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ORIGINAL PAPER

Electrochemical determination of Pb^{2+} using a carbon nanotube/Nafion composite film-modified electrode

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Abstract A carbon nanotube/Nafion composite film modified electrode is described for the sensitive and convenient determination of Pb^{2+}. In the presence of 1% Nafion, multi-walled carbon nanotubes (MWNT) were successfully dispersed into ethanol by ultrasonication. After evaporating the ethanol, a MWNT/Nafion composite film-modified electrode was achieved. The resulting MWNT/Nafion film modified electrode possesses high cation exchange capacity, large surface area, strong adsorption ability and catalytic activity. Compared with the unmodified electrode and Nafion film-modified electrode, the MWNT/Nafion film-modified electrode remarkably increases the stripping peak current of Pb^{2+}. Furthermore, the influences of supporting electrolyte, volume of MWNT/Nafion suspension, accumulation potential and accumulation time were investigated. The striping peak current of Pb^{2+} is proportional to its concentration over the range 8.0×10^{-8} to 6.0×10^{-6} mol L^{-1}. The limit of detection (S/N = 3) is as low as 5.0×10^{-9} mol L^{-1}. Finally, this newly developed method was used to determine Pb^{2+} in water samples.

Keywords Lead · Determination · Carbon nanotube · Nafion · Modified electrode

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1 Introduction

Lead is toxic and linked to various adverse health effects, promoting extensive attention in developing sensitive, reliable and rapid analytical methods. Until now, the widely used method for the determination of Pb^{2+} is atomic spectrometry, including atomic absorption spectrometry (AAS), atomic emission spectrometry (AES) and atomic fluorescence spectrometry (AFS). Apart from the atomic spectrometric methods, the electrochemical method has attracted increasing attention because of its high sensitivity, good selectivity, rapid response, extreme simplicity, easy data read-out and low cost. To date, a great number of electrochemical methods utilizing various chemically modified electrodes (CMEs) have been reported for the determination of Pb^{2+} [1–5]. However, to the best of our knowledge, determination of Pb^{2+} using carbon nanotube/Nafion composite film modified electrodes has not been reported.

Multi-walled carbon nanotube (MWNT) is a fascinating material made of concentric cylinders placed around a common central hollow, with a spacing between the layers close to that of the interlayer distance in graphite (0.34 nm). MWNT is of great potential for a vast variety of applications due to the unique structural, mechanical, thermal, electrical and optical properties [6]. Moreover, MWNT possesses subtle electronic properties and obvious catalytic activity, prompting the investigation of their applications in electrochemistry as novel electrode materials [7–13].

The main objective of this work is to develop a sensitive, selective and convenient electrochemical method for the determination of Pb^{2+} using the unique properties of MWNT and the favourable properties of Nafion. Nafion is a perfluorinated sulphonated cation exchanger with high cation exchange capacity and has been extensively used to modify electrodes for purposes such as improving the sensitivity and selectivity of the determination of positively charged species.

In this work, a stable and homogeneous MWNT/Nafion suspension was obtained by dispersing MWNT into ethanol in the presence of 1% Nafion. A MWNT/Nafion composite film was then coated onto a glassy carbon electrode (GCE) surface after evaporating the ethanol, resulting in a uniform and stable MWNT/Nafion film-modified GCE. The resulting MWNT/Nafion film not only possesses the cationic selectivity of Nafion but also exhibits the unique properties of MWNT such as catalytic activity, strong adsorption ability and high surface area. Therefore, the MWNT/Nafion film-modified GCE enhances the electrochemical response of Pb^{2+} and greatly improves the sensitivity and selectivity for determining Pb^{2+}.

2 Experimental

2.1 Reagents

MWNT was obtained from Shenzhen Nantotech Port Co. Ltd. Nafion (5%) was purchased from Aldrich. Stock solution of 1.00×10^{-2} mol L^{-1} Pb^{2+} was prepared by dissolving $Pb(NO_3)_2$ (Shanghai Reagent Corporation, China) into bidistilled water. Other chemicals used were of analytical grade. All the chemicals were used without further purification and the water was bidistilled.

2.2 Apparatus

Electrochemical experiments were carried out using a CHI 650B Electrochemical Workstation (CH Instrument, Austin, TX). A conventional three-electrode system, consisting of a MWNT/Nafion film-modified GC working electrode (3.0 mm in diameter), a saturated calomel reference electrode (SCE) and a platinum wire counter electrode, was employed.

