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Carbon Nanotubes/Ionophore Modified Electrode for Anodic Stripping Determination of Lead

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Environmental Analysis

CARBON NANOTUBES/IONOPHORE MODIFIED ELECTRODE FOR ANODIC STRIPPING DETERMINATION OF LEAD

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Bifunctional combination of carbon nanotubes and ionophore is introduced for anodic stripping analysis of lead (Pb^{2+}). Carbon nanotubes are employed to improve the detection sensitivity due to their excellent electrical conductivity and strong adsorption ability. An ionophore is utilized for its excellent selectivity toward Pb^{2+}. The proposed carbon nanotubes/ionophore modified electrode shows improved sensitivity and selectivity for Pb^{2+}. Low detection limit (1 nM), wide linear range (5 nM–8 μM) and excellent selectivity over other metal ions (Cd^{2+}, Cu^{2+}, and Hg^{2+}) was obtained. The practical application has been carried out for determination of Pb^{2+} in real water samples.

INTRODUCTION

The toxic effect of heavy metals has been widely recognized. Heavy metals can bio-accumulate in the food chain and cause health problems, such as digestive, neurological, cardiac, and mental diseases (Fouskaki and Chaniotakis 2005; Ghiaci, Rezaei, and Kalbasi 2007), and even the formation of malignant tumors because

the interaction of heavy metals with DNA can be carcinogenic (Tu et al. 2004; Wong, Chow, and Gooding 2007). Among various heavy metals, lead (Pb^{2+}) is of great concern to the public since its compounds are highly toxic. Lead has been widely applied in storage batteries, cable sheath, solders, and petrol additives (Ensafi, Far, and Meghdadi 2009). Lead in the environment is cycled through the biogeochemical cycle and has ended up in surface and ground water (Paoliello and Capitani 2005). Many techniques have been used to detect trace Pb^{2+}, including spectral methods (Tarley and Arruda 2004; Zachariadis and Sahanidou 2009; Wang et al. 2000; Chen et al. 2009; Yoosaf et al. 2007) and electrochemical methods. Traditional spectral methods are somewhat cumbersome, time consuming, and not especially suitable for in situ measurement because of their complicated and ponderous instruments. In contrast, the electroanalytical methods have more attractive features, such as low cost, favorable portability, and easy operating procedures. Anodic stripping voltammetry (ASV) is considered to be one of the most sensitive electroanalytical methods in trace analysis of heavy metals (Wang 2006). In the past years, mercury based electrodes, including hanging mercury, dropping mercury, and mercury membrane modified electrodes, were widely used in ASV due to their advantages of easy formation of amalgam with reduced metals, excellent reproducibility, and surface renewability.

Recently, bismuth (Bi) film electrode has become an attractive subject of electroanalytical investigations as a potential replacement for mercury film electrodes due to its environmentally friendly property and closest behavior to mercury (Kachoosangi et al. 2007; Pauliukaite and Brett 2005; Hocevar et al. 2002; Kefala et al. 2003; Legeai et al. 2005). Generally, Bi film electrode includes ex situ and in situ prepared electrode. However, ex situ Bi film electrode has relatively narrow potential window (below the oxidation potential of bismuth) and is easily oxidized in contact with air causing relatively low chemical stability (Korolczuk, Moroziewicz, and Grabarczyk 2005). For in situ Bi film electrode, Bi(III) ions very easily hydrolyze forming insoluble compounds, so only acidic media can be considered as plating solutions (Buckova, Grundler, and Flechsig 2004), which limits the use of the electrode. Thus, new alternative electrode materials are highly desired to meet the growing demands for on-site environmental monitoring of trace heavy metals.

Since the discovery of carbon nanotubes (CNTs) (Iijima 1991), there are enormous interests in exploring their unique electrochemical, physical and structural properties. Recently, CNTs have come to the forefront of electrochemistry due to their high surface area, excellent electrical conductivity, unique three-dimensional network structure and good chemical stability (Haddon 2002; Liao and Chen 2002; Zhang and Wang 2007; Musameh, Lawrence, and Wang 2005). CNTs have been applied to detect heavy metals as novel materials (Li et al. 2003; Hu et al. 2009; Li et al. 2005). Although CNTs modified electrodes exhibit excellent properties, the application in real water samples is still a matter of concern because of the serious interference from other coexisting heavy metal ions in stripping analysis.

