Sensors **2003**, 3, 544-554

sensors

ISSN 1424-8220

http://www.mdpi.net/sensors

Direct Electrochemistry of Glucose Oxidase at a Gold Electrode Modified with Single-Wall Carbon Nanotubes

Wang Liang[1,2] and Yuan Zhuobin [1,2,*]

[1]Department of Chemistry, Graduate School, University of Science and Technology of China, Beijing P. R. 100039

[2] Department of Chemistry, Graduate School, Chinese Academy of Science, Beijing P. R. 100039

* Author to whom correspondence should be addressed.

Received: 08 August 2003 / Accepted: 15 November2003 / Published: 31 December 2003

Abstract: The direct electrochemistry of glucose oxidase (GOD) was accomplished at a gold electrode modified with single-wall carbon nanotubes (SWNTs). A pair of well-defined redox peaks was obtained for GOD with the reduction peak potential at –0.465 V and a peak potential separation of 23 mV at pH 7.0. Both FT-IR spectra and the dependence of the reduction peak current on the scan rate revealed that GOD adsorbed onto the SWNT surfaces. The redox wave corresponds to the redox center of the flavin adenine dinucleotide(FAD) of the GOD adsorbate. The electron transfer rate of GOD redox reaction was greatly enhanced at the SWNT-modified electrode. The peak potential was shown to be pH dependent. Verified by spectral methods, the specific enzyme activity of GOD adsorbates at the SWNTs appears to be retained.

Keywords: Glucose oxidase ; SWNT-modified electrode; Direct Electrochemistry

---

Introduction

Carbon nanotubes(CNTs) possess superb electrical conductivity, high chemical stability, and extremely remarkable mechanical strength and modulus[1]. These tubes can be divided into two categories. Multiwall carbon nanotubes (MWNTs) and single wall carbon nanotubes (SWNTs).

MWNTs are made of concentric cylinders placed around a common central hollow, with an moterlayer distance close to that of graphite(0.34nm). Single-wall carbon nanotubes (SWNTs) are usually arranged in a regular pattern of bundles composed of tens to hundreds of carbon nanotubes in parallel and in contact with each other. CNTs have been shown to be advantageous for a wide range of potential and practical applications, such as electronic devices[2],probe for scanning probe microscopy[3],high sensitivity nanobalance for nanoscopic particles[4] and chemical sensors[5,6].Recent developments in carbon nanotubes have been reviewed[1,7].

Depending on its atomic structure, carbon nanotube behave electrically either as metals or as semiconductiors[8,9].The subtle electronic properties suggest that carbon nanotubes have the ability to promote electron transfer reactions when used as an electrode material in electrochemical reactions. The application of CNTs in electroanalytical chemistry have been received more and more attentions[10-26].Carbon nanotubes can serve as excellent substrates for the development of biosensors or as a modifier to promote electron transfer reactions between many biologically important species with the underlying electrode. The immobilization of protein and enzyme onto CNTs is leading to the development of new biosensors [27-29].

Study of the direct heterogeneous electron transfer of proteins and enzyme is a convenient and informative means for understanding the kinetics and thermodynamics of biological redox processes [30]. The direct electrochemistry of the flavoenzymes has been widely investigated. However, in the absence of mediating small molecules, well-defined direct electrochemical behavior of flavoprotein-oxidase systems is rendered extremely difficult as the flavin adenine dinucleotied(FAD) moiety is deeply embedded within a protective protein shell. Glucose oxidase is a typical flavin enzyme with FAD as redox prosthetic group. Its biological function is to catalyze glucose to form gluconolaction. The GOD molecule is a structurally rigid glycoprotein with a molecular weight of 152,000-186,000Da, and consists of two identical polypeptide chains, each containing a FAD redox center. However, in general the GOD is not oxidized electrochemically through the electrode reaction. The reason is that the FAD/$FADH_2$ redox centers are located deeply in the apoenzyme[31]. Recently, a great number of methods have been developed to achieve direct electron transfer between the GOD and various chemically modified electrodes [32-34].

In present, novel carbon materials are evaluated as transducers, stabilizers and mediators for the construction of amperometric biosensors [35]. It is shown that carbon nanotubes are promising materials as electrochemical mediators and enzyme stabilizers. Based on the consideration that carbon nanotubes might be the best candidate among the various carbonaceous substrates for promoting the electron transfer reaction of GOD and for biomolecular attachment [29,36], we explored the possibility of direct chemistry studies of GOD at SWNT-modified gold electrodes. We now wish to report the preparation of SWNT-modified gold electrodes for the studies of direct electrochemistry of GOD. The analytical performance of the SWNT-modified electrodes is described and a spectroscopic evidence is presented to show the retention of the specific enzyme activity of GOD at the SWNT-modified surfaces. Our work demonstrates that carbon nanotubes might be a unique material for the fabrication of useful biosensors.

