

Full Paper

Fabrication and Characterization of Carbon Nanotube-Hydroxyapatite Nanocomposite: Application to Anodic Stripping Voltammetric Determination of Cadmium

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Abstract

A novel chemically modified electrode for stripping determination of cadmium is presented in this paper, based on carbon nanotube-hydroxyapatite (CNT-HAP) nanocomposite, which can be prepared by an easy and effective one-step sonication. The newly synthesized nanocomposite was characterized with FTIR, TEM, and electrochemical methods. Due to the combination of the strong absorption ability of HAP and excellent electroanalytical properties of CNTs, the GC/CNT-HAP electrode has been successfully used for determination of Cd²⁺ by anodic stripping voltammetry with a linear range of 20 nM–3 μ M. The sensitivity and detection limit are 25.6 μ A/ μ M and 4 nM, respectively. The practical application of the proposed electrode has been carried out for the determination of trace levels of Cd²⁺ in real water samples.

Keywords: Carbon nanotube, Hydroxyapatite, Nanocomposite, Cadmium, Stripping analysis

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1. Introduction

Nowadays, the roles of trace heavy metals in nature environment and public health are widely recognized. The lack of these microelements in biological systems can cause many diseases and illnesses. On the other hand, the excess quantities of these elements can be toxic for a range of metabolic processes [1]. Among those heavy metals, cadmium (Cd) has been used extensively in industry for the production of pigments, anticorrosion coatings, plastics, alloys and batteries. Substantial amounts of Cd are continuously added to soil, water and air as a consequence of human pollution. Cd is of great toxicological interest due to its unusually long half-life and accumulation in soft tissues, chiefly in kidneys and liver. It has been shown to have a long resident time in the body making it essentially a cumulative poison or carcinogenic activity. For these reasons, the measurement of Cd is becoming more common in chemical, clinical and toxicology laboratories [2–7].

Anodic stripping voltammetry (ASV) is one of sensitive methods for the determination of trace heavy metal ions [8]. However, ordinary electrochemical solid electrodes such as glassy carbon, Pt, Au and graphite electrodes are not suitable for the determination of metal ions in ASV because of their poor sensitivity. One interesting approach to improve sensitivity is related to the use of novel chemically modified electrodes (CMEs). Many kinds of CMEs have been reported for determination of Cd [9–11]. In recent

years, bismuth film electrode has become an attractive new subject of electroanalytical investigations as a potential replacement for mercury and mercury film electrodes due to its environmentally friendly property and closest behavior to mercury, and been successfully applied to the detection of heavy metals including Cd [12–19]. However, bismuth 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 [20]. Thus, new alternative electrode materials are highly desired to meet the growing demands for on-site environmental monitoring of trace metals.

Since the discovery of carbon nanotubes (CNTs) [21], there has been enormous interest in exploring and exploiting their unique structural, electrical, mechanical, electro-mechanical and physical properties. Due to their significant mechanical strength, high surface area, excellent electrical conductivity, special size in nanometer and good chemical stability, CNTs have been applied to remove heavy metal ions from aqueous solution or determine the concentration of heavy metal as new material of chemically modified electrode [22–25]. Recently, many efforts have been focused on the design and preparation of nanocomposite based on CNTs in order to obtain new superior composite material that would be useful in particular applications [26]. The novel nanocomposite offers the possibility to produce three-dimensional nanostructured films that combine the functional organic or inorganic materials with the high

surface area and excellent conductivity of CNTs. Various types of nanocomposite based on CNTs, such as CNT-polymer and CNT-metals, have been reported [27–31].

Hydroxyapatite (HAP, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), a bioceramic material analogous to the mineral component of bone with great biocompatibility and particular multi-adsorbing sites, has recently been used as a promising adsorbent for divalent heavy metal ions [32–34]. Conventionally, HAP powders are synthesized by various methods including solid-state reactions, precipitation and hydrolysis of calcium phosphates and sol-gel. Lately, nanostructured HAP with a higher surface area have attracted much attention [35–39], and a few literatures about CNT-HAP nanocomposite have also been reported [40–43]. However, the synthesis procedures for the CNT-HAP nanocomposite are rather time-consuming and complex. More regrettably, the application of this nanocomposite in electroanalysis has not been exploited.

In this paper, a novel CNT-HAP nanocomposite has been prepared through an easy and effective one-step sonication synthesis, and the resulting nanocomposite can be used as a new chemically modified electrode material for stripping voltammetric analysis of trace amounts of Cd^{2+} . This is the first report on using CNT-HAP nanocomposite modified electrode for heavy metal detection by stripping voltammetry. The proposed electrode shows a wide linear range and high sensitivity. The experimental conditions related to the preparation and characteristic of the sensing system have been studied in detail.

2. Experimental

2.1. Reagents

Multi-walled carbon nanotubes with purity >95% synthesized by the chemical vapor deposition method were obtained from Shenzhen Nanotech Port (China) and acidic treatment according to the literature [44]. Stock solution of 0.01 M Cd^{2+} was prepared by dissolving $\text{Cd}(\text{NO}_3)_2$ (Shanghai Reagent Corporation, China) into deionized water, and then diluted to various concentrations of working solutions. Unless otherwise stated, 0.2 M HAc–NaAc buffer solution (pH 4.4) was used as the supporting electrolyte for Cd^{2+} determination. All other chemicals were analytical reagents and used without further purification. Deionized water (18.2 M Ω cm specific resistance) obtained with a Pall Cascada laboratory water system was used throughout.

