2008

Nanofiber mats from DNA, SWNTs, and poly(ethylene oxide) and their application in glucose biosensors

Jun Chen

University of Wollongong, junc@uow.edu.au

Chee O. Too

University of Wollongong, chee@uow.edu.au

Gordon G. Wallace

University of Wollongong, gwallace@uow.edu.au

Tuan A Nguyen

Vietnamese Academy of Science and Technology, Vietnam

Violetta Misoska

University of Wollongong

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/scipapers>

Part of the [Life Sciences Commons](#), [Physical Sciences and Mathematics Commons](#), and the [Social and Behavioral Sciences Commons](#)

Recommended Citation

Chen, Jun; Too, Chee O.; Wallace, Gordon G.; Nguyen, Tuan A; Misoska, Violetta; and Liu, Yong: Nanofiber mats from DNA, SWNTs, and poly(ethylene oxide) and their application in glucose biosensors 2008, K100-K103.

<https://ro.uow.edu.au/scipapers/3505>

Nanofiber mats from DNA, SWNTs, and poly(ethylene oxide) and their application in glucose biosensors

Abstract

Ultrafine fibers with diameters ranging from 50 to 300 nm were prepared from DNA/single-walled carbon nanotubes (SWNTs)/poly(ethylene oxide) blended dispersion. Well-defined electrospun fibers were obtained by good control of key dispersion properties related to electrospinning, such as ionic conductivity, surface tension, and viscosity. Raman spectroscopy confirmed the presence of SWNT in the resulting fibers, indicating good interaction between DNA and SWNT. The resulting fibers also exhibited electroactive behavior and could be used as an immobilization matrix for a glucose oxidase enzyme biosensor. The sensor response was linear up to 20 mM glucose with a sensitivity of 2.4 mA cm⁻² M⁻¹

Keywords

Nanofiber, mats, from, DNA, SWNTs, poly, ethylene, oxide, their, application, glucose, biosensors

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

Publication Details

Liu, Y., Chen, J., Nguyen, T., Too, C. O., Misoska, V. & Wallace, G. G. (2008). Nanofiber mats from DNA, SWNTs, and poly(ethylene oxide) and their application in glucose biosensors. *Electrochemical Society. Journal*, 155 (5), K100-K103.

Authors

Jun Chen, Chee O. Too, Gordon G. Wallace, Tuan A Nguyen, Violetta Misoska, and Yong Liu

Nanofiber Mats from DNA, SWNTs, and Poly(ethylene oxide) and Their Application in Glucose Biosensors

Yong Liu,^a Jun Chen,^{a,*} Nguyen Tuan Anh,^b Chee O. Too,^a Violeta Misoska,^a and Gordon G. Wallace^{a,*}

^aARC Centre of Excellence for Electromaterials Science, Intelligent Polymer Research Institute, University of Wollongong, Wollongong, New South Wales, NSW 2522, Australia

^bInstitute for Tropical Technology, Vietnamese Academy of Science and Technology, Cau Giay, Hanoi, Vietnam

Ultrafine fibers with diameters ranging from 50 to 300 nm were prepared from DNA/single-walled carbon nanotubes (SWNTs)/poly(ethylene oxide) blended dispersion. Well-defined electrospun fibers were obtained by good control of key dispersion properties related to electrospinning, such as ionic conductivity, surface tension, and viscosity. Raman spectroscopy confirmed the presence of SWNT in the resulting fibers, indicating good interaction between DNA and SWNT. The resulting fibers also exhibited electroactive behavior and could be used as an immobilization matrix for a glucose oxidase enzyme biosensor. The sensor response was linear up to 20 mM glucose with a sensitivity of 2.4 mA cm⁻² M⁻¹.

© 2008 The Electrochemical Society. [DOI: 10.1149/1.2890417] All rights reserved.

Manuscript submitted December 19, 2007; revised manuscript received February 8, 2008.

Available electronically March 20, 2008.

