Lead Determination on MWNT/Nafion Composite Modified Glassy Carbon Electrodes

XU, Qin(徐琴) LIU, Ni-Na(刘妮娜) ZHU, Jun-Jie*(朱俊杰)

Key Laboratory of Analytical Chemistry for Life Science, Department of Chemistry, Nanjing University, Nanjing, Jiangsu 210093, China

A composite material of nitric acid oxidized multiwalled carbon nanotube (MWNT) and Nafion was prepared. Such composite was modified on a glassy carbon electrode to determine trace of lead by differential pulsed voltammetry. In pH = 6.47 NaNO₃ solution, Pb²⁺ ions were accumulated on the modified electrode at -0.4 V. Compared with a bare and a Nafion film coated electrode, the composite coated GC electrode can reduce the accumulating potential and eliminate the toxic character of mercury. The calibration plots were linear at low concentration of 5.0×10⁻⁹—2.0×10⁻⁸ mol/L and high concentration of 2.5×10⁻⁸—5.0×10⁻⁶ mol/L. The performances characteristics indicate that the electrode can be used to determine trace Pb²⁺ ions.

Keywords composite, lead, electrochemistry, differential pulsed voltammetry

Introduction

Lead is a kind of heavy metal that can hurt human’s nerve. Excessive ingestion of it can cause accumulative poisoning, nervous system damage, etc. Due to its dangerous and harmful properties for the health of human being, the determination of it is very important. Many methods have been used to analyze trace of lead such as atomic absorption spectrometry,¹ ion chromatography and so on.² However, these processes are relatively complicated and the instruments are expensive. Electrochemical method, which is cheap and convenient, was widely used to determine lead concentration. The analysis for trace of lead by stripping voltammetry has been suggested as early as 1953.³ Some investigations including the mercury-coated glassy carbon electrode (GCE), polymeric membrane electrodes,⁴ boron-doped diamond film electrode, carbon electrode and MWNT film modified electrode⁵ have been applied. In these studies, an accumulation step was carried out followed by electrochemical measurement of the analyte in a free background electrolyte solution.

Carbon nanotubes (CNT) represent an important group of nanomaterials with attractive electronic, chemical and mechanical properties.⁶ The improved electrochemical behaviors of catecholamine neurotransmitters, cytochrome c, and ascorbic acid have been illustrated at CNT modified electrodes. CNT oxidized with nitric acid had a high cation adsorption capacity especially for lead.⁷ New fabrication schemes are highly desired to broaden the applications of the CNT-based electrodes. The major barrier for developing the practical CNT-based devices is the insolvability of CNT in most solvents.

Nafion is a perfluorinated sulfonated cation exchanger and has been widely used as an electrode modifier due to its attractive ion-exchange characteristics, thermal stability, chemical inertness, mechanical strength, and antifouling properties. Deo and Wang⁸ have demonstrated the catalytic oxidation of carbohydrates at a single-walled CNT-Nafion coated electrodes. Simple Nafion modified electrodes have been used for the analysis of lead and cadmium⁹ in the presence of surfactants. The combination of Nafion with the suitable carbon materials to fabricate the composite film electrode has very interesting properties and a wide range of applications.

In this article, multiwalled carbon nanotubes were uniformly solubilized in Nafion and the composite modified electrode was constructed. The presence of Nafion increased the solubility of MWNT and further immobilized MWNT on GC electrode. In this immobilization approach, Nafion acted as a membrane material, ion exchanger, and solvent for MWNT. The electrode showed good stability, reproducibility and strong ability against electrode fouling. Unlike early electrode, low accumulation potential was used in this study. Therefore, it can be severed as an effective sensor for lead determination.

