Short Communication

Electrocatalytic Oxidation of Catechol at Multi-Walled Carbon Nanotubes Modified Electrode

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Abstract
In 0.05 mol/L phosphate buffer solution (pH 7.0), carbon nanotubes modified electrode exhibits rapid response, strong catalytic activity with high stability toward the electrochemical oxidation of catechol. The electrochemical behavior of catechol on both the multi-walled and single-walled carbon nanotubes modified electrode was investigated. The experimental conditions, such as pH of the solution and scan rate were optimized. The currents (measured by constant potential amperometry) increase linearly with the concentrations of catechol in the range of $2.0 \times 10^{-5} - 1.2 \times 10^{-3}$ mol/L. Moreover, at the multi-walled carbon nanotubes modified electrode the electrochemical responses of catechol and ascorbic acid can be separated clearly.

Keywords: Carbon nanotube, Cyclic voltammetry, Catechol, Ascorbic acid

Measuring the secretion of neurotransmitters such as catechol and catecholamines has been considered to be of great importance to probe the brain chemistry [1] and many researches have been carried out to detect catechol [2, 3]. A carbon paste electrode modified with copper phthalocyanine and histidine based on the chemistry of the dopamine β-monooxygenase enzyme was constructed with rapid response and long lifetime [2]. Catechol could also be detected by inhibited chemiluminescence method [3]. While the major difficulty in electrochemical detection of neurotransmitters in vivo was the interference from excess ascorbate, which oxidized at the same potential as catecholamines [4]. Using Nafion film [5, 6] or self-assembled cationic monolayers [7] the influence of ascorbic acid (AA) could be eliminated. However, there were disadvantages such as the diffusion coefficients of the neurotransmitters inside the film were relatively low (typically $10^{-10} - 10^{-9}$ cm$^2 \cdot$ s^{-1}) [8] and the time needed for preparing the self-assembled monolayers on gold electrode was rather long.

Carbon nanotubes (CNTs), consisting of cylindrical graphene sheets with nanometer diameter wrapped into one-dimensional tubular structure, have high electrical conductivity, good chemical stability and significant mechanical strength and modulus [9]. These special properties of both single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) have attracted increasing interest because their great potential and real applications have been found in chemistry, physics and material science [10 – 14].

Carbon nanotube may behave as a metal or semiconductor depending on tube diameter and its helicity. Its specific electronic properties result in excellent performance in promoting electron transfer when used as an electrode in electrochemical reactions [15, 16]. Recently, the electrochemistry of SWNTs has been more and more studied because the SWNT is a well-defined system in terms of electronic properties. Many biomolecules such as dopamine, epinephrine, ascorbic acid [17], 3,4-dihydroxyphenylacetic acid [18], norepinephrine [19] showed favorable electrochemical behavior at the SWNTs-modified glassy carbon (GC) or Au electrode.

At the same time, MWNTs electrode was successfully constructed using bromoform as a binder and the oxidation of dopamine was achieved [20]. Also, other proteins such as cytochrome c and azurin showed well-behaved electrochemical response at MWNTs electrode compared with other carbon electrodes [21]. Luo's group subtly fabricated β-cyclodextrin incorporating MWNTs modified GC electrode for the detection of uric acid [22] and the MWNTs-intercalated graphite electrode to determine dopamine and serotonin [23]. A sensitive method was established to detect nitric oxide in aqueous solution using MWNTs-modified GC electrode [24].

Here the electrochemical behavior of the MWNTs- and SWNTs-modified electrode to catechol was studied, as far as our knowledge, there are few reports dealing with the comparison [25]. The simply prepared CNTs-modified electrode exhibits rapid response, strong catalytic activity with stability to the electrochemical oxidation of catechol. And then we utilized the MWNTs-modified GC electrode to detect the representative neurotransmitter catechol avoiding the interference from AA.