Experimental

Reagents and Instruments

Purified SWNTs were purchased from SES Research (Houston, TX). All solutions were prepared with deionized water treated with a Millipore water purification system (Millipore Corp.). Glucose Oxidase was acquired from Sigma and dissolved in a phosphate buffer solution (0.05 M, pH 7.0).

Voltammetric measurements were performed with a CHI 660 electrochemical workstation (CH Instruments, Austin, TX) in a conventional three-electrode cell. The working electrode was a Au disk electrode with a diameter of 2 mm. Prior to each measurement, the electrode was polished with diamond pastes and an alumina slurry down to 0.05 μm on a polishing cloth, followed by sonicating in water and ethanol. The electrode was rinsed with a copious amount of deionized water. A saturated calomel electrode (SCE) and a platinum electrode were used as the reference and auxiliary electrodes, respectively. Unless otherwise stated, the electrolyte solutions were thoroughly degassed with N_2 and kept under a N_2 blanket.

FT-IR spectra were collected using an Avatar 360 FT-IR spectrometer (Nicolet Instrument Corp., Madison, WI).

Preparation of GOD/SWNTs Modified Electrode

With the aid of ultrasonic agitation, 1 mg of purified SWNTs was dispersed in 10 mL of N,N-dimethylformamide (DMF). To modify the gold electrode with SWNTs, 15 μL of the SWNT suspension was cast onto the gold electrode and the solvent was allowed to dry under an infrared lamp. The preparative procedure was found to produce optimal voltammetric responses. Too little of the casting solution will not yield discernible voltammetric currents, whereas too much will increase the background current so much that the redox peaks became distorted. The resulting electrodes were sequentially rinsed with water and the working buffer just before carrying out CV experiment. In order to prepare GOD/SWNTs modified electrode, 5μL 1.0×10^{-4}M GOD solution was dropped onto the surface of the SWNTs modified electrode then allowed to dry under ambient conditions. Also, GOD/SWNTs electrodes were rinsed completely with water and the working buffer solution prior to carry out CV experiment.

To measure the FT-IR spectra, silicon (100) wafers were used as the substrate for supporting the SWNT films (prepared in a similar manner to that for the Au disk electrode except that SWNT was dispersed in ethanol).

Results and Discussion

Direct electrochemistry of GOD at the SWNT-modified Au electrode

Cyclic voltammograms (CVs) overlaid in Figure 1 show the redox behaviors of GOD in a 0.05 M phosphate buffer solution (pH 7.0) at a bare gold electrode (curve 1) and at a

GOD/SWNT-modified Au electrode (curve 3). The CV acquired at the SWNT-modified gold electrode in the absence of GOD (curve 2) is also given. As can be seen, while GOD at a bare gold electrode essentially exhibits no voltammetric response, a pair of well-defined redox peaks was observed at the GOD/SWNT-modified electrode. The absence of any discernable faradaic current in curve 2 suggests that the observed peaks in curve 3 is not given rise by the SWNTs. For curve 3, at pH 7.0 and *v*(scan rate) of 0.1 Vs^{-1}, the cathodic peak potential (E_{pc}) is –0.465 V *vs.* SCE and the peak potential separation (ΔE_p) is 23mV. The ratio of the cathodic current over the anodic one is close to 1, suggesting that GOD undergoes a quasi-reversible redox process at the SWNT-modified electrode. The peak potential and the voltammetric characteristics are consistent with reported values for free FAD and the FAD redox center of the flavoenzyme[31,37]. The large background current is attributable to the catalytically active surface of the modified electrode. SWNTs, with diameters in the range of 1-2 nm, and up to several microns in length, have very high aspect ratio (length versus diameter). When used as an electrode material, the surface area of the electrode is increased. Consequently, the background current at the SWNT-coated surface is greater than that at the bare surface.

