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Preparation in-situ of carbon nanotubes/polyaniline modified electrode and application for ascorbic acid detection

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ABSTRACT

A novel grown in-situ carbon nanotube/polyaniline chemically modified electrode (GSCNT/PANI-CME) was synthesized for the electrochemical detection of ascorbic acid (AA). First, nickel catalyst was obtained by direct current electrochemical deposition on a graphite electrode (GE) surface. Second, CNTs were grown in-situ to obtain CNTs chemically modified electrode (GSCNTs-CME) by catalytic chemical vapor deposition. Third, the grown CNTs were acid treated to carboxylate and remove nickel particles. Finally, PANI was prepared in-situ by electrochemical polymerization on the GSCNTs-CME to obtain GSCNTs/PANI-CME. The obtained electrodes were characterized by scanning electron microscopy and cyclic voltammetry. The results showed that CNTs grew uniformly on the GE surface and the original tubular structure was remained. PANI was uniformly coated on the surface of CNTs in the obtained composite, which was a typical three-dimensional network structure. The GSCNTs/PANI-CME exhibited an excellent electrocatalytic activity to AA. The oxidation peak current was increased linearly with the concentration of AA in the range from 1.0×10^{-6} mol L^{-1} to 4.5×10^{-4} mol L^{-1}, with a detection limit of 1.0×10^{-7} mol L^{-1} (S/N = 3). The experimental data showed that the obtained electrode was selective, stable and reproducible. The recoveries were between 97.4% and 102.1%.

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1. Introduction

Ascorbic acid (AA, Vitamin C) is an effective reducing agent and a powerful antioxidant in food and human organ [1]. Thus, it is important for the food and medicine safety to develop a simple and rapid method to determine accurately the AA. Compared with conventional methods: fluorimetry, chromatography, spectrophotometry and redox titration, electrochemical methods have the obvious advantages of low cost, high sensitivity, short response time and simple operation [2,3]. Although AA is an effective reductive compound, it cannot be detected directly by the electrochemical methods using the conventional electrode such as glassy carbon electrode, graphite electrodes and Pt electrode for its high overpotential, low selectivity, low reaction sensitivity and poor reproducibility on these electrodes [4,5]. In order to solve these problems, many kinds of modified electrodes were prepared to replace the conventional electrodes [6–8].

Polyaniline (PANI), an organic conducting polymer, has attracted much attention as the modified electrode material for its efficient electrocatalytic activity and high selectivity in the AA detection [9]. Carbon nanotubes (CNTs), discovered in 1991 [10], also have attracted considerable attention as the modified material to electrochemical sensors and biosensors for their unique properties such as high surface area, strong adsorptive ability, high electrical conductivity and good chemical stability [11–14]. There is π–π conjugation between the benzenoid rings of CNTs and PANI quinoid rings, which can urge the signal transmission between the two modified materials and thus CNT/PANI composite modified electrode may have better electrochemical detection performances. In fact, the researchers have proved that there is a good synergy between the CNTs and PANI, and the modified electrodes made from the two modified materials have excellent electrochemical detection performances [15–18].

According to current research reports [15–26], the CNTs/PANI chemically modified electrodes (CNTs/PANI-CMEs) can be prepared by two ways. One is fixing functionalized CNTs on the surface of the bare electrode by dropping and dipping method, then growing PANI on the CNTs by chemical oxidation or electrochemical polymerization [19–22]. The other is that the composite of CNTs/PANI is prepared in advance. Subsequently, the composite is fixed directly on the surface of the bare electrode by dropping and dipping method [23–26]. However, these ways may change the original novel nanometer hollow tube structure of the CNTs due to adding electrode materials (for example, the binder), which may decrease the utilization efficiency of the CNTs and increase the resistance of the composite. In addition, the binding between modified materials and electrode surface may be fragile, which could affect the stability and reutilization of the modified electrode. In order to avoid these defects mentioned above, we put forward to a new way to prepare the CNTs/PANI-CME: the CNTs were grown in-situ on the

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surface of the graphite electrode (GE) by catalytic chemical vapor deposition (CCVD) without binder. Then the PANI was prepared in-situ on the surface of the CNTs by electrochemical polymerization. So the CNTs/PANI-CME was prepared without any binder, named as the GSCNTs/PANI-CME. The obtained modified electrode was used for electrochemical detection of the AA in aqueous solution and showed a broader linear range of 1.0×10^{-6} mol L^{-1}–4.5×10^{-4} mol L^{-1} and the detection limit was 1×10^{-7} mol L^{-1}. The detection limit is lower than those of the similar electrodes obtained by other ways [27–30].