Ionophores, also known as ion carriers, are macrocyclic reagents that offer a defined cavity for metal ion complexation (Chen et al. 1999). They have been widely used in ion selective electrodes due to their excellent selectivity for specific metal ions (Hassan et al. 2003). Ionophores exhibit specific selectivity to certain metal ions, but the use of them in volt-amperometric analysis other than potentiometric analysis has received little attention (Pan et al. 2009a; Wang, Pan,

and Qin 2009), probably because of their nonconductive property. Recently, in our laboratory, the modified electrode based on nanosized hydroxyapatite and iono-phore for determination of Pb^{2+} has been reported (Pan et al. 2009a;b). However, linear range, reproducibility, and stability of this modified electrode were not quite satisfactory because nanosized hydroxyapatite is non-conductive and has rather weak dispersibility in aqueous solution.

In this paper, the unique properties of CNTs (i.e., excellent electrical conduc-tivity, good dispersibility, strong adsorptive capability, and large active surface area) with the specific complexing ability of ionophore have been bifuntionally combined to fabricate a new chemically modified electrode for stripping voltammetric analysis of trace Pb^{2+}. To sustain the neutral circumstance for cation extraction and supply the stability of the modifying layer, Nafion, a sulfonated cation-exchange polymer, has been utilized as the conductive membrane matrix, in which CNTs and ionophore can be tightly attached to the electrode surface. It will be presented that the proposed CNTs/ionophore/Nafion electrode can offer remarkably improved sensitivity and selectivity for stripping measurement of Pb^{2+}.

EXPERIMENTAL

Reagents and Chemicals

The CNTs with purity >95% synthesized by the chemical vapor deposition method were obtained from Shenzhen Nanotech Port (China) and treated according to the literature (Tsang, Harris, and Wan 1993). Nafion (5% w/w in a mixture of lower aliphatic alcohols and water), sodium hydroxide, and acetic acid were purchased from Sigma. Lead ionophore 4-tert-butylcalix [4] arene-tetrakis (N, N-dimethylthioacetamide) was obtained from Fluka. The solution of Pb^{2+} was prepared by dissolving $Pb(NO_3)_2$ (Sinopharm Chemical Reagent, China) in deionized water. All other chemicals used here were analytical reagent grade or better. All solutions were prepared with deionized water ($18.2\,M\Omega\,cm$ specific resistance) obtained with a Pall Cascada laboratory water system.

Apparatus

All electrochemical measurements were performed with a CHI 660 electrochemi-cal workstation (Chenhua Instruments Co., Shanghai, China). The electrochemical cell was composed of a three-electrode arrangement. A glass carbon (GC) electrode (3 mm in diameter) was used as working electrode, with a saturated calomel electrode (SCE) and platinum foil as the reference and counter electrodes, respectively. All potential values refer to SCE. Experiments were carried out at room temperature.

Preparation of CNTs/ionophore/Nafion Electrode

The procedure for preparation of CNTs/ionophore/Nafion electrode is as follows:

1. The GC electrode was polished with 0.3 and 0.05 μm alumina powder on slurry, respectively, rinsed with deionized water, and then cleaned by ultrasonication for 1 min. After that, the electrode was activated in 0.5 M H_2SO_4 solution by cycling between −0.15 and 1.3 V until a stable profile was obtained.

2. Original 5% w/w Nafion solution was diluted to 0.5% w/w solution with N, N-dimethylformamide (DMF); 10 mL of the above solution was used to dissolve 1.06 mg lead ionophore to obtain clear and pale yellow solution; 2 mg of CNTs was added into the mixture and sonicated for 20–30 min to get a homogeneous suspension.
3. A 5 μL amount of the CNTs/ionophore/Nafion suspension was added on the surface of GC electrode and dried under an infrared lamp.