Scanning electron microscopy (SEM) was performed with a FEI-Quanta 200 microscope. Atomic absorption spectrometric measurements were conducted with AA 6300 Atomic Absorption spectrophotometer (SHIMADZU, Japan).

2.3 Preparation of MWNT/Nafion composite film-modified GCE

MWNT/Nafion suspension was achieved by adding 5.0 mg MWNT in 10.0 mL, 1% Nafion ethanol solution and then sonicating for 30 min. Before coating, a GCE (3 mm in diameter) was polished with aluminium slurry, and then sonicated in re-distilled water. The GCE surface was then coated with 10.0 μL MWNT/Nafion suspension, and allowed to evaporate ethanol. The Nafion film was fabricated with the same procedure but without MWNT.

2.4 Determination of Pb^{2+}

Unless otherwise stated, pH 5.0 NaAc–HAc buffer (0.1 mol L^{-1}) was used as the supporting electrolyte. Firstly, Pb^{2+} was accumulated onto the surface of MWNT/Nafion film-modified GCE and reduced to Pb under −1.00 V. Secondly, the reduced Pb was oxidized to Pb^{2+} during the potential sweep from −1.00 to −0.30 V, resulting in a stripping peak at −0.62 V. Finally, the stripping peak current was measured for Pb^{2+}.

3 Results and discussion

3.1 SEM image of MWNT/Nafion film

The SEM image MWNT/Nafion composite film on the glassy carbon disk is illustrated in Fig. 1. It is clear that the GCE surface is coated with a MWNT thin film.

3.2 Electrochemical response of Pb^{2+}

Figure 2 shows the electrochemical behaviour of Pb^{2+} at different working electrodes, investigated by linear sweep voltammetry (LSV). In 0.1 mol L^{-1}, pH 5.0 NaAc–HAc buffer, a poor-shaped reduction peak is observed for

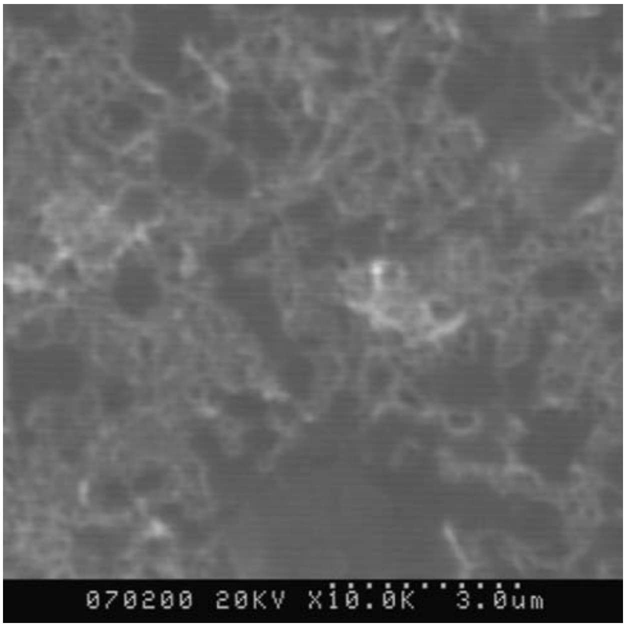

Fig. 1 SEM image of MWNT/Nafion film on GC surface

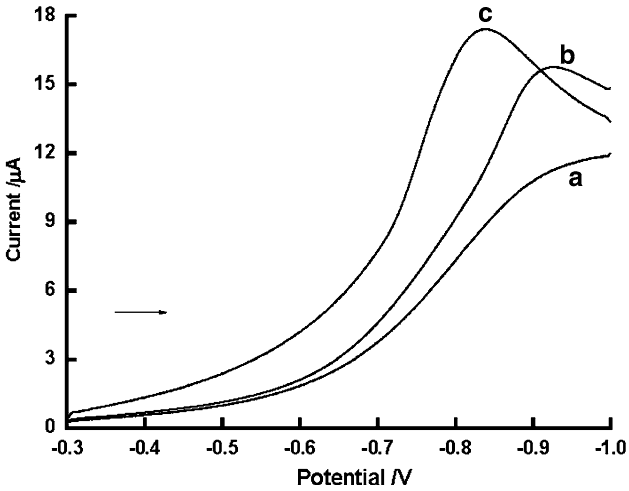

Fig. 2 Linear sweep voltammograms of 1.0×10^{-5} mol L^{-1} Pb^{2+} in pH 5.0 NaAc–HAc buffer at (a) bare GCE, (b) Nafion film-modified GCE, (c) MWNT/Nafion film-modified GCE

