

Spontaneous Coating of Carbon Nanotubes with an Ultrathin Polypyrrole Layer

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Abstract: A novel protocol for precisely coating individual multiwall carbon nanotubes (MWCNTs) with an ultrathin layer of polypyrrole was developed. The nanocoated MWCNTs were successfully prepared by in situ chemical deposition of polypyrrole in an aqueous suspension of MWCNTs. The coating layer was very uniform and the

thickness of the layer was determined by controlling the monomer concentration used, which gave nanometer precision. The products were characterized

by transmission electron microscopy, scanning electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, electron energy loss spectroscopy, and conductivity and current-voltage measurements. The ultrathin polypyrrole layer could electrically insulate individual MWCNTs.

Keywords: coating • materials science • nanotubes • polymers • polypyrrole

Introduction

Composite materials of carbon nanotubes (CNTs) and polymers have attracted great interest because they are expected to create advanced functional materials with superior characteristics than either of the individual components.^[1,2]

CNTs were used to improve the conductivity of polymers, to increase their toughness or to control their bioaffinity.^[3] CNTs coated with a precisely controlled polymer layer were fabricated for use as insulated AFM tips,^[4] as nanoelectrodes,^[5] and as nanowires in nanoelectronic devices.^[6,7]

It is particularly interesting to coupling the properties of CNTs with functional polymers, such as polypyrrole (PPy), polyaniline, and polythiophene.^[1] It is well known that PPy exists in two oxidation states, one that is doped (oxidized), which has good electrical conductivity, and one that is undoped (reduced), which has very low electrical conductivity.^[8] Coating CNTs with PPy by using chemical and electrochemical methods have been investigated by several groups, however, the formation of a uniform coating on individual CNTs has remained a challenge because it is not easy to control the agglomeration of conjugated polymers and the polymer chains are prone to forming deposits of irregular nanoparticles or sediments. CNTs have often been embedded in bulk PPy,^[9] or they were coated with thick and non-uniform layers, which range from 50^[10–13] to 80 nm,^[14–16] and often encapsulated more than one CNT in the bulk polymer,^[11] or they were covered by PPy nanoparticles with a diameter of about 50 nm.^[12,13]

We previously developed the polymerization-induced adsorption process for the preparation of ultrathin films of insoluble polymers on solid substrates^[17,18] and for nanocoating natural cellulose fibers.^[19] Herein we describe the preparation and characterization of nanocoated individual multiwall carbon nanotubes (MWCNTs) with an unprecedentedly

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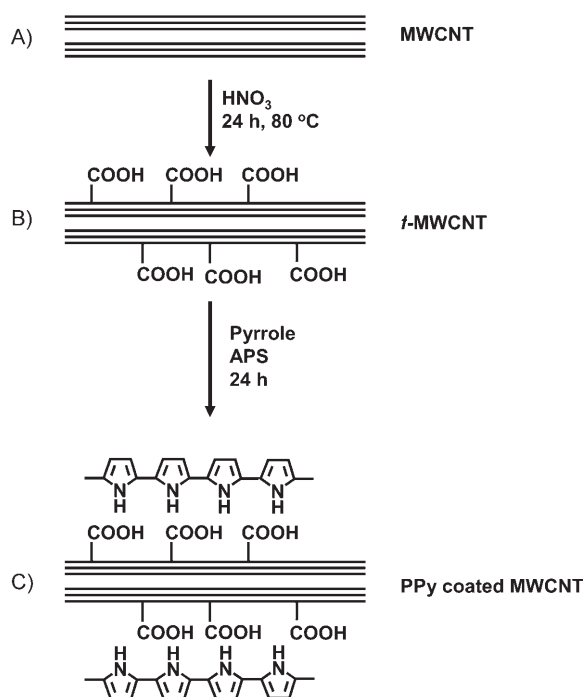
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uniform PPy layer that is less than 15 nm thick. Transmission electron microscopy (TEM) equipped with electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy, Raman spectroscopy, and conductivity measurements were used to characterize the nanocoated MWCNT.

Results and Discussion

We illustrate the coating process in Scheme 1. The MWCNTs (Scheme 1A) were first functionalized by heating them at reflux in 6 M nitric acid at 80 °C for 24 h to give sur-



Scheme 1. Schematic representation of the process of coating MWCNTs with PPy. MWCNT (A) was heated at reflux in HNO_3 to give carboxyl groups at the defect sites of the outer graphene layer (B). Such functionalized nanotubes were subsequently coated with PPy (C).

face carboxyl groups at the defect sites of the outer graphene layer of the nanotubes (Scheme 1B).^[20–22] Subsequently, the carboxylic acid-functionalized multiwall carbon nanotubes (f-MWCNT) were washed with distilled water and dried before they were dispersed in water (0.5 mg mL^{-1}). Subsequently, pyrrole solution in 2-propanol was added to reach the required pyrrole concentration in the final solution (typically 10 mM) and thereafter ammonium persulfate (APS) was added to initialize the polymerization. PPy was formed slowly and spontaneously deposited on the surface of the f-MWCNTs to form PPy-coated MWCNTs over a period of 24 h (Scheme 1C).