2.2. Apparatus

The CNT-HAP adduct was pressed into a KBr pellet for FTIR investigation (FTIR-8400S, SHIMADZU, Japan) and loaded onto GC electrode for electrochemical study. All electrochemical experiments were carried out in a conventional three-electrode cell controlled by CHI 660C Electrochemical Work Station (CH Instruments, Inc). A platinum foil served as the counter electrode, and a saturated calomel

electrode (SCE) was used as the reference electrode. All potential values given below refer to SCE. All the electrochemical experiments were carried out at room temperature. The TEM micrograph was recorded using a JEOL-3010 transmission electron microscope (operating at 300 kV). A drop of the prepared CNT-HAP aqueous solutions was placed on carbon-coated copper grids and dried under ambient conditions. Atomic absorption spectrometric (AAS) measurements were conducted with an AA6300 atomic absorption spectrophotometer (SHIMADZU, Japan).

2.3. Preparation of CNT-HAP Nanocomposite

CNT-HAP nanocomposite was prepared by one-step sonication synthesis. Briefly, 0.8 mg of CNTs was dispersed in 25 mL of 0.1 M $\text{Ca}(\text{NO}_3)_2$ solution with the aid of ultrasonication for 20 min, and the pH value was adjusted with ammonia to 10–12. To this mixture, 15 mL of 0.1 M $(\text{NH}_4)_2\text{HPO}_4$ aqueous solution was added drop-wise at a rate of 2–4 mL/min with continuous sonication. As a result, the total molar ratio of Ca and P was equal to 1.67. The pH of the above solution was controlled at about 10–12 using ammonia during the course of $(\text{NH}_4)_2\text{HPO}_4$ addition. The mixture solution was then kept in continuous sonication for 1 h. The resulting liquid crystalline mixture was centrifuged, washed with water and dried at 100 °C in an oven [45]. For comparison, pure HAP was prepared in the same manner.

2.4. Preparation of GC/CNT-HAP Electrode

Before coating, GC electrode (3 mm in diameter) was polished with 0.3 and 0.05 μm alumina slurries, washed with deionized water and acetone thoroughly, and then sonicated in deionized water for 1 min. After that, 10 μL of 1 mg/mL CNT-HAP ethanol solution was added on the surface of GC electrode and dried under an infrared lamp to obtain the uniform modifying layer. For comparison, HAP-modified and CNT-modified GC electrodes were fabricated with the same procedure described previously.

2.5. Analytical Procedure

The analysis of Cd^{2+} has two main steps including accumulation and stripping out. Cd^{2+} ions were first reduced to Cd under -1.20 V for a desired time onto the CNT-HAP film. In the following step, the reduced Cd was oxidized at -0.84 V during the potential sweep from -1.10 to -0.65 V. The stripping peak current was measured for Cd^{2+} quantification. Prior to the next measurements, the modified electrode was activated at 0.6 V for 150 s in the supporting electrolyte to remove the previous deposit completely.

Quantitative determinations of Cd^{2+} were performed with differential pulse anodic stripping voltammetry. The optimal conditions were as follows: deposition potential of -1.2 V

with stirring; deposition time of 5 min; quiet time of 15 s; quiet potential of -1.2 V; amplitude of 0.05 V; pulse width of 0.05 s; sampling width of 0.0167 s; pulse period of 0.2 s.

3. Results and Discussion

3.1. Characterization of CNT-HAP Nanocomposite

The formation of CNT-HAP nanocomposite was identified by analyzing its FTIR spectrum. For CNT with acidic treatment (Fig. 1a), five characteristic peaks are observed at 1117 , 1641 , 2854 , 2923 and 3409 cm^{-1} . The peak around 3409 cm^{-1} is attributed to the hydroxyl group (ν_{OH}). This band may be due to both water and the hydroxyl functional groups resulting from the chemical treatment during the purification process. Bands around 2923 and 2854 cm^{-1} are due to asymmetric and symmetric stretching of C–H bonds [46]. The band around 1641 cm^{-1} can be attributed to carbonyl ($\nu_{\text{C=O}}$), while the band around 1117 cm^{-1} can be assigned to $\nu_{\text{C-O}}$ groups. The appearance of peaks at 1117 and 1641 cm^{-1} can verify the purification and function of CNT [46]. From the spectrum of HAP (Fig. 1b), the bands at 564 , 602 , 962 , and 1068 cm^{-1} are attributed to the stretching modes of phosphate group [40]. The split bands, mainly at 1027 and 1094 cm^{-1} , seem to be coincided with the formation of a well-crystallized apatite [37]. Carbonate

bands were detected at 1389 cm^{-1} . The presence of hydroxyl group in HAP gives rise to characteristic bands at 1637 and 3428 cm^{-1} . The spectrum of HAP from our experiment is coincided with the standard HAP FTIR spectrum [37]. Figure 1c illustrates that the CNT-HAP composite shows the spectrum similar to that of HAP, which implies that the existence of CNT in the synthesis of CNT-HAP composites does not change the formation and structure of HAP. However, the band corresponding to the formation of apatite becomes sharp and is observed at 1035 cm^{-1} , which indicates the formation of CNT-HAP composites [42].