For comparison, the CNTs/Nafion, ionophore/Nafion modified electrodes were prepared in the same manner.

Safety Considerations

Because CNTs and most of the tested heavy metals ions, such as Pb^{2+}, Cd^{2+}, and Hg^{2+}, are toxic and have adverse effects on human body, all experiments involving in CNTs and heavy metal ions should be performed with protective gloves and face masks. The waste solutions that contain heavy metal ions should be collectively reclaimed to avoid polluting the environment.

Analytical Procedure

The analytical procedure has three detection steps including accumulation, electrochemical reduction, and anodic stripping detection. The accumulation step was carried out at open-circuit by immersing the modified electrode into Pb^{2+} solution for 10 min. After accumulating, the modified electrode was rinsed with deionized water and transferred to a lead-free fresh acetate buffer solution (0.1 M HAc/NaAc buffer of pH 4.4) which was deaerated by bubbling of N_2 for 10 min. Then, a potential of −1.1 V was applied to the electrode for about 30 s in order to electrochemically reduce Pb^{2+}. Finally, the reduced Pb ions were stripped from the electrode during the potential sweep from −0.9 V to −0.4 V and the stripped peak current was measured at −0.55 V. Quantitative determination of Pb^{2+} was performed with differential pulse anodic stripping voltammetry (DPV). The optimal conditions were as follows: amplitude of 0.05 V; pulse width of 0.01 s; sampling width of 0.005 s; pulse period of 0.2 s; quiet time of 15 s. After each measurement, the modified electrode was cleaned by controlling the potential at 0.3 V for 60 s in order to remove the previous deposited ions from the electrode surface. Before each determination experiment, blank current of modified electrode was scanned to make sure that no peak of Pb^{2+} was present.

RESULTS AND DISCUSSION

Electrochemical Properties of CNTs/ionophore/Nafion Modified Electrode

The voltammetric behavior of Pb^{2+} at the CNTs/ionophore/Nafion modified electrode was investigated in 2 μM $Pb(NO_3)_2$ solution with 10-min open-circuit accumulation. The electrode was subject to cyclic voltammetric measurement in a 0.1 M HAc/NaAc supporting electrolyte solution at pH 4.4 from −0.9 to −0.3 V. Compared to the voltammetric curve of CNTs/ionophore/Nafion modified

electrode without accumulation (dotted line in Figure 1), a large anodic peak at $-0.55\,V$ and a cathodic peak at $-0.76\,V$ was observed at the same electrode after 10-min open-circuit accumulation in solution containing Pb^{2+} (solid line in Figure 1). Since no potential was applied during the accumulation step, the chemical incorporation of Pb^{2+} into the modifying layer is the logical explanation of this result. The poor reversibility of the oxidation-reduction cycle of lead may possibly result from the electrochemical properties of the modifying layer. Such difference between reduction and oxidation potentials can also be observed at CNTs/Nafion and ionophore/Nafion electrodes.

