

Fabrication, Characterization and Electrocatalysis of an Ordered Carbon Nanotube Electrode

CHEN, Jing(陈静) BAO, Jian-Chun(包建春) CAI, Chen-Xin*(蔡称心)

Department of Chemistry, Nanjing Normal University, Nanjing, Jiangsu 210097, China

A method for fabrication of the ordered carbon nanotube (CNT) film, which was template-synthesized within the highly ordered pores of a commercially available alumina template membrane, modified glassy carbon (CNT/GC) electrode was established. The CNT/GC electrode showed excellent electrocatalytic activity toward dopamine electrochemical reaction without introducing any electrochemically active group into CNT film or activating the electrode electrochemically. DA undergoes ideal reversible electrochemical reaction on CNT/GC electrode at low scan rate (≤ 20 mV/s) with an excellent reproducibility and stability. The CNT/GC electrode might be used in biosensors because the highly ordered CNT may present a steric effect on more efficient redox reactions of biomolecules.

Keywords carbon nanotube, ordered carbon nanotube electrode, electrocatalysis, dopamine

Introduction

Because of their exciting physical properties and potential applications, carbon nanotubes (CNT), consisting of cylindrical graphene sheets with nanometer diameter, have been the major subject of numerous experimental and theoretical investigations^{1,2} since the initial finding by Iijima³ in 1991 and the subsequent report of the synthesis of large quantities by Ebbesen and coworkers⁴ in 1992. With novel structural, extraordinary electronic properties, high chemical stability and extremely high mechanical strength and modulus,¹ CNT finds a wide range of potential applications from structural materials^{5,6} to nanoelectronic components.⁷ The applications of CNT include high sensitivity microbalance,⁸ gas detectors^{9,10} and catalyst support.^{11,12} The single wall CNT (SWCNT) can also be used as electron sources in field emission mode for display,¹³ tiny tweezers for nanoscale manipulation¹⁴ and as probe tips for scanning probe microscopy,¹⁵ with the added advantage that the apex may be chemically functionalized. The recent theoretical and experimental studies indicate that the extremely thin carbon tubules, for instance, CNT of 0.4 nm in diameter, can be used as optical and super conductive materials.^{16,17}

Theoretical calculations have shown that, depending

on their symmetry and diameter, CNT can be metallic, semimetallic or semiconducting.¹⁸⁻²⁰ Furthermore, it has been proved that CNT has better conductivity than graphite.²¹ The subtle electronic properties suggest that the CNT has the ability to promote electron transfer in electrochemical reaction when used as an electrode, representing a new application of CNT. The disordered CNT, including SWCNT and multiwall CNT (MWCNT), has been used to fabricate electrode.²²⁻²⁶ In those studies, the CNT was mixed with a binder, such as bromoform, mineral oil, liquid paraffin or *N,N*-dimethylformamide, and then packed into a glassy capillary or cast onto the surface of glassy carbon, platinum or gold electrode. But the well-resolved voltammograms were only obtained at the electrode which made from the CNT functionalized with the electrochemically active group, such as carboxylic acid group,²³ or at the CNT modified electrode, which was activated in phosphate buffer solution first.²⁶ Campbell and coworkers²⁷ fabricated a single CNT electrode and they proposed that such an electrode could be used as a probe in scanning electrochemical microscopy. It is interesting to fabricate the electrode using the ordered CNT and examine the electrocatalytic activity of this type of electrode toward electrochemical reaction of some biologically active molecules because the ordered CNT may present a steric effect on more efficient redox reactions. This paper reports the fabrication and characterization of ordered CNT film modified glassy carbon (GC) electrode (CNT/GC electrode), and also studies the electrocatalysis of dopamine, as an example, at CNT/GC electrode. The results show that the performance of CNT is superior to other form of carbon, such as, glassy carbon, and a high degree of reversibility of the electrochemical reaction of dopamine at CNT/GC electrode is achieved.

