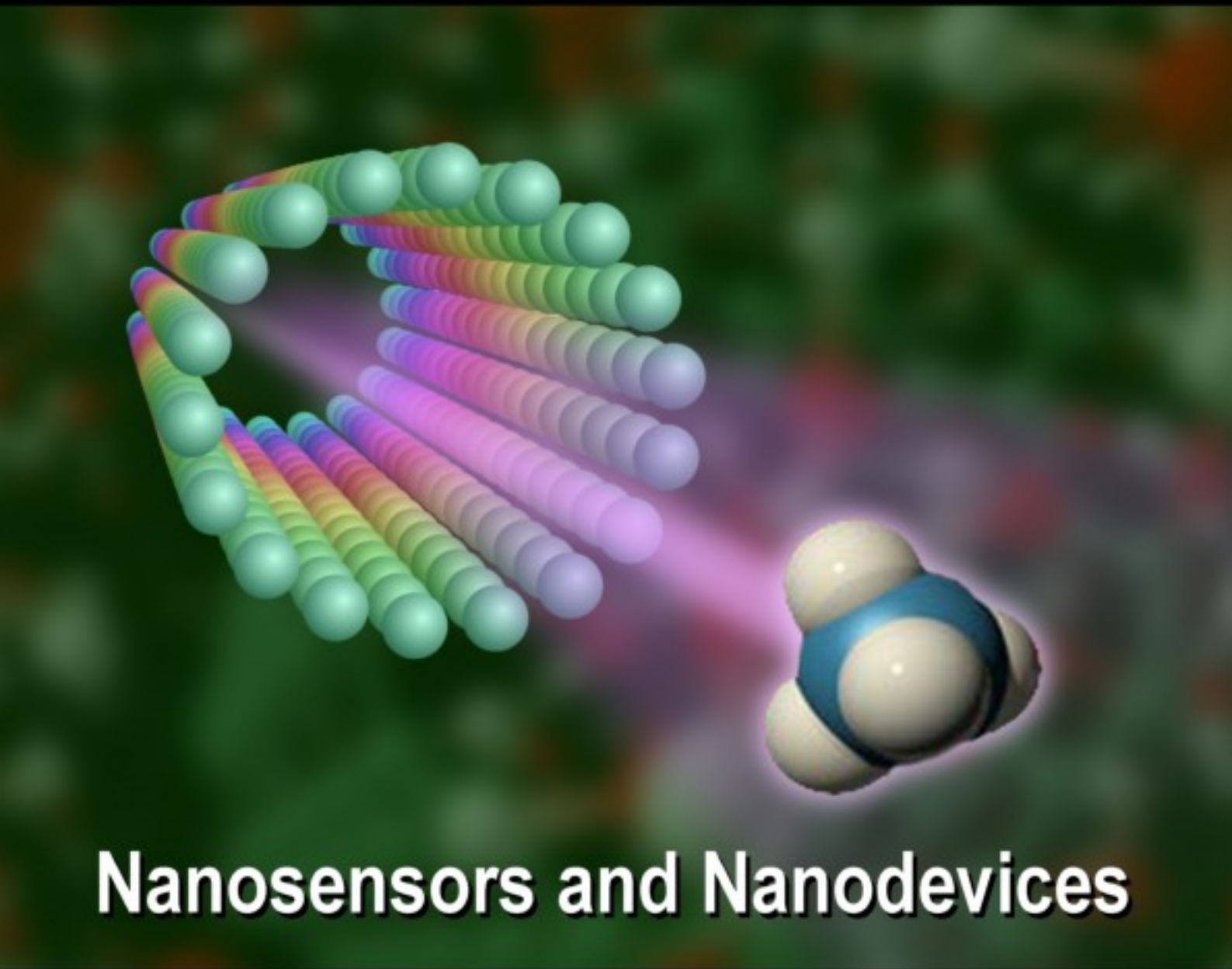
ISSN 1726-5749

SENSORS & TRANSDUCERS

vol. 73
11/06



Nanosensors and Nanodevices

International Frequency Sensor Association Publishing

IFSA

Sensors & Transducers

Volume 73
Issue 11
November 2006

www.sensorsportal.com

ISSN 1726-5479

Sensors & Transducers Journal, Vol.73, Issue 11, November **2006,** *pp.799-803*

Sensors & Transducers
ISSN 1726-5479

http://www.sensorsportal.com

Preparation of Multiwalled Carbon Nanotube-Poly (4-styrenesulfonic acid) Aqueous Dispersion for Dopamine Sensing