Figure 2 shows the TEM images of CNT, HAP and CNT-HAP nanocomposite, respectively. From Figure 2a, the diameter of the random CNT is 50 – 100 nm. Figure 2b shows that HAP nanoparticles are quite uniform spindle-like structure with width of 20 – 25 nm and length of 50 – 100 nm. The formation of CNT-HAP nanocomposite is shown in Figure 2c. It can be seen that the spindle-like HAP nanoparticles bind to the surface of CNT, thus forming an attractive three-dimensional structure.

3.2. Electrochemical Behaviors of Cd^{2+} at CNT-HAP Nanocomposite Modified GC Electrode

Figure 3 illustrates the potential application of CNT-HAP film in the determination of trace levels of Cd^{2+} . A very small stripping peak was obtained for 0.5 μM Cd^{2+} at bare GC electrode after reduction at -1.20 V for 5 min (Fig. 3a). Under the comparable conditions, a larger stripping peak at -0.84 V for HAP modified electrode was observed (Fig. 3b). Because HAP has particular multi-adsorbing sites for Cd^{2+} and can attracts Cd^{2+} from bulk solution to electrode surface, the stripping peak current increases. For CNTs modified electrode (Fig. 3c), the oxidation peak of Cd^{2+} was also increased but appeared at -0.87 V. With acidic treatment of CNTs, some oxygenous groups, such as carboxyl, carbonyl and hydroxyl, could be formed at the ends and defect sites on the surface of the CNTs. These functional groups can complex with Cd^{2+} for chemical adsorption [47–49], which results in the accumulation of Cd^{2+} and the increase of the stripping peak current. The highest peak at -0.84 V was obtained with CNT-HAP nanocomposite modified electrode (Fig. 3d). Additionally, the stripping peak currents of Cd^{2+} at bare GC, HAP-, CNT- and CNT-HAP modified electrodes are 0.83 , 1.24 , 1.66 , 9.01 μA , respectively, indicating that the current response obtained with the CNT-HAP modified GC electrode was increased by nearly 11-fold as compared to that with the bare GC electrode. More importantly, the peak current at CNT-HAP modified electrode is larger than the sum of that at CNTs and HAP modified electrode alone, i.e., $i_{\text{CNT-HAP}} > i_{\text{CNT}} + i_{\text{HAP}}$, indicating the synergetic effect of bifunctionality of CNTs and HAP. Such bifunctional properties of CNT-HAP nanocomposite include high specific surface areas, particular multi-adsorbing sites, uniform and tailored nano-structure and excellent electrochemical properties. Since the electrodeposition of Cd is carried out at a substantially

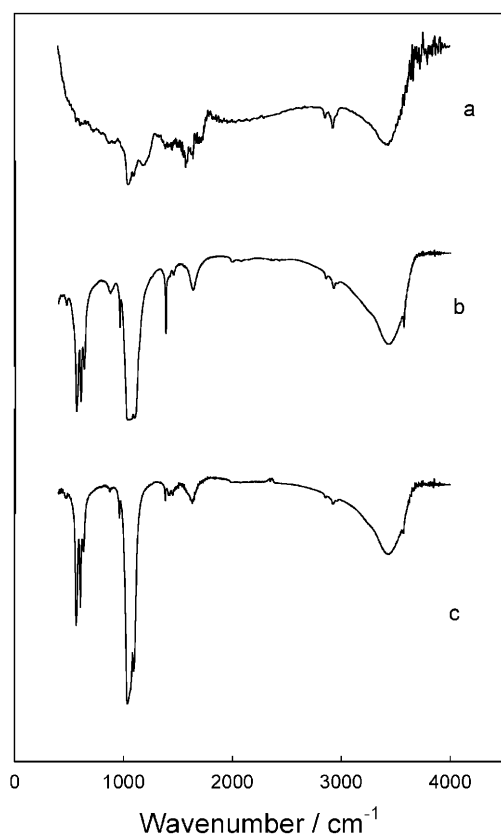


Fig. 1. FTIR spectra of a) CNT, b) HAP, and c) CNT-HAP nanocomposites.

