Journal of Electroanalytical Chemistry 755 (2015) 203–209

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

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

Mesoporous $MnFe_2O_4$ nanocrystal clusters for electrochemistry detection of lead by stripping voltammetry

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ARTICLE INFO

Article history:
Received 9 April 2015
Received in revised form 30 July 2015
Accepted 31 July 2015
Available online 1 August 2015

Keywords:
Lead
$MnFe_2O_4$
Stripping voltammetry

ABSTRACT

High-adsorption $MnFe_2O_4$ nanocrystal clusters ($MnFe_2O_4$ NC) with mesoporous structure were used for selective analysis of Pb^{2+} by square wave anodic stripping voltammetry (SWASV) in this work. The as-prepared $MnFe_2O_4$ NCs with diameter of 200–400 nm and mesoporous structure composed of nanocrystals with a size of about 8–12 nm were characterized using SEM, HRTEM and XRD. Electrochemical properties were characterized by cyclic voltammetry and electrochemical impedance spectroscopy. The chemical and electrochemical parameters influencing on deposition and stripping of metal ions, such as supporting electrolytes, pH value, deposition potential, and deposition time, were also studied. The $MnFe_2O_4$ NC modified GCE has a high selectivity toward Pb^{2+} with a favorable sensitivity (19.9 μA μM^{-1}) and LOD (0.054 μM) for Pb^{2+} under the optimized conditions while the response to Cd^{2+}, Hg^{2+}, Cu^{2+} and Zn^{2+} is poor. No interference from Cd^{2+}, Zn^{2+} and Hg^{2+}, favorable stability and potential practical applicability were recognized in the electrochemical determination of Pb^{2+}. The above results provided a potential material for the design of new sensing materials in the application field of electrochemical detection toward toxic metal ions.

1. Introduction

It is well known that environmental contamination by heavy metals has been a serious and complex problem and has remained a focus of attention all over the world [1,2]. Heavy metals, unlike organic contaminants, were not biodegradable and tended to accumulate in living organisms and most of them were known to be poisonous and carcinogenic [3]. Effective determination of heavy metals in low concentration was important due to their hazards to the physical health of human being [4–6]. The electrochemical technique, as an alternative to the conventional spectroscopic techniques, has been recognized as a promising method for trace and on-site analysis of toxic heavy metal ions due to portability, high sensitivity, good selectivity, low cost, and suitability [7–12]. It is known that the electrochemical performance is highly dependent on the sensing materials, which is reasonable when presumed that the materials with high adsorption capacity can improve the efficiency for accumulating analytes [13].

Materials with high adsorbability are leading a new opportunity for the sensing performance in electrochemical detection. Very recently, based on the remarkable adsorption ability, nanomaterials have been developed as a detection strategy toward heavy metal ions [14–18]. Due to the adsorption capacity, O_2-plasma oxidized multi-walled carbon nanotubes [15] and γ-AlOOH(boehmite)@SiO_2/Fe_3O_4 porous magnetic microspheres [19] were found to be useful for the electrochemical detection of heavy metal ions. Polypyrrole/reduced graphene oxide nanocomposites were used for identifying Hg^{2+} by means of their highly specific adsorption ability toward Hg^{2+} [17]. Porous Co_3O_4 microsheets presented a high sensitivity and a quite nice low detection limit toward Pb^{2+} because of their high adsorption capacities [13].

As ideal adsorbents, ferrite (MFe_2O_4; M = Fe, Mn, Zn, or Co) nanoparticles have attracted great attention for the characteristic of high adsorption capacity and superparamagnetism. With the high adsorption capacity of nanostructure, the superparamagnetic materials can disperse well in the solution due to the absence of any residual magnetization without the external applied magnetic field, avoiding the typical aggregation problems of ferromagnetic materials [20,21]. With a high adsorption performance, the $MnFe_2O_4$ NCs combined with uniform mesoporous structure and small constituent nanocrystals (about 8–12 nm in size) even provide a synergistic effect for enhanced adsorption performance toward As(III) [22]. However, to the best of our knowledge, the high-adsorption ferrite (MFe_2O_4; M = Fe, Mn, Zn, or Co) materials used as sensing materials for the detection of heavy metal ions have rarely been reported.