Aihua LIU* [a] **and Jin WANG** [b]
[a]Department of Chemistry , Michigan State University, East Lansing, MI 48824-1322, USA
[b]Nano-Medical Engineering Laboratory, Riken Institute,
2-1 Hirosawa, Wako, Saitama 351-0198, Japan,
Tel.: ++81-29-5080, e-mail: liuaihua@hotmail.com

Received: 21 May 2006 /Accepted: 30 November 2006 /Published: 4 December 2006

Abstract: A simple and facile method for the non-covalent functionalization of multi-walled carbon nanotubes (MWNTs) using poly(4-styrenesulfonic acid) (PSS) is proposed. The resulting PSS-MWNTs dispersion is readily soluble in water and can be left to stand for 2 weeks at room temperature, no phase separation with aggregation of nanotubes at the bottom of the vials was observed. The as-prepared PSS-MWNTs dispersions could facilitate the processing of the nanotubes into composites with high nanotube loading. The PSS-MWNTs complex shows high electrocatalytic activity to the oxidation of neutrontransmitter of dopamine, suggesting that the coating of PSS onto carbon nanotubes surface without destroying the electronic structures of the pristine carbon nanotubes; therefore, the unique properties including the catalytic property of the nanotubes retained. It is envisioned that the PSS-MWNTs aqueous dispersions may find possible applications in the development of biosensors, bioelectronics, separation and environment protection as well as other biological events where water-based environment is required. *Copyright © 2006 IFSA.*

Keywords: Dispersion of multi-walled carbon nanotubes, Poly(4-styrenesulfonic acid), Dopamine, Biosensing

1. Introduction

Recently, there is increasing interest in the study of carbon nanotubes (CNTs) because of their extraordinary physical and chemical properties. However, due to the poor solubility of CNTs in all solvents, their real applications were greatly impeded. Dispersions of CNTs by polymer in organic solvents [1, 2] or preparation of CNTs dispersions in water by using lower molecule-weight surfactants are not suitable for biochemical and biosensing application[3, 4]. Single-walled carbon nanotubes (SWNTs) can reversibly solubilize into water with their surface wrapped with polyanionic polystyrene sulfonate (PSS), however, there are no reports on biochemical application [3]. Non-covalent functionalization of CNTs holds great promise, because it does not disrupt the large ð-electronic surface, and thus it can open the possibility to organize CNTs into 3D networks. From the view of point of manipulation and processing, it remains a great challenge to develop efficient non-covalent functionalization of CNTs in water. It is important to prepare homogeneous, stable and relatively concentrated CNTs aqueous dispersions suitable for biological application. Dopamine (DA) is an important neurotransmitter, which involves in motor and cognitive functions; DA deficits in brain may cause Parkinson's disease in human beings [5, 6]. It is of significant physiological importance to monitor DA. It was reported that carbon nanotube-coated electrodes can electrocatalytic oxidation of biomaterials such as DA[7], NADH[8] and thymine[9]. However, there are few reports to use homogeneous CNT dispersion for the real bio-application.

In the present study, an alternative approach to generate multi-walled carbon nanotubes (MWNTs) aqueous dispersions using poly(4-styrenesulfonic acid) (PSS, Mw, 70 000) was proposed. Both MWNTs (outer diameter of 30-50 nm) and PSS were commercial from Wako Chemical Co, Japan). The chemical structure of PSS is illustrated in Fig.1.

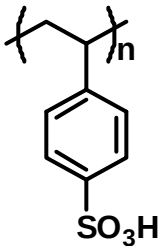


Fig. 1. Chemical structure of PSS used in this study.

2. Experimental Section

PSS-MWNTs complex was prepared as following: suitable amount of pristine MWNTs were first dispersed in different concentration of PSS in water under sonication for 30 min. The as-prepared dispersion was left to stand 3-6 hrs. A little precipitate (it may contain catalyst and segregated MWNTs particles) was removed by filter. PSS-MWNTs complex was obtained by freeze-drying the filtrate. The resulting PSS-MWNTs complex was re-dissolved in water to obtain homogeneous dispersions.

A 15-ìL aliquot PSS-MWNTs aqueous dispersion containing was uniformly cast onto the inverted GCE (denoted as PSS-MWNTs/GCE) and let to dry under ambient conditions for 2 hrs. In a control experiment, a 15-ìL aliquot PSS (1mg/mL) solution was uniformly cast onto the inverted GCE (denoted as PSS/GCE). Thus, uniform membrane was covered on the electrode. The as-prepared electrodes were let to dry at room temperature at least 24 hrs before use. The electrochemical response was measured in a conventional three-electrode system using a modified GCE as working electrodes, a

platinum wire as counter electrode, and an Ag/AgCl (3.3 M KCl) electrode as reference electrode. All potentials were reported in this context with respect to this reference. Cyclic voltammetry measurements were performed using an Autolab potentiostat/galvanostat (Eco Chemie, B. V, Utrecht, The Netherlands).