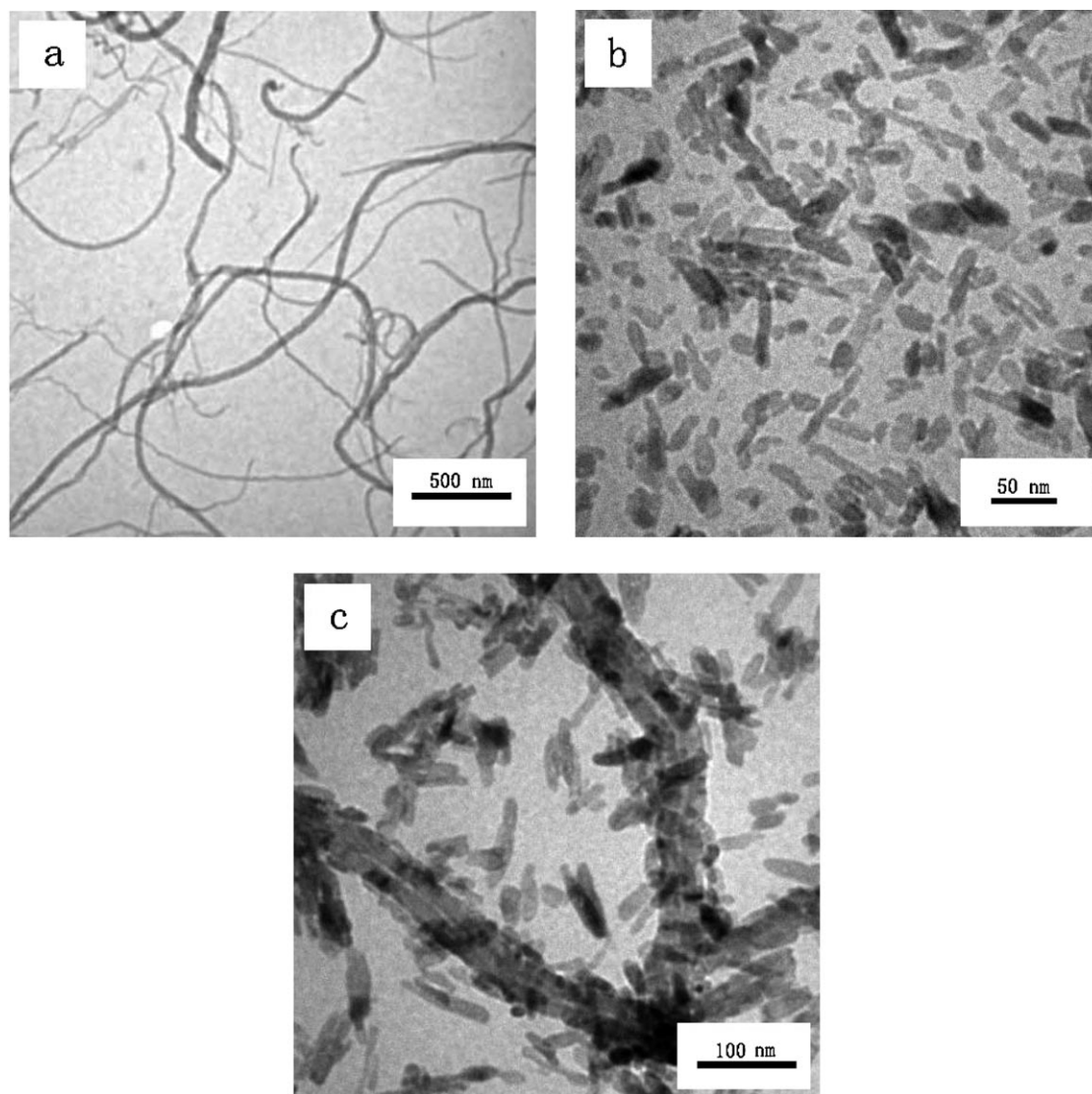
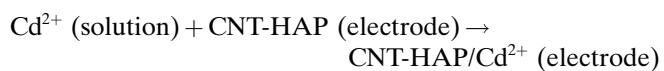


Fig. 2. TEM images of a) CNT, b) HAP, and c) CNT-HAP nanocomposites.

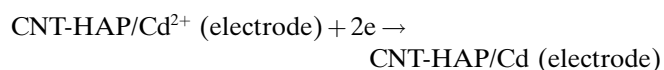
negative potential in all cases (-1.2 V), its electrochemical accumulation of Cd from the solution phase and onto the modified electrode is carried out under mass transfer control. The surface area of the modified electrode and its adsorption affinity for Cd^{2+} would affect the stripping efficiency. Indeed, higher surface area of the CNT-HAP modified layer would lead to thinner or well dispersed deposits having a better adherence and able to support a higher and stable metal loading, while higher adsorption affinity of the nanocomposite could promote the accumulation of the analyte ion with simultaneous reduction.

The mechanism of the electrochemical behavior of Cd^{2+} at the CNT-HAP modified electrode can be described as the following steps:

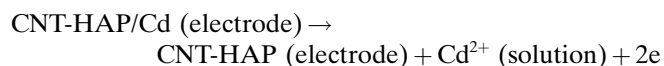
1. Adsorption:



2. Electrodeposition:



3. Stripping:



In the present experiments, since Cd^{2+} ions are accumulated by applying a cathodic potential during adsorption with CNT-HAP nanocomposite, step 1 occurs concurrently with step 2. The advantages of depositing metal simultaneously with adsorption include that the analysis becomes a two step process (adsorption/reduction and stripping) as in conventional ASV, and the deposition time and the overall time are shortened [50].