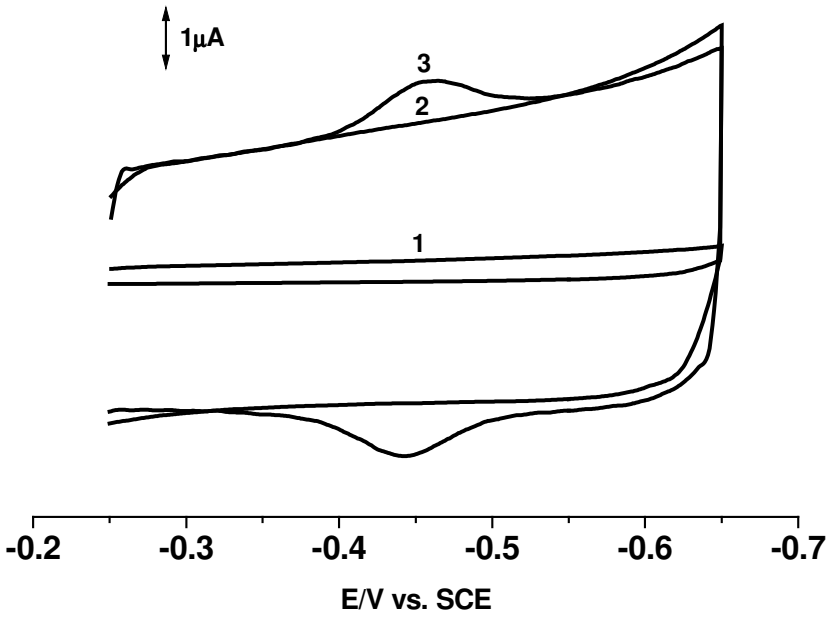

Fig.1. Cyclic voltammograms of glucose oxidase (1.0×10^{-4} M) at a bare gold electrode (1) and a SWNT-modified glod electrode (3). Curve (2) is a voltammogram acquired at a SWNT-modified gold electrode in the absence of glucose oxidase. The electrolyte solution used was a 0.05M phosphate buffer (pH 7.0) and the scan rate employed was $0.1Vs^{-1}$.

A voltammograms at unmodified glassy carbon electrodes and found that the voltammetric response (data not shown) was comparable to curve 1. Thus, it is conclusive that SWNT-modified surface indeed enhances the electron transfer rate.

Effect of Scan Rate on the Peak Current and Peak Potential of GOD at an SWNT Film-Modified Electrode

The influence of the scan rate on the electrochemistry of GOD at the SWNT film modified electrode was investigated by cyclic voltammetry. Figure 2 displays an overlap of CVs of GOD acquired at five different scan rates. The i_{pc}-ν plot shown in the inset exhibits a linear relationship (with r = 0.9991). Moreover, ΔE_p remains virtually constant within the range of scan rates studied. Thus, it is clear that GOD adsorbed onto the surface undergoes a reversible electron transfer with the SWNTs. The reason for the facile electron transfer reaction is that the surface of SWNTs are known to enhance many electrochemical reactions [13,38,39]. The better performance of the carbon nanotube electrodes has been found due to the carbon nanotube dimensions (of the tubes, the channels that are inherently present in the tubes), the electronic structure, and the topological defects present on the tube surface [39].