Experimental

Chemicals

Dopamine hydrochloride (DA) was purchased from

* E-mail: cxcai@njnu.edu.cn

Received August 24, 2002; revised December 23, 2002; accepted February 8, 2003.

Project supported by the Natural Science Foundation of Education Committee of Jiangsu Province (No. 2002HXXXLH1701).

Fluka (AG, Switzerland) and used without further purification. Nafion solution (5% in methanol) was obtained from Aldrich (Millwaukee, USA). All other chemicals were of analytical grade. All the solutions were prepared with doubly distilled water. The solution of DA was prepared freshly just before each experiment.

Preparation of ordered CNT film and fabrication of CNT/GC electrode

The array of ordered CNT was template-synthesized within the highly ordered pores (*ca.* 100 nm in diameter) of a commercially available alumina template membrane (Whatman, UK). Silver paste was spread on one side of the alumina membrane, which was used as a working electrode. A small amount of cobalt, which was used as catalyst in preparation of CNT, was electrodeposited into the bottom of the nanopores of the template by the direct current method. The electroplating solution was composed of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (50 g/L) and H_3BO_3 (20 g/L). Then, the Co-containing alumina template was placed in a horizontal quartz reactor and the temperature of the reactor was increased to 600 °C under flowing gas containing 2% H_2 and 98% Ar and kept constant for 1 h. Then, the temperature of furnace was increased to 650 °C, and the source gas containing 2% C_2H_2 , 2% H_2 and 96% Ar was passed through the reactor at a flow rate of 5×10^{-2} L/min for 20 min, to form CNT in the alumina template pores. Finally, the source gas stream was switched to the flowing gas containing 2% H_2 and 98% Ar and the CNT was annealed at that temperature for 4 h. The membrane was taken out after the reactor was cooled down to room temperature. The HCl acid was used to remove the catalyst of Co and the alumina was dissolved away in NaOH solution (3 mol/L) to obtain the desired freestanding CNT membrane.

Before casting the freestanding CNT on GC electrode surface to form CNT/GC electrode, the GC electrode (4 mm in diameter) was polished sequentially with metallographic abrasive paper (No. 6), slurries of alumina powder of 0.3 and 0.05 μm to a mirror finish. After rinsing with doubly distilled water, the GC electrode was sonicated in an ultrasonic bath with absolute ethanol and then with doubly distilled water for about 5 min. A piece of CNT membrane (after removal of the underlying alumina) was placed on the surface of GC electrode (area about of 0.12 cm^2) and one drop of Nafion solution was applied. The solvent was allowed to evaporate and the Nafion acted as an adhesive to hold the CNT membrane to the GC electrode surface to form CNT/GC electrode.

Apparatus

The scanning electron micrograph (SEM) of CNT film was obtained using a JEOL JSM-5610LV Scanning Electron Microscope. The transmission electron micrograph (TEM) of a single carbon nanotube was studied in a JEOL 4000FX Transmission Electron Microscope operating at

400 kV. The micro-Raman spectrum was recorded with a Spex1403 Raman spectrometer at ambient temperature using 514-nm excitation and a spectral slitwidth of 2 cm^{-1} . The XRD spectrum was recorded using a D/Max-RA diffractometer with $\text{Cu K}\alpha$ radiation.

The electrochemical measurements were carried out using an EG&G M273A Potentiostat/Galvanostat (EG&G, Princeton Applied Research, Princeton, NJ, USA) equipped with a PAR M270 electrochemical software for data acquisition at room temperature in a conventional three-electrode cell. The working electrode was CNT/GC or 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 experiments.

Results and discussion

Physical characterization

Fig. 1A is the SEM image of CNT membrane after removing the alumina. It shows that CNT is aligned, and the ends of the CNT are open. Fig. 1B shows a TEM image of a single CNT that was removed (by ultrasonification) from CNT membrane. It can be seen that the diameter of CNT is about 130 nm and the wall of CNT is sufficiently thin (about 5 nm) compared with its diameter.

