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Lead (II) carbon paste electrode based on derivatized multi-walled carbon nanotubes: Application to lead content determination in environmental samples

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ABSTRACT

For the first time a novel derivatized multi-walled carbon nanotubes-based Pb^{2+} carbon paste electrode is reported. The electrode with optimum composition, exhibits an excellent Nernstian response to Pb^{2+} ion ranging from 5.9×10^{-10} to 1.0×10^{-2} M with a detection limit of 3.2×10^{-10} M and a slope of 29.5 ± 0.3 mV dec^{-1} over a wide pH range (2.5–6.5) with a fast response time (25 s) at 25 °C. Moreover, it also shows a high selectivity and a long life time (more than 3 months). Importantly, the response mechanism of the proposed electrode was investigated using AC impedance technique. Finally, the electrode was successfully applied for the determination of Pb^{2+} ion concentration in environmental samples, e.g. soils, waste waters, lead accumulator waste and black tea, and for potentiometric titration of sulfate anion.

1. Introduction

In comparison with membrane electrodes, carbon paste electrodes as ion selective electrodes have gained considerable attention mainly due to their advantages such as renewability, stable response, low ohmic resistance, no need for internal solution [1–8]. The introduction of a chemical modifier, which is able to preconcentrate metallic ions on the electrode surface by either complexation or electrostatic attraction, can lead to more sensitive electroanalytical procedures with lower detection limit values [9]. Recently, carbon nanotubes (CNTs) have been used in carbon paste electrodes [10,11] for fabricating electrochemical sensors and biosensors due to their special physicochemical properties, such as ordered structure with high surface-to-volume ratio, ultra-light weight, excellent mechanical strength, high electrical conductivity, high thermal conductivity and chemical performance. The combination of these characteristics make CNTs unique materials with the potential for diverse applications [12–20]. However, to date their derivates have not been tested as ionophores in potentiometric analysis.

At present, the importance of controlling the level of environmental pollutants in natural waterways, potable water and soils has generated increasing interest in the development of novel sensors for the detection of heavy metals such as lead ions. Lead is a highly toxic substance and is present in various products (e.g. accumulators, ammunitions, pipes, paints, anti-radiation screens and tin-based welding alloys). Moreover, lead is easily found in high concentrations in industrial wastewaters which can gradually seep into surface water bodies. Lead in environment is generally present as inorganic Pb^{2+} and it has toxic effect to human health, such as renal disease, cardiovascular effects and reproductive toxicity [21]. Thus, the increasing industrial use of lead and its serious effect on human health make it necessary and challengeable to develop methods for the determination of lead (II) in various environmental samples.

In recent years, a number of lead ion-selective electrodes have been reported [22–36]. But most of them possess narrow working concentration ranges and suffer serious interferences from various cations. In this study, we synthesized an L-grafted MWCNTS (L-g-MWCNTS) using 2-aminothiophenol (L) and carboxylic acid-functionalized multi-walled carbon nanotubes (MWCNT-COOH), and for the first time we fabricated a lead (II) carbon paste electrode based on this L-g-MWCNTS. MWCNTS have high surface-to-volume ratio and electrical conductivity, which can combine more 2-aminothiophenol. Meanwhile, L-g-MWCNTS contains strong covalent bonds (amino groups covalently attached to the solid framework via an amino-carbonyl chain). Due to the existence of hard N, O, S donor atoms and aromatic rings, it is expected to provide a much-needed hydrophobic environment and high complex stability. At the same time, the possible cation–π interactions could

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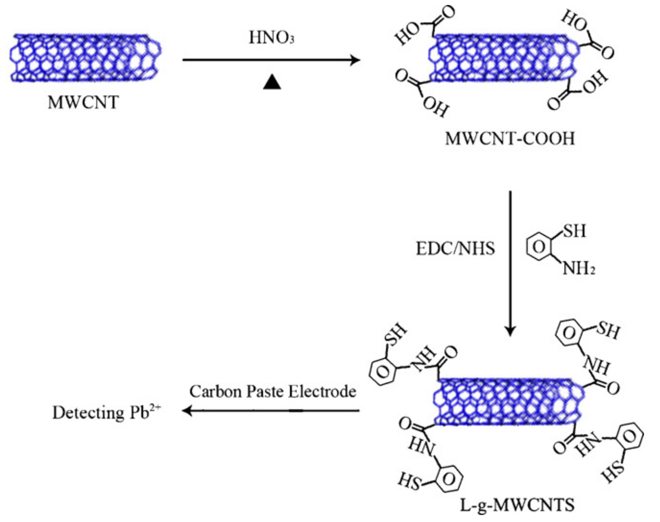

Fig. 1. Schematic representation of the synthetic procedure for L-g-MWCNTS.

have a marked influence on the coordination geometry at the metal center [37–39]. Thus, it can improve the selectivity and sensitivity of the sensor. The results reported in this paper show that we have overcome the limitations above and have largely improved the performance of the lead sensor, and it was successfully applied in the potentiometric titration of sulfate anion and the determination of Pb^{2+} ion concentration in environmental samples.