1.0×10^{-5} mol L^{-1} Pb^{2+} at the unmodified GCE (curve a). When the bare GCE surface is coated with 1% Nafion film, the reduction peak becomes well shaped at −0.92 V, and the reduction peak current increases (curve b). This is due to the fact that Nafion is a cation exchanger and attracts Pb^{2+} from bulk solution to the electrode surface. The reduction peak potential shifts positively from −0.92 V to −0.82 V, and the peak current further increases on the MWNT/Nafion film-modified GCE (curve c), compared with those at Nafion film-modified GCE. The positive shift of reduction peak potential and peak current enhancement indicate that MWNT has strong catalytic activity for the reduction of Pb^{2+}.

Because of its high sensitivity and excellent resolution, differential pulse voltammetry (DPV) is a perfect electrochemical method for trace level determination. So, the electrochemical response of a low concentration of Pb^{2+} at the unmodified GCE, Nafion film-modified GCE and MWNT/Nafion film-midified GCE was examined using DPV. After 2-min accumulation under −1.0 V, a negligible stripping peak is observed for 5.0×10^{-7} mol L^{-1} Pb^{2+} at the unmodified GCE (Fig. 3a). Under the identical conditions, an obvious stripping peak is observed at −0.62 V at the Nafion film-modified GCE (Fig. 3b). As above-mentioned, Nafion is a cation exchanger with high cation-exchange capacity. Therefore, Nafion film-modified GCE shows higher accumulation efficiency to Pb^{2+} and finally enhances the stripping current. However, the stripping peak current of Pb^{2+} increases remarkably at the MWNT/Nafion film-modified GCE (Fig. 3c), compared with that at the Nafion film-modified GCE. The MWNT/Nafion film-modified GCE not only possesses the cation exchange ability of Nafion but also exhibits the excellent properties of MWNT such as strong adsorptive ability, large surface area and catalytic ability. Without a doubt, the MWNT/Nafion film-modified GCE shows higher accumulation efficiency towards Pb^{2+}, greatly improving its stripping peak current. In brief, the MWNT/Nafion film-modified GCE notably improves the sensitivity of Pb^{2+} determination.

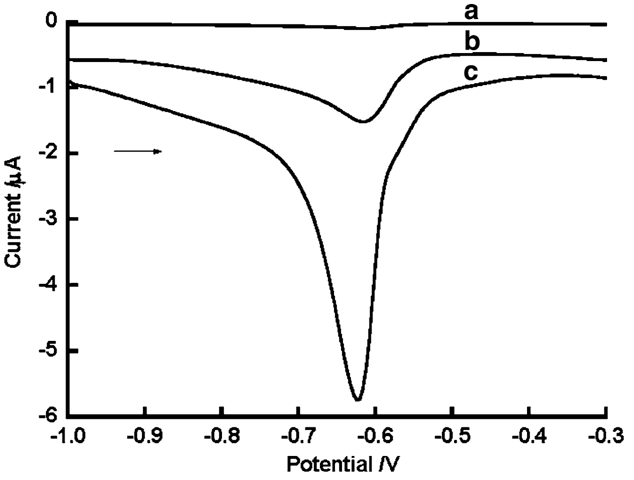

Fig. 3 Differential pulse voltammograms of 5.0×10^{-7} mol L^{-1} Pb^{2+} at (a) bare GCE, (b) Nafion film-coated GCE, (c) MWNT/Nafion film-coated GCE. Accumulation potential: −1.0 V, accumulation time: 2 min, pulse amplitude: 50 mV, pulse width: 50 ms, scan rate: 20 mV s^{-1}

3.3 Supporting electrolyte

In electrochemical determination, the choice of suitable supporting electrolyte is important since it not only influences the electrochemical response of the analyte but also affects the electrochemical activity of the working electrode. In this work, the anodic stripping response of Pb^{2+} in various supporting electrolytes, such as HCl, $HClO_4$, NaAc, KCl, Na_2SO_4, pH 3.5 ~ 5.6 NaAc–HAc buffer, pH 5.5 ~ 8.0 phosphate buffer (each 0.1 mol L^{-1}) was individually examined. It is found that the stripping peak current is highest and the peak shape is best defined in 0.1 mol L^{-1}, pH 5.0 NaAc–HAc buffer. Therefore, pH 5.0 NaAc–HAc buffer solution was employed for the determination of Pb^{2+}.

