Bucky-gel coated glassy carbon electrodes, for voltammetric detection of femtomolar leveled lead ions

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ABSTRACT

Femtomolar (fM) leveled lead ions were electrochemically detected using a bucky-gel coated glassy carbon electrode and differential pulse anodic stripping voltammetry. The bucky-gel was composed of dithizone, ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate), and multi-walled carbon nanotubes (MWCNTs). The fabrication of the bucky-gel coated electrode was optimized. The modified electrode was characterized with voltammetry, electrochemical impedance spectroscopy, and chronoamperometry. After the accumulation of lead ions into the bucky-gel modified electrode at -1.2 V vs. saturated calomel electrode (SCE) for 5 min in a pH 4.4 sodium acetate–acetate acid buffer solution, differential pulse anodic stripping voltammograms of the accumulated lead show an anodic wave at -0.58 V. The anodic peak current is detectable for lead ions in the concentration range from $1.0\,\mu M$ down to 500 fM. The detection limit is calculated to be 100 fM. The proposed method was successfully applied for the detection of lead ions in lake water.

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1. Introduction

Bucky-gel discovered by Aida and coworkers has been paid much attention recently not only as a unique elastic material but also as an electrode material. It consists of carbon nanotubes (CNTs) and ionic liquid (IL, "green" solvent). The bucky-gel displays both ionic and electronic conductivity. It has a three-dimensional structure, resulting in larger surface area. Due to the presence of CNTs, the bucky-gel reveals good biocompatibility and chemical/environmental stability [1,2]. It can be prepared by grinding with an agate mortar and pestle or sonicating highly dispersed CNTs in ILs, for example more than 0.5–1.0 (wt%) dispersion ratio [1].

Coating electrodes with the bucky-gel has been proved to be a straightforward way to fabricate functionalized electrodes. These bucky-gel coated electrodes showed the features of improved sensitivity, low susceptibility to electrode fouling, enhanced electrochemical reactions, and the advantage of easy preparation [1,2]. They therefore have been applied widely for electrochemical and biochemical sensing applications. For example, the electrochemical detection of bio-molecules like dopamine, [2,3] ascorbic acid

[2], NADH [2,3], uric acid [4], and nitric oxide [5] has been reported. Direct electron transfer processes of proteins [2,6,7] and enzymes have been obtained. Higher electron transfer rates were achieved after incorporating a catalyst like Pt and redox reagent into the three-dimensional bucky-gel [8–10]. However, the big drawback of bucky-gel coated electrodes is that the bucky-gel does not stick well on smooth Au or glassy carbon electrodes [8]. As for electrochemical applications, the utilization of bucky-gel modified electrodes for the environmental analysis like the detection of toxic metal ions was seldom reported in literature.

With an aim to extend the application of bucky-gel modified electrodes in environmental analysis, we functionalized the glassy carbon electrodes with bucky-gel and utilized the bucky-gel modified electrode to detect lead ions electrochemically. Thiol was added into the bucky-gel since the metal–S interaction is expected for the better accumulation of metal ions into three-dimensional structure of bucky-gel. The reason of lead ions as the target is because they are widely spread in various areas (like atmosphere, soil, and water) and heavily toxic. In this paper, we reported about the fabrication and the characterization of the bucky-gel coated glassy carbon electrodes, voltammetric response of lead ions on bucky-gel coated electrodes, and the optimization of the experimental conditions for the detection of lead ions. The proposed method was also applied for the detection of lead ions in lake water.

2. Experimental

2.1. Chemicals and solutions

Ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIMPF_6$) was purchased from Shanghai No. 1 Chemical Company (Shanghai, China). $Pb(NO_3)_2$ was from Beijing Hongxing Chemical Company (Beijing, China). Dithizone (DTZ), tetrachloromethane (CCl_4), and N,N-dimethylformamide (DMF) were from Shanghai National Chemical Company (Shanghai, China). Other reagents are analytical grade and used as received. Double-distilled water was used throughout experiments. Multi-walled carbon nanotubes (MWCNTs) with approximately 95% purity were obtained from Shenzhen Nanotech Port (Shenzhen, China). The MWCNTs were characterized, purified, and functionalized as reported previously [11,12].

