

# Simultaneous Determination of $\text{Cd}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Hg}^{2+}$ at a Carbon Paste Electrode Modified with Ionic Liquid-functionalized Ordered Mesoporous Silica

Penghui Zhang, Sheying Dong,\* Guangzhe Gu, and Tinglin Huang†

College of Sciences, Xi'an University of Architecture and Technology, Xi'an 710055, P. R. China

\*E-mail: dshiney2004@yahoo.com.cn

†College of Environmental and Municipal Engineering, Xi'an University of Architecture and Technology, Xi'an 71005, P. R. China

Received July 17, 2010, Accepted September 1, 2010

Ionic liquid-functionalized ordered mesoporous silica SBA-15 modified carbon paste electrode (CISPE) was fabricated and its electrochemical performance was investigated by cyclic voltammetry, electrochemical impedance spectra. The electrochemical behavior of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at CISPE was studied by differential pulse anodic stripping voltammetry (DPASV). Compared with carbon paste electrode, the stripping peak currents had a significant increase at CISPE. Under the optimized conditions, the detection limits were  $8.0 \times 10^{-8}$  M ( $\text{Cd}^{2+}$ ),  $4.0 \times 10^{-8}$  M ( $\text{Pb}^{2+}$ ),  $6.0 \times 10^{-8}$  M ( $\text{Cu}^{2+}$ ),  $1.0 \times 10^{-8}$  M ( $\text{Hg}^{2+}$ ), respectively. Furthermore, the present method was applied to the determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  in water samples and people hair sample.

**Key Words:** Carbon paste electrode, Ionic liquid, SBA-15, Heavy metal ion

## Introduction

Heavy metal pollution, always caused by the waste streams of many industries, such as metal plating facilities, mining operations, and tanneries, has become a serious threat to human health, living resources, and ecological systems. They are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders to the nervous, immune, reproductive and gastrointestinal systems.<sup>1</sup> Thus, different sensitive methods have been developed to the simultaneous determination of heavy metals. The typical methods for the simultaneous analysis include inductively coupled plasma-mass spectrometry (ICP-MS),<sup>2</sup> X-ray fluorescence spectrometry (XRF),<sup>3</sup> and atomic absorption spectrometry (AAS).<sup>4</sup> However, time consuming process, high cost of maintenance, expensive and sophisticated instruments severely restrict their practical applications.

Electrochemical method is one of the most favorable techniques for the determination of environmental pollutants because of its low cost, high sensitivity and easy operation. Among different electrochemical methods, anodic stripping voltammetry (ASV) has been proved to be a simple and effective method for the determination of heavy metal ions. Traditional working electrodes for simultaneously voltammetric determination were generally based on a hanging drop mercury electrode (HDME)<sup>5</sup> or a mercury film electrode (MFE).<sup>6</sup> However, the toxicity of Hg and its precursors made these materials undesirable for disposable *in situ* sensing applications. Therefore, various mercury-free electrodes including bismuth film electrode,<sup>7,8</sup> gold-coated electrode,<sup>9</sup> silver electrode,<sup>10</sup> carbon paste electrode (CPE)<sup>11-13</sup> and glassy carbon electrode<sup>14,15</sup> were applied for sensitive metal determinations. In the fabrication of these modified electrodes, CPE was usually preferred for its low cost and simple preparation procedure. Moreover, through the replacement of paraffin with different binders,<sup>16</sup> the modification of the electrode surface,<sup>17</sup> or the addition of new materials,<sup>18,19</sup> the modified CPE

exhibited an excellent electrochemical behavior.

Mesoporous materials attracted much attention for their large surface area, fast adsorption kinetics, controllable pore size and pore arrangement. Due to the abundant silanol groups located at the internal surfaces, the mesoporous materials could be functionalized with alkoxy silanes containing different organic groups.<sup>20-22</sup> These functionalized silica<sup>23,24</sup> behaved as effective sorbents in the removal of heavy metals from contaminated water, while the functionalized silica modified CPE also exhibited high selectivity to the simultaneous determination of heavy metal ions.<sup>25</sup> However, the poor conductivity of silica decreased the sensitivity of the determination.<sup>26</sup> To improve the conductivity of the silica, ionic liquid was immobilized on SBA-15, one of the mesoporous silica possessing large pores and thick pore walls that led to good thermal stability. This ionic liquid functionalized SBA-15 (ILs-SBA-15) not only had the unique structure of SBA-15, but also exhibited high conductivity and catalytic activity of ionic liquid. At the same time, the use of ILs-SBA-15 in the fabrication of CPE could avoid the high background current caused by the direct use of ionic liquid as a binder.<sup>27</sup>

In the present work, the first challenge was made to fabricate a novel ILs-SBA-15 functionalized carbon paste electrode (CISPE).  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  was selected as a probe to evaluate CISPE by cyclic voltammetry, electrochemical impedance spectra. Based on the good performance of CISPE, the electrochemical behaviors of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at CISPE were studied by differential pulse anodic stripping voltammetry (DPASV). In addition, a DPASV method for the simultaneous determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  with sensitive, simple and rapid characteristics was presented.

