# Catalytic Activity of Multiwalled Carbon Nanotubes for the Oxidation of Nitric Oxide

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The acid-treated Multiwalled Carbon Nanotubes (MWNTs) was dropped on the surface of glassy carbon electrode to form a modified electrode. The MWNTs showed the strong catalytic activity for the electrochemical oxidation of nitric oxide (NO) and the catalytic currents were proportional to the NO concentrations in submicromolar range.

Since the discovery of carbon nanotubes in 1991, much attention has been focused on their production, purification, mechanical and electronic properties, and their electrical conductivity.[1–6] The subtle electronic properties suggest that carbon nanotubes will have the ability to promote electron transfer reaction when used as an electrode. Recently, microelectrodes constructed from singlewalled carbon nanotubes (SWNTs) or MWNT bundle have been reported.[7,8] The cast film of SWNTs or nitric acid-purified SWNTs on Pt, Au and glassy carbon electrode[9,10] have been used as modified electrodes to catalyze the electrochemical reaction of some biomolecules, such as dopamine, epinephrine, ascorbic acid etc. On the other hand, due to their high surface areas, their central hollow cores and the outside walls, carbon nanotubes can be used as a superior material to adsorb and storage gases, such as oxygen, hydrogen and nitrogen oxides etc.[11–13] The investigations of gas sensors based on the adsorptive properties of carbon nanotubes to detect oxygen and carbon oxides have been reported.[14,15] We are interested in the adsorptive properties of carbon nanotubes for nitrogen oxides because it can be utilized to establishing a sensitive method to detect nitric oxide in aqueous solution through combining the adsorptive properties with electronic ones of carbon nanotubes.

Nitric oxide is an important biomolecule, and it is thought to be a retrograde messenger in the central nervous system.[16] Although a lot of researches focused on the determination of NO in aqueous solution with various modified electrodes have been reported,[17–19] it is interesting to develop new materials with high efficiency and small dimensions for the detection of NO. In this letter, a simple method to prepare MWNT-modified electrode was presented and the electrode showed a strong electrocatalytic activity for the oxidation of NO in aqueous solution.

MWNTs (10 mg, 10–40 nm in diameter, several microns in length, synthesized by catalytic decomposition of hydrocarbons using a floating catalyst) were dispersed in 10 mL mixed acid solution of nitric acid and perchlorate acid (7 : 3). The mixed solution was ultrasonically agitated for 7 h. The MWNTs were washed with double-distilled water to neutral, then washed with acetone and dried in air. The peaks at 1735 $\text{cm}^{-1}$ and 1590 $\text{cm}^{-1}$ on FTIR spectrum suggested that carboxylate groups were present on the surface of MWNTs, which TEM image was similar to that reported in the previous literature.[20]

2.5 milligram of mixed acid-treated MWNTs was dispersed in 10 mL of acetone with the aid of ultrasonic agitation. The glassy carbon (GC) electrode ($\phi = 3.0$ mm) was carefully polished with $Al_2O_3$ slurry and then 15 cyclic scans were carried out in the potential range of 2.0 V–−2.0 V (vs SCE) in the solution of 1.0 M $H_2SO_4$. 30 $\mu$L of dispersed MWNTs solution was dropped on GC electrode surface and then the solvent acetone was evaporated in air to form a MWNT-modified electrode.

The modified electrode was placed into pH 6.3 phosphate buffer solution and cyclic voltammetric experiments were performed in the potential range of −0.15 V–0.45 V (vs SCE) at room temperature. A couple of redox peaks were observed; the cathodic and anodic peak potentials were 0.095 V and 0.145 V, respectively (Figure 1). The peak currents of cathodic and anodic were both proportional to the scan rate, indicating that this is a surface wave. The peak potentials depended linearly on the pH of supporting electrolyte and the slope of linear equation was 64 mV/pH, which revealed that the electrode reaction was related to the concentration of proton. Therefore, the redox peaks corresponded to the reduction and reoxidation of carboxylic acid group on surface of MWNTs, which was a four-electron, four-proton reaction and similar to that of SWNTs.[10] The electrochemical behavior of MWNT-modified electrode was considerably stable, even being laid aside one week in air.

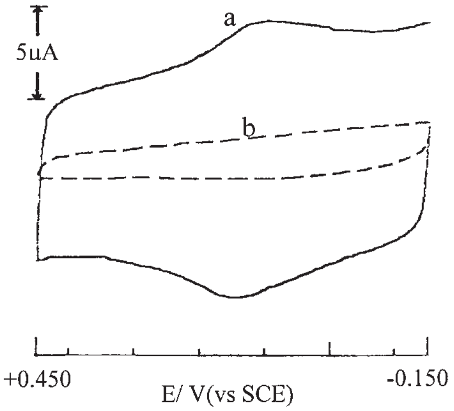

**Figure 1.** Cyclic voltammograms 100 mM phosphate buffer solution of pH 6.3 for: (a) MWNT-modified electrode and (b) bare GC electrode (Scan rate: 0.05 V/s).

