A Novel of Multi-wall Carbon Nanotubes/Chitosan Electrochemical Sensor for Determination of Cupric ion

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Abstract. A multi-wall carbon nanotubes/Chitosan electrochemical sensor had been fabricated by dropping CHS/MWNT solution directly onto the GC surface. The sensor was charactered by cyclic voltammetry and AC impedance with $K_3Fe(CN)_6$ as a electrochemical probe; Cyclic voltammograms(CV) and electrochemical impedance spectroscopy(EIS) indicated that the active area and electrochemical behavior of the sensor increased and improved significantly after the electrode was modified by carbon nanotubes dispersed by the chitosan. The sensor showed good electrocatalytic activity of $K_3Fe(CN)_6$. Also, from the cyclic voltammograms, we can see the process was diffusion controlled on the bare electrode and kinetics and diffusion controlled on the modified electrode. Finally Cu^{2+} responsed sensitively at the sensor which supplied a new method for the detection of Cu^{2+}.

1. Introduction

Electrochemical reaction is uaually happened in the vicinity of the electrode surface, so as to make the reactions occur with full efficiency, the electrode surface properties are very important factors to be considered. Due to the types of electrode materials restricting , how to improve the performance of the existing electrode and to give it desired properties will become a new field for electrochemical researchers. So, people have to look toward how to use chemical methods to modify the electrode surface.

In resent years, Multi-walled carbon nanotubes（MWNT）as new kind of nanomaterial, which are more surface reactive than the other graphite variantshave [1-4]. Electron transport is faster on MWNT as its pipe structural wall. MWNT can effectively reduces the overpotential of some reaction because its walls are more easily decorated with functional groups[5-8]. Multi-walled carbon nanotubes show functional porous three-dimensional network structure, which have effect of trapping on analysis material[9,10]. The peak current of the analytical material on the MWNT modified electrode is significantly increased[11,12].

The research of carbon nanotube modified electrode has been taken seriously[13–14]. However, because carbon nanotubes have a strong inter-tube van der Waals force and are easy to aggregate, they can`t dissolve in water and common organic solvents. They are very difficult to be directly used for modifying electrode.

Chitosan (CHS) with good dispersion and water-soluble can adsorb metal ions and non-metallic material for it has both hydrophilic and hydrophobic groups.

In this work, CHS which worked as a dispersant of MWNT and MWNT were used to modified glassy carbon electrode (CHS/MWNT/GCE) by dropping solution directly on the surface of GCE.

This method overcome the deficiencies that carbon nanotubes were difficult to modify the electrodes and improved the electrochemical activity of the GCE. The electrochemical behavior of the CHS/MWNT/GCE were investigated by cyclic voltammograms(CV) and electrochemical impedance spectroscopy(EIS).

2.   Materials and methods

2.1. Reagentswith
Chitosan was bought from the Shanghai reagent co., China, its deacetylation degrees was 91%. The MWNT (diameter:10–20nm, length: 10–30μm) was bought from Chengdu Organic Chemistry Co. Ltd. CAS (Chengdu, China) and used after oxidation. Glassy carbon electrode was bought from Shanghai Leici Co. Ltd.

2.2. Apparatus
Electrochemical tests were used to be a PARSTAT2273 electrochemical workstation (USA). CHS/MWMWNT/GCE as working electrode, reference electrode was saturated calomel electrode, and auxiliary electrode was platinum electrode. The frequency range of alternating-current impedance meas urement is 100 kHz to 10 mHz. The measurement electrolyte is KCl solution(0.1 mol/L).All tests were conducted at 25°C.

2.3. Preparation of Electrochemical Sensor
5.00 g MWNT (mass fraction > 95%) in nitric acid with reflux reaction for 5 hours. The pretreated MWNT was prepared by cooling, washed with deionized water, filtration, drying at 100 ℃.

The surface of glassy carbon electrode (GCE, Φ=3 mm) was polished to a mirro in 0.3μm, 0.05μm Al_2O_3 powders, then washed with distilled water. Ultrasonic cleaning with nitric acid solution, ethanol and distilled wate for 5 min. The cleaned electrode was inserted in 0.5 mol/L H_2SO_4 solution, and the performed potential range of cyclic scanning activation treatment was -1.0V to 1.0 V. The peak potential difference of the cyclic voltammetry is below 80 mV.

0.05 g chitosan were dissolved in 10 mL acetic acid(1%), then 3 mg MWNT were dispersed in 5mL chitosan solutions. The uniform black suspension is prepared After the ultrasonic oscillation. 4 μL MWNT suspension droplets onto a glass carbon electrode by microsyringe, drying used by infrared light. Then washing three times with distilled water.