Deoxyribonucleic acid (DNA) is a nucleic acid that contains the genetic instructions specifying the biological development of all cellular forms of life (and many viruses). There has been much work investigating techniques to prepare novel structures and/or devices by the modification of DNA chains through the sequence-specific pairing interactions.¹ Applications of DNA-based polymers have been investigated in many areas such as ionic liquid DNA,^{2,3} semiconductors,⁴ and nonlinear optics.⁵ Poly(ethylene oxide) (PEO) is known as a highly conductive polymer due to its ability to dissociate salts into ions and stabilizing them with relatively large dipole moment on its ether oxygens. PEO was previously reported as a host polymer to improve processability and biocompatibility of solutions of natural proteins and conducting polymers without the use of organic solvents,⁶⁻⁸ because it is known to be biocompatible.⁹ Nishimura et al. have reported that the ionic conductivity of DNA was improved by introducing PEO onto DNA chains through a covalent bond.¹⁰ To date, few studies have been published concerning electrospinning DNA/PEO blends, especially from aqueous solution. We have presented the synthesis of DNA/PEO ultrafine fibers from aqueous solution as described elsewhere.¹¹ The introduction of single-walled carbon nanotubes (SWNTs) into the DNA/PEO electrospun fibers gives rise to improvement in many properties, such as mechanical and electrochemical.

SWNTs have proven attractive for a wide range of applications due to their unique electronic, thermal, and mechanical properties.¹² Significant progress has been made in the application of both single- and multiwalled carbon nanotubes.¹³⁻¹⁵ The use of carbon nanotubes, especially SWNTs, as components of novel biomaterials has also been realized.¹⁶⁻¹⁸ The combination of DNA with SWNTs has been of interest due to the ability of the biomolecule to self-assemble carbon nanotubes (CNTs) to form molecular-scale electronic systems.^{19,20} The noncovalent binding of DNA to the side-walls of SWNTs has been reported by Zheng and co-workers.²¹ Zheng et al. have also dispersed CNTs into single-stranded DNA.²¹⁻²³

In our work, SWNTs were thoroughly dispersed in aqueous solution after being wrapped by DNA. PEO was then covalently conjugated with DNA chains. Ultrafine fibers were prepared from DNA/SWNT/PEO dispersions using an electrospinning technique. Electrospinning, first reported by Formhals,²⁴ provides a simple and fast way for the production of nano/micro-scaled fibers with the use of electrostatic forces. Polymer fibers are formed when electrostatic repulsion between charged polymer molecules is greater than the

surface tension holding them together.²⁵ The DNA/SWNT/PEO blended fibers exhibited electroactive behaviors during electrochemical characterization and were employed as an immobilization matrix for the construction of enzyme biosensors in the present work.

Glucose oxidase (GOx), the most popular oxidase enzyme, was entrapped in DNA/SWNT/PEO electrospun fibers in this work. GOx has been immobilized onto CNTs by electrodeposition within a conductive polymer,^{26,27} through CNT-based screen-printed electrodes²⁸ and CNT paper.²⁹ GOx has been attached to CNTs through covalent binding carbodiimide between amine groups of GOx and the carboxylic acid groups of chemically functionalized CNTs. In this research work, DNA was utilized to facilitate dispersion and separation of CNTs¹⁹⁻²¹ and also increase the effective surface area in contact between CNT coated electrodes and enzymes (increased the amount of immobilized enzyme). The resulting biosensor in our work showed a wide linearity range and good sensitivity.

Experimental

Reagents and materials.— DNA-Na (M_w 3,000,000, N% 15.5%, P% 7.96%) was supplied by Nippon Chemical Feed Co., Ltd, Japan. SWNT was obtained from Carbon Nanotechnologies (CNI lot no. P0275). PEO (M_w 300,000), glutaraldehyde, glucose oxidase, and glucose were all purchased from Sigma-Aldrich. Na₂HPO₄, NaH₂PO₄, NaCl, and KCl were from Asia Pacific Specialty. Glass slides were obtained from Delta Technologies, Limited. All chemicals were used without further purification.

Dispersion preparation.— 4% (w/w) DNA was dissolved in Milli-Q water by magnetic stirring over 60 min and heated at 90°C for 30 min to break the double chains of DNA.²¹⁻²³ 0.3% (w/w) SWNTs were then added into the DNA solution and sonicated for 60 min in a model 102C Branson Digital Sonifier at 30% power (150 W, 20 kHz, pulse: 2 s on/1 s off). Subsequently, 6% (w/w), 8% (w/w), 10% (w/w), and 12% (w/w) PEO were added into the dispersions and these were magnetically stirred overnight.