## Experimental

**Reagents and solutions.** The chemicals used in this study

include tri-block copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (P123, MW: 5800), 1-methylimidazole from Aldrich, tetraethyl orthosilicate (TEOS), 3-(chloropropyl)-trimethoxysilane (CPTe), high purity graphite powder, paraffin liquid,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Hg}(\text{NO}_3)_2$  from China National Medicine Corporation, ethyl acetate, hydrochloric acid (36 - 38%),  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{KNO}_3$  and  $\text{KCl}$  from Xi'an Chemical Reagent Factory. All the chemicals were of analytical reagent grade and used without further purification.

0.10 M PBS ( $\text{NaH}_2\text{PO}_4$ - $\text{Na}_2\text{HPO}_4$ ) was employed as supporting electrolyte and adjusting the pH with  $\text{H}_3\text{PO}_4$  or  $\text{NaOH}$ . Stock solutions (1.0 mM) of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  were prepared by dissolving their corresponding nitrate salts into water and diluted to various concentrations. The hair sample was prepared as follows: the hair was washed with detergent and water to remove the external contamination or unnecessary dirt and grease from its surface. The washed hair was dried and digested with  $\text{HNO}_3$ - $\text{HClO}_4$  (4/1) solution for 2 h at room temperature. Then the digested solution was diluted to prepare 1.00 g  $\text{mL}^{-1}$  hair sample. The tap water sample and river water sample were used without further treatment. All solutions were prepared with twice-distilled water.

**Apparatus.** All electrochemical measurement was carried out with a CHI660B electrochemical workstation (Shanghai Chenhua Co.) controlled by a microcomputer with CHI660 software. A three-electrode system was used, where a saturated calomel electrode (SCE) served as the reference electrode, a platinum wire electrode served as the auxiliary electrode and a CPE, a SBA-15 modified carbon paste electrode (CSPE) or a CISPE served as the working electrode. All potentials reported were referred to the SCE. In the measurements of electrochemical impedance spectra (EIS), the applied perturbation amplitude was 0.005 V, the frequencies swept from  $10^5$  to  $10^{-2}$  Hz, the number of points per frequency decade was 12 and initial potential was 0.20 V.

**Preparation of the modified carbon paste electrodes.** The ILs-SBA-15 based on imidazolium ionic liquid was prepared following the similar procedures according to the literature.<sup>28</sup> The CISPE was prepared as follows: graphite powder was mixed with ILs-SBA-15, then 0.80 g of the mixture was added to 0.20 g of paraffin liquid and mixed for at least 20 min to produce the final paste containing 5.0% ILs-SBA-15 (w/w). Then the prepared carbon paste was tightly packed into a PVC tube (3 mm internal diameter) and a copper wire was introduced into the other end for electrical contact. The preparation of CSPE was similar to that of CISPE but only SBA-15 was used for the construction of CSPE, while CPE was prepared by mixing graphite powder and paraffin liquid with a ratio of 80/20 (w/w). A new surface was obtained by smoothing the electrode onto a weighing paper.

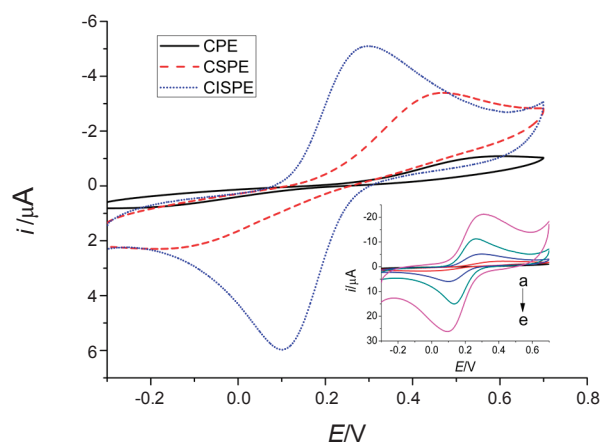
**Analytical procedure.** A certain amount of standard or sample solution was mixed with 0.10 M PBS into 20 mL volumetric flask. The prepared solution was transferred into electrochemical cell. The electrochemical behavior of CISPE was investigated by cyclic voltammetry (CV) and EIS in  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  solution. The analysis of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  using DPASV was carried out in the following steps: (a) pre-

conditioning step: potential 0.6 V for 60 s was applied before each measurement to ensure dissolution of the remaining deposits; (b) the pre-concentration step proceeded at -1.2 V for 6 min while the mixture solution was stirred; (c) the stripping voltammograms were recorded when swept from -1.0 V to 0.6 V after a 20 s quiescence. All the experiments were conducted by CHI660B electrochemical workstation at room temperature.