To further clarify the function of each component in the modifying layer, the differential pulse voltammograms recorded from -0.85 to $-0.40\,V$ for stripping analysis of $0.5\,\mu M\ Pb^{2+}$ at various electrodes are shown in Figure 2. A rather small stripping peak was observed at bare GC electrode (curve a in the inset). Under the same conditions, a slightly larger stripping peak at Nafion-modified electrode was observed (curve b in the inset), which is probably due to the ion-exchange property of the Nafion film. Larger stripping peaks at $-0.55\,V$ and $-0.56\,V$ were found at ionophore/Nafion and CNTs/Nafion modified electrodes, respectively (Figure 2c and 2d). The CNTs and the ionophore both have particular multi-adsorbing sites for Pb^{2+} which can attract Pb^{2+} from bulk solution to electrode surface, thus increasing the stripping peak currents. The highest stripping peak at $-0.56\,V$ was obtained at CNTs/ionophore/Nafion modified electrode (Figure 2e). The stripping peak currents of Pb^{2+} at bare GC, Nafion, ionophore/Nafion, CNTs/Nafion, and CNTs/ionophore/Nafion modified electrodes are 0.007, 0.03, 0.3, 0.7, and $1.5\,\mu A$, respectively. These results indicated that the current response obtained at the
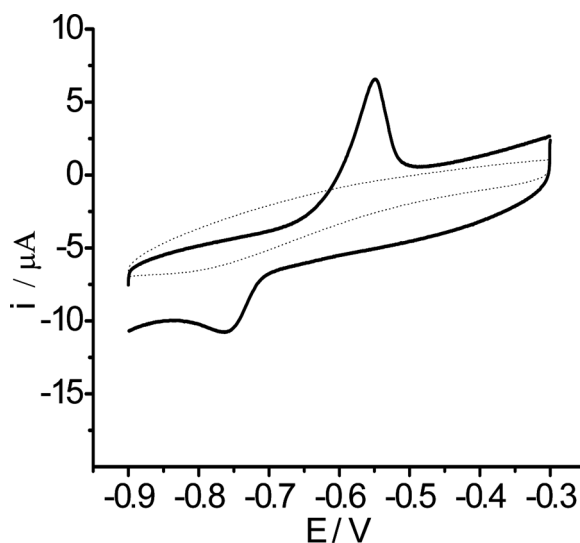

Figure 1. Cyclic voltammograms of CNTs/ionophore/Nafion modified electrode in 0.1 M HAc/NaAc buffer (pH 4.4) with (solid line) and without (dotted line) 10-min open-circuit accumulation. Accumulation solution: buffer solution containing $2\,\mu M\ Pb^{2+}$. Scan rate: $50\,mV/s$. Reduction potential: $-1.1\,V$. Deposition time: $30\,s$.
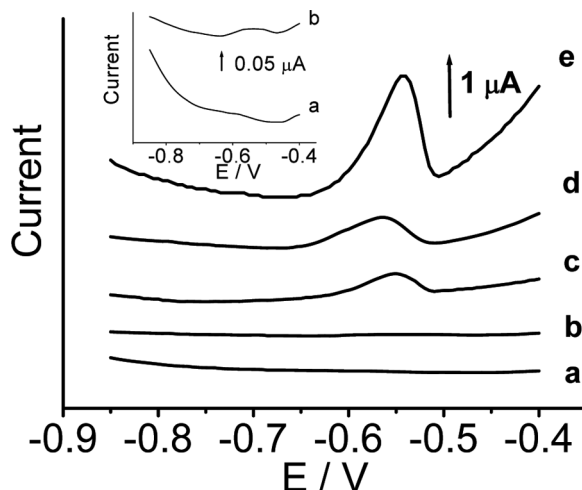
Figure 2. Anodic stripping differential pulse voltammograms at (a) bare GC electrode (b) Nafion modified (c) ionophore/Nafion modified, (d) CNTs/Nafion modified, and (e) CNTs/ionophore/Nafion modified GC electrode in 0.1 M HAc/NaAc buffer (pH 4.4) containing 0.5 μM Pb^{2+}. Accumulation time: 10 minutes. Pulse amplitude: 50 mV. Scan rate: 20 mV/s. Pulse width: 50 ms. Quiet time: 15 s. Other conditions are the same as in Figure 1.

CNTs/ionophore/Nafion modified GC electrode increased almost 200 times as compared to that at the bare GC electrode.

On the other hand, in order to find whether such a significant increase of response current is simply due to the large surface of the CNTs modified electrode, the electroactive surface areas of the modified electrodes were estimated by using ferrocyanide as redox probe. Figure 3 represents cyclic voltammograms (CVs) of the ionophore/Nafion modified electrode (dotted line) and CNTs/ionophore/Nafion modified electrode (solid line) in a 5 mM $Fe(CN)_6^{3-/4-}$ solution containing 0.1 M KCl at 50 mV/s. Well-defined oxidation and reduction peaks due to the $Fe(CN)_6^{3-/4-}$ redox couple were observed at both modified electrodes. The average electroactive surface area was calculated according to the Randles–Sevcik equation (Bard and Faulkner 2002):