Experimental

Reagent and apparatus

Stock solutions of 1.0×10⁻² mol/L Cd²⁺, Pb²⁺ and...
Cu²⁺ were prepared by dissolving Cd(NO₃)₂ and Pb(NO₃)₂ (Shanghai Reagent Corporation, China) into redistilled water, and then diluted to various concentrations. Nafion was purchased from Fluka E-Merck company (Germany). Other chemicals used were of analytical grade. All the chemicals were used without further purification. The MWNT used in the experiments (obtained from Shenzhen NTP) was refluxed in the concentrated HNO₃. Deionized doubly-distilled water was used for making the solutions (18.6 MΩ).

Transmission electron microscopy (TEM) images were recorded on a JEOL-JEM 200CX transmission electron microscope, using an accelerating voltage of 200 keV. All electrochemical experiments were performed on a CHI 630 electrochemical analyzer (Shanghai Chenghua Company) in a three-electrode configuration. A Nafion/MWNT composite modified glassy carbon electrode was used as working electrode. A saturated calomel electrode (SCE) and a platinum wire were used as the reference electrode and auxiliary electrode respectively.

**Electrode modification**

The MWNT was purified by refluxing in the aqueous HNO₃ solution (2.6 mol/L, 48 h), washed repeatedly with water, and sonicated to shorten. The nanotube-bound carboxylic acids were associated with the defect sites and the terminal carbons in chemically shortened nanotubes as a result of the purification process. Then 5 mg of MWNT were dispersed in 1 mL of ethanol containing 1% Nafion by sonication for about 5 h to yield a stable and uniform suspension. Prior to modification, a GCE was polished with 0.015 µm aluminum slurry (BDH Chemicals Ltd., Poole, England), then rinsed thoroughly with redistilled water, successively sonicated in redistilled water and ethanol, and finally dried by flowing pure N₂.

**Determination of Pb²⁺**

A certain volume of Pb²⁺ solution was added into pH 6.47 NaNO₃ solution, and then accumulated at −0.4 V for 600 s while stirring the solution. The electrode was then moved to pH 2.68 HCl solution containing 0.01 mol/L NaCl, left for 30 s, and the differential pulse voltammograms were recorded from −1.0 to 0 V. The peak heights were measured at −0.532 V. For repeated determinations of the same electrode, the potential was held at 0.20 V in 0.1 mol/L HNO₃ for 60 s to remove previous deposits.

**Results and discussion**

**Physical characterization**

A homogeneous, well-dispersed viscous solution of MWNT/Nafion could be easily prepared by sonication and the solution was stable even after several months. Increasing Nafion content resulted in the remarkable enhancement of solubility of MWNT. The combination of MWNT and Nafion to fabricate a lead sensor was appealing since the latter exhibited unique ion-exchange and discriminative properties and could improve the solubility of MWNT. However, when the concentration of Nafion was too large, it was difficult to renew the electrode, and thus 1% Nafion was selected.

Transmission electron microscopy image revealed the MWNT sizes and the nature of association between the Nafion and MWNT (Figure 1). Figure 1a clearly shows the pristine nature of the raw MWNT, and that the diameters of the MWNT are ca. 20 nm. Figure 1b shows the size and morphology of the MWNT/Nafion composite. It was known that the cylindrical shape, the perfect straightness, and the exceptional rigidity of the carbon nanotubes make their surfaces good candidates for the growth of helical crystals of proteins. From the image, it can be seen that Nafion formed helical structure around the MWNT. The combination of Nafion and MWNT has enhanced the solubility of MWNT in ethanol because of the structure of Nafion.

![Figure 1](image_url)