2.2. Electrochemical measurements

Electrochemical measurements were performed on a CHI 760B electrochemical working station (Shanghai Chenhua, China) with a conventional three-electrode system at room temperature. Either a bare or a bucky-gel modified glassy carbon electrode acted as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum foil as the counter electrode. For the detection of lead ions, the solutions were purged with nitrogen gas for at least for 15 min.

The bucky-gel coated electrodes were fabricated as following. Firstly, the glassy carbon electrode 3.0 mm in diameter was polished carefully with a 1000-meshed emery paper and then continuously using 1.0, 0.3, 0.05 μm Alpha alumina slurry (CH Instruments, Austin, USA). After each polishing, the electrode was cleaned with water copiously and then in sonication bath for 10 min. The bucky-gel was then prepared by suspending the functionalized MWCNTs (1.0 mg) in 1 mL the mixture of $BMIMPF_6$ with DMF or in the mixture of $BMIMPF_6$ with CCl_4. A drop of this suspension with a volume of 3–5 μL was finally spin-coated onto the rough electrode surface. Several drops of the thiol (DTZ) in microlitres were added onto the bucky-gel coated electrode. After drying in air at room temperature and washing with water, the bucky-gel coated electrode was fabricated and then used for electrochemical characterizations and voltammetric detection of lead ions.

3. Results and discussion

3.1. Preparation and characterization of bucky-gel coated glassy carbon electrodes

The activity and active surface area of modified electrodes were investigated using cyclic voltammetry and the redox couple of $Fe(CN)_6^{3-/4-}$ as probes. Fig. 1 shows cyclic voltammograms of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl solution on the electrode with and without bucky-gel coating. The scan rate was 100 mV s^{-1}. Well-defined redox waves with identified peak potentials were obtained on the bare glassy carbon electrode (a), bucky-gel coated in the absence (b) and the presence of thiol (c). For three electrodes, the peak splittings are around 80 mV. This couple of redox waves obviously come from the quasi-reversible redox reaction of $[Fe(CN)_6]^{4-} \leftrightarrow [Fe(CN)_6]^{3-}$. The peak current was enhanced slightly on bucky-gel coated electrodes (b and c) and the background currents were enlarged too. The capacitance current on bucky-gel coated electrode after adding thiol (c) is larger than that of only bucky-gel coated electrode (b). The three-dimensional and highly conductive gels having larger surface area lead to the enhanced redox and capacitive current.
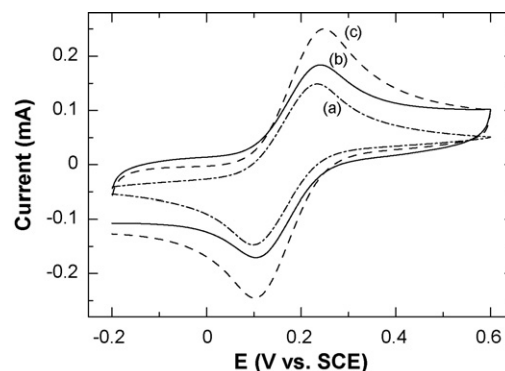

Fig. 1. Cyclic voltammograms of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl solution on the bare glassy carbon electrode (a) and on the bucky-gel coated electrode in the absence of thiol (b) and in the presence of thiol (c). The scan rate is 100 mV s^{-1}.
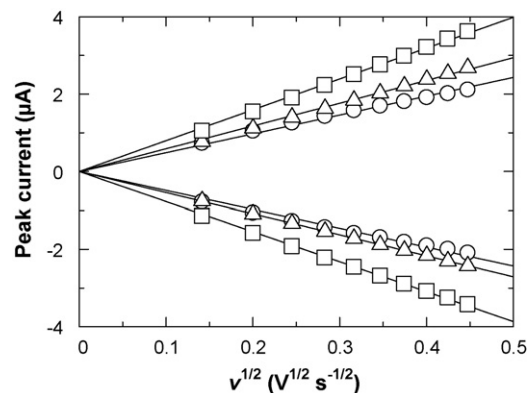

Fig. 2. Peak currents of 5.0 mM $[Fe(CN)_6]^{3-/4-}$ in 0.1 M KCl solution as a function of square root of scan rates on the bare glassy carbon electrode (circles) and on the bucky-gel coated electrode in the absence of thiol (triangles) and in the presence of thiol (squares).