$$I_p = 2.69 \times 10^5 A D^{1/2} n^{3/2} \gamma^{1/2} C \tag{1}$$

where n is the number of electrons participating in the redox reaction, A is the area of the electroactive surface (cm^2), D is the diffusion coefficient of the molecule in solution (cm^2 s^{-1}) (Hrapovic and Luong 2003; Zeng et al. 2006), C corresponds to the bulk concentration of the redox probe (mol cm^{-3}), and γ is the scan rate of the potential perturbation (V s^{-1}). The $Fe(CN)_6^{3-/4-}$ redox system used in this study is one of the most extensively studied redox couples in electrochemistry and exhibits a heterogeneous one-electron transfer ($n = 1$). According to the equation, the value of the electroactive surface area is proportional with the peak current. From Figure 3, the peak current at the CNTs/ionophore/Nafion modified electrode is 24.1 μA, while that at ionophore/Nafion modified electrode is 3.3 μA. The electroactive
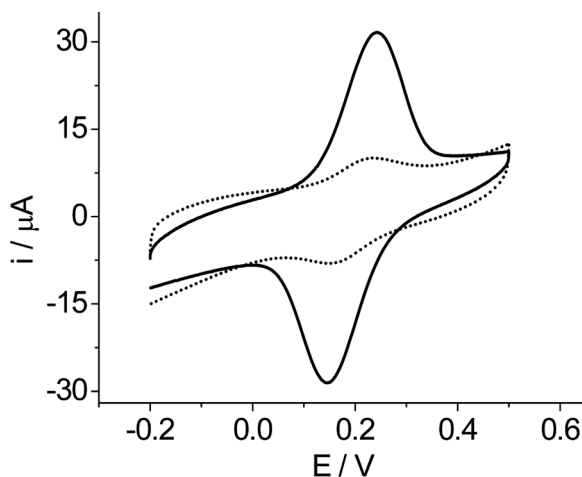
Figure 3. Cyclic voltammograms of ionophore/Nafion (dotted line) and CNTs/ionophore/Nafion (solid line) modified electrodes in 5 mM $Fe(CN)_6^{3-/4-}$ containing 0.1 M KCl.

surface area of the CNTs/ionophore/Nafion modified electrode is 7.3 times larger than that of ionophore/Nafion modified electrode, which is coincident with the results of Figure 2. These results indicate the significant increase of response current is consistent with the increase of electroactive surface area. CNTs with excellent electrical conductivity form a unique three-dimensional network structure which offers a larger surface area with more active sites for Pb^{2+} accumulation and provides docking sites for the ionophore or the ionophore-Pb complex.

Determination of Pb^{2+} at CNTs/ionophore/Nafion Modified Electrode

Effect of the pH of the detection solution. Generally, the response characteristics of the heavy metal sensor are affected by the pH value of the detection solution. The effect of the pH values of the detection solution on the response behavior of the CNTs/ionophore/Nafion electrode has been investigated and the corresponding results are shown in Figure 4. From Figure 4, a wide pH range (pH 2.6–5.8) for the CNTs/ionophore/Nafion electrode was used. From pH 2.6 to pH 4.4, the stripping current gradually increased and the maximum current was observed at pH 4.4. This may be ascribed to the multi-hydroxyl groups of CNTs and fewer protons are competing with Pb^{2+} for these binding sites with the increase of pH value. But, at pH values above 4.4, the current decreased, which might be caused by the formation of metal hydroxide complexes that may be partially soluble. These hydroxide complexes may precipitate either on the wall of the electrolytic cell or on the electrode surface, thereby causing a significant decrease in the quantity of solution phase metal ions that may reach the electrode surface (Walcarius et al. 1999). Therefore, a moderately acidic environment is important for the detection of the divalent heavy metal Pb^{2+}. In this work, 0.1 M NaAc-HAc buffer solution of pH 4.4 was chosen as the detection solution.
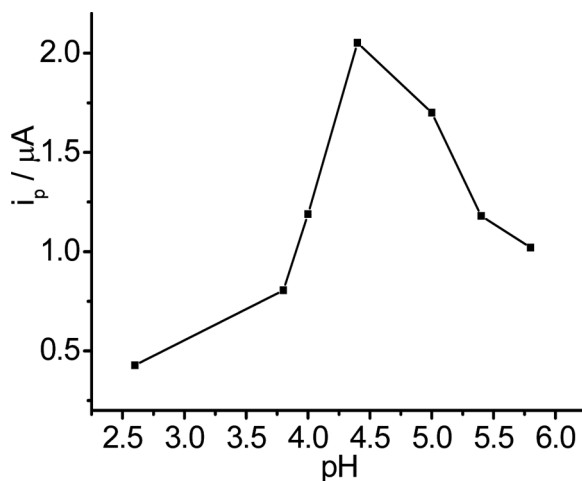
Figure 4. Effect of pH values on the stripping peak currents of CNTs/ionophore/Nafion modified electrode for $0.5 \mu M$ Pb^{2+}. Other conditions are the same as in Figures 1 and 2.

