

Direct Electrochemical Oxidation of Dihyronicotiamide Adenine Dinucleotide (NADH) at An Ordered Carbon Nanotubes Electrode

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Abstract: An ordered carbon nanotubes (CNTs) film, which was template-synthesized within the porous of an alumina template, modified glassy carbon electrode is fabricated. The electrode exhibits potent electrocatalysis for NADH oxidation in PBS (pH 6.8) with a diminution of the overpotential of more than 600 mV. The anodic peak current increases linearly with NADH concentration from 2×10^{-5} mol/L to 1×10^{-3} mol/L with the detection limit of about 5×10^{-7} mol/L.

Keywords: Carbon nanotube, ordered carbon nanotube electrode, electrocatalysis, NADH.

With novel structure, extraordinary electronic properties, high chemical stability and extremely high mechanical strength¹, carbon nanotubes (CNTs) have found a wide range of potential applications²⁻⁶. The subtle electronic properties suggest that CNTs have the ability to promote electron transfer when they are used as an electrode. The disordered CNTs have been used to fabricate electrode⁷⁻¹⁰. Thus, it is very interesting to fabricate the electrode using the ordered CNTs and to examine its electrocatalytic activity toward electrochemical reaction of some biologically active molecules because the ordered CNTs may present a steric effect for more efficient redox reactions. Here, we fabricate the ordered CNTs films modified glassy carbon (GC) electrode using Nafion as a binder (Nafion/CNTs/GC electrode), and study the electrochemical oxidation of dihydronicotiamide adenine dinucleotide (NADH) on it.

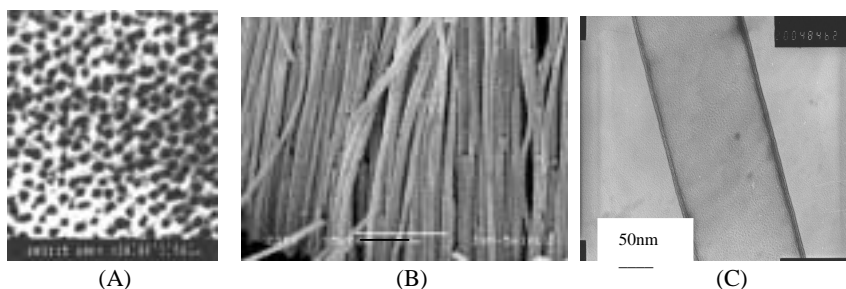
The direct electrochemical oxidation of NADH at a bare electrode takes place at high overpotential. Using of mediators can move the oxidation potential to the range of 100 to 200 mV (*vs.* SCE)¹¹⁻¹⁶. Recently, Musameh *et al.*¹⁷ reported the electrocatalytic oxidation of NADH at a GC electrode modified with disordered CNTs with decreasing of 490 mV in overpotential. The present results indicate that the NADH can be directed oxidized at about 0 V on a Nafion/CNTs/GC electrode with a diminution of the overpotential more than 600 mV, the anodic peak current increases linearly with NADH concentration from 2×10^{-5} mol/L to 1×10^{-3} mol/L with the detection limit of about 5×10^{-7} mol/L.

NADH (from Shanghai Lizhu Dongfeng Biotechnology Co. Ltd.) and Nafion solution (5% in methanol, from Aldrich) were used without further purification. The

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solution of NADH was prepared freshly *prior to* each experiment. The scanning electron micrograph (SEM) of CNTs film and the transmission electron micrograph (TEM) of a single carbon nanotube (CNT) were obtained using a JEOL JSM-5610LV Scanning Electron Microscope and a JEOL 4000FX Transmission Electron Microscope, respectively. The electrochemical measurements were carried out using a CHI 600A Electrochemical Workstation (CH Instruments) in a conventional three-electrode cell. The working electrode was a Nafion/CNTs/GC or a bare GC electrode. The coiled Pt wire and saturated calomel electrode (SCE) were used as the counter electrode and the reference electrode, respectively. Before the electrochemical experiments, the solution was deaerated by passing through highly pure nitrogen for 20 min, and a continuous flow of nitrogen was maintained over the sample solution during the experiments.

Figure 1 The SEM image



(A) a porous alumina template, (B) a CNTs film after dissolving the alumina template and (C) a TEM image of a single carbon nanotube.