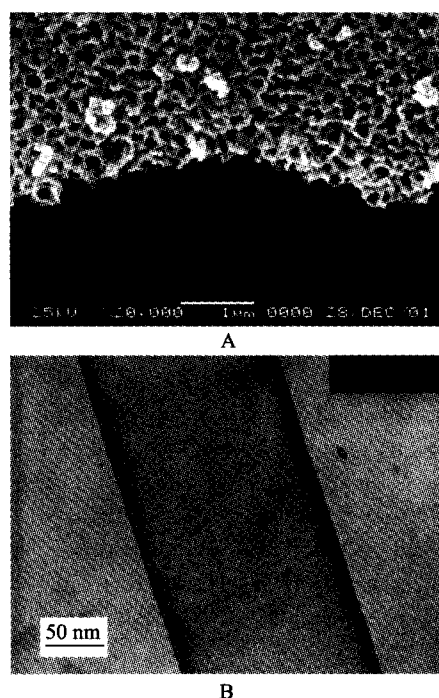


Fig. 1 Electron micrographs of carbon nanotubes. (A) Scanning electron micrograph of a template-synthesized carbon nanotube film after dissolving the alumina template. (B) transmission electron micrograph of single carbon nanotube.

The CNT membrane was characterized by Raman spectroscopy, which has been identified as a sensitive probe for the structure of carbon materials.^{28,29} The Raman spectrum of CNT membrane (Fig. 2) shows two distinct peaks in the range of 1000 cm^{-1} to 2000 cm^{-1} . The Raman-allowed E_{2g} graphitic peak appears at 1585 cm^{-1} (G). The D band at 1340 cm^{-1} indicates that the presence of amorphous carbon in the sample. The amorphous carbon can be removed or reorganized by thermal treatments.³⁰ Fig. 3 is the XRD spectrum of CNT. The diffraction peaks in the $10^\circ < 2\theta < 70^\circ$ can be indexed as C(002) and C(101), which belong to the graphitic structure.

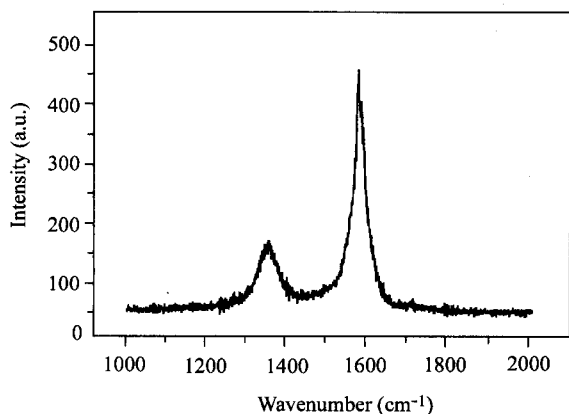


Fig. 2 Raman spectrum of CNT.

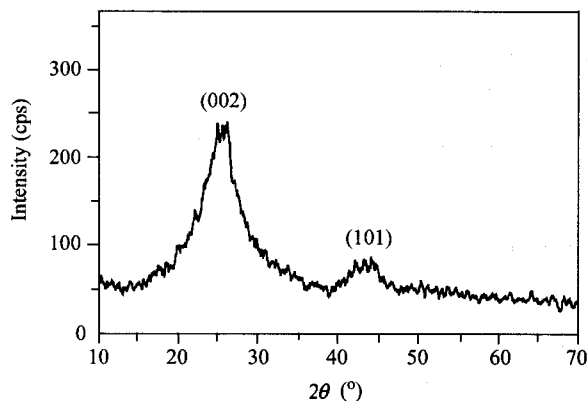


Fig. 3 XRD spectrum of CNT.