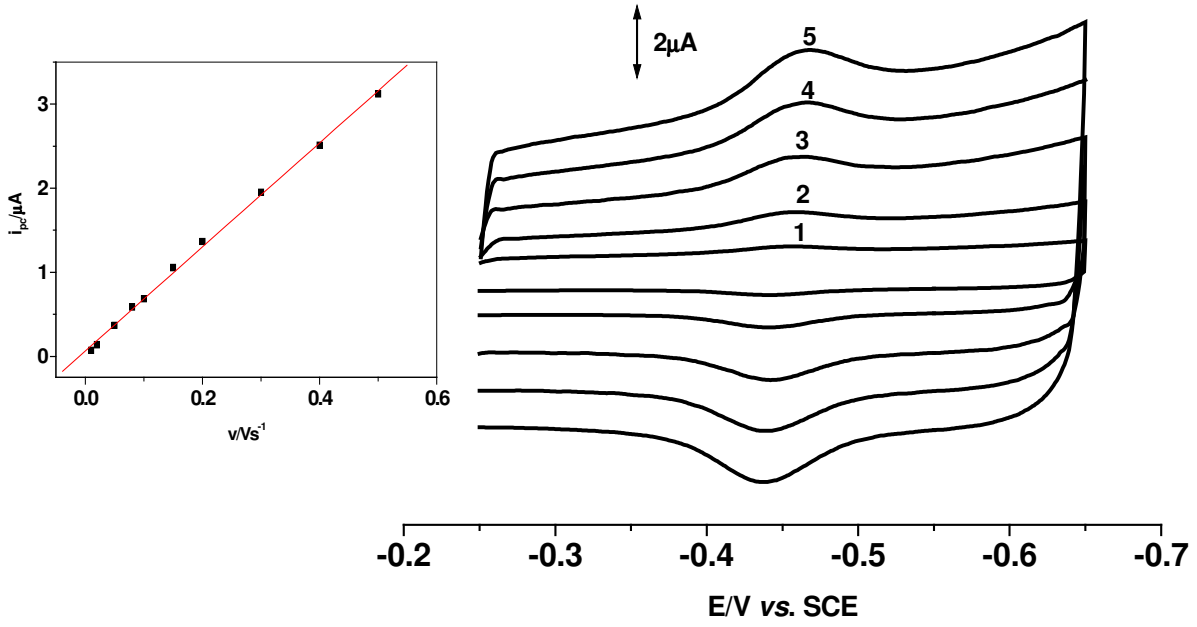

Fig.2. Cyclic voltammograms of glucose oxidase (1.0 ×10^{-4} M) at a SWNT-modified gold electrode in a 0.05M phosphate buffer solution (pH 7.0) at scan rates of (1) 0.02, (2) 0.05, (3) 0.10, (4) 0.15, (5) 0.20 Vs^{-1}. The inset is a plot of the reduction peak current i_{pc} against the scan rate.

Effect of pH on the Peak Current and Peak Potential of GOD at an SWNT Film-Modified Electrode

Figure 3 depicts a series of CVs of GOD collected from 0.05 M phosphate buffer solutions of different pH values. As can be seen, the peak potential of GOD is dependent on the solution pH. Within the pH range of 5.0-9.1, the peak potential shifts to the cathodic direction with a slope of 48 mV per decade of $[H^+]$. Therefore, it appears that there are tow protons involved per transfer of two electrons. Thus, the electrode reaction could be descried as below:

$$GOD - FAD + 2e + 2H^+ \rightarrow GOD - FADH_2$$

At about pH 7.0, the GOD redox peaks were found to best defined. Therefore, we fixed the solution pH at 7.0 for the investigations of the analytical performance of SWNT-modified electrodes covered with GOD.