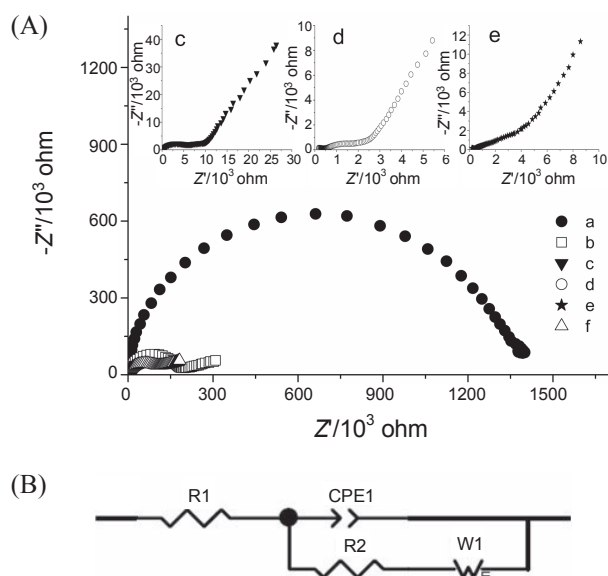
## Results and Discussion

**Characterization of different electrodes.**  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  was selected as a probe to evaluate the performance of the prepared electrodes. Fig. 1 presented the electrochemical responses of CPE, CSPE, and CISPE in 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  solution. It was observed that the peak current of CISPE greatly increased together with an obvious decrease of  $\Delta E_p$ , behaving as a quasi-reversible electron transfer process. The inset of Fig. 1 showed the effect of CISPE compositions on the CV responses. It was found that the redox peak currents significantly increased with the increase of ILs-SBA-15. But when the modified silica was more than 10% (w/w), the reversibility of the electrode reaction and the stability of CISPE decreased obviously, which attributed to the water adsorption of ILs-SBA-15. These results presented that the reversibility of the electrode reaction and the conductivity of CISPE were greatly improved.

To further study the capability of the electron transfer on these electrodes, EIS of CPE, CSPE and CISPE were determined in 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  solution. As shown in Fig. 2(A), the semicircular part at higher frequencies corresponded to the electron transfer-limited process and its diameter was equal to the electron transfer resistance ( $R_{ct}$ ), which controlled the electron transfer kinetics of the redox probe at the electrode interface. Meanwhile, the linear part at lower frequencies fitted in with the diffusion process. The equivalent circuit (Fig. 2(B)) used to model the above behavior was a modification of the well-known Randles circuit,<sup>29</sup> which approximated the behavior



**Figure 1.** CV curves of CPE, CSPE and CISPE in 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  (1:1, pH = 6.9) solution containing 0.10 M  $\text{KNO}_3$ , scan rate  $0.10 \text{ V s}^{-1}$ . Inset shows CV curves (a-e) of CISPE with different compositions (containing ILs-SBA-15 (w/w) 0%, 2.5%, 5.0%, 7.5% and 10.0%, respectively).

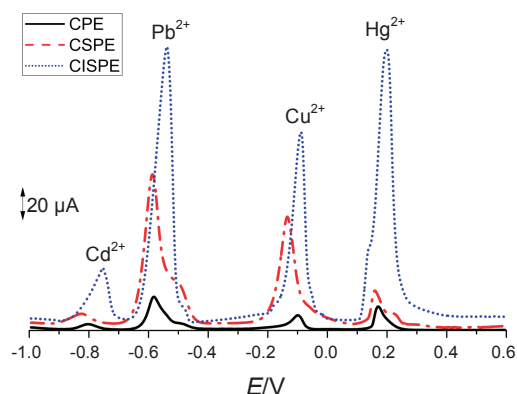


**Figure 2.** (A) Electrochemical impedance spectroscopy of (a) CPE, (b-e) CISPE (containing ILs-SBA-15 (w/w) 2.5%, 5.0%, 7.5%, 10.0%, respectively), (f) CSPE (containing SBA-15 5.0%) in 5.0 mM  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  (1:1) solution containing 0.10 M  $\text{KNO}_3$ . The applied perturbation amplitude was 0.005 V, the frequencies swept from  $10^5$  to 0.01 Hz and initial potential 0.20 V. (B) Equivalent circuit model of the electrochemical impedance behavior of the electrodes.  $R_{sol}$ : the resistance of the solution;  $R_{ct}$ : charge transfer resistance;  $CPE$ : constant phase element, which is a complex of various elements;  $W$ : Warburg resistance, which reflects diffuse barrier at low-frequency part.