Electrochemical characterization

To study the electrochemical characteristics of CNT/GC electrode, the electrochemical performance of $\text{K}_3\text{Fe}(\text{CN})_6$ at the electrode was carried out. Fig. 4 is the cyclic voltammograms of $\text{K}_3\text{Fe}(\text{CN})_6$ ($4 \times 10^{-3}\text{ mol/L}$) in KCl (0.1 mol/L) solution at a bare GC electrode (curve a) and a CNT/GC electrode (curve b) at a scan rate of 50 mV/s . The anodic and cathodic peak potentials (E_{pa} and E_{pc}), the peak potential separation (ΔE_p) and the formal potential ($E^{\circ'}$) are presented in Table 1.

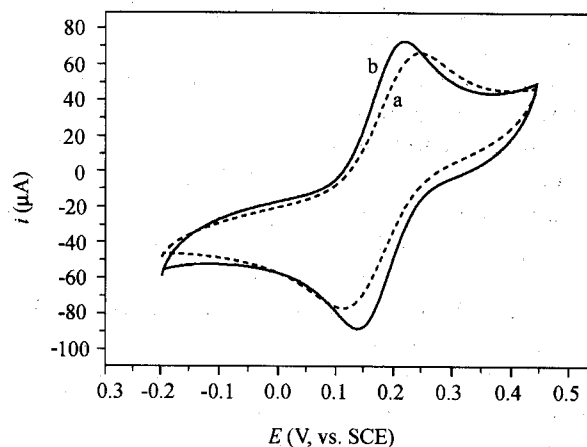


Fig. 4 Cyclic voltammograms of $\text{K}_3\text{Fe}(\text{CN})_6$ ($4 \times 10^{-3}\text{ mol/L}$) in KCl (0.1 mol/L) solution on a bare GC electrode (curve a) and a CNT/GC electrode (curve b) at a scan rate of 50 mV/s .

Table 1 Electrochemical parameters of $\text{K}_3\text{Fe}(\text{CN})_6$ at a bare GC electrode and a CNT/GC electrode

| Electrode | E_{pc} (mV) | E_{pa} (mV) | $E^{\circ'}$ (mV) | ΔE_p (mV) |
|-----------|---------------|---------------|-------------------|-------------------|
| CNT/GC | 150 | 207 | 178.5 | 57 |
| Bare GC | 138 | 225 | 181.5 | 87 |

From Table 1, it can be seen that the anodic and cathodic peak potentials of $\text{K}_3\text{Fe}(\text{CN})_6$ at a CNT/GC electrode shift toward the negative and positive direction, respectively, compared with those at a bare GC electrode. The peak separation (ΔE_p) of 87 mV indicates that $\text{K}_3\text{Fe}(\text{CN})_6$ undergoes a one-electron quasi-reversible reaction at a bare GC electrode, while the ΔE_p of 57 mV at CNT/GC electrode shows that the $\text{K}_3\text{Fe}(\text{CN})_6$ undergoes a one-electron ideal reversible reaction, because it is almost the same as the theoretical value which is 59 mV for one-electron ideal reversible reaction.³¹ These results show that CNT has catalytic activity toward electrochemical reaction. Most importantly, no any electrochemically active group was introduced into the CNT film. And also, the CNT/GC electrode was not activated electrochemically. The reason for the superior performance of CNT/GC in comparison with the GC electrode may originate from the CNT dimensions (of the tubes, the channels that are inherently present in the tubes), the electronic structure and the topological defects present on the tube surfaces.²⁴

Electrochemical reaction of DA at CNT/GC electrode

It is interesting to investigate the electrocatalytic activity of highly ordered CNT electrode, CNT/GC, toward the electrochemical reaction of biologically active molecules, such as DA, which is an important neurotransmitter. As showed in Fig. 5, curve b, DA showed a quasi-reversible electrochemical reaction with an oxidation