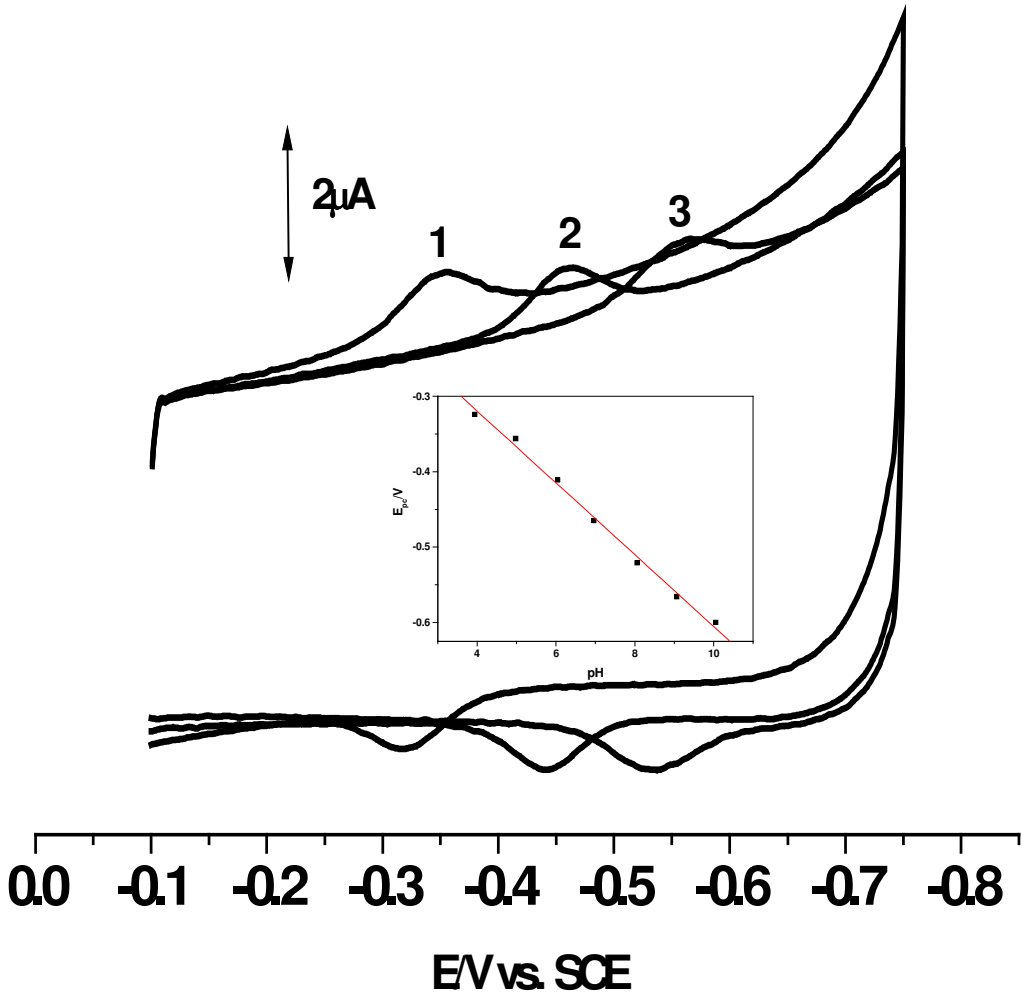

Fig.3. Cyclic voltammograms of glucose oxidase (1.0×10^{-4} M) at a SWNT-midified gold electrode in 0.05M phosphate buffer at pH values of (1)5.0, (2)7.0, (3)9.1. The inset shows the relationship between the reduction peak current E_{pc} and the solution pH value.The scan rate employed was $0.1Vs^{-1}$.

Stability of the SWNT Film-Modified Electrode

The preparative procedure for forming SWNT-modified electrodes was found to yield highly repeatable GOD redox currents. For example, five SWNT-modified gold electrodes fabricated using the same protocol produced an average i_{pc} of 0.75 μA with a relative standard deviation (%R.S.D.) of 6.5%, when the GOD concentration was 1.0×10^{-4} M and ν was 0.1 Vs^{-1}. Such a value is acceptable for most well-established analytical methods, indicating that the effective area constituting SWNTs for the GOD adsorption remains constant between preparations.

The surface coverage (Γ) of GOD on the SWNT Film-Modified Electrode

The surface coverage (Γ) of GOD was calculated. In order to obtain the effective surface area of SWNT, $K_3Fe(CN)_6$ was used as a probe. CV experiments of 1mM $K_3Fe(CN)_6$ at SWNT modified Au electrode were performed .For a reversible process , $i_p=(2.69\times10^5)n^{3/2}AD^{1/2}v^{1/2}C_0$ for $K_3Fe(CN)_6$, n=1, $D=7.6\times10^{-6}cm^2s^{-1}$, then the effective surface area of SWNT on the electrode could be calculated and $0.040cm^2$ was obtained. Then according to the coulometer charge in the cyclic voltammeter peaks of GOD/SWNT, the amount of GOD adsorbed on the SWNT surface could be also obtained. It was found that Γ is 5.1×10^{-11} mol cm^{-2}, indicating that GOD maybe has a saturated monolayer adsorption on SWNT surface.

FT-IR spectra of GOD on the SWNTs Films

The adsorbed GOD still retains its specific enzyme activity, which is verified by FT-IR measurements. The amide I and II infrared bands have been widely used for monitoring conformational changes in proteins [40,41]. The amide I band (1700-1600cm^{-1}) is caused by C=O stretching vibrations of peptide linkages in the protein's backbone. The amide II band (1600-1500cm^{-1}) results from a combination of N-H in plane bending and C-N stretching of the peptide groups. As shown in Figure 4, two amide bands, within ranges of 1700-1600 cm^{-1} and 1600-1500 cm^{-1}, were observed at both a GOD film cast onto a Si wafer and a SWNT film covered with GOD. The former (1652 cm^{-1}, amide I band) is caused by C=O stretching vibrations of peptide linkages in the GOD backbone, whereas the latter (1574 cm^{-1}, amide II band) results from a combination of N-H in-plane bending and C-N stretching of the peptide groups. A SWNT-modified surface did not produce any spectral absorption in the wavelength range. The presence of these two distinctive absorption bands in Figure 4 clearly suggests that the attachment of GOD onto SWNTs does not perturb the GOD conformations drastically. The small difference of the two spectra in Figure 4 indicated that GOD retained its native conformation in SWNT film despite the small perturbation. Purposely denatured samples of GOD showed completely different spectral characteristics in spectra in amide I and II regions.