Figure 1 shows the cyclic voltammograms of catechol at the bare GC electrode (A), the MWNTs-modified (B) and the SWNTs-modified electrode (C) in 0.05 M phosphate buffer solution recorded at 50 mV/s. At bare GC electrode,

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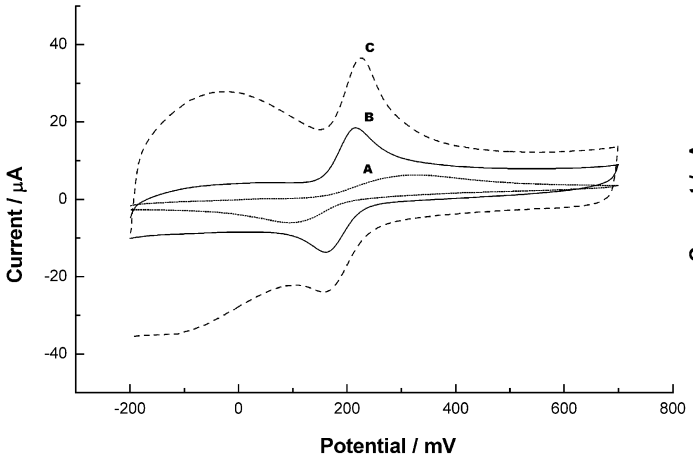

Fig. 1. Cyclic voltammograms of 2.0×10^{-4} M catechol at a bare GC electrode (A); a MWNTs- (B) and SWNTs-modified electrode (C) in 0.05 M phosphate buffer solution (pH 7.0). Scan rate: 50 mV/s.

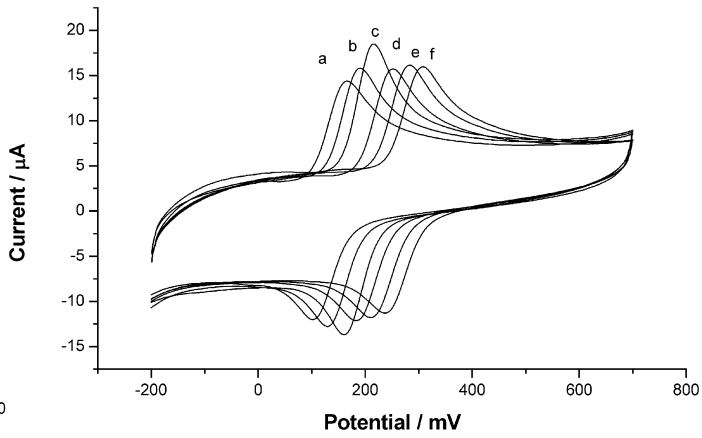

Fig. 2. Cyclic voltammograms of catechol at a MWNTs-modified electrode at different solution pH: (a) 8.00, (b) 7.53, (c) 7.00, (d) 6.47, (e) 6.02 and (f) 5.55. Scan rate: 50 mV/s.

the oxidation and reduction of catechol result in broad waves with the corresponding peak potentials of +324 mV and +99 mV. So it shows irreversible behavior with ΔE_p, the difference between the anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}), 225 mV. However, at the nanotube-modified GC electrodes, the reversibility of catechol is significantly improved together with the current signal increasing. The oxidation peak potential negatively shifts to 215 mV and the reduction peak positively shifts to 161 mV with $\Delta E_p = 54$ mV at the MWNTs-modified electrode, and that of 67 mV at the SWNTs-modified electrode. The peak currents are 2.41 and 3.14-fold larger than the corresponding ones at the bare GC surface, respectively. This is consistent with the result of NADH detection at the CNTs-modified electrode [25]. These suggest that the CNTs can act as a promoter to enhance the electrochemical reaction. Due to the high porosity of the nanotube, the real surface area of the modified electrode is far greater than other forms of carbon electrode. So the peak current increases evidently together with the background voltammetric response at the nanotube-coated GC stronger than that at the bare surface. In order to obtain a well-behaved electrochemistry of catechol, the MWNTs-modified electrode was chosen for the following experiments.

The dependence of 2.0×10^{-4} M catechol on pH over the range of 5.5 – 8.0 in 0.05 M phosphate buffer solution at the MWNTs-modified electrode is illustrated in Figure 2. The peak potentials shift negatively as solution pH increases. An optimum response and the smallest ΔE_p occur at pH 7.0, so we chose pH 7.0 as the operational pH in the subsequent experiments. The linear regression equation between the formal potential $E^{0\prime}$ and solution pH, $E^{0\prime}$ (mV) = 587.53 ± 10.22 – (56.783 ± 1.50) pH, suggests that the loss of electrons is accompanied by the loss of an equal number of protons.