at 230 mV and a reduction at 91 mV on a bare GC electrode in phosphate buffer solution (PBS, 0.1 mol/L, pH 6.8), at a scan rate of 50 mV/s. From the cyclic voltammogram, it can be concluded that the rate of electrochemical oxidation of DA at a bare GC electrode is slow and irreversibility is high because the anodic and cathodic peaks are broad and the peak separation ($\Delta E_p = 139$ mV) is relatively large. Curve c in Fig. 5 is the cyclic voltammogram of DA (1×10^{-3} mol/L) on CNT/GC electrode in PBS (0.1 mol/L, pH 6.8) at a scan rate of 50 mV/s. The redox peak current increases significantly and the anodic and cathodic peak potentials shift toward negative and positive directions, respectively, in comparison with curve b. The anodic and cathodic peak potentials are 170 mV and 136 mV, respectively. The peak potential difference is 34 mV, suggesting DA is undergoing a two-electron oxidation with high reversibility at CNT/GC electrode since the peak potential difference is very close to the theoretical value, 30 mV, for two-electron ideal reversible electrochemical reaction.³¹ Curve a in Fig. 5 shows the cyclic voltammogram of CNT/GC electrode in PBS (0.1 mol/L, pH 6.8) in the absence of DA, and no any redox reaction can be found. These results indicate that the CNT/GC electrode has an excellent electrocatalytic activity toward DA electrochemical reaction.

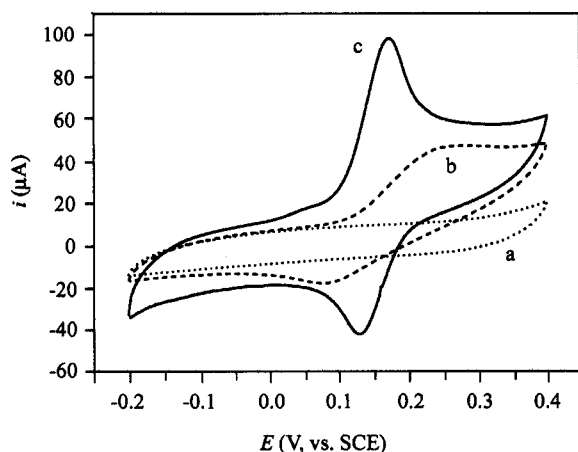


Fig. 5 Cyclic voltammograms of a CNT/GC electrode in phosphate buffer solution (0.1 mol/L, pH 6.8) in the presence (curve c) and the absence (curve a) of DA (1×10^{-3} mol/L) at a scan rate of 50 mV/s. Curve b is cyclic voltammogram of a bare GC electrode in the same solution and the same scanning rate as curve c.

Fig. 6 shows the cyclic voltammograms of DA (1×10^{-3} mol/L) in PBS (0.1 mol/L, pH 6.8) on a CNT/GC electrode at various scan rates. The dependence of the peak potential and current on the scan rate are summarized in Table 2.

From Table 2, it can be seen that the anodic and cathodic peak potentials shift to positive and negative direction, respectively, and the peak potential difference increases with the increase of the scan rate. The important

results concluded from Table 2 show that DA undergoes an ideal reversible electrochemical reaction on CNT/GC electrode at low scan rates, for example, 20 mV/s, since the ΔE_p at the scan rate is 30 mV, which is the same as the theoretical value.³¹ This result suggests that intramolecular cyclization of dopaminequinone, which is the product of DA oxidation, is absent on CNT/GC electrode surface.^{32,33} Perhaps the oxidation occurring on the CNT/GC electrode surface is stabilized in comparison with the product formed elsewhere in the sample. From the Table 2, it can be also noted that the current function, $i_p \cdot v^{-1/2}$, is not a constant with increase of the scan rate, but it has an increasing tendency. This may be because the inner surface of CNT is also electrochemically accessible. The current function increases with the increase of the scan rate, the more DA can enter the inside of CNT.