As well known, the stability of electrode surface is critical to the performance of electrodes, its stability and reproducibility of results. Due to considerable chemical stability, carbon nanotubes is a superior electrode material and in fact the properties of electrode constructed from carbon nanotubes are very stable as shown in this letter. On the other hand, because of the porous structure and small dimensions, the nanotube provide a good wetting property for the solvents, a better electrode/electrolyte interface, and a larger surface area. These result in that the peak current at MWNT-modified electrode is larger than that at bare GC electrode. Considering the stability and its adsorptive properties for nitrogen oxides, carbon nanotube is expected to use as a new electrode material to catalyze directly the oxidation of NO in aqueous solution.

Saturated NO solutions were prepared according to the previous report.[19] It is necessary to carefully remove oxygen in solution before preparation, because NO can be rapidly oxidized by $O_2$. NO standards were prepared by making serial dilutions of saturation NO solutions with deoxygenated phosphate buffer solutions (pH 6.0). Figure 2 shows the cyclic voltammograms of NO in deoxygenated phosphate buffer solution. No voltammetric response was observed on a bare GC electrode for NO, as shown in Figure 2d. At MWNT-modified electrode, an obvious anodic peak was observed at 0.73 V and the peak current increased significantly with NO concentration increased (Figures 2b, 2c). The MWNT-modified electrode displayed a voltammetric behavior towards NO similar to the electropolymerized metall-porphyrin film sensors.[16–18] The fact that the five times cyclic voltammograms in 20 $\mu$M NO solution were the same and that the voltammetric response in five NO solutions were similar suggested that the MWNT-modified electrode had a good reproducibility and stability.

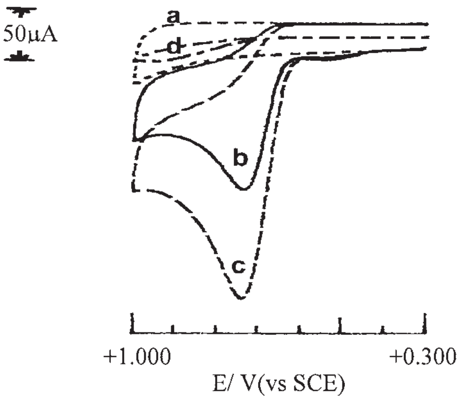

**Figure 2.** Cyclic voltammograms of NO in 300 mM phoshate buffer solution of pH 6.0 for: (a) MWNTs electrode, without NO, (b) MWNTs electrode, 20 $\mu$M NO, (c) MWNTs electrode, 40 $\mu$M NO and (d) bare GC electrode, 40 $\mu$M NO.

The mechanism of NO oxidation can be assumed as following; nitric oxide is adsorbed by carbon nanotubes firstly and then the removal of electrons from NO to carbon nanotubes does occur. In this process, the adsorption of NO by carbon nanotubes plays a key role. These results demonstrated that the MWNT-modified electrode could be used as a sensor for the detection of NO in aqueous solution.

In order to examine the response character of MWNTs electrode to NO, we have undertaken the detection of NO in phosphate buffer solution with a constant potential voltammetry. Figure 3 shows typical constant potential amperogram obtained with MWNTs electrode with successive addition of NO. This amperogram obviously showed an increase in measured current with the addition of NO, and the analytical procedure presented here can be used to determine NO at expected submicromolar concentration range. Further work is under way in our group.

In conclusion, the multiwalled carbon nanotube-modified electrode has the ability to catalyze the oxidation of NO. The results in this letter display that carbon nanotube is a superior electrode materials and can be used as electrochemical sensors to detect directly NO in aqueous solution. Compared with that of other carbon nanotube electrodes,[7–9] the preparation of MWNTs electrode hereof was an economical, simple and convenient way to utilize MWNTs in electrochemistry.

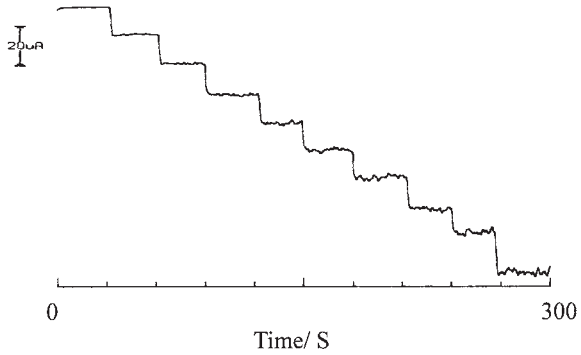

**Figure 3.** Amperogram obtained with successive addition of NO in 300 mM phsphate buffer solution of pH 6.0. Constant potential: 0.73 V, each addition of 4 $\mu$M NO.

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