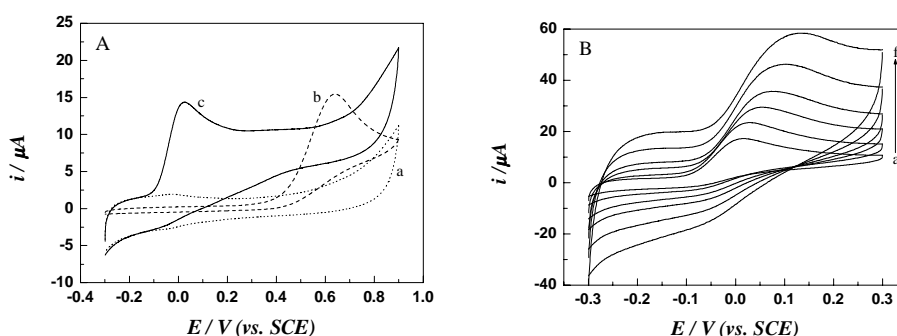
The ordered CNTs was template-synthesized within the ordered pores of an alumina template membrane (whatman, UK)¹⁸. **Figure 1A** is a SEM image of a porous alumina template membrane. It can be seen that the diameter of the pores distributes mainly in the range of 150 to 220 nm with the smallest pore of about 100 nm and the largest pore of about 280 nm in diameter. **Figure 1B** is a SEM image of CNTs, which was a freestanding film after alumina was dissolved away in NaOH solution (3 mol/L). It shows that CNTs are aligned. **Figure 1C** shows a TEM image of a single CNT which was removed (by ultrasonification) from CNTs film. It can be concluded that the diameter of CNT is about 160 nm and the wall of CNT is sufficiently thin (about 5 nm) in comparison with its diameter. The surfaces of CNT, including inner and outer surface, are smooth. The micro-Raman spectra of CNTs (not shown here) show two distinct peaks in the range of 1000 cm^{-1} to 2000 cm^{-1} . The Raman-allowed E_{2g} graphitic peak appears at 1595 cm^{-1} (G), indicating the presence of the graphite structure in the prepared sample. The appearance of D band at 1332 cm^{-1} indicates the presence of amorphous carbon, which may be due to the partial destructive of CNTs in the process of their formation. The integrated relative intensities of the D mode *versus* the graphitic G mode shows that only a minor fraction of amorphous carbon presents in the sample.

A piece of ordered CNTs film (after removal of the underlying alumina) was placed on the surface of a GC electrode (3 mm in diameter), which was pre-treated as

previously¹⁹, and one drop of Nafion solution was applied. The solvent was allowed to evaporate and the Nafion covered over the surface of CNTs and acted as an adhesive to hold the ordered CNTs film to the GC electrode surface forming the Nafion/CNTs/GC electrode.

Figure 2A, curve a is a cyclic voltammogram of a Nafion/CNTs/GC electrode in 0.1 mol/L phosphate buffer solution (PBS, pH 6.8) at a scan rate of 10 mV/s. A pair of very small redox peaks appear at about -50 mV. This may be due to redox reaction of some oxygen-contained groups⁸, which were presented on CNTs surface and were introduced during the CNTs preparation¹⁷. Curve b is a cyclic voltammogram of a bare GC electrode in PBS containing 2×10^{-3} mol/L NADH. NADH occurs an irreversible electrochemical reaction with the anodic peak at 645 mV. Curve c is a cyclic voltammogram of a Nafion/CNTs/GC electrode in PBS containing 2×10^{-3} mol/L NADH. From the cyclic voltammogram, one can conclude that NADH can be directly oxidized at the Nafion/CNTs/GC electrode with the anodic peak at about 15 mV, hence, a decrease in overpotential of 630 mV is achieved. The reason, that the ordered CNTs can electrocatalyze the oxidation of NADH, may be proposed due to some oxygen- contained groups presented on the CNTs surface and also the small dimension of CNTs, but the exact reason is not fully understood. The value of anodic peak potential of NADH oxidation obtained at present case is much more negative than that obtained by Musameh *et al.*¹⁷ at a disordered CNTs modified GC electrode (0.33 V and 0.36 V at multi-wall CNTs and single-wall CNTs, respectively, modified GC electrode). These results show that the ordered CNTs have potent electrocatalytic activity toward NADH oxidation. It should be noted that no any electrochemical active group was introduced into CNTs film purposefully and the electrode was also not activated electrochemically.

Figure 2 Cyclic voltammograms of a Nafion/CNTs/GC electrode in 0.1 mol/L PBS (pH 6.8)



(A) in the presence (curve c) and absence (curve a) of 2×10^{-3} mol/L NADH at a scan rate of 10 mV/s. Curve b is cyclic voltammogram of a bare GC electrode in the same solution and same scanning rate as curve c. (B) 2×10^{-3} mol/L NADH at various scan rate. The scan rate is (from a to f) 10, 20, 40, 60, 100 and 150 mV/s, respectively.

The anodic peak potentials and currents are scan rate dependent (**Figure 2B**). The peak potential moves to positive direction and the peak current increases with the

increasing of the scan rate. Moreover, the peak current increases linearly with the square root of the scan rate, indicating the current is limited by the diffusion of NADH in solution.

Both the anodic current and the anodic potential also depend on the concentration of NADH. The anodic potential shifts slightly to positive direction with the increasing of the concentration. For example, the oxidation potential is -36 mV when the NADH concentration was 2×10^{-5} mol/L (at a scan rate of 10 mV/s), this value becomes 76 mV when NADH concentration increased to 5×10^{-3} mol/L. The anodic current increases with the increasing of NADH concentration. The linear range of the current to NADH concentration was from 2×10^{-5} mol/L to 1×10^{-3} mol/L and the detection limit is about 5×10^{-7} mol/L.

In conclusion, an ordered CNTs film modified GC electrode has been fabricated using Nafion as a binder (Nafion/CNTs/GC). The Nafion/CNTs/GC electrode showed excellent electrocatalytic activity toward NADH oxidation with reducing the overpotential more than 600 mV. The oxidation current increased linearly with the NADH concentration in the range of 2×10^{-5} mol/L to 1×10^{-3} mol/L and the detection limit is about 5×10^{-7} mol/L. The linear range can be used as a calibration to determine NADH in sample.

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