The influence of scan rate on oxidation of catechol at the MWNTs-modified electrode is obvious for the peak current while slight for the ΔE_p. The peak current increases linearly

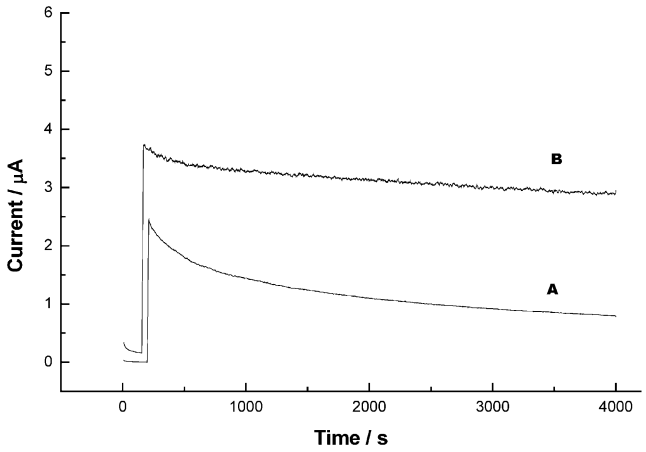

Fig. 3. Stability of the response to 2.0×10^{-4} M catechol at bare GC (A) and MWNTs-modified GC (B) electrodes in 0.05 M phosphate buffer solution (pH 7.0). Operating potential: 180 mV; Stirring rate: 300 rpm.

with the square root of the scan rate from 10 to 200 mV/s, indicating that the redox reaction of catechol at the modified electrode is a diffusion-controlled process. The linear regression equation is expressed as I_{pa} (μA) = −0.48 ± 0.16 + (1.96 ± 0.02) (ν/mV s^{-1})$^{1/2}$.

An attractive feature of the CNTs-modified electrodes is their stable amperometric response to catechol. Figure 3 shows the amperometric response to 2.0×10^{-4} M catechol, at the bare (A) and MWNTs-modified (B) GC electrodes recorded over a continuous 60-min period. The response of the MWNTs-coated GC electrode remains stable during the experiment, with only 6.2%, 12.4%, 20.3% current decreases at 10, 30 and 60 min, respectively. In contrast, the bare GC electrode displays a rapid decay of the signal with 38%, 55%, 67% current depressions, respectively, at the corresponding time, indicating an inhibition of the redox process as a result of fouling effect on the electrode surface. The reproducibility of the current response of 2.0×10^{-4} M catechol was investigated at the MWNTs-modified elec-

trode and the relative standard deviation was 1.4%. For the inter-electrode repeatability of five electrodes fabricated in the same manner, the relative standard deviation was 7.1% with a catechol concentration of 2.0×10^{-4} M at the scan rate of 50 mV/s.

In order to examine the response character of the modified electrode to catechol, we have undertaken the detection of catechol in phosphate buffer solution with a constant potential voltammetry. When an aliquot of catechol was added into the buffer solution, the modified electrode responded rapidly to the substrate and could achieve the steady-state current within 5 s. The fast response can be attributed to its significant advantages within the realm of heterogeneous electron transfer. A linear relationship between peak current and catechol concentrations was obtained in a range of 2.0×10^{-5} M – 1.2×10^{-3} M with correlation coefficient $r = 0.999$. The detection limit has been estimated to be 1.0×10^{-5} M.

Neurotransmitters and AA coexist in biological environments. Considering the large charging current contribution to the background current, differential pulse voltammetry (DPV) was used to examine the separation of the electrochemical responses of catechol and AA. Figure 4A (a) shows the DPV obtained at the bare GC electrode in 0.05 M phosphate buffer solution (pH 7.0) containing 2.0×10^{-4} M ascorbic acid + 2.0×10^{-4} M catechol. A rather broad oxidation peak resulted and the peak potential of catechol and AA were indistinguishable. However, at the MWNTs-modified electrode (b), the two separate oxidation peaks were resolved with a potential separation of 160 mV. Another interference in the detection of catecholamines in the presence of AA is the homogeneous catalytic oxidation of AA by the oxidized form of catecholamines [26, 27] and this needs to be eliminated for the precise determination of catecholamines. Figure 4B shows the DPV of AA at different concentrations of catechol .The homogeneous catalytic oxidation has not been observed and the voltammetric peak of AA was unaltered by the addition of catechol. So the MWNTs-modified GC electrode could be used to detect the representative neurotransmitter, catechol, avoiding the interference from AA.