3.4 Influence of the volume of MWNT/Nafion suspension

From Fig. 3, it is well known that the MWNT/Nafion composite film can remarkably enhance the stripping peak current of Pb^{2+}. However, further studies show that the volume of MWNT/Nafion suspension used to modify the GCE also influences the stripping peak current as shown in Fig. 4. With increasing volume of MWNT/Nafion

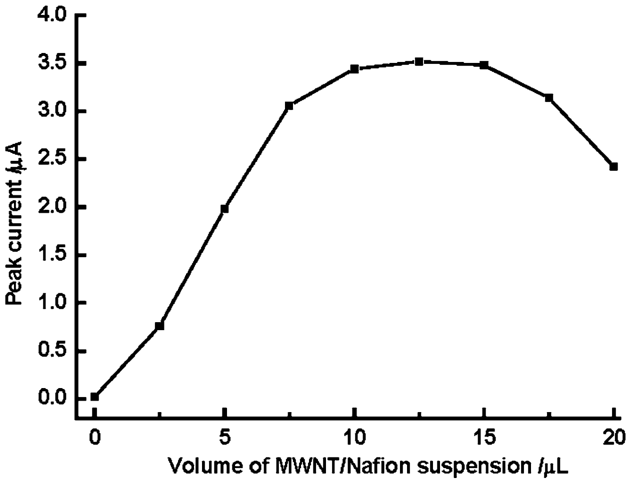

Fig. 4 Plot of stripping peak current of 5.0×10^{-7} mol L^{-1} Pb^{2+} as a function of the volume of MWNT/Nafion suspension

suspension, the stripping peak current of Pb^{2+} greatly increases at first, then changes slightly and finally decreases. When the volume of MWNT/Nafion suspension increases, the accumulation efficiency of MWNT/Nafion film-modified GCE to Pb^{2+} also increases, resulting in the peak current enhancement. However, Nafion is an insulator and lowers the electrical conductivity of MWNT/Nafion film-modified GCE. Therefore, the stripping peak current of Pb^{2+} decreases when the MWNT/Nafion film is too thick. In order to achieve high sensitivity, 10.0 μL of MWNT/Nafion suspension was used.

3.5 Effect of accumulation potential

Figure 5 depicts the effect of accumulation potential on the stripping peak current of Pb^{2+} after 2-min accumulation. When the accumulation potential shifts from −0.70 V to −1.00 V, the stripping peak current increases. However, the stripping peak current increases slightly when the accumulation potential is more negative than −1.00 V. Moreover, the background current begins to increase. Thus, the accumulation potential is located at −1.00 V to achieve better response.

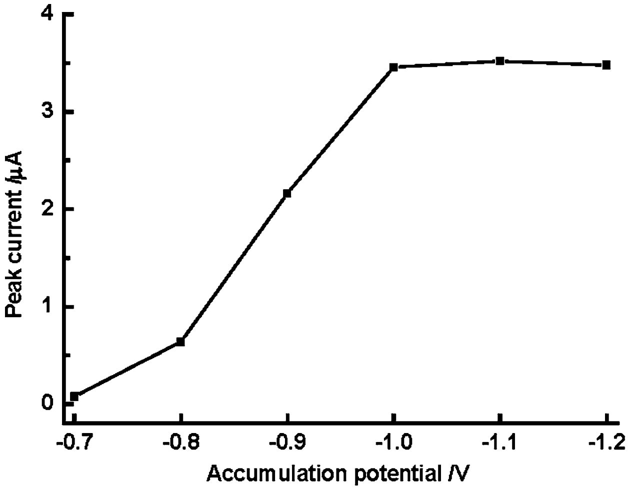

Fig. 5 Effect of accumulation potential on the stripping peak current of 5.0×10^{-7} mol L^{-1} Pb^{2+}