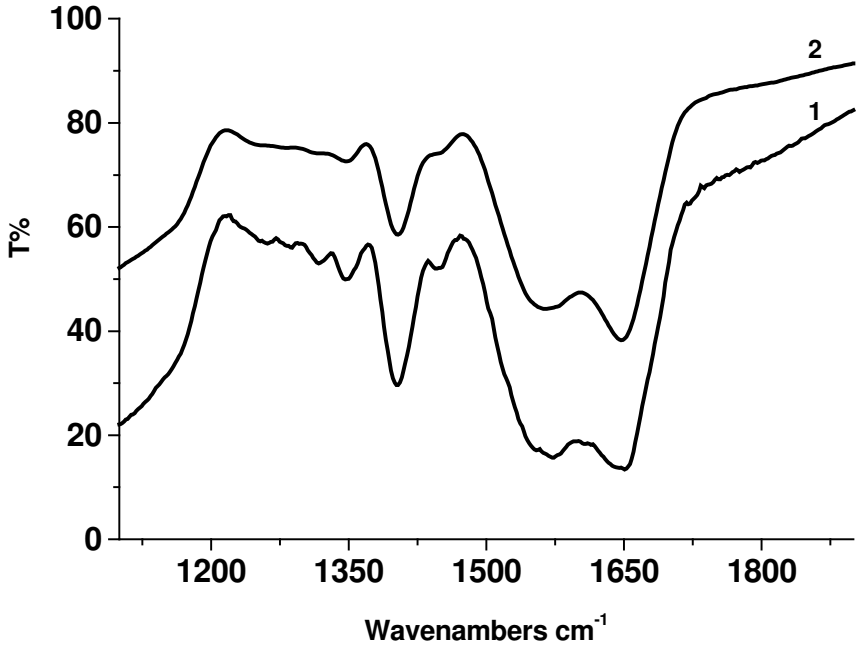

Fig.4. FT-IR spectra of a cast glucose oxidase film on a silicon wafer (1) and a glucose oxidase film covering a SWNT-modified silicon wafer(2).

It is well known that carbon nanotubes are promising materials as electrochemical mediators and enzyme stailizers[35]. It is possible to adsorb a variety of enzymes on carbon nanotube while their specific enzyme activity were retained. Davis's group demonstrated that catalytic response at glassy carbon electrode modified with GOD-SWNTs (glucose oxidase immobilized on SWNTs) was observed upon the addition of glucose[42]. Zhao reported direct electrochemistry of horseradish peroxidase(HRP) at carbon nanotube powder microelectrode(CNTPME).Furthermore the adsorbing HRP still retains its catalytic activity to H_2O_2[43].The combination of carbon nanotube with redox active enzymes would appear to offer an excellent and convenient platform for a fundamental understanding of biological redox reactions as well as the development of reagentless biosensors and nanobiosensors.

Conclusions

This work demonstrates that direct electrochemistry of glucose oxidase can be conducted at SWNT-modified Au electrodes. A reversible reduction wave can be observed with E_{pc} at -0.465 V (*vs*. SCE) and ΔE_p of 23 mV at pH 7.0. The peak potential is pH-dependent and shifts to the cathodic direction by 48 mV per unit of pH. The cathodic peak current, i_{pc}, was found to be proportional to the scan rate, suggesting that the redox wave was given rise by the GOD adsorbate at the SWNTs. The specific enzyme activity of the GOD adsorbates at the SWNTs was found to

be retained. The results suggest that SWNT-modified electrodes covered with redox-active enzymes can retain the enzyme activities and provide an attractive route for the development of biosensors and nanobiosensors.

Acknowledgements

This project was supported by National Science Foundation of China (No.29875027, 20175025), the grant the State Key Laboratory for eletroanalytical chemistry (Changchun Insititute of applied chemistry of CAS).