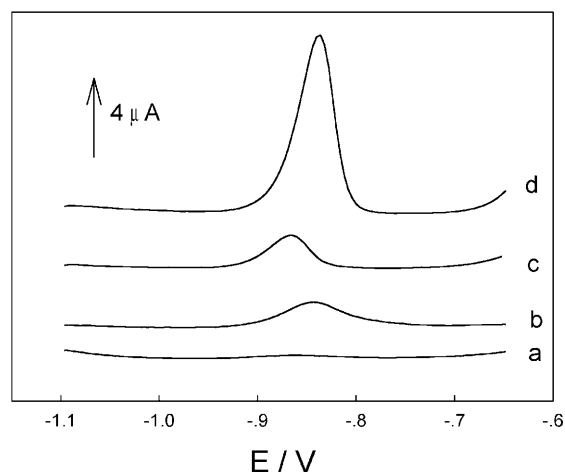


Fig. 3. Anodic stripping differential pulse voltammograms of a) bare GC, b) HAP-modified, c) CNT-modified, and d) CNT-HAP nanocomposites modified GC electrodes in 0.2 M HAc-NaAc buffer (pH 4.4) containing $0.5 \mu\text{M Cd}^{2+}$: accumulation potential, -1.2 V ; accumulation time, 5 min; pulse amplitude, 50 mV; scan rate, 20 mV/s; pulse width, 50 ms.

3.3. Optimization for Measurement of Cd^{2+} at GC/CNT-HAP Electrode

3.3.1. Effect of Volume of the CNT-HAP Suspension

The voltammetric response of Cd^{2+} is dependent on the thickness of CNT-HAP film, which is determined by the volume of CNT-HAP ethanol suspension added onto the GC electrode surface. The relationship between the volume of CNT-HAP ethanol suspension and the stripping peak current was investigated and the corresponding results are shown in Figure 4a. The stripping peak current gradually increases with the volume of CNT-HAP suspension until $10.0 \mu\text{L}$, which is due to the increase of the active sites for Cd^{2+} accumulation onto the GC electrode surface. However, further increase of the volume of CNT-HAP suspension can result in the decrease of the peak current. Indeed, with thicker films of CNT-HAP, the mass transport might conversely decrease, while ohmic losses through a three-dimensional electrode coating with CNT-HAP material could increase. Therefore, the optimized amount of CNT-HAP suspension is chosen as $10.0 \mu\text{L}$.