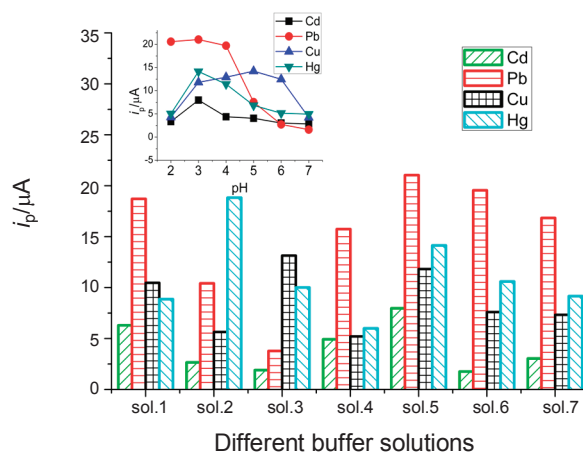
of a solid electrode participating in single-electron faradaic charge-transfer process. It was found that the fitted plots obtained were quite well in agreement with the measured plots. The resistances of solution at different electrodes had slight change, while  $R_{ct}$  of CPE and CSPE were far higher than that of CISPE (CISPE < CSPE < CPE).

The obtained results showed that with the addition of SBA-15, the electron transfer ability of the electrode was improved a little because the uniform pore structure and high surface area of the SBA-15 provided a microenvironment to accelerate the electron transfer of the electrode reaction. However, the poor conductivity of silica led to the dissatisfactory performance. The improved electron transfer kinetics at CISPE was likely associated with the interaction between  $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$  inner-sphere redox couple and imidazolium cation at the ILs-SBA-15.<sup>30</sup> On the other hand, the large surface area of mesoporous material resulted in the high concentration of imidazolium cation on the surface of ILs-SBA-15. Thus, the unique structure and electrocatalytic effect of the ILs-SBA-15 contributed to the promotion of the electron transfer, improvement of the reversibility and enhancement of the sensitivity at CISPE.

**Effect of electrode composition.** The effect of electrode composition on the electrochemical behaviors of  $1.0 \times 10^{-7}$  M  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  was investigated in pH 3.0  $\text{NaH}_2\text{PO}_4\text{-H}_3\text{PO}_4$  buffer solution. The stripping peak currents of the four metal ions increased with the amount of ILs-SBA-15 in the paste up to 5.0% (w/w). When the modified silica was more than 5.0%, the determination sensitivity of  $\text{Cd}^{2+}$  decreased dramatically



**Figure 3.** DPASV curves of  $1.0 \times 10^{-7}$  M  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at CPE, CSPE and CISPE in pH 3.0 PBS buffer solution. Accumulation potential:  $-1200$  mV; accumulation time: 6 min; pulse amplitude: 60 mV; scan rate:  $20 \text{ mV s}^{-1}$ ; pulse width: 60 ms.



**Figure 4.** The effect of different electrolytes (sol. 1: 0.10 M HAc-NaAc, 2: 0.10 M sodium citrate-HCl, 3: Mcllvaine buffer solution, 4: 0.20 M potassium biphthalate-NaOH, 5: 0.10 M PBS, 6: 0.10 M KCl, 7: 0.10 M  $\text{KNO}_3$ ) on the stripping peak currents of  $1.0 \times 10^{-7}$  M  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at CISPE. Inset shows the stripping peak currents in 0.10 M PBS with different pH (2.0 - 7.0). Other conditions are the same as in Fig. 3.

for the increase of the background current. Therefore, a carbon paste composition of 5.0% (w/w) ILs-SBA-15, 75.0% (w/w) graphite and 20.0% (w/w) paraffin liquid was used for further experiments.

**The electrochemical responses of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at different electrodes.** Fig. 3 showed differential pulse anodic stripping voltammograms of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at CPE, CSPE and CISPE. The stripping peak potential separations of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at the three electrodes were all sufficient for simultaneous determination. It was obvious that the stripping peak currents at CPE were low, while the performance of CSPE had a little improvement. At CISPE, four well-defined stripping peaks were obtained and the stripping currents significantly increased. The reason might be that the nitrogen atom of the imidazolium group at the surface of ILs-SBA-15 was a very strong N-ligating donor for d-metal ions.<sup>31</sup> The co-

ordination of the metal ions and imidazolium group led to an enhancing response. At the same time, ILs-SBA-15 could promote the electron transfer rate, so more metal ions were deposited on the electrode surface in a shorter time and the large stripping currents were obtained.<sup>13</sup> In addition, the unique structure of ILs-SBA-15 might also accelerate the enrichment of metal ions.

**Effect of electrolyte and pH.** The speciation of metal ions in an aqueous solution significantly affects their interaction with a solid adsorbent.<sup>32</sup> In a dilute solution,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  are mainly present in the form of mononuclear hydrolysis products, but their species distributions are related to many factors, such as pH, ionic strength, anions, and metal ion concentration. As shown in Fig. 4, the influence of different electrolytes in the stripping peak currents of  $1.0 \times 10^{-7}$  M  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  was investigated. The results showed when 0.10 M PBS was chosen as the electrolyte, the larger stripping peak currents, the lower background current and the better shape of peaks were obtained.