Electrospinning.— The electrospinning setup consisted of a Gamma high-voltage power supply (ES50P-10W/DAM), a 5 mL glass syringe, and a PrecisionGlide 19 G needle (1.1 mm diameter). The electrospinning was conducted at 15 cm tip-to-collector distance, 20 kV applied potential, and 100 μL/min feed rate. Electrospun fibers were collected onto Pt-coated glass slides. Pt was sputter coated onto glass slides for 10 min at 30 mA.

Characterization.— The conductivity of each solution was measured using a model 20 pH/conductivity meter (Denver Instru-

* Electrochemical Society Active Member.

^z E-mail: junc@uow.edu.au

Table I. Properties of aqueous dispersions containing DNA/SWNT/PEO.

Solution no.	PEO (%)	DNA (%)	SWNTs (%)	Conductivity ($\mu\text{S}/\text{cm}$) ^a	Surface tension (mN/m) ^b	Viscosity (mPa s) ^c
1	6	4	0.3	68.6	67.28	563.2
2	8	4	0.3	65.3	66.18	1105.3
3	10	4	0.3	52.5	65.32	2537.6
4	12	4	0.3	41.8	64.99	9128.0

^a Determined by a model 20 pH/conductivity meter (Denver Instruments).

^b Determined by a KSV contact angle analyzer (goniometer, KSV Instruments, Ltd).

^c Determined by a DV-II viscometer (Brookfield Engineering Laboratory, Inc.), shear rate using 20 s^{-1} for viscosity testing.

ments). The surface tension of solutions was determined using a KSV contact angle analyzer (goniometer, KSV Instruments, Ltd.), and the viscosity of solutions was tested by a DV-II viscometer (Brookfield Engineering Laboratory, Inc.). The resulting mats' morphology was determined using a Leica Cambridge 440 stereoscan scanning electron microscope (SEM). The average diameter of the electrospun fibers was measured from SEM micrographs by using Video Pro 32 (Leading Edge Pty., Ltd.). Samples were sputter coated with gold prior to SEM imaging.

The presence of SWNTs in the composite fibers was confirmed using a Raman JYHR800 at 632.8 nm.

A Princeton Applied Research 363 potentiostat/galvanostat was used to measure the electrochemical properties of the fibers. Cyclic voltammograms for DNA/SWNT/PEO nanofibers on Pt/glass slide were obtained in 0.15 M NaCl/phosphate buffer solution (PBS, containing 0.2 M Na_2HPO_4 and 0.2 M NaH_2PO_4 , pH 7.4) (electrode size $1 \times 1 \text{ cm}^2$). In all cases, a Ag/AgCl (3 M NaCl) reference and Pt mesh auxiliary were employed.

Enzyme biosensors based on DNA/SWNT/PEO electrospun fibers.— DNA/SWNT/PEO electrospun fibers coated on the Pt/glass slides were soaked in a glutaraldehyde solution [2.5% (w/w) in 0.4 M PBS, and 0.05 M KCl, pH 7.4] at 4°C overnight. The electrodes were subsequently washed and soaked in a GOx solution (5 mg/mL GOx in PBS, pH 7.4) at 4°C overnight. After a further washing, the enzyme electrode was ready for use.

Using this enzyme electrode, amperometry³⁰ was used to detect glucose in solution. A constant anodic potential (+0.5 V) was applied to detect hydrogen peroxide produced in the enzyme reaction. The current was monitored continuously until a steady-state value was reached. The enzyme electrode was measured in 0.4 M PBS (pH 7.4) (electrode size $1 \times 1 \text{ cm}^2$). Glucose was added gradually (5 mM each time) into the working solution.

Results and Discussion

A number of solution properties, such as solution conductivity, surface tension, and viscosity, have been shown to be key parameters in determining the morphology of electrospun mats.³¹ These properties of the resulting DNA/SWNT/PEO dispersions are summarized in Table I.

