



Simultaneous label-free and pretreatment-free detection of heavy metal ions in complex samples using electrodes decorated with vertically ordered silica nanochannels

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ABSTRACT

In this work, indium tin oxide coated glass (ITO) decorated with vertically-ordered mesoporous silica film (VMSF/ITO) is synthesized and applied as electrochemical sensor for simultaneous label-free and pretreatment-free detection of Pb²⁺, Cu²⁺, and Cd²⁺ in human serum and soil leaching solution. Using differential pulse voltammetry (DPV), the electrochemical detection consists of electro-deposition of metal species and subsequent anodic stripping in the silica nanochannels. Because of the electrostatic enrichment and nano-confinement effects, VMSF/ITO is able to simultaneously detect Pb²⁺, Cu²⁺, and Cd²⁺ in a mixture with low detection limits (2.6 nM, 32 nM and 230 nM, respectively). Moreover, VMSF confer the electrode with excellent anti-fouling and anti-interference property through steric exclusion and electrostatic repulsion. Direct analysis of complex biological (human serum) and environmental (soil leaching solution) samples could be finished within 10 min without the usual need of tedious pretreatment. Furthermore, the VMSF/ITO sensor can be reused for several times without performance degradation.

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1. Introduction

With ever-increasing industrialization, heavy metal ion species have become common contaminants in water, soil and food. Due to the non-biodegradability, toxic heavy metal ions impose a great threat to living organisms [1–4]. For instance, even at a trace concentration, lead(II) (Pb²⁺, 10 ng/mL) could cause fearful damage to brain, immune system, liver, kidney, and central nervous system especially to young people and children [5–7]. And a small amount of cadmium(II) (Cd²⁺) may cause renal dysfunction, metabolism disorders, and increase cancer incidence [8,9]. Though appropriate quantity of copper(II) (Cu²⁺) is nutrient as the co-factor of some enzymes, elevated concentrations of Cu²⁺ may lead to gastrointestinal disturbance and liver or kidney damage [10–12]. Hence, realizing simple, sensitive and simultaneous detection of heavy metal ion species are of great importance. Comparing to other techniques including flame or graphite furnace atomic absorption spectrophotometry (FAAS/GFAAS), inductively-coupled

plasma mass spectrometry (ICP-MS) and fluorescence detection, electrochemical sensing is particularly attractive because of high sensitivity, rapid analysis, no need of bulky instrumentation and easy operation [2,13–16]. Current electrochemical sensors, however, are often unpractical for analysis of complex clinical (e.g. serum or whole blood) or environmental (e.g., soil leaching solution, waste water) samples due to unsatisfactory selectivity, stability and reproducibility, because of interference from other redox molecules and non-specific fouling on the sensor surface [17,18]. Various strategies have been developed to improve the anti-fouling and anti-interference characteristics of electrochemical sensors. Commonly, molecular passivation layers are coated on the sensor surface, which reduce non-specific interactions by introducing electrostatic repulsion (e.g., perfluorinated ionomer Nafion or other polyelectrolyte [19–21]) or steric hindrances (e.g., spatial spacers of alkyl chains with certain lengths or polymer brushes [22,23]). However, the detection efficiency is unavoidably compromised to some extent due to obstruction of diffusion and charge transfer.

Recently, vertically-ordered mesoporous silica film (VMSF) has attracted tremendous interests as the selectivity layer for electrochemical sensors [17,24–32]. VMSF exhibits uniform nanochannels (2–3 nm) perpendicular to the underlying electrode with a high

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pore density ($\sim 40000 \mu\text{m}^{-2}$). Such unique nanostructure is advantageous [33–40] in term of (1) anti-fouling and anti-interface effects because non-specific adsorption of macromolecules onto the electrode could be remarkably eliminated via steric hinderance; (2) anti-interference ability due to repulsion of negatively charged redox compounds (e.g. ascorbic acid, uric acid) by the negatively charged deprotonated silanol groups on the channel surface; (3) improved sensitivity towards positively charged analytes resulting from the enrichment effect enabled by electrostatic attraction and spatial confinement inside the channel; (4) fast detection due to unhindered molecular transport inside the channel.

In this work, simultaneous label-free and pretreatment-free detection of heavy metal ion species in complex biological and environmental samples is presented using ITO electrodes decorated with vertically-ordered mesoporous silica nanochannels (VMSF). The detection is based on metal ion enrichment through electrostatic and coordination effects by negatively charged VMSF nanochannels, subsequent electrochemical deposition and anodic stripping (Fig. 1). The VMSF/ITO sensor demonstrated outstanding performance for simultaneous analysis of Pb^{2+} , Cu^{2+} and Cd^{2+} in human serum and soil leaching solution in terms of excellent anti-interference and anti-fouling property, fast detection, high sensitivity and selectivity, and good reusability.

2. Material and methods

2.1. Reagents and apparatus

Standard Pb^{2+} , Cu^{2+} and Cd^{2+} solutions were obtained from National standard materials center (China). Tetraethyl orthosilicate (TEOS), cetyltrimethylammonium bromide (CTAB), potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), potassium hydrogen phthalate (KHP), ammonia aqueous solution (wt. 25%), sodium acetate (NaAc), acetic acid (HAc) and high-purity HNO_3 were obtained from Aladdin Chemistry Co. Ltd. (China). ITO coated glass (ITO thickness: $\sim 100 \text{ nm}$, resistance: $< 14.5 \Omega/\text{square}$) was obtained from Zhuhai Kaivo Electronic components (Zhuhai, China). All aqueous solutions were prepared with ultrapure water ($18.2 \text{ M}\Omega \text{ cm}$, Milli-Q, Millipore).