In this work, we modified a glass carbon electrode (GCE) using mesoporous $MnFe_2O_4$ nanocrystal clusters ($MnFe_2O_4$ NC) for selective analysis of Pb^{2+} by square wave anodic stripping voltammetry

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http://dx.doi.org/10.1016/j.jelechem.2015.07.054

(SWASV), and the selective detection toward Pb^{2+} was achieved. The optimizing of experimental conditions, such as supporting electrolytes, pH values, deposition potential, and deposition time were investigated. Other heavy Metal ions, such as Cd^{2+}, Hg^{2+}, Cu^{2+} and Zn^{2+}, were chosen as potential interfering ions for investigating the electrochemical selective behavior of mesoporous $MnFe_2O_4$ NC toward Pb^{2+}. Furthermore, the stability of mesoporous $MnFe_2O_4$ NC modified electrode was also studied.

2. Experimental

2.1. Chemical reagents

All chemicals are of analytical grade, which are commercially available from Shanghai Chemical Reagent Co. Ltd and without further purification in this study. Acetate buffer solution of 0.1 M with different pH was prepared by mixing stock solutions of 0.1 M NaAc, HAc and NaOH. Phosphate buffer solutions (PBS) of 0.1 M were prepared by mixing stock solutions of 0.1 M H_3PO_4, KH_2PO_4, K_2HPO_4, and NaOH. NH_4Cl-$NH_3 \cdot H_2O$ (0.1 M) solution was prepared by mixing stock solutions of 0.1 M NH_4Cl and $NH_3 \cdot H_2O$ in different proportions. The water (18.2 MΩ cm) that was used to prepare all solutions was purified with the NANO pure Diamond UV water system.

2.2. Apparatus

All electrochemical measurements were performed using a CHI 660D computer-controlled potentiostat (ChenHua Instruments Co., Shanghai, China). A conventional three-electrode configuration was employed, consisting of a bare or modified glassy carbon electrode (GCE) as a working electrode, an Ag/AgCl/saturated KCl electrode as a reference electrode, and a platinum wire as a counter electrode. The morphology of $MnFe_2O_4$ NCs was investigated by scanning electron microscopy (SEM, Quanta 200 FEG, FEI Company, USA). High Resolution Transmission electron microscopy (HRTEM) was carried out on a JEM-2010 microscope. X-ray diffraction (XRD) was carried out using a PW1710 instrument with Cu Kα radiation $\lambda = 0.15406$ Å.

2.3. Synthesis of $MnFe_2O_4$ NCs

$MnFe_2O_4$ NCs were synthesized according to a previous report [23]. In brief, 5 mmol of $FeCl_3 \cdot 6H_2O$ (1.35 g) and 2.5 mmol $MnCl_2 \cdot 4H_2O$ (0.50 g) were dissolved in ethylene glycol (40 mL) to form a clear solution, followed by the addition of NaAc (3.6 g) and polyethylene glycol (1.0 g). The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined autoclave (50 mL capacity), heated at 200 °C in an electric oven for 8 h, and then cooled to room temperature naturally. The black products were centrifuged and washed with deionized water and absolute alcohol for several times and finally dried at 60 °C for 6 h.

2.4. Preparation of $MnFe_2O_4$ NC modified electrode

Prior to modification, the bare glassy carbon electrode was sequentially polished with 0.3 μm and 0.05 μm alumina power slurries to a mirror-shiny surface, and then sonicated with 1:1 HNO_3 solution, absolute ethanol and deionized water for 1 min, respectively. The $MnFe_2O_4$ film on the surface of glassy carbon electrode was performed in the following manner: 2 mg of $MnFe_2O_4$ NCs was added into 2 mL of Milli-Q water, and sonicated for 3 min to obtain a uniform dispersion. A drop of the above solution was pipetted onto the fresh surface of GCE and dried in air. After evaporation, a thin $MnFe_2O_4$ film was formed on the electrode surface.