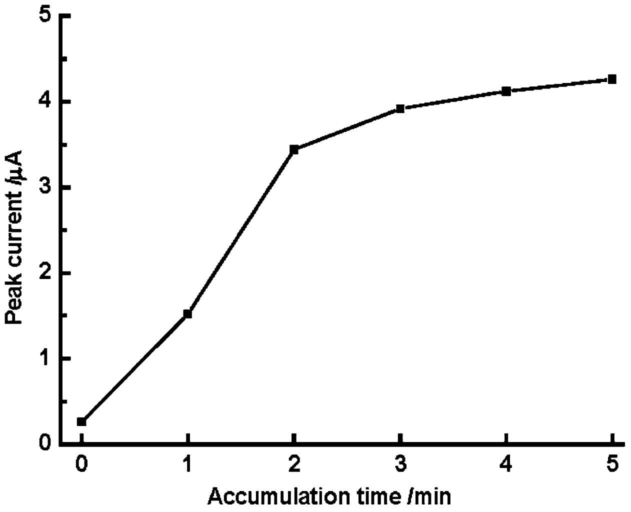

Fig. 6 Influence of accumulation time on the stripping peak current of 5.0×10^{-7} mol L^{-1} Pb^{2+}

3.6 Influence of accumulation time

The dependence of stripping peak current on the accumulation time was also studied (Fig. 6). With extended accumulation time an increasing amount of Pb^{2+} accumulated at the MWNT/Nafion film-modified GCE surface. Therefore, the stripping peak current of Pb^{2+} increases. In order to shorten analysis time and achieve higher sensitivity an accumulation time of 2 min was selected.

3.7 Interferences

The possible interferences of foreign species on the determination of Pb^{2+} were tested. It was found that 5.0×10^{-3} mol L^{-1} Ca^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Fe^{3+}, Al^{3+}, SCN^-, Cl^-, F^-, Br^-, SO_4^{2-}, NO_3^-, PO_4^{3-}; 1.0×10^{-4} mol L^{-1} Cd^{2+}, As^{3+}; 1.0×10^{-5} mol L^{-1} Cu^{2+} and Hg^{2+}, have no influence on the signal of 5.0×10^{-7} mol L^{-1} Pb^{2+} since the peak current change is below 6%.

3.8 Calibration curve

The relationship between the stripping peak current (i_p) and the concentration of Pb^{2+} (C) was studied by DPV. The i_p after 2-min accumulation is proportional to C over the range 8.0×10^{-8} to 6.0×10^{-6} mol L^{-1}, obeying the

Table 1 Determination of Pb^{2+} in wastewater samples

Water sample	By AAS (mol L^{-1})	By this method (mol L^{-1})	RSD (%)
A	4.17×10^{-7}	4.64×10^{-7}	5.3
B	1.98×10^{-7}	2.46×10^{-7}	5.5
C	5.36×10^{-7}	4.98×10^{-7}	5.4
D	1.06×10^{-7}	1.38×10^{-7}	5.6
E	8.64×10^{-8}	8.26×10^{-8}	5.7

equation: $i_p = 0.09 + 0.67 \times 10^7\ C$, $r = 0.996$, i_p in μA, C in mol L^{-1}. The lowest detectable concentration of Pb^{2+} is estimated to be 2.0×10^{-8} mol L^{-1} after 2-min accumulation. The lowest detectable concentration decreases further if the accumulation time is extended. For example, the lowest detectable concentration of Pb^{2+} for 6-min accumulation is as low as 5.0×10^{-9} mol L^{-1}.

Because of the high cationic-exchange capacity of Nafion and strong adsorptive ability of MWNT, the MWNT/Nafion film-modified GCE was used for single measurements. The reproducibility of multiple MWNT/Nafion film-modified GCEs was estimated by comparing the stripping peak current of 5.0×10^{-7} mol L^{-1} Pb^{2+}. The RSD is 6.3% for 10 MWNT/Nafion modified-GCEs, indicating good reproducibility.

3.9 Determination of Pb^{2+} in water samples

The newly developed method was employed to determine Pb^{2+} in wastewater samples to ascertain its potential application. 5.00 mL of the sample was added to 5.00 mL pH 5.0 Hac–NaAc buffer, and accumulated at −1.00 V for 2-min. Differential pulse anodic stripping voltammograms were recorded and the stripping peak current was measured for Pb^{2+}. The content of Pb^{2+} was detected using the standard addition method. Results are summarized in Table 1. Each sample was analysed in triplicate and the RSD was below 6%, suggesting good reproducibility. To test the accuracy of the method, atomic absorption spectrometry (AAS) was also used to determine Pb^{2+}. The results obtained by the two methods are in good agreement.

4 Conclusion

Based on the high cation exchange capacity of Nafion and the unique properties of MWNT such as catalytic activity, high surface area and strong adsorptive ability, a highly sensitive and rapid electrochemical method was proposed for the determination of Pb^{2+}, and was successfully used to determine Pb^{2+} in water samples.

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