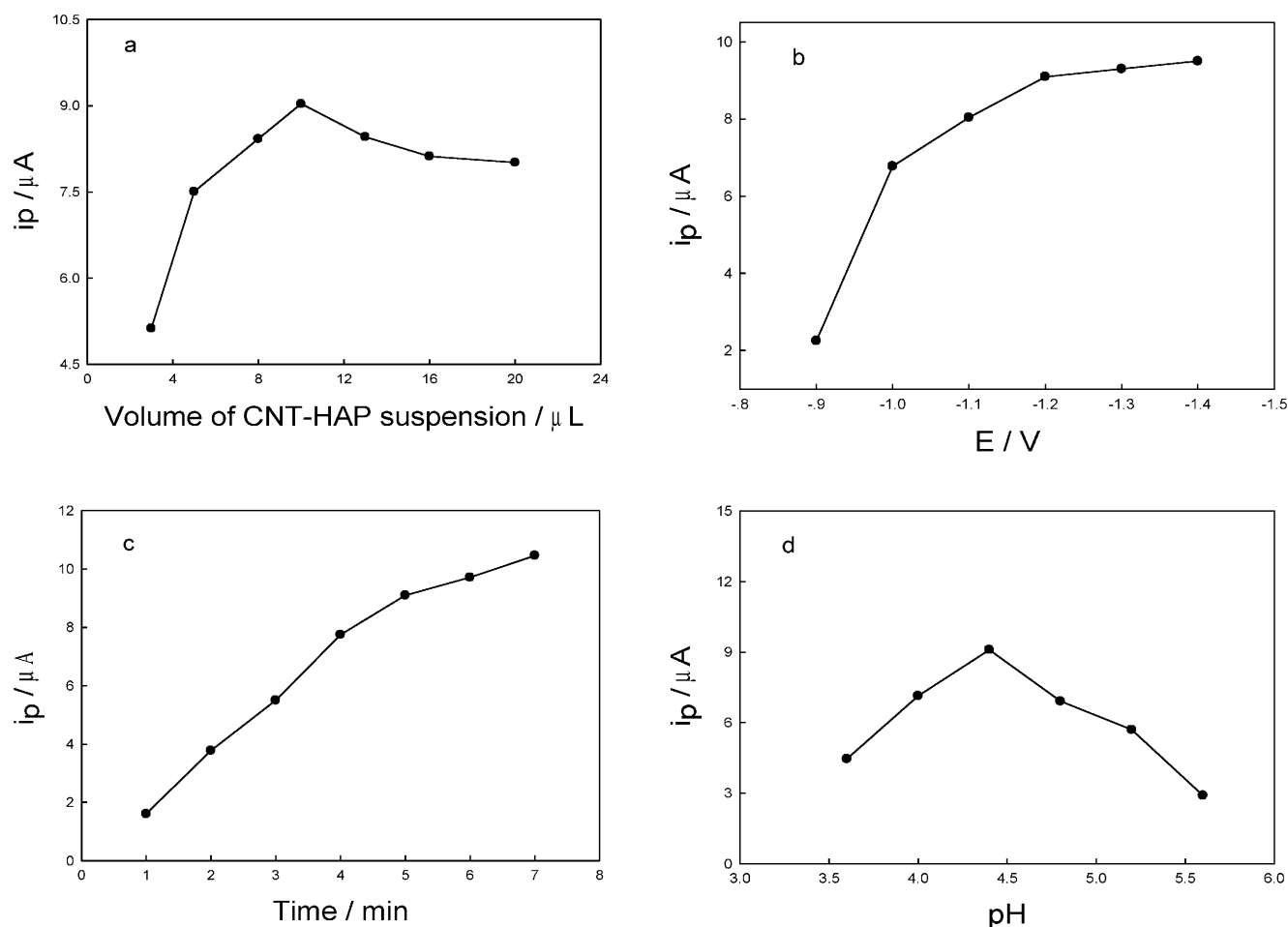


Fig. 4. Effect of a) volume of CNT-HAP suspension (1 mg/mL), b) accumulation potential, c) accumulation time, and d) pH value of buffer solution on the stripping peak current of $0.5 \mu\text{M Cd}^{2+}$. Other conditions are the same as in Figure 3.

3.3.2. Effect of Accumulation Potential

Figure 4b depicts the effect of the accumulation potential on the stripping peak currents with 5 min deposition. When the deposition potential shifted from -0.9 to -1.2 V, the stripping peak currents increased greatly, which is due to the fact that Cd^{2+} can be reduced more efficiently at more negative deposition potentials. Experiments also showed that further negative shift of the accumulation potential could not increase obviously the peak current but cause a relatively higher background current, which is mainly attributed to the cohydrogen evolution at such negative potentials. So, -1.2 V was used in the following experiments.

3.3.3. Effect of Accumulation Time

The sensitivity of the proposed method for detection of Cd^{2+} was undoubtedly promoted with the increase of the accumulation time because of the increased amount of Cd on the GC/CNT-HAP electrode. However, this tendency would not be prolonged all through due to the limited active sites for Cd accumulation. The response of the GC/CNT-HAP electrode to $0.5 \mu\text{M}$ Cd^{2+} increased rapidly with the accumulation time up to 5 min, and then tended to increase slowly, as shown in Figure 4c. Though increasing the accumulation time improves the sensitivity, it also lowers the upper detection limit due to the rapid surface saturation at high Cd concentrations [30]. Therefore, to achieve lower detection limit and wider response range, 5 min was chosen as the accumulation time for the following experiments.

3.3.4. Effect of pH Value of the Buffer Solution

Buffer solution has the ability to fix pH value and ionic strength. In the practical analysis, buffer solution, therefore, was widely employed as supporting electrolyte. The pH value of the accumulation solution was found to exert a significant but predictable effect on the accumulation process. Figure 4d shows pH dependency of the stripping current of metal ions in 0.2 M NaAc-HAc buffer solutions in the pH range of 3.6–5.6. In this case, the chemical deposition was done in $0.5 \mu\text{M}$ Cd^{2+} solution for 5 min at -1.2 V. The current response was strongly influenced by the pH value of the deposition solution. From pH 3.6 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 CNT-HAP and fewer protons are competed with Cd^{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 [51]. Therefore, a moderately acidic environment is important for the detection of the divalent heavy metal Cd^{2+} . In this work,

0.2 M NaAc-HAc buffer solution of pH 4.4 was chosen as the supporting electrolyte.

3.4. Calibration Curve

The calibration curve of the Cd^{2+} sensor was derived from the differential pulse stripping voltammetry curves obtained at the GC/CNT-HAP electrode with a 5-min accumulation period (Fig. 5). The stripping peak current (i_p) is proportional to the concentration of Cd^{2+} from 20 nM to $3 \mu\text{M}$ ($i_p = 25.55C + 0.12$, $r = 0.995$, i_p in μA , C in μM). The sensitivity of the GC/CNT-HAP electrode to Cd^{2+} is $25.6 \mu\text{A}/\mu\text{M}$. The detection limit was given by the equation $C_L = 3s_{bl}/S$, where s_{bl} is the standard deviation of the blank measurements and S is the sensitivity of the calibration graph. The detection limit of Cd^{2+} for 5-min accumulation was calculated to be 4 nM . The relative standard deviations for 80 nM Cd^{2+} were found to be 6.2% for one electrode with five measurements and 8.5% for five electrodes prepared with identical procedures. The response characteristics of the proposed method were compared with those reported in the literature and the results are shown in Table 1. It can be seen that the proposed GC/CNT-HAP electrode system has a wider linear dynamic range, lower detection limit and larger sensitivity than most of other methods for voltammetric stripping determination of Cd^{2+} .