Fig. 2 shows the proportional relationship of the cathodic peak currents as a function of the square root of the scan rates, indicating a diffusion-controlled process. The electroactive area, A, is then determined from the slope of a plot of the voltammetric peak current, I_p, versus the square root of sweep rate, $v^{1/2}$:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_0^{1/2} C_0 v^{1/2} \tag{1}$$

where n (= 1) is the electron transferred number of the reaction $[Fe(CN)_6]^{4-} \leftrightarrow [Fe(CN)_6]^{3-}$, D_0 (= 7.6×10^{-6} cm^2 s^{-1}) is the diffusion coefficient and C_0 (= 5×10^{-3} M) is the concentration of the redox couple, $Fe(CN)_6^{3-/4-}$. The averaged slopes of I_p versus $v^{1/2}$ are 4.86, 5.50 and 7.85 μA s$^{1/2}$ V$^{-1/2}$ for the bare (circles), bucky-gel coated electrode in the absence (triangles) and in the presence of thiol (squares), respectively. According to the equation, the effective area of bucky-gel coated electrode is about 1.3 times larger than a bare electrode. Adding thiol into the bucky-gel led to further enhancement (1.6 times) of electroactive surface area of the modified electrode. One possible reason is that more bucky-gel can be adsorbed on the electrode surface in the presence of thiol.

Moreover, the chronoamperomegrams (not shown) of the electrodes were recorded in 1.0 M H_2SO_4 solution. The bucky-gel coated electrode in the presence of thiol shows the fastest attenuation of current, indicating a faster mass transfer process. The capability of electron transfer on these electrodes was then checked using electrochemical impedance spectroscopy (EIS). Basically, a typical Faradaic impedance spectrum presented as a Nyquist plot consists of a semicircle portion at higher frequencies and a linear line portion at lower frequencies, which correspond to the electron transfer
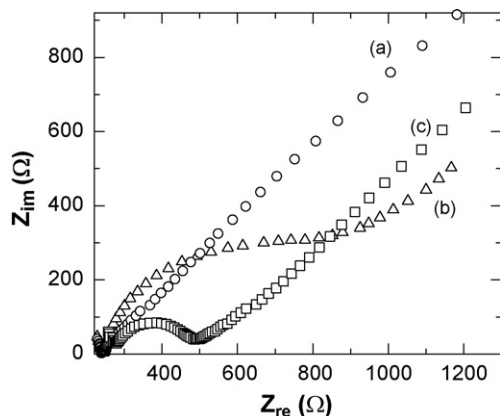
Fig. 3. Nyquist plots in 5.0 mM [Fe(CN)$_6$]$^{3-/4-}$ in 0.1 M KCl solution on the bare glassy carbon electrode (circles) and the bucky-gel coated electrode in the absence of thiol (triangles) and in the presence of thiol (squares). The potenital applied was 0.25 V vs. SCE.

Fig. 4. Cyclic voltammograms of 0.1 μM lead ions on the bare electrode (a) and on the bucky-gel coated electrode (b) in the pH 4.4 NaAc–HAc solution at a scan rate of 100 mV s^{-1}.

Fig. 5. Differential pulse anodic stripping voltammograms of 0.1 μM lead ions on the bucky-gel coated electrode (a) and on the bare electrode (b). Curve (c) is the response of the bucky-gel coated electrode in buffer solution. The buffer is pH 4.4 NaAc–HAc solution. The accumulation time was 5 min and the accumulation potential was −1.2 V. The scan rate was 100 mV s^{-1} with an amplitude of 2.5 mV.

limited process and the diffusion process, respectively. Additionally the diameter of semicircular is equivalent to the interfacial charge transfer resistance (R_{ct}). The resistance to charge transfer (R_{ct}) and the diffusion impedance (W) are both in parallel to the interfacial capacitance. Fig. 3 shows Nyquist plots of the bare electrode (a), the bucky-gel coated electrode in the absence (b) and in the presence (c) of thiol. The solution is 5 mM [Fe(CN)$_6$]$^{3-/4-}$ in 0.1 M KCl. The potenital applied was 0.25 V (vs. SCE, the open circle potential). The semicircular for the bare electrode (a) has not been observed due to very low R_{ct}. After the modification with bucky-gel (b), R_{ct} increased markedly, indicating that the bucky-gel is not transparent to redox probes. It might act as a barrier and block interfacial charge transfer partially. However, the addition of thiol (c) led to a decrease of R_{ct}, an sign of fast electron transfer process in the presence of thoil. This agrees with what we observed using chronoamperometry. Therefore the bucky-gel coated electrode in the presence of thiol was applied for the detection of lead ions.