The production of nanofibers using electrospinning with 4% (w/w) DNA/0.3% (w/w) SWNT dispersions with the addition of PEO was successful. Continuous jets were observed during electrospinning, and nonwoven mats were collected on the Pt-coated glass slides. SEMs (Fig. 1a and b) showed that beads were deposited when the percentage of PEO in the dispersion was less than 10% (w/w). This may be attributed to the low viscosity and high conductivity of the dispersion (Table I solutions 1 and 2). The low viscosity results in small viscoelastic forces that are insufficient to counter the higher coulombic forces and consequently, the charged jet broke up

Figure 1. (Color online) SEM micrographs of the electrospun fibers from 4% (w/w) DNA/0.3% (w/w) SWNT dispersions with the addition of (a) 6% (w/w), (b) 8% (w/w), (c) 10% (w/w), and 12% (w/w) PEO at (i) low resolution and (ii) high resolution.

into droplets as a result of surface tension.³² It is also known that if a solution of high conductivity is used formation of beads during electrospinning is observed.³³ With the addition of PEO, ionic conductivity decreased due to the decreased comparative concentration of SWNTs. Concomitantly, a slight decrease in surface tension and a dramatic increase in viscosity were observed with increasing concentration of PEO (Table I). Formation of a small number of fibers was observed when the concentration of PEO was increased to 10% (w/w) (Fig. 1c). However, larger beads were present. As shown in Fig. 1d, a well-defined electrospun fibrillar network was obtained when the PEO was added at 12% (w/w). These well-interconnected, ropelike bundles of fibers exhibited various degrees of porosity and were quite uniform in diameter (50–300 nm). The average diameter of SWNT/DNA/PEO electrospun fibers was estimated at 150 nm.

Raman spectroscopy.— Raman spectra of electrospun fibers obtained from 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO dispersion were obtained (Fig. 2 and 3). As shown in Fig. 2, three bands were found in the Raman spectra of DNA/SWNT/PEO composite fibers in the 1200–1600 cm^{-1} range that could be attributed to the G-band of SWNTs: 1590 cm^{-1} (from the graphitic sheets), 1561 cm^{-1} (stretching mode of SWNTs), and 1308 cm^{-1} (defects in SWNTs).^{34,35} This confirms the presence of SWNTs in the electrospun fibers. There were also four bands observed in both spectra of electrospun fibers and raw SWNTs in the 150–300 cm^{-1} range (Fig. 3). These peaks originate from the radial breathing mode (RBM) of SWNTs.^{34,35} The shifts observed in RBM peaks (Fig. 3) indicate interactions between DNA/PEO and SWNTs. Furthermore, the diameter of a SWNT is inversely proportional to RBM frequency,^{34,36} according to

$$\omega_R = 224 \text{ cm}^{-1}/d \quad [1]$$

where d represents the diameter of the tube in nanometers and ω_R is the RBM frequency. According to Eq. 1, the upshift in RBM fre-

Figure 2. Raman spectra obtained for (a) nanofibers electrospun from 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO and (b) SWNTs. Laser excitation wavelength was 632.8 nm.

quency in the Raman spectra of electrospun fibers correlated with a decrease in tube diameter, indicating that SWNTs were well dispersed in the DNA solution and interacted strongly with the DNA molecules. Raman spectra were consistent across the electrospun mats over the glass slide, suggesting that SWNTs were well dispersed through the composite fibers.

Cyclic voltammetry.—Cyclic voltammograms (CVs) were obtained using mats spun onto the Pt/glass (Fig. 4). The CV of electrospun fibers before the adsorption of GOx was quite flat and exhibited a similar rectangular shape (Fig. 4a), indicating a highly capacitive nature of fibers.³⁷ The weak responses observed at 0.32 V (peak A) and 0.18 V (peak B), respectively, are probably due to a trace of residual iron in the SWNTs (used as a catalyst in the prepa-

Figure 3. Radial breathing mode Raman spectra obtained for (a) nanofibers electrospun from 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO and (b) SWNTs. Laser excitation wavelength was 632.8 nm.

Figure 4. CVs in 0.15 M NaCl/phosphate buffer solution (pH 7.4) of 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO electrospun fibers (a) without and (b) with incorporation of GOx (scan rate = 50 mV s⁻¹).

Figure 5. Typical current-time curves as a function of glucose concentration: 1–7 represents the successive injection of 0, 5, 10, 15, 20, 25, and 30 mM glucose into phosphate buffer solution (0.4 M, pH 7.4). Electrode: (a) 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO electrospun fibers in the absence of GOx and (b) 4% (w/w) DNA/0.3% (w/w) SWNT/12% (w/w) PEO electrospun fibers with immobilized GOx. Constant potential: +0.5 V vs Ag/AgCl (3 M NaCl).

ration of carbon nanotubes). Only minimal changes in peak currents were observed during 20 potential cycles, indicating that the electrospun fibers are quite electrochemically stable. The SWNT/DNA/PEO electrode that was incubated overnight at 4°C in GOx solution resulted in spontaneous adsorption of the enzyme onto the nanofibers. After the immobilization of GOx onto electrospun fibers, a clear oxidation peak was found at 0.45 V (peak C), while a reduction peak was observed at -0.5 V (peak D) (Fig. 4b), as expected for the electroactivity of GOx.²⁹ This suggests that the GOx immobilized on nanofibers still maintains its electrochemical properties, which would play a key role in its further electrochemical performance.