Calibration curve. The calibration curve of the proposed CNTs/ionophore/ Nafion modified electrode was derived from the differential pulse stripping volta- mmetry curves with a 10-min open-circuit accumulation and the corresponding results are shown in Figure 5. The stripping peak current (i_p) is proportional to the concentration of Pb^{2+} from 5 nM to 8 μM ($i_p = 4.2C - 0.63$, $r = 0.996$ i_p in μA, C in μM). The sensitivity of the modified electrode to Pb^{2+} is $4.2 \mu A/\mu M$. The detection limit is given by the equation $C = 3\sigma/S$, where σ is the standard deviation of the blank
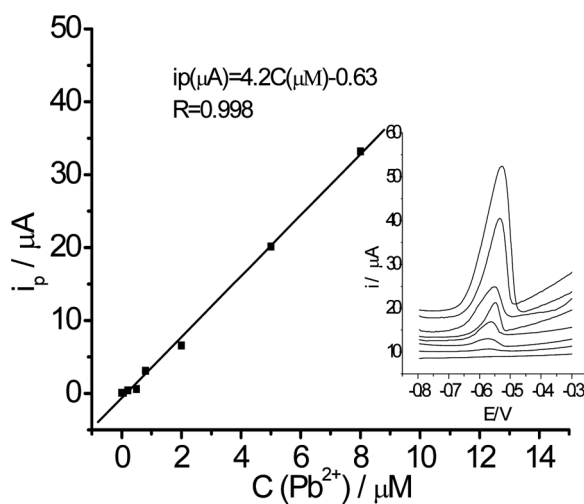

Figure 5. Calibration curves of Pb^{2+} on the CNTs/ionophore/Nafion modified electrode. The values for the inset curves are 0, 5 nM, 50 nM, 0.5 μM, 0.8 μM, 2 μM, 5 μM, and 8 μM from bottom to top, which are in the linear range. Other conditions are the same as in Figures 1 and 2.

measurements and S is the sensitivity of the calibration graph. The detection limit of Pb^{2+} for 10-min open-circuit accumulation was calculated to be 1 nM. The proposed electrode has a wider linear dynamic range, lower detection limit, and larger sensitivity than many other mercury free electrodes for determination of Pb^{2+} (Ghiaci, Rezaei, and Kalbasi 2007; Zhu et al. 2008; Hwang et al. 2008a; Guell et al. 2008; Hwang et al. 2008b). However, compared with our earlier work (Pan et al. 2009), the sensitivity and the detection limit of the proposed electrode have not been improved maybe due to the large background current of CNTs (Wang, Kawde, and Musameh 2003).

Additionally, the reproducibility of four CNTs/ionophore/Nafion modified electrode and the repeatability of CNTs/ionophore/Nafion electrode with nine measurements for 50 nM Pb^{2+} were estimated, and the results revealed the CNTs/ionophore/Nafion modified electrode had satisfactory reproducibility and repeatability with a relative standard deviation of 8.9% and 6.7%, respectively. The response current at CNTs/ionophore/Nafion modified electrode did not change significantly after two weeks under ambient conditions. Good reproducibility, repeatability, and stability may attribute to the excellent dispersibility of CNTs and the CNTs/ionophore entrapped strongly in the Nafion film which is very stable.