**Figure 1** TEM images of the bare MWNT (a) and the MWNT/Nafion composite (b).

Figure 2 is the differential pulse voltammograms in pH 2.68 HCl solution (containing 0.01 mol/L NaCl) of a bare electrode, a Nafion film modified electrode and a MWNT/Nafion film modified electrode after accumulation at −0.4 V in 1.4×10⁻⁶ mol/L Pb²⁺ solution for 600 s. As can be seen in Figure 2, the peak currents at both Nafion-modified electrode and MWNT/Nafion modified electrode are significantly higher than that at the bare electrode because of the preconcentration ability of the electrode coatings. At the MWNT/Nafion modified electrode, the peak current is noticeably higher.
than that at the Nafion-modified electrode. It clearly indicated the favorable and feasible stripping of the Pb\(^{2+}\) ions from the MWNT/Nafion modified electrode. The reason for the strong response of the MWNT/Nafion modified GCE is that MWNT has a smooth, straight, one-dimensional channel in its center, which can hold atoms or molecules. Meanwhile, MWNT with closed topology and much larger specific surface area exhibits strong adsorptive ability toward lead ions and hence improves their surface concentration. Figure 2 also indicates that the peak width at half height (\(W_{1/2}\)) is about 34 mV, which is near the expected value of 24 mV for a two-electron transfer process. The narrow width of the stripping indicates that both the electrochemical and subsequent chemical processes are fast.

### Effect of operational parameters

In order to optimize the procedure for the determination of lead, some effects have been investigated.

**Effect of pH** The effect of pH on the accumulation step was investigated in the range of pH values from 1.49 to 7.44. The result is shown in Figure 3. It was found that at low pH, the peak current of Pb\(^{2+}\) was so small that it could be neglected. With the increase of pH, the peak current increased sharply, and at the pH range of 5.5—7.5 the current reached the highest. In this experiment pH 6.47 was selected. The reason may be that the isoelectric point of the oxidized MWNT was shifted to a lower pH value than that of the as-grown MWNT\(^{13}\) due to the higher surface functionalized acidic groups. The deprotonated carboxylate groups would form complexes with lead ions. At low pH, many carboxylate groups on MWNT could be protonated and unavailable to complex Pb\(^{2+}\). At high pH, the deviation of the electrode response is due to the formation of certain hydrogen complexes of Pb\(^{2+}\) ions. The influence of the pH on the anodic stripping peaks of lead was studied in the pH range of 0.8—4.0. In Figure 4, it could be seen that the peak currents increased with the increase of pH. The maximum peak current was obtained at pH 2.5. No peak of lead was observed at the modified electrode when the pH was higher than 4. Therefore, pH 2.5 was adopted for further studies. Among various electrolytes examined in the stripping study, the best results were obtained in the chloride containing media. The chloride ion was able to form the complex with the metal ion formed during the anodic scan.

**Effect of ionic strength** The effect of various ionic strengths on the peak current for the accumulation of 10\(^{-6}\) mol/L Pb\(^{2+}\) was studied by varying the ionic strength of electrolyte solution in the range of 0.005—0.05. The ionic strength of electrolyte solution was adjusted by varying NaNO\(_3\) concentration. In view of these results, the electrolyte at pH 6.47 and ionic strength 0.01 was chosen as supporting electrolyte in the accumulation cell, thus the highest analytical signals were obtained. The effect of NaCl concentration was also studied in the range of 0.01—0.5 mol/L, and the optimal concentration was 0.01 mol/L.
and it was due to the formation of the complex between Cl\(^-\) and Pb\(^{2+}\).

**Effect of accumulation potential** The effect of accumulation potential on the peak currents was examined in the range of \(-0.2\) to \(-1.0\) V. As it can be seen in Figure 5, unlike other methods,\(^{14}\) the anodic peak current began to appear at an applied potential of \(-0.2\) V, when the potential was increased to \(-0.4\) V, a well-defined peak at \(-0.532\) V in the stripping solution could be obtained. However, when the accumulation potential was further increased to \(-0.9\) V, the current decreased and then sharply increased at \(-1.0\) V. The increase of the current at \(-0.4\) V may be due to the under-potential deposition of lead ions on the modified electrode. It is well known that the occurrence of under-potential deposition always comes with the strong interaction between the metal atoms and the substrate surface. MWNT, containing carboxyl ligand on the electrode surface, may form a particular surface with Nafion for the lead accumulation. On the other hand, MWNT was also used as the chelating agent to form the complex with lead ions. Therefore, during the accumulation process, the faradaic [reduction of Pb(II) to Pb] and non-faradaic (ion-exchange by the Nafion and complexation) by MWNT occurred. Both of them contributed to the increase of the stripping current. When the deposition potential reached \(-1.0\) V, almost all the lead ions in the solution were accumulated by the faradaic process,\(^{14}\) consequently the current was increased again. However, the background current was increased greatly, and hydrogen was electrolyzed as the accumulation potential became more negative than \(-1.0\) V. The bubbles generated in the electrode could destroy the modified electrode. To eliminate the influence, \(-0.4\) V was chosen as the accumulation potential.