3.   Results and discussion

3.1. Cyclic voltammetry
The capacity of CHS/MWNT/GCE to the electrocatalytic oxidation of $K_3Fe(CN)_6$ was investigated by CV. Figure 4 shows cyclic voltammetry at activated bare glassy carbon electrode, carbon nanotubes modified electrodes(MWNT/GCE)and CHS/MWNT/GCE in the presence of 1mM $K_3Fe(CN)_6$.
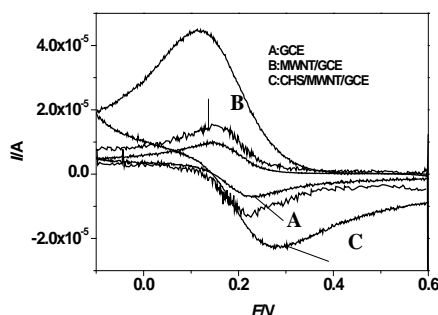

Figure 1 CV Curve of different modified electrodes in 1mmol/L $K_3Fe(CN)_6$, scan rate: 50 mV/s GC(A), MWNT/GCE(B), CHS/MWNT/GCE (C)

From figure 1 we can see, by modifying the mixture of chitosan and carbon nanotubes to the electrode, its electrochemical performance has been improved, response current of $K_3Fe(CN)_6$ at Chitosan/ carbon nanotubes modified electrode increased significantly than the bare electrode and carbon nanotube modified electrode which indicated that chitosan played a good role at dispersing carbon nanotubes.

This is due to reactive group after activation of MWMWNT. The unique electronic properties and surface microstructure of MWMWNT and chitosan`s good dispersion to carbon nanotubes is beneficial to catalytic or promote electron transfer reaction of potassium ferricyanide, electron transfer rate was greatly improved too.

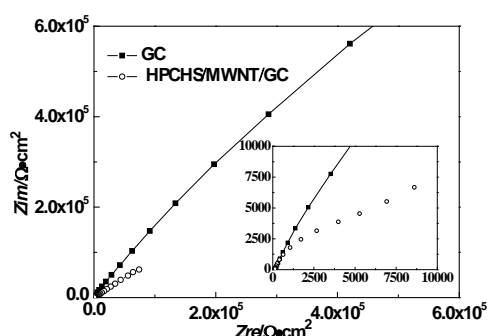*3.2. Electrochemical impedance spectroscopy(EIS)*

Figure 2 Nyquist plots of GCE and CHS/MWNT/GCE in 1mM $K_3Fe(CN)_6$

As we can see, EIS(Figure 2) of bare electrode was almost a straight line, due to the bare electrode is only commanded by diffusion. CHS/MWNT/GCE showed semicircle in high frequency area, linear low-frequency area, the characteristics of this modified electrode showed that the electrode process was affected by the joint of dynamics and diffusion. capacitance arc of high-frequency in the figure was not rule semi-circular, but the flattening of the capacitance arc, the equivalent capacitance deviate compared with the pure capacitance ,that was the dispersion effect. It also shows the size of dispersion effect.

3.3. Cyclic voltammetry behavior of Cu^{2+} at different electrodes

Figure 3 showed cyclic voltammetry of Cu^{2+} in the GCE (A) and MWNT/GCE, CHS/GCE, CHS/MWNT/GCE (B, C, D).We can see by the chart, at GCE there was no stripping peak visible. However With the MWNT/GCE, CHS/GCE, CHS/MWNT/GCE as working electrode, a sensitive stripping peak appeared in 0mV. The peak current increased significantly, indicating MWNT and CHS has obvious enrichment on Cu^{2+}. The mechanism may be Cu^{2+} is first adsorbed to the electrode surface, at the accumulation potential of Cu^{2+} is reduced to copper, in the process of potential changes copper was oxidized and dissolution.
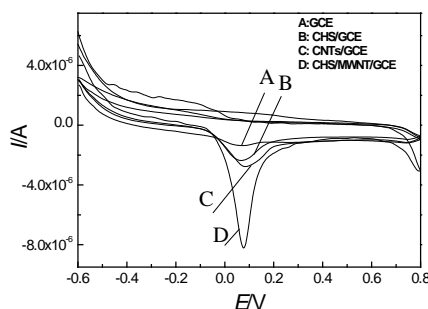

Figure 3 Cyclic voltammetric grams of Cu^{2+} (2.5×10^{-4}mol/L)at GCE and MWNT/GCE, CHS/GCE, CHS/MWNT/GCE
Scan rate: 50mV.s^{-1}. Supporting electrolyte: NaAc-HAc(0.1 M, pH 4.54).