Interference study. The stripping analysis of Pb^{2+} can be affected by interferences from other heavy metal ions. Cd^{2+} can compete with Pb^{2+} for available deposition and/or coordination sites on the electrode surface. Cu^{2+} has been found to suppress the peak current probably due to the formation of the intermetallic compound between Cu and Pb. Hg^{2+} interferes with the stripping analysis of Pb^{2+} because of the formation of mercury film during the reduction step (Wang 1985). In this work, these three typical metal ions were chosen as interfering ions for investigation of the electrode's selectivity and the corresponding results are shown in Table 1. Experiments showed that a 50-fold excess Cd^{2+}, 10-fold Cu^{2+} and 5-fold Hg^{2+} had no influence on the signal of 50 nM Pb^{2+} at CNTs/Nafion modified electrode. However, at the CNTs/ionophore/Nafion modified electrode, 200-fold excess Cd^{2+}, 100-fold Cu^{2+} and 50-fold Hg^{2+} had no influence on the signal of 50 nM Pb^{2+}. This implies that the existence of the lead ionophore can effectively improve the selectivity of the modified electrode due to the selective transportation of Pb^{2+} ions for the sample solution to the modifying layer via the specific complexation with the ionophore during the open-circuit accumulation procedure.

Practical Application of CNTs/ionophore/Nafion Modified Electrode

To evaluate the applicability of proposed electrode, determination of Pb^{2+} in real lake waters and waste waters by using standard addition method was carried

Table 1. Interferences of other heavy metals with the stripping peak current of 50 nM Pb^{2+}

Heavy metal ions	Tolerance level at CNTs/Nafion modified electrode (μM)[a]	Tolerance level at CNTs/ionophore/Nafion modified electrode (μM)
Cd^{2+}	2.5	10
Cu^{2+}	0.5	5
Hg^{2+}	0.25	2.5

[a]For 5% error.

Table 2. Determination of Pb^{2+} in real water samples

Samples	Added (nM)	Found (nM)	Recovery (%)
Lake water 1	–	ND^a	
	10.0	10.3	103.0
	20.0	20.2	101.0
	30.0	29.1	97.0
	40.0	41.2	103.0
Lake water 2	–	ND	
	10.0	10.2	102.0
	20.0	20.8	104.0
	30.0	28.7	95.6
	40.0	41.2	103.0
Lake water 3	–	ND	
	10.0	9.6	96.0
	20.0	20.6	103.0
	30.0	29.2	97.3
	40.0	38.9	97.3
Waste water 1	–	57.2	–
	20.0	75.8	93.0
	40.0	93.7	91.3
Waste water 2	–	81.3	–
	20.0	102.5	106.0
	40.0	119.0	94.3

[a]Not detectable.

out and the results are shown in Table 2. The lake samples were filtered through a standard 0.45 μm membrane and treated with UV digestion for release of the trace lead from the organic complexes, then adjusted to pH 4.4 using sodium acetate and acetic acid before analyzed. The recoveries of the CNTs/ionophore/Nafion modified electrode varied between 91.3% and 106%, indicating the potential application of this proposed electrode in real water sample analysis with a high accuracy and good reliability.

CONCLUSIONS

By combining unique properties of CNTs (excellent electrical conductivity, good dispersibility, strong adsorptive capability, and large active surface area) with the specific complexing ability of ionophore, a bifunctional CNTs/ionophore modified electrode has been developed for determination of trace levels of Pb^{2+}. Compared with bare GCs, CNTs, and ionophore modified electrodes, the proposed CNTs/ionophore modified electrode significantly enhances the sensitivity and selectivity for Pb^{2+}. The electrode system has provided an excellent platform for electroanalysis and has a large potential application for the fabrication of other heavy metals sensors.

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