3.5. Study of Interferences

The interference of several common metal ions (Pb^{2+} , Cu^{2+} , Hg^{2+}) to the detection of Cd^{2+} was investigated and the results are shown in Figure 6. When GC/CNT-HAP electrode was immersed in a mixture of Cd^{2+} , Pb^{2+} , Cu^{2+} and Hg^{2+} at the same concentration of $0.5 \mu\text{M}$ (solid line), the oxidation signal attributed to Cd^{2+} at -0.79 V was observed,

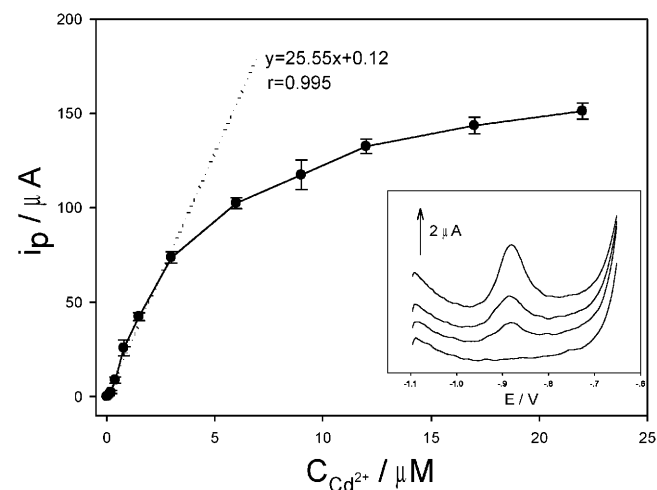


Fig. 5. Calibration curves of Cd^{2+} on the CNT-HAP nanocomposites modified GC electrode ($n = 3$). The values for the inset curves are 0, 20, 50, and 100 nM from bottom to top, which are in the linear range. Other conditions are the same as in Figure 3.

Table 1. Comparisons of response characteristic of the present work with other studies.

Detection limit (nM)	Linear range (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}$)	References
20	0.031–310	NR [a]	[4]
9.8	0.20–3.2	NR	[5]
20	0.18–1.8	NR	[6]
6.0	0.018–0.11	20.3	[16]
4.0	0.040–4.0	6.2	[22]
6.0	0.025–10	15.1	[23]
2.2	0.044–0.89	15.6	[30]
500	0.70–5.6	NR	[32]
40	0.25–25	NR	[52]
100	0.56–35	2.83	[53]
9.8	0.089–0.71	9.24	[54]
4.0	0.020–3.0	25.6	Present work

[a] NR means not reported

while the oxidations of Pb^{2+} , Cu^{2+} and Hg^{2+} occurred at -0.57 , -0.24 , -0.13 V, respectively. This implies that the proposed electrode could be used for simultaneous detection of several heavy metals including Cu^{2+} and Hg^{2+} , which can not be determined by bismuth film electrode due to the oxidation of bismuth at higher stripping potentials. The positive change of peak position of Cd (from -0.84 V to -0.79 V) indicates the interference of the co-existing metal ions. The simultaneous detection of several other trace elements was done in the presence of mercury, which may result in the in-situ formed mercury film. Another supplemental experiment was carried out in the mixture solution without mercury present (dotted line). Indeed, well resolved stripping peaks were obtained in the absence of mercury. In spite of the interaction of other metals with the CNT-HAP film, their oxidation peaks can be obviously observed and the peak potentials are far from that of Cd^{2+} . The peak

potential difference between Cd^{2+} and Pb^{2+} is at least 220 mV.

On the other hand, tests were done by analyzing a standard solution ($0.5 \mu\text{M}$ Cd^{2+}) to which amounts of interfering metals were added under the optimal experiment conditions, and the corresponding results were shown in Table 2. Experiments showed that more than a 1000-fold excess of Na^+ , K^+ , Ca^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Mg^{2+} , Al^{3+} , Cl^- , NO_3^- , H_2PO_4^- , and SO_4^{2-} , less than a 100-fold excess of Pb^{2+} , 3-fold Cu^{2+} and 2-fold Hg^{2+} had no influence on the signal of $0.5 \mu\text{M}$ Cd^{2+} . However, 300-fold Pb^{2+} could decrease 50% of the peak current of Cd^{2+} , which might be due to the fact that many available deposition and/or adsorption sites could be occupied by Pb^{2+} at high concentrations. 10-fold Cu^{2+} was found to completely suppress the peak current probably due to the formation of the intermetallic compound between copper and cadmium deposited in the electrode. 10-fold Hg^{2+} heavily interfered with the measurement of Cd^{2+} due to the formation of mercury film at the modified electrode surface, which causes Cd^{2+} to be reduced more easily and increases the stripping peak current due to the formation of amalgam consequently. In addition, 100-fold I^- dramatically increased the peak current, which is due to the fact that I^- could induce Cd^{2+} to adsorb at the electrode surface [23]. However, experiments showed that the effect of interferences for real samples analysis can be eliminated effectively by using the standard addition method (see below).