Reference

1. Ajayan, P. M. Nanotubes from Carbon.*Chem. Rev.* **1999**, *99*,1787-1800.
2. Saito S. Carbon Nanotubes for Next-Generation Electronics Devices. *Science*.**1997,** *278,* 77-78.
3. Wong S. S.; Woolley A. T.; Joselevich E.; Cheung C. L.; Lieber C.M. Covalently-Functionalized Single-Walled Carbon Nanotube Probe Tips for Chemical Force Microscopy. *J. Am. Chem. Soc.* **1998**, *120*, 8557-8558.
4. Poncharal P.; Wang Z. L.; Ugarte D.; Heer W. A. de. Electrostatic Deflections and Electromechanical Resonances of Carbon Nanotubes. *Science*.**1999**,*283*,1513-1516.
5. Collins P. G.; Bradley K.; Ishigami M.; Zettl A. Extreme Oxygen Sensitivity of Electronic Properties of Carbon Nanotubes. *Science*. **2000**, *287*,1801-1804.
6. Kong J.; Franklin N. R.; Zhou C.; Chapline M. G.; Peng S.; Cho.K.; Dai H.J. Nanotube Molecular Wires as Chemical Sensors. *Science.* **2000**, *287*, 622-625.
7. Heer W.A.de. Recent developments in carbon nanotubes.*Current Opinion in Solid State and Materials Sciecne* . **1999**, *4*, 355-359.
8. Odom T. W.; Huang J. L.; Kim P.; Lieber C.M.Atomic structure and electronic properties of single-walled carbon nanotubes. *Nature*. **1998**, *391*, 62-64.
9. Wilder J. W. G.; Venema L. C.; Rinzler A. G.; Smalley R. E.;Dekker C. Electronic structure of atomically resolved carbon nanotubes. *Nature.* **1998**,*391*,59-62.
10. Campbell J.K.; Sun L.; Croods R.M. Electrochemistry using single carbon nanotubes. *J. Am. Chem. Soc.* **1999**,*121*,3779-3780.
11. Sherigara B.S.; Kulner W.; D'Souza F. Electrocatalytic properties and sensor applications of fullerenes and carbon nanotubes. *Electroanalysis.* **2003**,*15*,753-771.
12. Zhao Q.;Gan Z.H.; Zhuang Q.K. Electrochemical sensors based on carbon nanotubes. *Electroanalysis.* **2002**,*14*,1609-1613.
13. Wang J.X.; Li M.X.; Shi Z.J.; Li N.Q.; Gu Z.N. Investigation of the electrocatalytic behavior of single-wall carbon nanotube films on an Au electrode. *Microchem. J.* **2002**,*73*,325-333.
14. Wang J.X.; Li M.X.; Shi Z.J.; Li N.Q.; Gu Z.N. Direct electrochemistry of cytochrome *c* at a glassy carbon electrode modified with single-wall carbon nanotubes. *Anal. Chem.* **2002**,*74*,1993-1997.

15. Luo H.X.; Shi Z.J.; Li N.Q.; Gu Z.N.; Zhuang Q.K. Investigation of the electrochemical and electrocatalytic behavior of single-wall carbon nanotube film on a glassy carbon electrode. *Anal. Chem.* **2001**,*73*,915-920.
16. Wang J.X.; Li M.X.; Shi Z.J.; Li N.Q.; Gu Z.N. Electrocatalytic oxidation of norepinephine at a glassy carbon electrode modified with single wall carbon nanotubes. *Electroanalysis.* **2002**,*14*,225-230.
17. Zhao Y.D.; Zhang W.D.; Chen H.; Luo Q.M. Anodic oxidation of hydrazine at carbon nanotube powder microelectrode and its detection. *Talanta.* **2002**,*58*,529-534.
18. Wang G.; Xu J.J.; Chen H.Y. Interfacing cytochrome *c* to electrodes with a DNA-carbon nanotube composite film. *Electrochem. Comm.* **2002**,*4*,506-509.
19. Zhao Y.D.; Zhang W.D.; Chen H.; Luo Q.M. Electrocatalytic oxidation of cysteine at carbon nanotube powder microelectrode and its detection. *Sensors and Actuators B* **2003**,*92*,279-285.
20. Wang Z.H.; Wang Y.M.; Luo G.A. The electrocatalytic oxidation of thymine at α-cyclodextrin incorporated carbon nanotube-coated electrode. *Electroanalysis.* **2003**,15,1129-1133.
21. Wang Z.H.; Wang Y.M.; Luo G.A. selective voltammetric method for uric acid detection at β-cyclodextrin modified electrode incorporating carbon nanotubes. *Analyst.* **2002**,*127*,1353-1358.
22. Wang Z.H.; Liu J.; Liang Q.G.; Wang Y.M.; Luo G.A. Carbon nanotube-modified electrodes for the simultaneous determination of dopamine and ascorbic acid. *Analyst*. **2002**,*127*,653-658.
23. Wang J.; Musameh M.; Lin Y. Solubilization of Carbon Nanotubes by Nafion toward the Preparation of Amperometric Biosensors. *J. Am. Chem. Soc.* **2003**,*125*,2408-2409.
24. Musameh M.; Wang J.; Merkoci A.; Lin Y. Low-potential stable NADH detection at carbon-nanotube-modified glassy carbon electrodes. *Electrochem. Comm.* **2002**,*4*,743-746.
25. Wang Z.H..; Liang Q.L.; Wang Y.M.; Luo G.A. Carbon nanotube-intercalated graphite electrodes for simultaneous determination of dopamine and serotonin in the presence of ascorbic acid. *J. Electroanal. Chem.* **2003**,*540*,129-134.
26. Wu K.B.; Fei J.J.; Hu S.S. Simultaneous determination of dopamine and serotonin on a glassy carbon electrode coated with a film of carbon nanotubes. *Anal. Biochem.* **2003**, *318*, 100-106.
27. Davis J.J.; Green M.L.H.; Hill H.A.O.; Leung Y.C.; Sadler P.J.; Sloan J.; Xavier A.V.; Tsang S.C. The immobilisation of proteins in carbon nanotubes. *Inorg. Chim. Acta,* **1998**, *272,*261-266.
28. Azamian B.R.; Davis J.J.; Coleman K.S.; Bagshaw C.B.; Green M.L.H. Bioelectrochemical single-walled carbon nanotubes. *J.Am.Chem.Soc.* **2002**,*124*,12664-12665.
29. Huang W.J.; Taylor S.; Fu K.F.; Lin Y.; Zhang D.H.; Hanks T.W.; Rao A.M.;Sun Y.P. Attaching proteins to carbon nanotubes via diimide-activated amidation. *Nano Letters*. **2002**,*2*,311-314.
30. Guo Y.Z.; Guadalupe R. Direct electrochemistry of horseradish peroxidase adsorbed on glassy carbon electrode from organic solutions. *Chem.Commun.* **1997**,1437-1438.
31. Chi Q.; Zhang J.D.; Dong S.J.; Wang E.K. Direct electrochemistry and surface characterization of glucose oxidase adsorbed on anodized carbon electrodes. *Electrochimica Acta.* **1994**,*39*,2431-2438.
32. Zhao Y.D.; Zhang W.D.; Chen H.; Luo Q.M. Direct electron transfer of glucose oxidase molecules adsorbed onto carbon nanotube powder microelectrode. *Anal. Sci.* **2002**,*18*,939-941.