The experimental conditions for the fabrication of the best bucky-gel coated electrode were optimized, including the type of the solvent, the proportion of BMIMPF$_6$ and DMF, the amount of thiol and the volume of buck gel. For the preparation of the bucky-gel, it is easier to use the mixture of BMIMPF$_6$ with DMF to suspend the functionalized MWCNTs than to use the mixture of BMIMPF$_6$ with CCl$_4$. We used 5.0 mM redox probes of Fe(CN)$_6$$^{3-/4-}$ to characterize the bucky-gel modified electrodes. Too much BMIMPF$_6$ for the preparation of the bucky-gel coated electrode made it hard for the modified electrode dry in air due to the non-volatile characteristics of BMIMPF$_6$. Too less resulted in a peak splitting of 150 mV for Fe(CN)$_6$$^{3-/4-}$ redox couples, indicating a poor electron transfer process. The best ratio we found in the mixed solution is BMIMPF$_6$:DMF = 1:4 (v/v). The prepared electrode using this bucky-gel shows a peak splitting of around 80 mV for Fe(CN)$_6$$^{3-/4-}$ redox couples. As for the amount of bucky-gel used, we chose 3 μL (1 mg/mL) since smaller volumes of MWCNTs than 2 μL did not cover the electrode surface fully and larger volume than 4 μL resulted in high capacitance current [11,12]. As for the amount of thiol, 10 μL drops of dithizone solution results in not only the best electrochemical response (the peak splitting of Fe(CN)$_6$$^{3-/4-}$ redox couples is 82 mV), but also the more stable and durable composite membrane (the electrode stability is over 2 weeks, see the section below). Please note that, experimentally the 10 μL dithizone solution has to be dropped onto electrode in two steps. After dropping 5 μL onto the electrode, the electrode surface needs to be semi-dry, followed by the second drop. The whole process takes about 15 min.
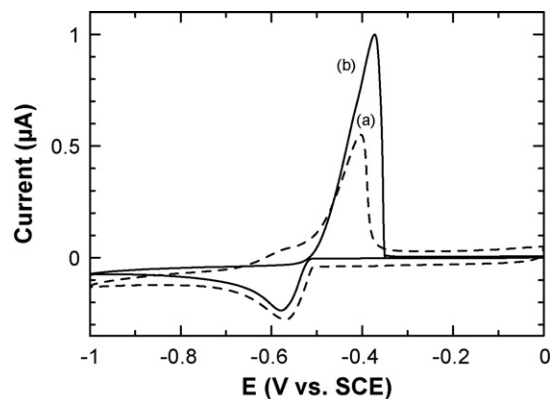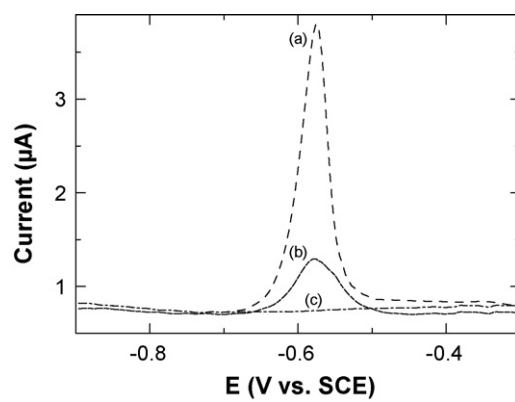
3.2. Voltammetric detection of lead ions on bucky-gel coated electrodes

Fig. 4 shows the cyclic voltammogram of 0.1 μM lead ions on the bare electrode (a) and on the bucky-gel coated electrode (b) in the potential range from 0 to −1.0 V. The buffer used is a pH 4.4 sodium acetate–acetate acid buffer solution (NaAc–HAc) and the scan rate is 100 mV s^{-1}. On the bare electrode (a), a cathodic wave at −0.58 V and an anodic wave at −0.40 V were noticed. On the bucky-gel coated electrode (b), the cathodic wave was at −0.57 and the anodic one at −0.37 V. Moreover, two-times larger anodic peak current was obtained on the bucky-gel coated electrode. Only capacitance currents were recorded for the bare electrode and the bucky-gel coated electrode in the pH 4.4 NaAc–HAc buffer (not shown). Therefore we applied anodic stripping voltammetry to detect lead ions using the bucky-gel coated electrodes.

