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A Multiwall Carbon Nanotube-chitosan Modified Electrode for Selective Detection of Dopamine in the Presence of Ascorbic Acid

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Abstract: A novel multiwall carbon nanotube-chitosan modified electrode has been prepared. The modified electrode resolves the overlapping voltammetric response of dopamine and ascorbic acid into two well-defined peak by 212 mV. The mechanism of discrimination of dopamine from ascorbic acid is discussed. Dopamine can be determined selectively with the carbon nanotube-chitosan modified electrode. The electrode shows good sensitivity, selectivity and stability.

keywords: Nanotube-chitosan modified electrode, dopamine, ascorbic acid.

Dopamine (DA) is a very important neurotransmitter in mammalian central nervous system, and low levels of DA have been found in patients with Parkinson's disease[1]. So its detection with high selectivity and sensitivity is of great significance in the investigation of its physiological functions and diagnose of nervous diseases resulted from abnormal metabolite. When solid electrodes are used to detect DA, the main and foremost difficulty is the interference of ascorbic acid (AA), which is oxidized at almost the same potential as DA[2]. So it is very important to develop an electrochemical method for highly selective and sensitive detection of DA.

Chitosan, which is derived from chitin by deacetylation, has excellent biologic compatibility. Due to chitosan possesses many active groups, it can be used as modifier of electrode[3]. Besides, macromolecule dispersant is of benefit to environment protection. So in this study, multiwall carbon nanotube (MWNT)-chitosan solution was initially used as modifier. MWNT-chitosan modified electrode (MC/GCE) has many advantages with regard to low detection limit, fast response in case of detection for DA in the presence of AA.

Experimental

All the electrochemical measurements were carried out with a BAS CV-50w bioelectrochemical analyzer. A three-electrode system consisted of a working electrode MC/GCE, a saturated calomel reference electrode, and a platinum auxiliary electrode.

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All potentials were referred to the SCE. The transmission electron microscopy image was performed with TEM-100CXⅡ. The MWNTs used in this work were obtained from the Institute of Nanometer of Central China Normal University.

The GCE was polished with 0.3 μm, 0.05 μm aluminum slurry to a mirror face and smeared evenly with 10 μL MWNT-chitosan (0.5%) solution (1 mg MWNT into 5 mL chitosan solution, ultrasonic agitation for a few minutes to give 0.2 mg/mL black suspension), dried under the infrared lamp for 10 min.

0.1 mol/L phosphate buffer (pH=7.2) was used as the supporting electrolyte for DA and AA determination. Before and after every measurement, the MC/GCE was activated by the successive cyclic voltammetric sweeps between -0.20 V and 0.5 V at 100 mV/s in the blank phosphate buffer.

Results and Discussion

Figure 1 showed the transmission electron microscopy image of chitosan-MWNT. It can be observed that the MWNT were equably dispersed in the chitosan solution and their average diameter ranged from 30 to 40 nm.

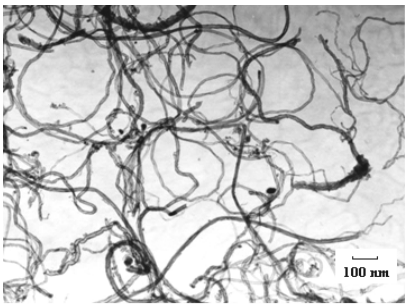
Figure 2 showed one cathodic peak and anodic peak of DA (1×10^{-4} mol/L). Comparing with the bare electrode, the cathodic peak potential of DA (Ep_c) shifted positively to 0.117 V, and the anodic peak potential (Ep_a) shifed negatively to 0.183 V, the reversibility of electrode became better. Meanwhile, the cathodic peak current (ip_c) and anodic peak currents (ip_a) both increased and the figure of curve became better. These results indicated that the MWNT-chitosan modified electrode exerted an obvious electrocatalysis effect on DA. By using cyclic voltammetric sweep, we found that ip of DA were directly proportional to the scan rate（**Figure 3**）, suggesting that the redox reaction of DA is an absorption-controlled behavior.

It was discovered that the redox peak current (ip) of DA at MC/GCE in the phosphate buffer was higher than that supported on the other electrolytes such as HAC-NaAC, B.R buffer. And the ip of DA also depends on the phosphate concentration, the highest current was obtained in 0.1 mol/L phosphate buffer. So the following experiments were carried out in pH 7.2 phosphate buffer. The Ep_a of DA shifted negatively with the increase of pH in the range of 3.2~8.2, obeyed the equation: Epa=0.571-0.056pH (r=0.998), the slope of -56 mV/pH suggested that two protons and two electrons took part in the redox of DA, which agreed with the reference[4].

When the amount of MWNTS on the surface of electrode exceeded 45 $\mu g/cm^2$, the background current rised while ip_a of DA falled. Because the thicker film on the electrode surface blocked the electron transfer between DA and electrode. In this study, the amount of MWNTS was 38 $\mu g/cm^2$.