33. Liu S.; Ju H.X. Reagentless glucose biosensor based on direct electron transfer of glucose oxidase immobilized on colloidal gold modified carbon paste electrode. *Biosensors and Bioelectron.* **2003**, *in press*,1-7.
34. Wu Z.Y.; Wang B.Q.; Dong S.J.; Wang E.K. Amperometric glucose biosensor based on lipid film. *Biosensors and Bioelectron.* **2000**,*15*,143-147.
35. Sotiropoulou S.; Gavalas V.; Vamvakaki V.; Chaniotakis N.A. Novel carbon materials in biosensor systems. *Biosensors and Bioelectron.* **2003**,*18*,211-215.
36. Shim M.; Kam N.W.S.; Chen R.J.; Li Y.M.; Dai H.J. Functionalization of carbon nanotubes for biocompatibility and biomolecular recognition. *Nano Letters* . **2002**,*2*,285-288.
37. Rodrigues C. G.; Wedd A.G.; Bond A. M. Electrochemistry of xanthine oxidase at glassy carbon and mercury electrodes.*J. Electroanal. Chem.* **1991**,*312*,131-140.
38. Davis J.J.; Coles R.J.; Hill H.A.O. Protein electrochemistry at carbon nanotube electrodes. *J. Electroanal. Chem.* **1997**,*440*,279-282.
39. Britto P. J.; Santhanam K. S. V.; Ajayan P. M. Carbon nanotube electrode for oxidation of dopamine. *Bioelectrochem. Bioenerg.* **1996**,*41*,121-125.
49. Kumosinski T.F.; Unruh J.J. *Molecular Modeling*.ACS Symp.Ser. 576;In:Kumosinski T.F.; Leibman M.M.(Eds.);Washington,DC,**1993**,pp71-98
41. Chen X.H.; Xie H.; Kong J.L.; Deng J.Q. Characterization for didodecyldimethylammonium bromide liquid crystal film entrapping catalase with enhanced direct electron transfer rate. *Biosensor and Bioelectron.* **2001**,*16*,115-120.
42. Azamian B.R.; Davis J.J.; Coleman K.S.; Bagshaw C.B.; Green M.L.H. Bioelectrochemical single-walled carbon nanotubes. *J.Am.Chem.Soc.* **2002**,*124*,12664-12665.
43. Zhao Y.D.; Zhang W.D.; Chen H.; Luo Q.M.; Li S.F.Y. Direct electrochemistry of horseradish peroxidase at carbon nanotube powder microelectrode. *Sensors and Actuators B.* **2002**,*87*,168-172.

Sample Availability: Available from the authors.