3.4. Effect of electrolyte and acidity.

The effect of 0.1 mol/L of different supporting electrolyte such as KNO_3, H_2SO_4, HAc-NaAc buffer solution on the peak current of Cu^{2+} was investigated. The result showed in acetate buffer (HAc-NaAc), peak current of Cu^{2+} was highest, the background current was small and the peak shape was best. The acetate buffer was selected and used in following experiment.

The effect of acidity for peak current of Cu^{2+} on the CHS/MWNT/GCE was studied. In the CV curve, the changes of the peak current of Cu^{2+} in the sodium acetate buffer solution were investigated under different pH values (3.92 ~ 5.50) （Fig.4）. In Fig.4, the peak current increases of Cu^{2+} with the increase of pH. Peak current reaches the maximum, when the pH is 4.54. and then peak current decreases with the increase of pH, as pH was 4.54-5.50. so the pH value of 4.54 was selectd and used, and the detection of Cu^{2+} has high electrochemical response at pH 4.54.
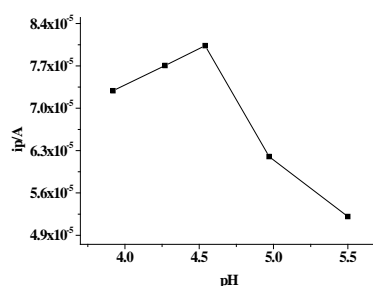

Figure 4 Efect of pH on the peak current of Cu^{2+}

3.5. Effect of accumulation potential and time

Fixed the concentration of Cu^{2+} at 2.5×10^{-4}, the affect of accumulation potential on electrochemical property was investigated in the -200 ～ -1000 mV(Fig.5.). In Fig.5, the peak potential of Cu^{2+} increased with the negative shift of accumulation potential, when accumulation potential was -1000mv, peak current was not increased, and side effects occured. So -800 mV was chosen as the accumulation potential.

Fixed concentration of Cu^{2+} at 2.5×10^{-4} mol/L, accumulation potential for 800 mV, changed the accumulation time. The experiment result indicates with the accumulation time, the stripping peak current increased, as accumulation time was 400s or less, peak current of Cu^{2+} was linear with accumulation time; and then the peak current was basically unchanged indicating the enrichment of Cu^{2+} saturated. So we chose accumulation time was 400s.
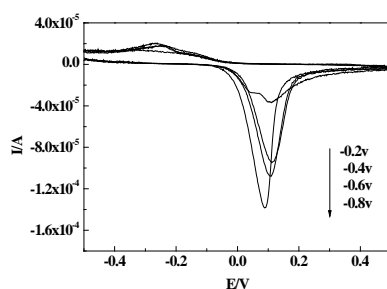

Figure 5 CV of Cu^{2+} at modified electrode of different accumulation potentials

3.6. detection experiment

The copper standard solution was diluted into a series of standard working solutions, and the standard curve was measured in optimum experimental conditions. the results showed that concentration of Cu^{2+} is in linear relation with the peak current in concentration range from 10 to 25μmol/L, and the linear equation is I(A)=-3.02 + 88367.27 c(mol/L) (R = 0.9972). The detection limit of Cu^{2+} was 1.0×10^{-7} mol/L.

3.7. Reproducibility

The Cu^{2+} solution of 2.0 x 10^{-5} mol/L was measured 10 times under the same condition. The relative standard deviation(RSD) is 2.1%. Compared with five days ago, the peak current of Cu^{2+} was reduced 5.1%, indicative of excellent reproducibility.

3.8. Effects of coexisting ions on determination of Cu^{2+}

The effect of various ions on Cu^{2+} dissolution peak current was investigated. The experiment indicated that 200-fold of K^+，Na^+，Cl^-，NO_3^-, SO_4^{2-} and 50-fold of Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{3+} did not interfere with the determination of Cu^{2+}

4. Conclusions

A CHS/MWNT/GCE was prepared by dropping the solution of CHS and MWNT directly on the GCE. The electrochemical properties of CHS/MWNT/GCE were characterized by CV and EIS. Compared with GCE, peak current of Cu^{2+} on CHS/MWNT/GCE exhibited electrocatalytic activity significant increase. In addition, some optimum conditions were chosen, such as the electrolyte and acidity were calculated.

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