3. Preparation of PSS-MWNTs Composite

The as-received MWNTs dispersed in water are quickly aggregated to the bottom of the vials. PSS-MWNTs dispersion can be left to stand for two weeks at room temperature, no phase separation with aggregation of nanotubes at the bottom of the vials was observed, which suggests the formation of homogeneous dispersions of nanotubes (photographs not shown). The solubility strongly indicates that PSS-MWNTs complex is stable and irreversibly bound rather than a simple mixture. PSS is polymeric weak acid with conjugated side-chain, which may form ð-ð stacking with CNTs surface, therefore, facilitate the formation of stable complex. It is reported that a nonionic surfactant or polymer's ability to suspend nanotubes originating from the size of the hydrophilic group, with high molecular weights suspending much amount of nanotubes because of the enhanced steric stabilization with long polymeric groups [10].

The surface morphology of PSS-MWNTs composite was examined by using scanning electron microscopy (Leo Gemini Supra 35, Carl Zeiss). Figure 2 shows SEM images of the pristine MWNTs powder and the PSS-MWNTs complex. The surface of pristine MWNTs is smooth, and the tubes are heavily entangled with snake-like shape (Fig. 2a). The surface of PSS-coated MWNTs demonstrates polymer protuberances (Fig. 2b). Similar results were reported with chitosan-functionalized MWNTs [11]. Polymer film was connected to the nanotubes, which favors the stability of the nanotube dispersion. The nanotubes are generally accumulated together as bundles in most solvents due to the intrinsic van der Waals force. The hydrophobic interaction of the polymer backbone to the graphene surface makes PSS wrap around MWNTs; the styrenesulfonic acid group of the side chain of the polymer around tubes makes them hydrophilic, which should decrease the intrinsic van der Waals force of nanotubes. Furthermore, the conjugated side-chain in PSS may interact with MWNTs surface to form ð-ð stacking, accordingly, to stabilize the complex. Therefore, the nanotubes are well dispersed.

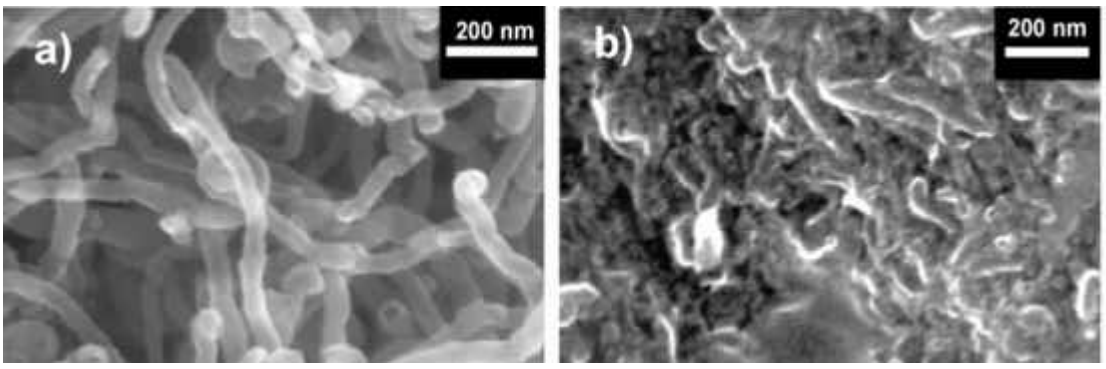


Fig.2. SEM images of pristine MWNTs(a) and PSS-MWNTs complex (b).

4. Dopamine-sensing Using PSS-MWNTs Composite Covered Glassy-Carbon Electrode

The catalytic activity of PSS-MWNT complex may be an indicator to whether the nanotubes in the complex still retain its native structure, considering that PSS is of no catalytic activity. The

electrocatalytic oxidation of DA by the PSS-MWNTs film-covered glassy carbon electrode (GCE) was examined.

Figure 3 shows typical cyclic voltammograms of modified-electrodes in the absence and in the presence of DA. The direct oxidation of DA at PSS/GCE is reversible with a small oxidation peak locates at 0.2 V (Fig. 3A, lines b and c), which is in agreement with oxidation of DA at bare GCE(b). The redox peaks of DA at PSS-MWNTs/GCE was a little negatively shifted (Fig. 3B, lines b and c) with the anodic peak current and cathodic peak current linearly increased with the scan rate. In addition, the symmetry of the anodic peak and cathodic peak for DA oxidation at PSS-MWNTs/GCE is obviously improved compared with DA with PSS/GCE. Moreover, the anodic peak current and cathodic peak current are greatly increased. For example, the oxidation peak current at PSS-MWNTs/GC electrode is 11 times higher than that for PSS/GC electrode in 0.1 mM DA solution. These observations clearly suggest the excellent catalytic role of entrapped MWNTs. It should be pointed here that the increment of the current may in part come from the enlargement of the surface area because of incorporating of CNTs. Therefore, the present study proves that PSS is an alternate polymer to functionalize MWNTs without destroying the electronic structures of the pristine carbon nanotubes, thus, the unique properties including the catalytic property of the nanotubes retained. Extensive studies on the observed electrocatalytic properties and the use of this DA transducer for bioanalytical applications are under way.