2. Experimental

2.1. Materials and reagent

All chemicals used in this paper were analytical reagent. The purity of the gases (Ar, H_2 and C_2H_2) used in the experiment was 99.99%. The GEs (5.3 mm in diameter, 7.0 mm in length) were produced by Sichuan Hengli Electrical Carbon Co. Ltd. The phosphate buffer solution (PBS) was prepared by Na_2HPO_4 and NaH_2PO_4, which was used as the supporting electrolyte during all measurements. Deionized water was used to rinse the materials and prepare the solutions.

2.2. Preparation of modified electrodes

2.2.1. Electrochemical deposition of Ni catalyst on the GE

The GE was polished to a mirror-like surface and fastened into polytetrafluoroethylene electrode set with silicone; only the polished surface was exposed to the air. To prepare Ni catalyst, a conventional two-electrode system was assembled by using Ni slice (99.99%) and the polished GE as the auxiliary electrode and working electrode, respectively. The electrochemical deposition solution was composed of nickel sulfate ($NiSO_4 \cdot 7H_2O$, 300 g L^{-1}), nickel chloride ($NiCl_2 \cdot 6H_2O$, 45 g L^{-1}), boric acid (H_3BO_3, 40 g L^{-1}), saccharin sodium ($C_6H_4COSO_2NNa \cdot 2H_2O$, 5 g L^{-1}), sodium dodecyl sulfate ($CH_3(CH_2)_{11}OSO_3Na$, 0.1 g L^{-1}) and deionized water [31]. The direct current electrochemical deposition of Ni catalyst was carried out at a constant potential of 2.05 V for 5 min. Finally, the GE was carefully removed from the electrode set and washed with deionized water.

2.2.2. Preparation of the GSCNTs-CME

The CNTs were grown by CCVD in the tubular resistance furnace, which has been reported in our previous papers [32]. The pretreated GE was placed in a quartz boat, and the quartz boat was put into the quartz tube ($\phi = 60$ mm, $l = 1000$ mm) of the tubular resistance furnace. Then, a flow rate of 50 sccm of Ar gas was introduced into the quartz chamber for eliminating the air in the quartz tube, meanwhile the tube furnace was heated up to 800 °C from room temperature at 10 °C per minute. The temperature was kept at 800 °C for 30 min and at the same time, H_2 gas was introduced into the tube at the flow rate of 50 sccm instead of the Ar gas. After that, the temperature was cooled down to 700 °C with Ar gas flowing at the flow rate of 50 sccm. Then the temperature was held at 700 °C for 20 min while a mixture gas composed of C_2H_2 and Ar (C_2H_2/Ar, 20/160) flew into the quartz tube to grow CNTs. Finally, the system was cooled down to ambient temperature under the protection of Ar gas at a flow rate of 25 sccm. After that, the electrode was taken out and treated by concentrated nitric acid for 1 h. The electrode was rinsed with deionized water and dried.

2.2.3. Preparation of the GSCNTs/PANI-CME and the PANI-CME

The GSCNTs/PANI-CME was prepared by in-situ electrochemical polymerization of aniline on the surface of the GSCNTs-CME. PANI was prepared by cyclic voltammetric scanning between −0.2 and 1.0 V for 10 cycles at a scan rate of 0.02 V s^{-1} in the 50 mL supporting electrolyte solution containing aniline (0.1 mol L^{-1}) and sulfuric acid (0.5 mol L^{-1}). As a contrast electrode, the PANI-CME was prepared by directly depositing PANI on the surface of the GE as the same operations.