Fig. 5 shows differential pulse anodic stripping voltammograms of 0.1 μM lead ions on the bucky-gel coated electrode (a) and on the bare electrode. As a control experiment, the response of the bucky-gel coated electrode in the buffer is presented in Fig. 5(c), where shows featureless. The buffer is pH 4.4 NaAc–HAc solution. The accumulation time was 5 min and the accumulation potential was −1.2 V. The differential pulse anodic stripping voltammograms show the same anodic potential (−0.58 V) for the accumulated lead on the bucky-gel coated electrode (a) and the bare electrode (b). However, almost three-times larger anodic peak current was detected on the bucky-gel coated electrode, indicating high effi-
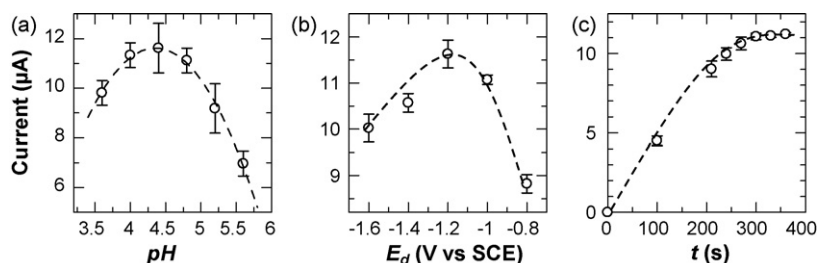
Fig. 6. Optimization of the detection conditions: the anodic peak current as a function of pH value of the buffer (a), the accumulation potential (b), and the accumulation time (c). The current was obtained from the differential pulse anodic stripping voltammograms. The concentration of lead ions was 0.1 μM. The scan rate was 100 mV s^{-1} with an amplitude of 2.5 mV. The buffer was NaAc–HAc solution. The dashed lines are for guiding the eyes.

ciency of the bucky-gel coated electrode for the detection of lead ions. We attribute this high efficiency to the porous structure and large surface area of bucky-gel. The interaction of lead ions with added thiol molecules is another main reason of high efficiency because the thiol molecules provide better chance and more sites for lead ions to nucleate.

The detection conditions were optimized including supporting electrolyte, pH values of the buffer applied, the accumulation potential, and the accumulation time. The anodic peak current as shown in Fig. 5 was adopted as the parameter to optimize the detection conditions. The results about the optimization of the experimental conditions are shown in Fig. 6. Various types of buffers including acids, bases, phosphate buffer, saline–sodium phosphate–EDTA buffer (SSPE), NaAc–HAc, Tris–hydrogen chloride (Tris–HCl), Britton–Robison buffer have been applied. The type of the buffer affected the solution stability greatly. Strong acid buffers resulted in gas evolution (hydrogen, chlorine) during electrochemical detection process while strong basic buffers led to the deposition of lead ions, which was also observed in phosphate buffer. The surfactant in SSPE blocked the electrode active sites, resulting in low anodic stripping current. Taking into account the stability of solution after adding lead ions, the sensitivity and the reproducibility of the measurements, the NaAc–HAc buffer solution was chosen.

As shown in Fig. 6(a), the pH value of buffer has a big effect on the detection of the accumulated lead. In the pH range of 3.6–5.6, the maximum anodic peak current is obtained at pH 4.4. As for the accumulation potentials (Fig. 6(b)), the accumulation of lead ions at −1.2 V gives the highest anodic peak current. The effect of accumulation time (Fig. 6(c)) on the anodic peak current follows the general tendency. The peak current increases with the accumulation time within 5 min, and then reaches the plateau, indicting a saturated state. In the measurement section, the pH 4.4 NaAc–HAc, the accumulation potential of −1.2 V, and the accumulation time of 5 min were then applied.