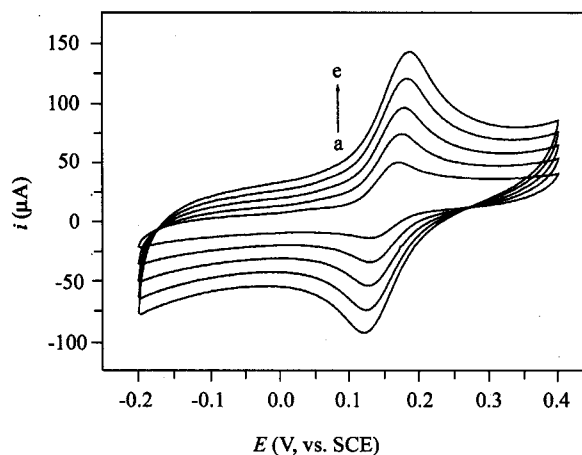


Fig. 6 Cyclic voltammograms of a CNT/GC electrode in phosphate buffer solution (0.1 mol/L, pH 6.8) containing DA (1×10^{-3} mol/L) at various scanning rates. The scan rate (from curves a to e) is 20, 40, 60, 80 and 100 mV/s, respectively.

Table 2 Dependence of peak potential and current on the scan rate for DA at a CNT/GC electrode

| v (mV/s) | E_{pc} (mV) | E_{pa} (mV) | ΔE_p (mV) | $i_{pa} \cdot v^{-1/2}$ [$(\mu A \cdot s^{1/2})/mV^{1/2}$] |
|---------------|------------------|------------------|----------------------|---|
| 20 | 138 | 168 | 30 | 7.0 |
| 40 | 137 | 169 | 32 | 8.1 |
| 60 | 133 | 170 | 37 | 8.4 |
| 80 | 130 | 177 | 47 | 8.8 |
| 100 | 127 | 182 | 55 | 9.2 |
| 150 | 120 | 188 | 68 | 10.3 |
| 200 | 111 | 193 | 82 | 10.4 |

It was reported³⁴ that the electrode surface is easy to be contaminated owing to the electrochemical polymerization of DA in the electrochemical process and the malan-like compounds will be produced on the surface of the electrode. But the cyclic voltammetric response of the CNT/GC electrode is almost unchanged after the electrode has been cycled several times in one DA solution and one

CNT/GC electrode in five DA solutions (the same concentration) produces the same voltammetric response. The fact suggests that the CNT/GC electrode has an excellent reproducibility and stability. These results also indicate that DA is not adsorbed or polymerized on the surface of the CNT/GC electrode.

Conclusion

The CNT/GC electrode showed excellent electrocatalytic activity toward DA electrochemical reaction even though no any electrochemically active group was introduced into CNT film and the electrode was not activated electrochemically. DA can undergo a two-electron ideal reversible electrochemical reaction on CNT/GC electrode at low scan rates (≤ 20 mV/s) with an excellent reproducibility and stability. The CNT/GC electrode might be used in biosensors to study the electrocatalytic reaction of biological important systems because the method of preparation of the CNT/GC is simple and the highly ordered CNT may present a steric effect on more efficient redox reactions of biomolecules.