In summary, the CNTs-modified GC electrode shows promising electrocatalytic behavior toward the oxidation of catechol. The electrochemical behavior of catechol at the MWNTs-modified electrode is a diffusion-controlled process. The peak current increases linearly with the concentration of catechol in the range of 2.0×10^{-5} M – 1.2×10^{-3} M, and the detection limit is 1.0×10^{-5} M. In the mixed solution of catechol and AA, the two oxidation peaks can be separated by about 160 mV at the MWNTs-modified electrode. This modified electrode provided a simple and convenient way to detect catechol and study the electrochemistry of biomolecules.

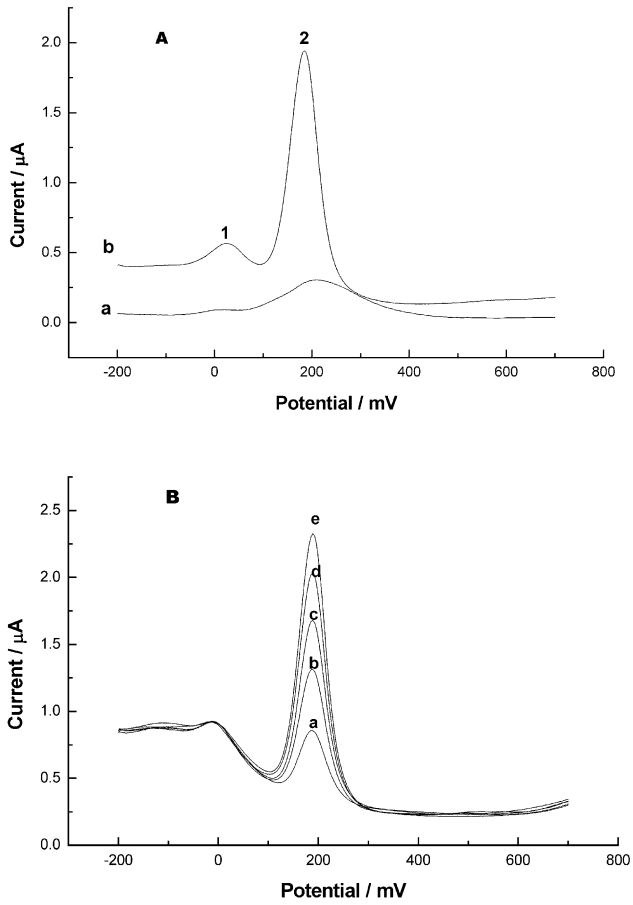

Fig. 4. A) Differential pulse voltammograms of 2.0×10^{-4} M ascorbic acid (1) + 2.0×10^{-4} M (2) catechol in 0.05 M phosphate buffer solution (pH 7.0) at a) a bare GC electrode, b) the MWNTs-modified electrode. B) DPV of AA (0.2 mM) at the MWNTs-modified electrode in the presence of different concentrations of catechol. Concentrations of catechol: a) 20, b) 40, c) 60, d) 80 and e) 100 μM. Scan rate: 5 mV/s; pulse height: 50 mV; pulse width: 50 ms.

Experimental

Amperometric experiments were performed with a BAS 100B electrochemical analyzer (West Lafayette, USA). The working electrode, the Ag/AgCl reference electrode and platinum wire counter electrode were inserted into a 10 mL cell through the fit holes in a plastic cover. During the amperometric measurement, a magnetic stirrer was used to provide the convective transport of analyte species. High-purity nitrogen was used for deaeration.

CNTs were obtained from Shenzhen Nanotech Port Co, Ltd (China) with typical diameter 1.4 nm and length 1 – 10 μm. The purity is about 80%. CNTs were purified, cut and functionalized through a well-established way with slight modification [28]. Catechol was from Beijing Chemical Factory (Beijing, China). All other chemicals were of analytical-reagent grade and were used without further purification. All solutions were prepared using doubly distilled, de-ionized water.

GC electrodes (diameter = 4 mm) were polished before each experiment with 1, 0.3 and 0.05 μm α-alumina powder, respectively, rinsed thoroughly with doubly distilled water between each polishing step. Then the electrodes were

sonicated in 1:1 nitric acid, acetone and doubly distilled water successively; finally the electrodes were allowed to dry at room temperature.

0.5 mg of purified CNTs were dispersed in 1 mL DMF with the aid of ultrasonic agitation to give a 0.5 mg/mL black solution. Then 10 μL of the mixed solution was deposited on the surface of GC electrode and allowed to dry under an infrared lamp. The SEM images indicated that MWNTs uniformly adsorbed on the surface of the electrode.

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