Fig. 7 shows differential pulse anodic stripping voltammograms of lead ions on the bucky-gel coated electrode under the optimized experimental conditions. The concentration of lead ions varied from 1.0 μM to 500 fM. After the accumulation of lead ions at −1.2 V for 5 min, the anodic peak current changes as a function of the concentration of lead ions, c. Most importantly, it is quite clear to see that even 500 fM lead ions can be detected using our modified electrode.

Fig. 8 summarizes the peak current obtained from Fig. 7 as a logarithmic function of the concentration of lead ions. As shown in the inert, in the concentration range from 0.1 to 1.0 μM, the anodic current is linear with the concentration of lead ions. The linear regression equation is I_p (μA) = 2.8 (μA) + 5.0c (μM), (R = 0.9990). In the lower concentration range (<0.1 μM), various functions (like logarithmic function, square-root function) can be applied to obtain the mathematically fitted linear relationship between the peak currents and the concentration of lead ions in different concentration
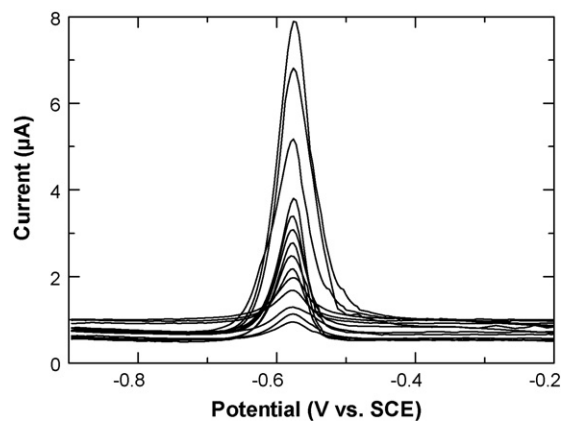

Fig. 7. Differential pulse anodic stripping voltammograms of lead ions on the bucky-gel coated electrode with different concentrations. The concentrations of lead ions from bottom to top are 500 fM, 1 pM, 2 pM, 5 pM, 8 pM, 10 pM, 100 pM, 1 nM, 10 nM, 100 nM, 200 nM, 500 nM, 800 nM, 1.0 μM. The buffer is pH 4.4 NaAc–HAc solution. The accumulation time was 5 min and the accumulation potential was −1.2 V. The scan rate was 100 mV s^{-1} with an amplitude of 2.5 mV.

ranges. However, they are not true linear equations since the errors using these mathematically fitted relationships are very high. For example, if we apply logarithmic function, 1% error in the current obtained will cause about 30% error in the calculated concentration. The detection limit was calculated to be 100 fM according to IUPAC regulations (S/N = 3).

The stability of the electrodes was examined. Ten electrodes were prepared and characterized using 5.0 mM redox probes of Fe(CN)$_6^{3-/4-}$ at different dates. On the same electrode the peak current and the peak potential did not change within two weeks.
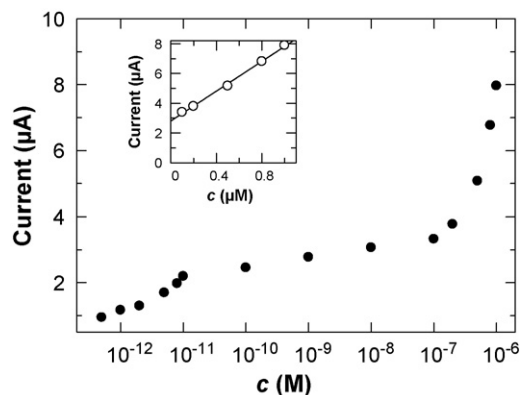