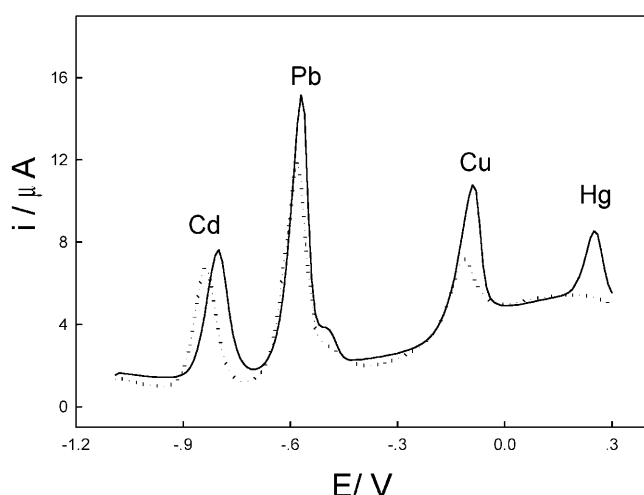


Fig. 6. Anodic stripping differential pulse voltammograms of the GC/CNT-HAP electrode in 0.2 M HAc-NaAc buffer (pH 4.4) containing Cd^{2+} , Pb^{2+} , Cu^{2+} and Hg^{2+} (solid line) or Cd^{2+} , Pb^{2+} , and Cu^{2+} (dotted line) at the same concentration of $0.5 \mu\text{M}$. Other conditions are the same as in Figure 3.

Table 2. Interferences of ions on the stripping peak current of $0.5 \mu\text{M}$ Cd^{2+} at GC/CNT-HAP electrode.

Ions	Tolerance level (μM) [a]
Na^+ , K^+ , Ca^{2+} , Zn^{2+} , Mn^{2+} , Co^{2+} , Mg^{2+} , Al^{3+}	500
Cl^- , NO_3^- , H_2PO_4^- , SO_4^{2-}	500
Pb^{2+}	50
I^-	5
Cu^{2+}	1.5
Hg^{2+}	1.0

[a] For 6% error.

Table 3. Comparison of GC/CNTs-HAP electrode and AAS for determination of Cd²⁺ in real water samples.

Sample	Detected by GC/CNT-HAP electrode (μM) [a]	Detected by AAS (μM)	Bias (μM)
Tap water 1	0.128 ± 0.003	0.172	−0.044
Tap water 2	0.112 ± 0.003	0.173	−0.061
lake water 1	0.113 ± 0.005	0.091	+0.022
lake water 2	0.352 ± 0.011	0.384	−0.032
lake water 3	0.507 ± 0.018	0.563	−0.056

[a] Average value of three determinations ± standard deviation.

3.6. Practical Application of GC/CNT-HAP Electrode

The GC/CNT-HAP electrode exhibits high sensitivity and good selectivity for the determination of Cd²⁺ under the optimum experimental conditions. In order to illustrate its accuracy in practical analysis, the comparison between the proposed GC/CNT-HAP electrode and atomic absorption spectrometry (AAS) for detection of Cd²⁺ in real samples was carried out. Several different types of lake water and tap water samples were filtered through a standard 0.45 μm filter and analyzed by the standard addition method. The results are shown in Table 3. It can be seen that the GC/CNT-HAP electrode indeed has a great potential for real sample analysis with a high accuracy and good reliability.

4. Conclusions

By combining the strong adsorption capacity of HAP with the unique properties of CNTs (the ability to facilitate electron transfer and huge specific surface area), CNT-HAP nanocomposite has been developed as novel chemically modified electrode materials for sensitive determination of Cd²⁺. Compared with the bare GC, HAP- and CNT-modified electrode, the proposed CNT-HAP nanocomposite modified GC electrode significantly enhances the sensitivity for Cd²⁺. The CNT-HAP nanocomposite has attractive properties including wide potential window, excellent chemical stability and unique three-dimensional structures, which can be used as a new alternative electrode material to provide an excellent platform for electroanalysis of heavy metal ions.

5. Acknowledgements

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6. References

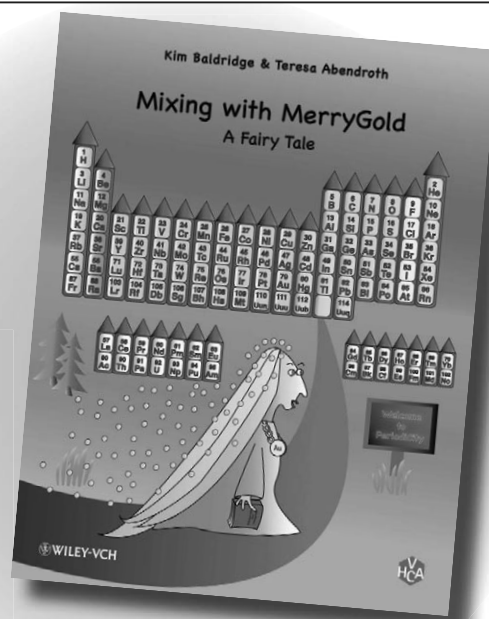
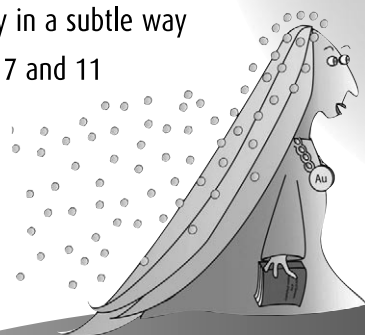
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