The inset of Fig. 4 showed the effect of pH on the stripping peak currents in 0.10 M PBS in the range of 1.0 - 7.0. As  $\text{pH} < 2.0$ , the current signals measured at CISPE were not steady and the interferences were serious. With the increase of pH, the currents of the four metal ions increased at first and then decreased. The reason might be that at  $\text{pH} < 5.0$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  species were totally present in ionic states. While increasing pH, these species started to hydrolyze and entirely precipitate at high pH value. The largest stripping currents of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Hg}^{2+}$  were obtained at pH 3.0, while the currents of  $\text{Cu}^{2+}$  had a slight change from 3.0 to 6.0. Thus, 0.10 M pH 3.0 PBS was chosen as the electrolyte in the following experiments.

**Optimization of experimental parameters.** In order to optimize the experimental parameters that might affect the determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ , the accumulation time,

deposition potential, amplitude and scan rate were evaluated.

As shown in Fig. 5(A), the stripping peak currents were proportional to the accumulation time up to 6 min. For longer preconcentration times, currents were found to level off and reach to constant values after 10 min owing to the saturation loading of active sites at the electrode surface. Furthermore, the long accumulation time might lead to the separation of the stripping peak which attributed to the formation of intermetallic compounds. Thus, the accumulation time of 6 min was chosen in the following experiments.

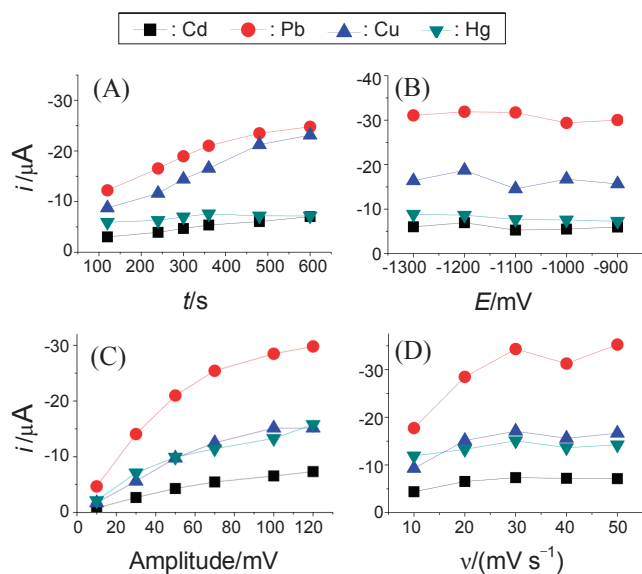
Fig. 5(B) displayed the effect of the deposition potential from -900 to -1300 mV on the stripping signals of the four metal ions. The negative shifts of deposition potential could improve the reduction of the metal ions on the surface of modified electrode and increase the peak currents. However, when deposition potentials were more negative than -1300 mV, the background currents increased and some interferences might be reduced at these potentials, which depressed the sensitivity of the determination. So the deposition potential of -1200 mV was used in the following experiments.

The stripping peak currents for  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  in DPASV were evaluated as a function of pulse amplitude from 10 to 120 mV and scan rate between 10 and 50  $\text{mV s}^{-1}$  in Fig. 5(C) and Fig. 5(D). It was observed that with the increase of scan rate and amplitude, the stripping peak currents and background currents both increased. To achieve higher sensitivity and better response, 80 mV and 30  $\text{mV s}^{-1}$  were employed in the following experiments.

**Calibration graph.** A series of standard solutions of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  were determined by DPASV under the optimized working conditions described above. The results presented that the stripping peak currents of the four metal ions had linear relationships with the concentrations in the range of  $6.0 \times 10^{-7}$  to  $3.0 \times 10^{-5}$  M ( $i(\mu\text{A}) = -20.51c(\mu\text{M}) + 8.817$ ,  $R = 0.9984$ ) for  $\text{Cd}^{2+}$ ,  $4.0 \times 10^{-7}$  to  $9.0 \times 10^{-5}$  M ( $i(\mu\text{A}) = -37.35c(\mu\text{M}) + 9.958$ ,  $R = 0.9986$ ) for  $\text{Pb}^{2+}$ ,  $3.0 \times 10^{-7}$  to  $1.0 \times 10^{-4}$  M ( $i(\mu\text{A}) = -27.15c(\mu\text{M}) + 1.926$ ,  $R = 0.9970$ ) for  $\text{Cu}^{2+}$  and  $8.0 \times 10^{-8}$  to  $5.0 \times 10^{-5}$  M ( $i(\mu\text{A}) = -75.29c(\mu\text{M}) - 3.037$ ,  $R = 0.9983$ ) for  $\text{Hg}^{2+}$ . When the signal noise ratio (SNR) was 3, the detection limits were  $8.0 \times 10^{-8}$  M ( $\text{Cd}^{2+}$ ),  $4.0 \times 10^{-8}$  M ( $\text{Pb}^{2+}$ ),  $6.0 \times 10^{-8}$  M ( $\text{Cu}^{2+}$ ),  $1.0 \times 10^{-8}$  M ( $\text{Hg}^{2+}$ ), respectively. Compared with other modified electrodes at Table 1, CISPE had a better sensitivity and larger linear range, indicating its potential in simultaneous determination of practical samples containing  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ .

**Stability of CISPE.** The reproducibility of CISPE was investigated by repetitively determining the mixed solution containing  $1.0 \times 10^{-7}$  M  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$ . It was found that the relative standard deviations (RSD) of peak currents for the four metal ions were 2.0% ( $\text{Cd}^{2+}$ ,  $n = 5$ ), 1.1% ( $\text{Pb}^{2+}$ ,  $n = 5$ ), 2.8% ( $\text{Cu}^{2+}$ ,  $n = 5$ ) and 3.4% ( $\text{Hg}^{2+}$ ,  $n = 5$ ), respectively. The response sensitivity retained more than 90% over two weeks when the electrodes was kept at 4 °C. In addition, RSD of peak currents using CISPE prepared at the same time were 2.4% ( $\text{Cd}^{2+}$ ,  $n = 5$ ), 1.8% ( $\text{Pb}^{2+}$ ,  $n = 5$ ), 2.8% ( $\text{Cu}^{2+}$ ,  $n = 5$ ) and 3.2% ( $\text{Hg}^{2+}$ ,  $n = 5$ ). The high reproducibility and stability indicated that CISPE was suitable for analysis of practical samples.

**Interferences.** The possible mutual Interferences of the four

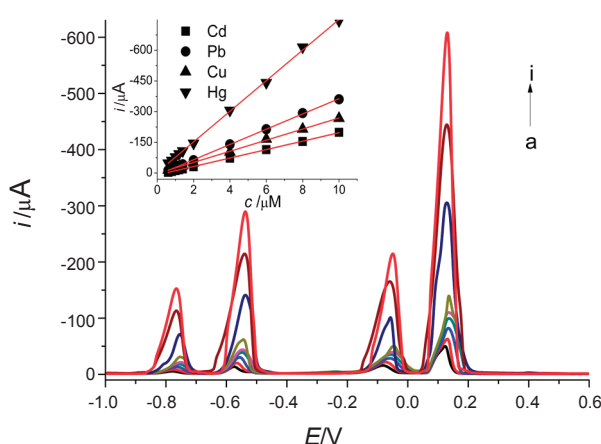


**Figure 5.** Effects of (A) time, (B) accumulation potential, (C) amplitude and (D) scan rate on the stripping peak currents of  $1.0 \times 10^{-7}$  M  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at CISPE in 0.10 M PBS.

**Table 1.** The detection ranges and detection limits of metal ions at different electrodes

Electrode		Cd <sup>2+</sup> (μM)	Pb <sup>2+</sup> (μM)	Cu <sup>2+</sup> (μM)	Hg <sup>2+</sup> (μM)	Reference
CISPE	DR	0.6 - 30	0.4 - 90	0.3 - 100	0.08 - 50	This work
	DL	0.08	0.04	0.06	0.01	
GC	DR	0.2 - 2	0.4 - 4	0.8 - 8	-	[33]
	DL	0.09	0.08	0.6	-	
BTPSBA-MCPE	DR	-	0.3 - 7	0.8 - 10	2 - 10	[26]
	DL	-	0.04	0.2	0.4	

DR: detection range; DL: detection limit. GC: glass carbon electrode. BTPSBA-MCPE: a carbon paste electrode modified with SBA-15 silica organofunctionalised with 2-benzothiazolethiol.

**Figure 6.** DPASV curves of different concentrations of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> (a-i, 0.6, 0.8, 1.0, 1.2, 1.4, 2.0, 4.0, 6.0, 8.0 μM) at CISPE in 0.10 M pH 3.0 NaH<sub>2</sub>PO<sub>4</sub>-H<sub>3</sub>PO<sub>4</sub> buffer solution. Accumulation potential: -1200 mV; accumulation time: 6 min; pulse amplitude: 80 mV; scan rate: 30 mV s<sup>-1</sup>; pulse width: 80 ms.

metal ions were evaluated by the single or simultaneous determination of 1.0 × 10<sup>-6</sup> M Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>. The results showed that there was no obvious shift for the stripping peaks obtained by simultaneous and single determination, while their stripping currents had a deviation below 5.0%. The possible interferences in the wastewater were also tested in Table 2. A great of species, including Ca<sup>2+</sup>, Co<sup>2+</sup>, Cr<sup>3+</sup>, Mn<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Sr<sup>2+</sup>, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> (each of c = 1.0 × 10<sup>-3</sup> M) had no significant influence on the signals of 1.0 × 10<sup>-6</sup> M Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> with deviations below 5.0%. The concentrations of Al<sup>3+</sup>, Bi<sup>3+</sup>, Fe<sup>2+</sup> and Fe<sup>3+</sup> should be taken into account due to their interfere with the determination. Ag<sup>+</sup> was a strong interferent to the determination of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>, which must be separated or masked before determination.