Fig. 8. Peak currents obtained from Fig. 7 as a logarithmic function of the concentration of lead ions in the range from 500 fM to 0.1 μM. The insert is the linear relationship of the peak current with the concentration of lead ions in the range of 0.1–1.0 μM. The solid line is the best fitted linear relationship.
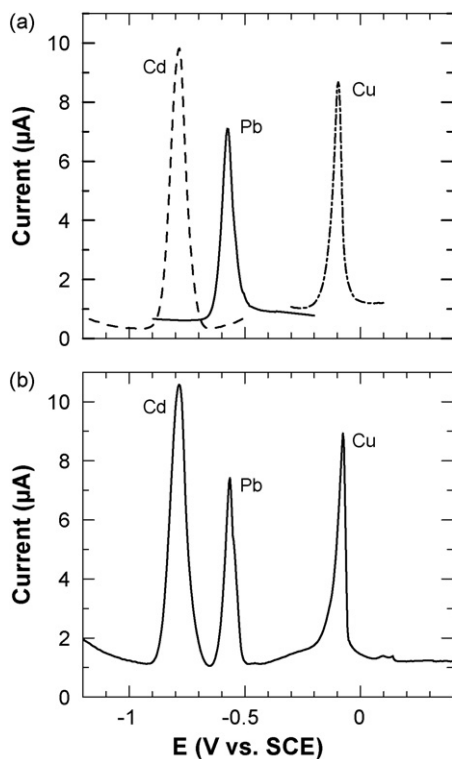
Fig. 9. (a) Differential pulse anodic stripping voltammograms of 0.1 μM Cu^{2+} (dotted line), 1.0 μM Pb^{2+} (solid line), and 1.0 μM Cd^{2+} (dashed line) ions on the bucky-gel coated electrode. (b) Differential pulse anodic stripping voltammogram of the mixture of 0.1 μM Cu^{2+}, 1.0 μM Pb^{2+}, and 1.0 μM Cd^{2+} ions on the bucky-gel coated electrode. The buffer is pH 4.4 NaAc–HAc solution. The accumulation time was 5 min and the accumulation potential was −1.2 V. The scan rate was 100 mV s^{-1} with an amplitude of 2.5 mV.

The relative standard deviation (RSD) of peak currents/potentials on different electrodes is in the range of 0.3–0.8%. The measurement of lead ions in the concentrations of 1.0 μM and 500 fM were also conducted on these electrodes. The pH 4.4 NaAc–HAc buffer, the accumulation potential of −1.2 V, and the accumulation time of 5 min were applied. The RSD values of the anodic current at −0.58 V during measurements as the reference to test the stability and sensitivity of the bucky-gel coated electrodes. These electrodes can be used for measurements continuously for over two weeks. On the same electrode, the RSD for the measurements of 1.0 μM lead ions is in the range of 1.2–2.7% and the RSD for the measurements of 500 fM lead ions is in the range of 4.5–6.7%. For different electrodes, the RSD for the measurements of 1.0 μM lead ions is in the range of 1.9–3.5 and for the measurements of 500 fM lead ions is in the range of 5.0–7.7%. These results indicate that the bucky-gel coated electrode has a good stability and the proposed method is sensitive and accurate. Please note that before each new measurement of lead ions the electrode has to be refreshed. The refreshment of the electrode was conducted by sweeping the electrode potential in the range of −1.0 to 0.5 at a scan rate of 100 mV s^{-1} for 20 cycles in the pH 4.4 NaAc–HAc buffer.

Interferences of Cd^{2+} and Cu^{2+} ions on the detection of lead ions were investigated. Fig. 9(a) shows the differential pulse anodic stripping voltammograms of 1.0 μM Pb^{2+} (solid line), 1.0 μM Cd^{2+} (dashed line), 0.1 μM Cu^{2+} (dotted line) ions on the bucky-gel coated electrode. The buffer is the pH 4.4 NaAc–HAc solution, the accumulation potential is −1.2 V and the accumulation time is 5 min. The anodic peak potentials are −0.08 V for copper ions, −0.58 V for lead ions, and −0.79 V for cadmium ions. The peak splitting from each other is more than 200 mV. Their different anodic

Table 1
Analytical results of the content of lead ions in lake water.