References

- 1 Ajayan, P. M. *Chem. Rev.* **1999**, *99*, 1787.
- 2 Wang, S.-G.; Wang, J.-H.; Qin, Y. *Acta Chim. Sinica* **2002**, *60*, 957 (in Chinese).
- 3 Iijima, S. *Nature* **1991**, *354*, 56.
- 4 Ebbesen, T. W.; Ajayan, P. M. *Nature* **1992**, *358*, 220.
- 5 Treacy, M. M. T.; Ebbesen, T. W.; Gibson, J. M. *Nature* **1996**, *381*, 678.
- 6 Schlittler, R. R.; Seo, J. W.; Gimzewski, J. K.; Durkan, C.; Saifullah, M. S. M.; Welland, M. E. *Science* **2001**, *292*, 1136.
- 7 Tans, S. J.; Verschueren, R. M.; Dekker, C. *Nature* **1998**, *393*, 40.
- 8 Poncharal, P.; Wang, Z. L.; Ugarte, D.; de Heer, W. A. *Science* **1999**, *283*, 1513.
- 9 Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science* **2000**, *287*, 622.
- 10 Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. *Science* **2000**, *287*, 1801.
- 11 Vieira, R.; Pham-Huu, C.; Keller, N.; Ledoux, M. J. *Chem. Commun.* **2002**, 954.
- 12 Jin, Y.-X.; Liu, Z.-J.; Chen, W.-X.; Xu, Z.-D. *Acta Phys.-Chim. Sin.* **2002**, *18*, 459 (in Chinese).
- 13 Fan, S.; Chapline, M. G.; Franklin, N. R.; Tomblor, T. W.; Cassell, A. M.; Dai, H. *Science* **1999**, *283*, 512.
- 14 Kim, P.; Lieber, C. M. *Science* **1999**, *286*, 2148.
- 15 Dai, H.; Hafner, J. H.; Rinzler, A. G.; Colbert, D. T.; Smalley, R. E. *Nature* **1996**, *384*, 147.
- 16 Liang, W.-L.; Yokojima, S.; Ng, M.-F.; Chen, G.-H.; He, G.-Z. *J. Am. Chem. Soc.* **2001**, *123*, 9830.
- 17 Tang, Z.-L.; Zhang, L.; Wang, N.; Zhang, X.-X.; Wen, G.-H.; Li, G.-D.; Wang, J.-N.; Chan, C.-T.; Sheng, P. *Science* **2001**, *292*, 2462.
- 18 Saito, R.; Fujita, M.; Dreesselhaus, G.; Dreesselhaus, M. S. *Appl. Phys. Lett.* **1992**, *60*, 2447.
- 19 Wildöer, J. W. G.; Venema, L. C.; Rinzler, A. G.; Smalley, R. E.; Dekker, C. *Nature* **1998**, *391*, 59.
- 20 Odom, T. W.; Huang, J. L.; Kim, P.; Lieber, C. M. *Nature* **1998**, *391*, 62.
- 21 Pennisi, E. *Sci. News* **1992**, *142*, 36.
- 22 Liu, C. Y.; Bard, A. J.; Wudl, F. *Electrochem. Solid State Lett.* **1999**, *2*, 577.
- 23 Luo, H.; Shi, Z.; Li, N.; Gu, Z.; Zhuang, Q. *Anal. Chem.* **2001**, *73*, 915.
- 24 Britto, P. J.; Santhanam, K. S. V.; Ajayan, P. M. *Bioelectrochem. Bioenerg.* **1996**, *41*, 121.
- 25 Davis, J. J.; Coles, R. J.; Hill, H. A. O. *J. Electroanal. Chem.* **1997**, *440*, 279.
- 26 Wang, J.; Li, M.; Shi, Z.; Li, N.; Gu, Z. *Anal. Chem.* **2002**, *74*, 1993.
- 27 Campbell, J. K.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3779.
- 28 Wu, C.-G.; Bein, T. *Science* **1994**, *266*, 1013.
- 29 Rao, A. M.; Richter, E.; Bandow, S.; Chase, B.; Eklund, P. C.; Williams, K. A.; Fang, S.; Subbaswamy, K. R.; Menon, M.; Thess, A.; Smalley, R. E.; Dresselhaus, G.; Dresselhaus, M. S. *Science* **1997**, *275*, 187.
- 30 Martínez, M. T.; Callejas, M. A.; Benito, A. M.; Maser, W. K.; Cochet, M.; Andrés, J. M.; Schreiber, J.; Chauvet, O.; Fierro, J. L. G. *Chem. Commun.* **2002**, 1000.
- 31 Bard, A. J.; Faulkner, L. R. *Electrochemical Methods, Fundamentals and Applications*, 2nd Edn., John Wiley & Sons, Inc., New York, **2001**.
- 32 Kawade, R. B.; Laxmeshwar, N. B.; Santhanam, K. S. V. *Bioelectrochem. Bioenerg.* **1994**, *34*, 83.
- 33 Kawade, R. B.; Santhanam, K. S. V. *Bioelectrochem. Bioenerg.* **1995**, *38*, 405.
- 34 Lane, R. F.; Hubbard, A. T. *Anal. Chem.* **1976**, *48*, 1287.