Glucose biosensors.—GOx was entrapped in DNA/SWNT/PEO electrospun fibers in this work. Responses of currents with increasing glucose concentration were recorded. No oxidant current was observed in DNA/SWNT/PEO fiber electrodes without GOx after the addition of glucose (Fig. 5a). A current response, however, was found after the immobilization of GOx in electrospun fibers. The current response of the fiber electrode with GOx to glucose was recorded in Fig. 5b. These results proved that the current response was due to the oxidation of hydrogen peroxide produced by the oxidation of glucose by the enzyme rather than direct oxidation of glucose on the electrode.

The calibration curve for the response of glucose at the GOx-DNA/SWNT/PEO fiber electrode is shown in Fig. 6, which is linear up to 20 mM glucose. The sensitivity of the biosensor is determined by the slope of the calibration curve. This biosensor had a sensitivity of 2.4 mA cm⁻² M⁻¹, compared with previous reported sensitivities in the 2–5 mA cm⁻² M⁻¹ range but that were for GOx-conducting polymer biosensors.³⁸ The reproducibility was evaluated by measuring the GOx-DNA/SWNT/PEO fiber electrode prepared on different days in the same solution. The variation between response currents was found to be 0.6% at low concentrations and up to 6.2% at the saturation concentration. The resulting biosensor exhibits a wide linearity range, good sensitivity, and excellent reproducibility, suggesting potential application in analyzing clinical samples over a wide range of physiological conditions.

Conclusions

Ultrafine fibers with an average diameter of 150 nm were electrospun from DNA/SWNT/PEO dispersions. Suitable solution properties for good electrospinning DNA/SWNT/PEO blends was determined. The successful introduction of SWNTs into DNA/PEO

Figure 6. Calibration curve obtained for glucose determination at 0.5 V vs Ag/AgCl (3 M NaCl) in 0.4 M PBS (pH 7.4) at a SWNT/DNA/PEO electrospun fiber electrode with immobilized GOx.

composite fibers was confirmed by Raman spectroscopy. Raman spectra also indicated a good dispersion of SWNTs throughout the electrospun fibers. DNA/SWNT/PEO electrospun fibers exhibited electroactive behaviors during electrochemical characterization, indicating improved electrochemical properties with the addition of SWNTs. Glucose oxidase was immobilized in DNA/SWNT/PEO fibers and a current response was observed with the addition of glucose. The biosensor showed a broad linearity range and high sensitivity.

Acknowledgment

Continued financial support of the Australian Research Council is gratefully acknowledged.

University of Wollongong assisted in meeting the publication costs of this article.