2.2. Materials characterizations

Scanning electron microscopy (SEM) was conducted on a field-emission scanning electron microscopy (S-4800, Hitachi, Japan). Transmission electron microscopic (TEM) photograph was taken on a JEM-2100 transmission electron microscope (JEOL Ltd., Japan) at operating voltage of 200 kV. Vertically-ordered mesoporous silica film (VMSF) was mechanically scrapped from the surface of ITO electrodes, dispersed in ethanol by sonication and dropped onto the copper grid. Zeta potential for solid phase was recorded on Surpass zeta potential system (Anton parr, Austria). Electrochemical experiments were carried out on an Autolab PGSTAT302N electrochemical workstation (Metrohm, Switzerland). A three electrodes system was adopt with bare or modified ITO as working electrode, Ag/AgCl (saturated KCl solution) as reference electrode and Pt-sheet electrode as counter electrode. Graphite furnace atomic absorption spectroscopy 900T (GFAAS, PE, USA) were used to measure Pb^{2+} , Cu^{2+} and Cd^{2+} as the current golden standard.

2.3. Preparation of VMSF/ITO electrode

ITO electrode was used as the supporting electrode. It was firstly immersed in 1 M NaOH overnight followed with successive clean by acetone, ethanol and ultrapure water under ultrasonication. VMSF was then fabricated on ITO electrode using Stöber-solution growth

approach as previously reported [41]. Briefly, TEOS hydrolyzes and assembles in presence of CTAB surfactant micelles (SM) in ammonia-ethanol medium. After removal of SM by solvent extraction in 0.1 M HCl of ethanol solution, VMSF/ITO sensor was obtained.

2.4. Simultaneous electrochemical detection of Pb^{2+} , Cu^{2+} and Cd^{2+}

NaAc-HAc buffer (0.1 M, pH 5.0) was used as the medium for metal detection. Standard stock solutions of Pb^{2+} and Cu^{2+} and Cd^{2+} (50.0 mM) were prepared and further diluted stepwise to obtain different concentrations. Electrochemical detection of metal ions consists of electrochemical deposition and the following stripping. Firstly, metal species were deposited on VMSF/ITO at -0.9 V for 300 s by reduction of Pb^{2+} , Cu^{2+} and Cd^{2+} . Secondly, anodic stripping (-0.95 to 0.4 V) of the electrodeposited Cd, Pb and Cu was detected using differential pulse voltammetry (DPV, modulation amplitude: 0.05 V , modulation time: 0.05 s , interval time: 0.4 s).

Human blood serum (healthy man) and soil leaching solution (SLS, soil from uncontaminated vegetable field, 2 g soil/10 mL solution, pH 5.5) were provided by Center for Disease Control and Prevention (Hangzhou, China) for real sample analysis. The electrochemical measurement was directly performed by dilution SLS using buffer ($v/v = 1:1$) for pH adjustment. For serum, protein-bound Pb^{2+} and Cu^{2+} ions are firstly released (WS/T 174–1999, WS/T 93–1996, China). Briefly, serum (2 mL) was mixed with diluted nitric acid (0.7 M, 4 mL) and stirred for 1 min. After pH was adjusted to 5.0 using NaOH (2 M), the final volume of the solution was modified to 10 mL using buffer solution for further electrochemical analysis. The reliability of electrochemical detection was also evaluated using standard addition method. A defined amount of ions was added into original serum or soil leaching solution. The obtained samples with artificial concentrations were also determined using the same procedure as described above. For measurement using standard GFAAS, samples were treated using the same methods and the supernatants after high speed centrifugation are analyzed.

3. Results and discussion

3.1. Preparation and characterization of VMSF/ITO electrodes

As previously reported [41] and illustrated in Fig. 1, vertically-ordered mesoporous silica film (VMSF) was readily prepared on ITO electrode using Stöber-solution growth where the silica precursor, tetraethyl orthosilicate (TEOS), hydrolyzes and assembles in the presence of cetyltrimethylammonium bromide (CTAB) surfactant micelles (SM) in ammonia-ethanol medium. CTAB micelles were then easily removed by solvent extraction in HCl-ethanol solution [29–33]. As shown in Fig. 2A and B, the cross-section SEM images of SM@VMSF/ITO and VMSF/ITO exhibit three layers from top to bottom corresponding to SM@VMSF or VMSF, ITO and glass, respectively. Fig. 2C and D display the high-resolution TEM (HRTEM) images of SM@VMSF and VMSF scrapped from the ITO surface. As seen, both films are continuous and uniform with mesopores ($\sim 2.6 \text{ nm}$) homogeneously distributed over the entire film. After removal of SM, no obvious changes in morphology or thickness were observed, indicating the stability of the VMSF. Although the structure of SiO_2 is easy to collapse under high-energy electron beams, some vertical channels can still be seen from the cross-section TEM image of VMSF (Fig. S1).

The permeability of silica nanochannel modified electrode was investigated by cyclic voltammetry measurement of the standard redox probes. Before removal of CTAB micelles, almost no redox responses are produced by positively charged $\text{Ru}(\text{NH}_3)_6^{3+}$ probe

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