![Figure 5](image)

**Effect of accumulation time** Another important parameter is the accumulation time of Pb\(^{2+}\). The anodic peak current of differential pulse voltammetry was increased with the increase of the accumulation time, which indicated an enhancement of Pb\(^{2+}\) at the modified electrode. The result indicated that before adsorptive equilibrium was reached, the longer the accumulation time, the more the metal ions were adsorbed and thus the larger the peak currents became. However, after a period of accumulation time, the peak currents tended to level off, illustrating that adsorptive equilibrium was achieved. To increase the sensitivity for lower concentrations, the accumulation time was set at 600 s.

**Linear ranges and detection limits**

To verify the linear relationship between peak currents and metal concentrations, six calibration graphs were constructed under optimum conditions and after 600 s accumulation time. The results of this study (correlation coefficients greater than 0.99) indicated that in all cases the current-concentration relationships were linear in the concentration range of \(5.0 \times 10^{-9} \) to \(2.0 \times 10^{-8}\) mol/L (\(i_p = 1.89 + 0.7 \times 10^{-9} c\), \(R = 0.997\), \(i_p\) in µA, \(c\) in mol/L) and \(2.5 \times 10^{-8} \) to \(5.0 \times 10^{-7}\) mol/L (\(i_p = 2.50 + 0.318 \times 10^{-8} c\), \(R = 0.994\), \(i_p\) in 10⁻⁷ A, \(c\) in mol/L). At high concentrations deviation from linearity occurred due to the saturation of the electrode surface. The detection limit (3σ) was found to be \(1.0 \times 10^{-7}\) mol/L.

**Interferences**

The influence of other ions in the analyte solution on the current response was investigated. Several ions such as K\(^+\), Na\(^+\), NH\(_4\)\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Ba\(^{2+}\), F\(^-\) and SO\(_4^{2-}\) have only negligible effect on the determination of Pb\(^{2+}\), equal molar amount of Cu\(^{2+}\) and Cd\(^{2+}\) have no effect too, but 100 folds molar of them was found to interfere slightly with the determination of Pb\(^{2+}\). The competitive adsorption capacities of Pb\(^{2+}\), Cu\(^{2+}\) and Cd\(^{2+}\) ions by the acid treated MWNT have been studied. Pb\(^{2+}\) ions showed greater adsorption capacities than the other two ions.\(^{15}\) Therefore, all Pb\(^{2+}\) ions would be accumulated on the modified electrode at low concentration and stripped. With the increase of the Cu\(^{2+}\) and Cd\(^{2+}\) ions in the solution, any interaction of these metals would happen during their co-deposition on the modified electrode, and then the Pb response would be decreased as has been reported.\(^{16}\)

**Conclusion**

In this paper, the MWNT/Nafion composite modified electrode was developed for the determination of Pb\(^{2+}\) at trace levels by differential pulse anodic stripping voltammetry. The existence of Nafion can increase the solubility of MWNT, which can improve the sensitivity of the electrode. The effects on the amount of Pb\(^{2+}\) accumulated at the electrode such as the accumulation voltage, the accumulation time and the pH value of the solution have also been studied. Compared with previous studies, the electrode can accumulate Pb\(^{2+}\) at \(-0.4\) V, which can prevent engendering of hydrogen from the electrolysis of water. The method presented here had a lower detection limit than the bare electrode and was not interfered strongly by other metal ions.
References


(E0501173  LI, W. H.; ZHENG, G. C.)