	Original (nM)	Added (nM)	Found (nM)	Recovery (%)	RSD (%)
East Lake	5.135	2.0	7.022	98.42	5.2
		5.0	10.02	98.86	4.5
		8.0	13.28	101.1	5.4
South Lake	2.267	2.0	4.348	101.9	5.8
		5.0	7.361^9	101.3	6.3
		8.0	10.07	98.08	4.7

stripping potentials are probably due to the different interaction of metal ions with the thiols and/or bucky-gel on the electrode. The anodic peak currents for three metal ions were enhanced with an increase of their concentrations. Fig. 9(b) shows the voltammogram obtained in the mixture of 1.0 μM Pb^{2+}, 1.0 μM Cd^{2+}, and 0.1 μM Cu^{2+} ions under the identified conditions used in Fig. 9(a). The differential pulse anodic stripping voltammogram shows three well-defined anodic waves at −0.79, −0.58, and −0.08 V. These peak potentials agree with those in Fig. 9(a) for Cd^{2+}, Pb^{2+}, and Cu^{2+} ions, respectively. Moreover, compared with those obtained in Fig. 9(a), the amplitudes of their anodic peak currents obtained from the mixture (Fig. 9(b)) did not change very much. Therefore, no interference of Cd^{2+} and Cu^{2+} ions was found for the detection of Pb^{2+} ion on the bucky-gel coated electrode. However, please note that what we show here is only one qualitative sign for interference experiments. For the more quantitative information, the slopes of calibration curves for the detection of lead ions in the presence and absence of possible interferents are needed. Subsequently, the bucky-gel coated electrode is promising to be used as an electrochemical sensor for the simultaneous detection of Cd^{2+}, Pb^{2+} and Cu^{2+} ions.

The method was then applied to determine the content of lead ions in East Lake and South Lake at Wuhan, China. No special treatment procedure of lake water was applied. Three parallel experiments were done for each sample. Table 1 shows the analysis results on these water samples from East Lake and South Lake. The recovery was found in between 98.08 and 101.9%. The RSD for the measurements is in the range of 4.5–6.3%. The contents of lead ions in two lakes we measured agree well with those released officially. Consequently, this method is sensitive, selective, and reproducible for the detection of lead ions in real samples.

4. Conclusion

Lead ions in the fM level were detected electrochemically on the bucky-gel coated glassy carbon electrode. The bucky-gel coated electrode showed high sensitivity, long stability, good reproducibility and excellent selectivity towards the detection of lead ions. The high sensitivity results from large surface area of bucky-gel, multi-reaction sites of MWCNTs, and strong interaction of lead ions with thiol inside bucky-gel. The addition of thiol might be a good way to improve the electrochemical activity of bucky-gel coated electrode. In summary, the bucky-gel coated electrode is promising for the detection of metal ions in environment. The method proposed has the potential to being adopted as an official route to monitor the concentration of lead ions and other metal ions in environment.

References

[1] T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, T. Aida, Science 300 (2003) 2072.

[2] Y. Liu, X. Zou, S. Dong, Electrochem. Commun. 8 (2006) 1429.

[3] R.T. Kachoosangi, M.M. Musameh, I. Abu-Yousef, J.M. Yousef, S.M. Kanan, L. Xiao, S.G. Davies, A. Russell, R.G. Compton, Anal. Chem. 81 (2009) 435.

[4] Q.P. Yan, F.Q. Zhao, G.Z. Li, B.Z. Zeng, Electroanalysis 18 (2006) 1075.

[5] C.M. Li, J.F. Zang, D.P. Zhan, W. Chen, C.Q. Sun, A.L. Teo, Y.T. Chua, V.S. Lee, S.M. Moochhala, Electroanalysis 18 (2006) 713.

[6] W. Tao, D. Pan, Q. Liu, S. Yao, Z. Nie, B. Han, Electroanalysis 18 (2006) 1681.

[7] H. Zhu, X. Lu, M. Li, Y. Shao, Z. Zhu, Talanta 79 (2009) 1446.

[8] F. Zhao, X. Wu, M. Wang, Y. Liu, L. Gao, S. Dong, Anal. Chem. 76 (2004) 4960.

[9] K. Mukai, K. Asaka, K. Kiyohara, T. Sugino, I. Takeuchi, T. Fukushima, T. Aida, Electrochim. Acta 53 (2008) 5555.

[10] P. Yu, J. Yan, H. Zhao, L. Su, J. Zhang, L.Q. Mao, J. Phys. Chem. C 112 (2008) 2177.

[11] Q. Wan, X. Wang, F. Yu, X. Wang, N. Yang, J. Appl. Electrochem. 39 (2009) 785.

[12] Q. Wan, X. Wang, F. Yu, X. Wang, N. Yang, J. Appl. Electrochem. 39 (2009) 1145.