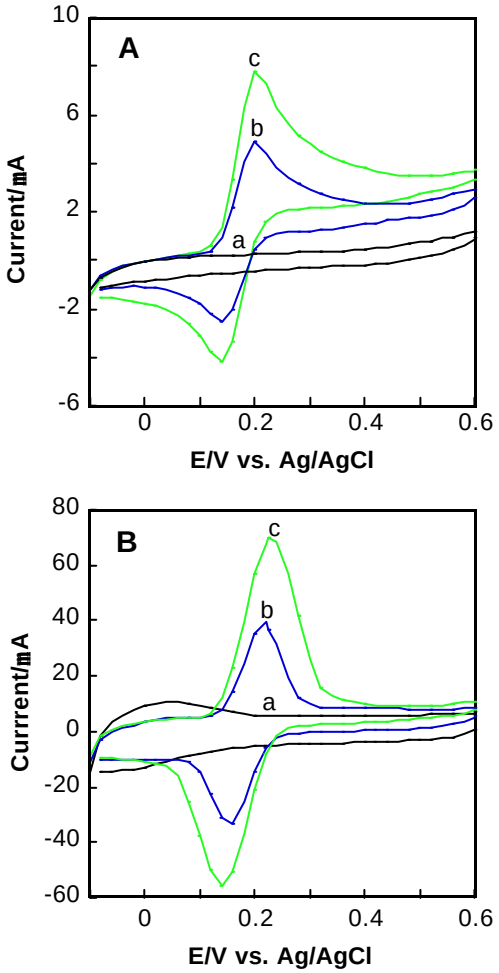


Fig.3. A Cyclic voltammograms of PSS/GCE (A) and PSS-MWNTs/GCE (B) in the presence of 0(a), 0.1 mM(b), 0.2 mM dopamine (c). Cyclic voltammograms were measured in 0.1 M phosphate buffer solution (pH 7.0). Scan rate, 0.1 V s^{-1}.

5. Conclusions

PSS-wrapped MWNTs complex is readily soluble and stable in water. The PSS-MWNTs complex film-covered electrode demonstrates stable, excellent electrocatalytic activity to oxidize neurotransmitter of dopamine, which makes it possible to prepare dopamine sensor with greatly improved sensitivity. The unique properties of the pristine CNTs have not been changed. Therefore, the homogeneous PSS-MWNTs complex aqueous dispersions may find potential applications in the development of biosensors, bioelectronics, gene and drug delivery as well as other biological events where water-based environment is required.

References

[1]. T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, *Science*, Vol. 300, 2003, 2072.
[2]. J. Chen, H. Y. Liu, W.A. Weimer, M. D. Halls, D.H. Waldeck, G. C. Walker, *J. Am. Chem. Soc.* Vol. 124, 2002, 9034.
[3]. M.J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. H. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, R. E. Smalley, R. E., *Chem. Phys. Lett.* Vol. 342, 2001, 265.
[4]. M.F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, A. G.Yodh, *Nano Lett.* Vol. 3, 2003, 269.
[5]. A. Liu, I. Honma, H. Zhou, *Biosens. Bioelectron.* Vol. 21, 2005, 809.
[6]. A. Liu, M. Wei, I. Honma, H. Zhou, Adv. Funct. Mater., Vol. 16, No. 3, 2006, 371.
[7]. P.J. Britto, K.S.V. Santhanam, P.M. Ajayan, *Bioelectrochem. Bioenerg.* Vol. 41, 1996, 121.
[8]. M. Musameh, J. Wang, A. Merkoci, Y. Lin, *Electrochem. Commun.* Vol. 4, 2002, 743.
[9]. Z. Wang, Y. Wang, G. Luo, *Electroanal.* Vol. 15, 2003, 1129.
[10]. V.C. Moore, M.S. Strano, E. H. Haroz, R. H. Hauge, R.E. Smalley, J. Schmidt J, et al., *Nano Lett.* Vol. 3, 2003, 1379.
[11]. Y.Y. Liu, J. Tang, X.Q.Chen, J. H. Xin, Carbon Vol. 43, 2005, 3178.