**Applications.** To evaluate the proposed method, CISPE was employed to determine Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> in tap water samples, river water samples and people hair samples. As shown in Table 3, the recovery and RSD were acceptable. In addition, to testify the accuracy of this method, the results obtained by CISPE were compared with that by atomic absorption spectrometry. The satisfactory RSD indicated the proposed method had great potential in the practical sample analysis.

**Table 2.** Interferences of some inorganic species on the stripping peak currents of 1.0 × 10<sup>-6</sup> M Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup>

Interferent	Concentration (mM)	Signal change (%)			
		Cd <sup>2+</sup>	Pb <sup>2+</sup>	Cu <sup>2+</sup>	Hg <sup>2+</sup>
Ca <sup>2+</sup>	1.0	1.3	1.3	0.7	2.8
Al <sup>3+</sup>	0.5	4.4	4.4	3.6	4.0
Co <sup>2+</sup>	1.0	3.2	1.9	2.7	0.1
Cr <sup>3+</sup>	1.0	3.5	1.9	1.8	4.7
Mn <sup>2+</sup>	1.0	0.5	0.8	0.1	0.4
Ni <sup>2+</sup>	1.0	2.2	0.4	1.4	2.1
Zn <sup>2+</sup>	1.0	3.9	1.0	1.2	0.5
Bi <sup>3+</sup>	0.1	2.3	1.9	2.6	1.5
Sr <sup>2+</sup>	1.0	2.3	2.1	2.5	4.7
Fe <sup>2+</sup>	0.1	1.2	3.5	2.2	3.6
Fe <sup>3+</sup>	0.1	1.3	7.9	3.1	5.7
Ag <sup>+</sup>	0.1	-	11.3	10.9	10.1
SO <sub>4</sub> <sup>2-</sup>	1.0	1.5	0.9	1.8	2.1
Cl <sup>-</sup>	1.0	0.2	0.1	0.3	0.2

**Table 3.** Recovery of Cd<sup>2+</sup>, Pb<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> (n = 3)

Samples	Ions	Added (μM)	Expected (μM)	Found (μM)	RSD (%)	Recovery (%)
1	Cd <sup>2+</sup>	0		ND		
		1.00	1.00	1.05	1.37	105.0
	Pb <sup>2+</sup>	0		ND		
		1.00	1.00	1.02	1.62	102.0
	Cu <sup>2+</sup>	0		0.71		
		1.00	1.71	1.69	1.64	98.8
2	Hg <sup>2+</sup>	0		ND		
		1.00	1.00	1.04	0.68	104.0
	Cd <sup>2+</sup>	0		ND		
		1.00	1.00	1.02	1.85	102.0
	Pb <sup>2+</sup>	0		1.59		
		1.00	2.59	2.57	1.35	99.2
3	Cu <sup>2+</sup>	0		11.65		
		1.00	12.65	13.02	0.98	104.3
	Hg <sup>2+</sup>	0		0.14		
		1.00	1.14	1.19	2.04	104.4
	Cd <sup>2+</sup>	0		ND		
		1.00	1.00	1.04	2.35	104.0
3	Pb <sup>2+</sup>	0		11.53		
		1.00	12.53	12.37	1.26	98.7
	Cu <sup>2+</sup>	0		69.85		
		1.00	70.85	71.20	1.19	100.5
	Hg <sup>2+</sup>	0		1.07		
		1.00	2.07	2.04	0.77	98.6

<sup>a</sup>ND: not detectable. <sup>b</sup>Sample 1: tap water sample; 2: river water sample (from Bahe river in Xi'an); 3: people hair sample. <sup>c</sup>The working conditions are the same as in Figure 6.

## Conclusions

In conclusion, CISPE modified with ILs-SBA-15 exhibited excellent electrocatalytic activity, electron transfer ability and stability owing to the advantages of both ionic liquids and heterogeneous supports. The unique structure and imidazolium cation

of ILS-SBA-15 made the simultaneous determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  at CISPE by DPASV present high sensitivity. The proposed DPASV method was applied to the determination of  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Hg}^{2+}$  in practical samples and satisfactory results were obtained. Thus, this study was expected to provide important insight into the application of ILS-SBA-15 in electroanalysis.

**Acknowledgments.** The authors appreciate the support from the National Natural Science Foundation of China (No. 5083 0303), Program for Changjiang Scholars and Innovative Research Team in University (PCSIRT) (Grant No. IRT0853) and the Research Achievements Foundation of Xi'an University of Architecture and Technology (No.ZC1004).