References

- See, for example, C. A. Mirkin, *Inorg. Chem.*, **39**, 2258 (2000); *DNA Microarrays: A Practical Approach*, M. Schena, Editor, Oxford University Press, Oxford (1999).
- A. M. Leone, S. C. Weatherly, M. E. Williams, H. H. Thorp, and R. W. Murray, *J. Am. Chem. Soc.*, **123**, 218 (2001).
- N. Nishimura and H. Ohno, *J. Mater. Chem.*, **12**, 2299 (2002).
- C. A. Mirkin and T. A. Taton, *Nature (London)*, **405**, 626 (2000).
- L. Wang, J. Yoshida, N. Ogata, S. Sasaki, and T. Kajiyama, *Chem. Mater.*, **13**, 1273 (2001).
- H. J. Jin, S. V. Fridrikh, G. C. Rutledge, and D. L. Kaplan, *Biomacromolecules*, **3**, 1233 (2002).
- L. Huang, K. Nagapudi, R. P. Apkarian, and E. L. Chaikof, *J. Biomater. Sci., Polym. Ed.*, **12**, 979 (2001).
- J. D. Norris, M. M. Shaker, F. K. Ko, and A. G. MacDiarmid, *Synth. Met.*, **114**, 109 (2000).
- Polymeric Biomaterials*, S. Dumitriu, Editor, Marcel Dekker, New York (1994).
- N. Nishimura, S. Kokubo, and H. Ohno, *Polym. Adv. Technol.*, **15**, 335 (2004).
- Y. Liu, J. Chen, V. Misoska, and G. G. Wallace, *React. Funct. Polym.*, **67**, 461 (2007).
- R. H. Baughman, A. A. Zakhidov, and W. A. De Heer, *Science*, **297**, 787 (2002).
- J. C. Charlier, A. De Vita, X. Blasé, and R. Car, *Science*, **275**, 647 (1997).
- D. C. Li, L. M. Dai, S. M. Huang, A. W. H. Mau, and Z. L. Wang, *Chem. Phys. Lett.*, **316**, 349 (2000).
- S. P. Frank, P. Poncharal, Z. L. Wang, and W. A. De Heer, *Science*, **280**, 1744 (1998).
- A. Bianco, K. Kostarelos, C. D. Partidos, and M. Prato, *Chem. Commun.*, **2005**, 571.
- Y. Lin, S. Taylor, H. Li, K. A. S. Fernando, L. Qu, W. Wang, L. Gu, B. Zhou, and Y.-P. Sun, *J. Mater. Chem.*, **14**, 527 (2004).
- Y. Liu, K. J. Gilmore, J. Chen, V. Misoska, and G. G. Wallace, *Chem. Mater.*, **19**, 2721 (2007).
- C. Dwyer, M. Guthold, M. Falvo, S. Washburn, R. Superfine, and D. Erie, *Nanotechnology*, **13**, 601 (2002).
- K. Keren, R. S. Berman, E. Buchstab, U. Sivan, and E. Braun, *Science*, **302**, 1380 (2003).
- M. Zheng, A. Jagota, M. S. Strano, A. P. Santos, P. Barone, S. G. Chou, B. A. Diner, M. S. Dresselhaus, R. S. Mclean, G. B. Onoa, et al., *Science*, **302**, 1545 (2003).
- M. Zheng and B. A. Diner, *J. Am. Chem. Soc.*, **126**, 15490 (2004).
- M. Zheng, A. Jagota, E. D. Semke, B. A. Diner, R. S. Mclean, S. R. Lusting, R. E. Richardson, and N. G. Tassi, *Nat. Mater.*, **2**, 338 (2003).
- A. Formhals, U.S. Pat. 1,975,504 (1934).
- Y. M. Shin, M. M. Hohman, M. P. Brenner, and G. C. Rutledge, *Polymer*, **42**, 09955 (2001).
- M. Gao, L. Dai, and G. Wallace, *Synth. Met.*, **137**, 1393 (2003).
- K. P. Loh, S. L. Zhao, and W. D. Zhang, *Diamond Relat. Mater.*, **13**, 1075 (2004).
- J. Wang and M. Musameh, *Analyst (Cambridge, U.K.)*, **129**, 1 (2004).
- A. Guiseppi-Elie, C. Lei, and R. H. Baughman, *Nanotechnology*, **13**, 559 (2002).
- M. Situmorang, J. J. Gooding, D. B. Hibbert, and D. Barnett, *Biosens. Bioelectron.*, **13**, 953 (1998).
- Z. M. Huang, Y. Z. Zhang, M. Kotaki, and S. Ramakrishna, *Compos. Sci. Technol.*, **63**, 2223 (2003).
- C. Mit-uppatham, M. Nithitanakul, and P. Supaphol, *Macromol. Symp.*, **216**, 293 (2004).
- H. Fong, I. Chun, and D. H. Reneker, *Polymer*, **40**, 4585 (1999).
- A. Rao, J. Chen, and E. Richter, *Phys. Rev. Lett.*, **86**, 3895 (2001).
- W. S. Bacsa, D. Ugarte, and A. Chatelain, *Phys. Rev. B*, **50**, 15473 (1994).
- W. Weber and R. Merlin, *Raman Scattering in Materials Science*, Springer, Berlin (2000).
- B. E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Application*, Kluwer Academic/Plenum Publishers, New York (1999).
- M. Trojanowicz, O. Geschle, T. Krawczynski, and K. Cammann, *Sens. Actuators B*, **28**, 191 (1995).