2.5. Electrochemical measurements

Square wave anodic stripping voltammetry (SWASV) was used for the observation of electrochemical behavior under optimized conditions. Pb, Cd, Hg, Cu, and Zn were deposited at the potential of 1.0 V for 150 s by the reduction of Pb^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, and Zn^{2+} in 0.1 M HAc-NaAc (pH = 5.0). The anodic stripping (reoxidation of metal to metal ions) of electrodeposited metal was performed in the potential range of −1.0 to −0.2 V at the following condition: frequency, 25 Hz; amplitude, 25 mV; increment potential, 4 mV; vs Ag/AgCl. A desorption potential of −0.1 V for 150 s was performed to remove the residual metals under stirring condition. The same experiment conditions were applied in the interference and stability studies. Cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) were performed in mixing solution of 5 mM $Fe(CN)_6^{3-/4-}$ with 0.1 M KCl and the scanning rate was 100 mV s^{-1}.

3. Results and discussion

3.1. Characterization of $MnFe_2O_4$ NCs

Fig. 1a shows monodisperse, uniform and clean spherical shape of $MnFe_2O_4$ microspheres with diameter of 200–400 nm at a large scale. Fig. 1b indicates that the typical individual ferrite microsphere is a loose cluster, and clearly, the cluster is composed by small nanocrystals with the size of about 8–12 nm. Between the small nanocrystals, the structure of mesoporous can be found in Fig. 1b. This architecture might render them with a large surface area for adsorption of guest molecules [24–26]. The selected-area electron diffraction (SAED) pattern showed that the diffraction spots are widened into narrow arcs (insets of Fig. 1b), indicating the clusters are made up of many misaligned ferrite nanocrystals [24,27], in agreement with the analysis of HRTEM (Fig. 1b). The d value of crystal plane (311) in Fig. 1c and characteristic peaks in Fig. 1d verify the crystalline structure of $MnFe_2O_4$ NCs. And the broad diffraction peaks shown in Fig. 1d suggest the small size of ferrite NCs formed. Based on the calculations with the Scherrer formula for the strongest (311) diffraction peak, the average primary grain size is estimated to be 11 nm for $MnFe_2O_4$ NCs, which is consistent with the analysis of Fig. 1b. Taking the analyses of SEM, HRTEM, and XRD mentioned above, the as-prepared $MnFe_2O_4$ NCs with diameter of 200–400 nm and mesoporous structure are composed of nanocrystals with a size of about 8–12 nm, might render them with large surface area for adsorption and detection of heavy metal ions.

3.2. CV and EIS characterization of $MnFe_2O_4$ NC modified GCE

The fabricated $MnFe_2O_4$ NC modified GCE was firstly electrochemically characterized using cyclic voltammograms (CV) and electrochemical impedance spectra (EIS) (Fig. 2). Fig. 2a displays the CV response of bare GCE and $MnFe_2O_4$ NC modified GCE electrodes. As compared with the bare GCE, the anodic and cathodic peak currents were decreased at $MnFe_2O_4$ NC modified GCE. This was due to the poor conductivity of $MnFe_2O_4$ NCs. Fig. 2b shows that the impedance spectra of $MnFe_2O_4$ NC modified GCE electrodes include a semicircle portion and a linear portion. The semicircle diameter at higher frequencies corresponds to the electron transfer resistance (R_{et}), and the linear part at lower frequencies corresponds to the diffusion process [28]. As seen in Fig. 2b, it was observed that the R_{et} of the $MnFe_2O_4$ NC modified GCE was about 1.8 kΩ, while the EIS of the bare GCE displays an almost straight line. It means that the R_{et} of the $MnFe_2O_4$ NC modified GCE is much higher than the bare GCE, showing that the modification of $MnFe_2O_4$ NCs can hinder the electron-transporting on surface of the electrode. The nanocrystal cluster structure of $MnFe_2O_4$ could create a further barrier and hinder the access of the redox probe to the electrode surface, resulting in a large electron transfer resistance of the $MnFe_2O_4$ NC modified GCE, which is consistent with the CV results.