### References

1. Darwish, I. A.; Blake, D. A. *Anal. Chem.* **2002**, *74*, 52.
2. Vogl, J.; Heumann, K. G. *Fresenius' J. Anal. Chem.* **1997**, *359*, 438.
3. Dariusz, W.; Barbara, H. *Appl. Radiat. Isot.* **1993**, *44*, 1101.
4. Fernando, B.; Francisco, J. K.; Éder, C. L. *Spectrochim. Acta, Part B* **1999**, *54*, 1155.
5. Shams, E.; Babaei, A.; Soltaninezhad, M. *Anal. Chim. Acta* **2004**, *501*, 119.
6. Ali, A.; Ensafi, T.; Khayamian, S.; Khaloo, S. *Anal. Chim. Acta* **2004**, *505*, 201.
7. Wang, J.; Lu, J.; Hocevar, S. B.; Farias, P. A. M. *Anal. Chem.* **2000**, *72*, 3218.
8. Li, J.; Guo, S. J.; Zhai, Y. M.; Wang, E. K. *Anal. Chim. Acta* **2009**, *649*, 196.
9. Zhang, X. H.; Wang, S. F. *Sens. Actuators, B* **2005**, *104*, 29.
10. Ostrega, B. K.; Piekarska, J. *Electroanalysis* **2005**, *17*, 815.
11. Hu, C.; Wu, K.; Dai, X.; Hu, S. *Talanta* **2003**, *60*, 17.
12. Gabriela, R. M.; Ramirez-Silva, M. T.; González, R. L.; Galicia, L.; Romero-Romo, M. *Electroanalysis* **2005**, *17*, 694.
13. Li, Y. H.; Liu, X. Y.; Zeng, X. D.; Liu, Y.; Liu, X. T.; Wei, W. Z.; Luo, S. L. *Sens. Actuators, B* **2009**, *139*, 604.
14. Yuan, S.; Chen, W. H.; Hu, S. S. *Talanta* **2004**, *64*, 922.
15. Zheng, H.; Yan, Z. N.; Dong, H. M.; Ye, B. X. *Sens. Actuators, B* **2007**, *120*, 603.
16. Albertúsa, F.; Llerena, A.; Alpízar, J.; Cerdáb, V.; Luquec, M.; Ríosc, A.; Valcárcel, M. *Anal. Chim. Acta* **1997**, *355*, 23.
17. Zhang, S. H.; Wu, K. B.; Hu, S. S. *Anal. Sci.* **2002**, *18*, 1089.
18. Shahrokhian, S.; Fotouhi, L. *Sens. Actuators, B* **2007**, *123*, 942.
19. Mashhadizadeh, M. H.; Khani, H. *Anal. Methods* **2010**, *2*, 24.
20. Christabel, E. F.; Burkett, S. L.; Mann, S. *Chem. Commun.* **1997**, *18*, 1769.
21. Lim, M. H.; Blanford, C. F.; Stein, A. *J. Am. Chem. Soc.* **1997**, *119*, 4090.
22. Bambrough, C. M.; Slade, R. C. T.; Williams, R. T. *J. Mater. Chem.* **1998**, *8*, 569.
23. Benhamou, A.; Baudu, M.; Derriche, Z.; Basly, J. P. *J. Hazard. Mater.* **2009**, *171*, 1001.
24. Algarra, M.; Jiménez, M. V.; Castellón, E. R.; López, A. J.; Jiménez, J. *Chemosphere* **2005**, *59*, 779.
25. Cesarino, I.; Cavalheiro, E. T. G.; Brett, C. M. A. *Electroanalysis* **2010**, *22*, 61.
26. Cesarino, I.; Marino, G.; Matos, J. R.; Cavalheiro, T. G. *Talanta* **2008**, *75*, 15.
27. Liu, H. T.; He, P.; Sun, C. Y.; Shi, L. Y.; Zhu, G. Y.; Li, J. Y. *Electrochem. Commun.* **2005**, *7*, 1357.
28. Liu, Y.; Peng, J. J.; Zhai, S. R.; Li, J. Y.; Mao, J. J.; Li, M. J.; Qiu, H. Y.; Lai, G. Q. *Eur. J. Inorg. Chem.* **2006**, *15*, 2947.
29. Randles, J. E. B. *Discuss. Faraday Soc.* **1947**, *1*, 11.
30. Maleki, N.; Safavi, A.; Rajabadi, F. *Anal. Chem.* **2006**, *78*, 3820.
31. Zhang, J. P.; Chen, X. M. *Chem. Commun.* **2006**, *16*, 1689.
32. Lv, L.; Hor, M. P.; Su, F. B.; Zhao, X. S. *J. Colloid Interface Sci.* **2005**, *287*, 178.
33. Staden, J. F.; Matoetoe, M. C. *Anal. Chim. Acta* **2000**, *411*, 201.