2.3. Characterization and instrumentations

A conventional three-electrode system was assembled by using the saturated calomel electrode (SCE) as the reference electrode, platinum electrode as the counter electrode and the modified electrodes as the working electrode and employed to electrochemical measurements. Cyclic voltammetry (CV) was used in the electrochemical measurement. And differential pulse voltammetry (DPV) was used to verify the testing results' reliability from the CV. Optical micrograph was used to observe the morphology of the GE surface by using a DMRX-type polarization microscope (Leica Microsystems, Germany). A JEOL JSM-7001F field emission scanning electron microscope (SEM) was used for surface image measurements of the modified electrodes. All the cyclic voltammetry (CV) measurements were carried out on a galvanostatic-voltage instrument (ZF-9, Shanghai, China) using Ar gas to move the air of the solutions. The electrochemical impedance spectroscopic (EIS) was carried out with supporting electrolyte solution (5.0 mmol L^{-1} $[Fe(CN)_6]^{3-/4-}$ in pH = 6 PBS). The AC amplitude was 5 mV and the testing frequency ranged from 10 kHz to 0.01 Hz. The applied potential was 0.172 V.

3. Results and discussion

Fig. 1A and B is the CV curves of the PANI electrochemical polymerization on the GE and GSCNTs-CME with 20 mV s^{-1} scan rate, respectively. It can be seen that the two CV curves both have three couples of redox peaks (marked as a, b and c) with the potential from −0.01 V to 0.85 V. The oxidation peak a corresponds to the transformation of PANI from leucoemeraldine form (fully reduced state) to emeraldine salt. The oxidation peak b is due to the oxidation of head to tail dimers (intermediate). The oxidation peak c is related to the state transformation from emeraldine to pernigraniline (fully oxidized state), which indicates that PANI has successfully grown on the surface of the electrode [33]. Moreover, with the increase of scan cycle numbers, there is a significant increase of the redox peak current, which is due to the fact that the PANI electrochemical polymerization is an autocatalytic process. Compared with Fig. 1A and B, we can find that the peak a current value of the GSCNTs-CME reaches 1.17 mA after 10 cycles, which is five times more than that of the GE. The peak b current value of the GSCNTs-CME is up to 0.85 mA, which is five times more than that of the GE. The peak c current value from the GSCNTs-CME reaches 1.14 mA, which is seven times more than that from the GE. These phenomena, we consider, should be attributed to the excellent electron transfer rate and high specific surface area of CNTs, indicating that grown in-situ CNTs could improve the modified electrode electrochemical performances.

Fig. 1C shows the CV curves of the four obtained electrodes in 5.0 mmol L^{-1} $[Fe(CN)_6]^{4-/3-}$ solution containing 0.1 mol L^{-1} KCl with 20 mV s^{-1} scan rate. Oxidation/reduction characteristics of $[Fe(CN)_6]^{4-/3-}$ could be seen in all the CV curves. However, the oxide peak current (210.1×10^{-6} A) based on the GSCNTs/PANI-CME is much higher than those based on the GE, GSCNTs-ME (121.3×10^{-6} A) and PANI-CME (69.7×10^{-6} A). So the electroactive areas of the electrodes can be obtained by the Randles–Sevcik equation [34]. The electroactive areas of PANI-CME, GSCNTs-CME and GSCNTs/PANI-CME are 4.1, 7.1 and 12.4 cm^2, respectively. The electroactive area of the GSCNTs/PANI-CME is the biggest and which is bigger than the total of the PANI-CME and GSCNTs-CME, indicating that there is a synergistic effect between the PANI and CNTs. If the oxide peak currents observed by CVs in the presence of AA are normalized with their electroactive areas, we can have the current densities 17.0×10^{-6} (PANI-CME), 17.1×10^{-6} (GSCNTs-CME) and 16.9×10^{-6} $A \cdot cm^{-2}$ (GSCNTs/PANI-CME). The differences of the current densities are very small, indicating that there is a close relationship between the electroactive area and its oxide peak current.

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