2. Experimental

2.1. Apparatus

Potentiometric measurements were performed with a MP230 pH meter (Metter Toledo, Switzerland) and a pHS-3C digital ion analyzer (Shanghai Dazhong Analytical Instruments, Shanghai, China). The AC impedance was recorded with an impedance measurement unit (IM6e, ZAHNER elektrick Co., Germany) and the frequency range used was 10^{-2}–10^{6} Hz (25 °C). A Model TAS-986 atomic absorption spectrophotometer (AAS) (Purkinje, Beijing, China) was used for the analysis of environmental samples.

2.2. Reagents

MWCNTs (purity > 95%, diameter within 10–20 nm) were purchased from Chengdu Organic Chemicals Co., Ltd. of the Chinese Academy of Science. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC), *N*-hydroxy succinimide (NHS) and 2-aminothiophenol (L) were purchased from Chongqing chemicals (Chongqing, China). The graphite powder with a 1–2 μm particle size (Sigma–Aldrich, America) along with the paraffin oil (Sigma–Aldrich, America) was of high purity and was used for the preparation of the carbon pastes. The nitrate and chloride salts of all the used cations (all from Chongqing, China) were of the highest purity available and used without any further purification. Double distilled water was used to prepare all aqueous solutions.

2.3. Synthesis of ionophore

Oxidation of MWCNTs (MWCNT-COOH) was performed as described previously [40–42]. For the preparation of 2-aminothiophenol grafted MWCNTs (L-g-MWCNTS) [43] (Fig. 1), the MWCNT-COOH (200 mg) was activated with excess EDC and NHS in ethanol and the mixture was stirred for 8 h at room temperature. In the next step, excess of 2-aminothiophenol was added to the mixture above and stirred at room temperature for 12 h. Then the L-g-MWCNTS was washed repeatedly with ethanol to remove unreacted 2-aminothiophenol. About 178 mg of the L-g-MWCNTS was obtained after drying under vacuum.

2.4. Carbon paste electrode preparation

The modified carbon paste electrodes were prepared as follows: different amounts of the ionophore L-g-MWCNTS along with appropriate amount of graphite powder and paraffin oil were thoroughly mixed. The paste was carefully packed into the end of a disposable polyethylene syringe 3 mm i.d. and 3 cm in length, the tip of which was cut off with arazor blade. A copper wire was inserted into the opposite end to establish electrical contact. The fresh electrode surface was polished with soft paper until the surface had a shiny appearance. A new surface was obtained by scraping out the old surface. The electrode was finally conditioned for 24 h in 1.0×10^{-3} M $Pb(NO_3)_2$ solution at pH 4.0 (adjusted with a 0.01 M HNO_3).

2.5. Potential measurements

The potential measurements were carried out using saturated calomel electrodes as reference electrodes with the following assembly:

$Hg–Hg_2Cl_2$, KCl (satd.) | test solution || carbon paste electrode || Cu.

A digital ion analyzer was used for the potential measurements at 25 °C. Activities were calculated according to the Debye–Hückel procedure [44].

3. Results and discussion

3.1. Composition and potential response characteristics of the carbon paste electrode

In preliminary experiments, variously carbon paste electrodes modified with L-g-MWCNTS were prepared and electrode No. 3 (Table 1) was used for the detection of different cations (Fig. 2A and B). As can be seen, among different tested cations, Pb^{2+} ion showed a Nernstian behavior and the most sensitive response over a wide concentration range. Meanwhile the slopes of the linear parts of the potential responses to other cations were much lower than those expected by the Nernst equation. Hence, L-g-MWCNTS was suitable to act as a selective carrier to construct a Pb^{2+} ion-selective electrode. It is well known that the sensitivity, selectivity and the linear range of an ion-selective electrode are significantly affected by the membrane composition. Thus, a number of carbon paste electrodes of different compositions based on L-g-MWCNTS were prepared and their potential responses to lead were determined and the results are summarized in Table 1. The results suggested that the electrode composed of 6.0 wt.% L-g-MWCNTS, 62.5 wt.% graphite powder and 31.5 wt.% Paraffin oil (No. 3) was found to be optimal for the Pb (II) detection (the data of the slope, detection limit and linear range of the electrode No. 1 were not given in Table 1. Because the electrode No. 1 without the carrier exhibited a very small response to Pb^{2+} ion, it is probably due to the sorption of a small amount of Pb^{2+} ions on the electrode surface, and the small response can be neglected). Thus, we selected the composition of the electrode No. 3 for the detection of Pb^{2+} in the following experiments.

3.2. Effect of pH on the response of the electrode

The effect of pH on the potentiometric response of the electrode was tested at two Pb^{2+} concentrations (1.0×10^{-2} and 1.0×10^{-4} M)