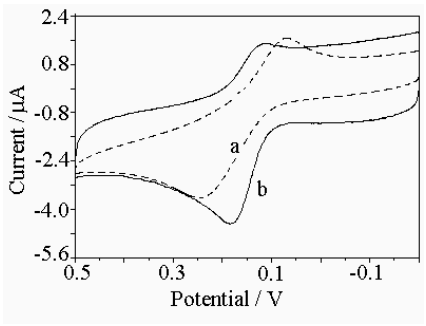
The electrochemical behavior of coexisting DA (1×10^{-4} mol/L) and AA (1×10^{-3} mol/L) at the MC/GCE was investigated. Two totally divided anodic peak were observed in the CV figure (Ep_{DA}=183 mV, Ep_{AA}=-29 mV) (**Figure 4**). The affect of different concentration of AA on oxidation behavior of DA and different amount of DA on ip_a of AA were further researched by using differential pulse voltammetry (DPV) mode under optimum conditions. **Figure 5(a)** showed that AA hardly interfered the

Figure 1 The transmission electron microscopy image of chitosan-MWNT



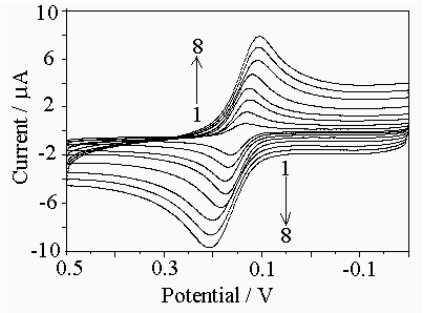
Magnification 19000×

Figure 2 Cyclic voltammograms of 1×10^{-4} mol/L DA



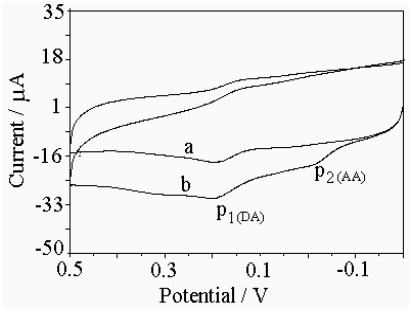
at (a) bare GCE and (b) MC/GCE scan rate 100 mV/s

Figure 3 Cyclic voltammograms of 1×10^{-4} mol/L DA at MC/GCE



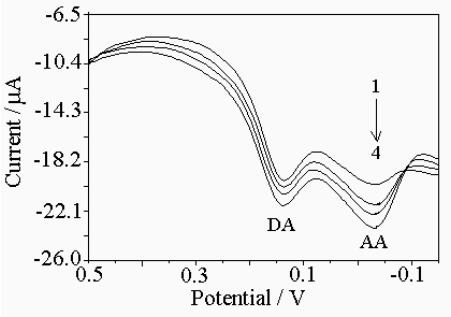
scan rates 25, 50, 75, 100, 125, 150, 175, 200 mV/s

Figure 4 Cyclic voltammograms of a, b at MC/GCE

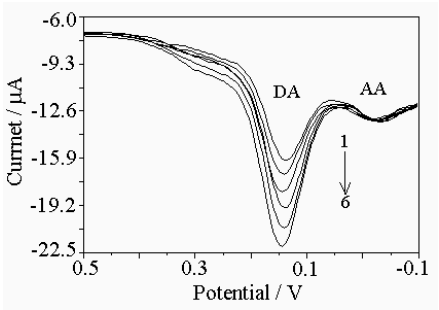


(a) 1×10^{-4} mol/L DA
(b) 1×10^{-4} mol/L DA+1×10^{-3}mol/L AA
scan rate 100 mV/s

Figure 5 Differential pulse voltammograms of DA and AA at MC/GCE



(a)
DA 1×10^{-4} mol/L
AA 1) 1×10^{-3} mol/L, 2) 3×10^{-3} mol/L
3) 4×10^{-3} mol/L, 5) 5×10^{-3} mol/L



(b)
AA 1×10^{-4} mol/L
DA 1) 1.5×10^{-4} mol/L, 2) 3×10^{-4} mol/L,
3) 4.5×10^{-4} mol/L, 4) 6×10^{-4} mol/L,
5) 7.5×10^{-4} mol/L, 6) 9×10^{-4} mol/L

detection of DA in condition that AA concentration was 50 times as that of DA. When the concentration of AA was increased to 100 times, the ip_a of DA decreased by 9.8%, while the Ep_a of DA did not shift. Similarly, **Figure 5(b)** showed DA did not affect the oxidation behavior of AA. The anodic peak current of DA was linearly related to the DA concentration over the range of 5×10^{-7}~1×10^{-4} mol/L in the presence of 1×10^{-3} mol/L AA (r =0.997). The detection limit (3σ) was 2×10^{-7} mol/L. Accordingly, determination of low concentration level of DA in the presence of high concentration level of AA was possible. The R.S.D of the MC/GCE was found to be 4.07 % for ten successive determinations of 1×10^{-4} mol/L DA and the electrode could be used for at least seven days.

The mechanism of electrocatalysis towards DA and AA by the chitosan-MWNT modified electrode were also discussed. Because chitosan has many active groups such as amino groups and hydroxy groups, there was intensive H-bond interaction between modifier and -OH which existed in the structure of DA and AA. Meanwhile, the subtle carbon nanotube provided many active sites, which enhanced the transfer of charge between electrode and reagents, all of which lead to the great electrocatalysis towards DA and AA. And chitosan would attract AA due to the amino groups' positive charge, which further catalyzed the oxidation of AA and resulted in that the Ep_a of AA shifted to -0.20 V. As a result, the separation between the two anodic peak potentials (ΔEp_a) of DA and AA was almost 212 mV in CV and 185 mV in DPV, and AA did not interfere the determination of DA.

The MC/GCE was used to detect DA in the sample which consisted of DA injection (10 mg/mL). The R.S.D for six successive determinations for DA was 3.65%. The average value was 10.2 mg/mL which agreed with the standard.

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