1.0%, *v*/v) was obtained by dispersing 10 mg chitosan in 10 mL acetic acid solution [34]. 6 mg Co_3O_4/rGO nanocomposite was dispersed in 3 mL chitosan solution under ultrasonication [35].

Before modification, GCE was polished with alumina powder (0.05 μm) on chamois leather for 5 min, and sonicated in doubly distilled water, absolute ethanol and doubly distilled water for 5 min, respectively. 5 μL of Co_3O_4/rGO/chitosan solution was added dropwise on the surface of electrode and dried under an infrared lamp. Thus, Co_3O_4/rGO/chitosan/GCE was obtained. For the same procedure, Co_3O_4/chitosan and rGO/chitosan modified GCEs were prepared by adding dropwise Co_3O_4/chitosan and rGO/chitosan onto bare GCE.

2.5. Differential stripping anodic voltammetry measurement of Pb(II) at the modified electrodes

The analysis of Pb(II) was performed using differential pulse anodic stripping voltammetry (DPASV) method after purging with nitrogen for 10 min. To be briefly, the modified electrode was immersed in NaAc-HAc (pH 5.0) and then deposition step was conducted at − 1.2 V for 360 s with stirring. After the stirring stopped, the stripping process was swept from − 0.75 V to − 0.35 V. The parameters setting are as follows: potential step is 4 mV and amplitude is 50 mV. All the results are subjected to statistical analysis and are presented as the mean ± SD (standard deviation). The schematic illustration for preparation of Co_3O_4/rGO/chitosan/GCE and electrochemical determination of Pb(II) were illustrated in Scheme 1.



Scheme 1. Schematic diagram for the fabrication of Co_3O_4/rGO/chitosan/GCE and the electrochemical detection of Pb(II).