Functionalization of the MWCNTs by carboxyl groups could be identified by comparing the Raman spectra of the untreated MWCNTs (Figure 1A) and the f-MWCNTs (Fig-

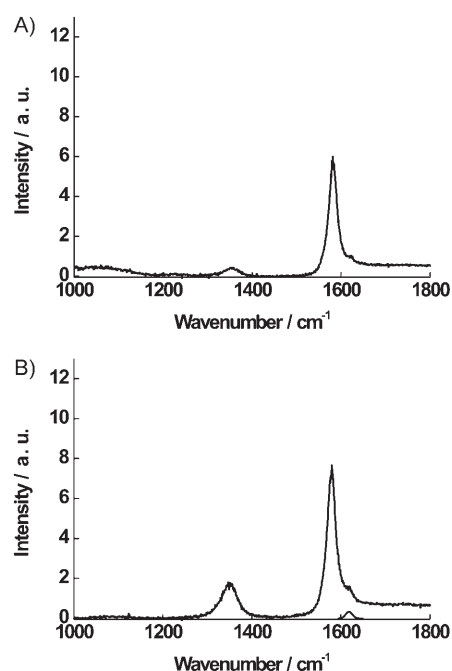


Figure 1. Raman spectra of A) the MWCNT and B) the acid-functionalized f-MWCNT.

ure 1B) in the region of the D band, which is the disordered sp^3 band at around 1350 cm^{-1} , and the G band, which corresponds to the stretching mode in the graphene plane at around 1580 cm^{-1} , of graphene sheet.^[20] It is possible to identify two features in the spectrum. First, there is a significant increase in the intensity of the D-band, which is attributed to sp^3 hybridization of the outer graphene sheet owing to functionalization with oxygen-containing groups. The ratio of the G/D bands decreased from 16.8 for untreated MWCNTs to 4.4 for f-MWCNTs, which reflects strong oxidation of the outer layer of the MWCNTs. Second, there is the clearly observed energy dispersion of the D' mode (about 1620 cm^{-1}), which appears to be owing to the strained C=C vibration as a result of oxidation of the outer graphene sheet (see the fitted peak in Figure 1B).^[20–24]

In Figure 2 we show typical TEM images of a PPy-coated MWCNT obtained after 24 h. The images reveal a coaxial structure of the resulting PPy-coated MWCNT in which the MWCNT is encapsulated by a nanometer thick layer of PPy. The surface of the resulting PPy-coated MWCNT nanowires appears to be very smooth; the thickness is about 7 nm with a variation of 1 nm in thickness for the same nanotube. There is a clearly visible MWCNT core with a crystalline lattice structure and an amorphous PPy-coating layer. The crystalline structure of the MWCNT was revealed by its electron diffraction (ED) pattern (not shown). In the ED pattern, the pairs of bright diffractions that correspond to the (002), (004), and (006) reflections of the graphene sheets are visible along the direction perpendicular to the tube axis, which suggests that the tube wall consists of cylindrically stacked graphitic (002) planes with a lattice spacing of

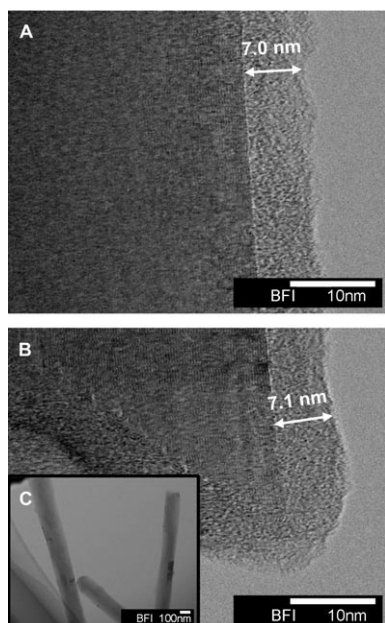


Figure 2. TEM images of PPY-coated MWCNT. Detailed view of PPY A) at the side and B) the end of the PPY-coated MWCNT. Inset C shows a TEM image of several PPY-coated MWCNTs at lower magnification. Coating conditions: concentration of pyrrole, 10 mM; coating time, 24 h.

0.340 nm.^[25] The uniform coating presented in this work is a result of polymerization-induced adsorption of the polymer chains that is based on optimization of van der Waals interactions between the atomic arrangement of the CNT surface and the polymer chains.^[17] Previously described electrochemical deposition of PPY onto MWCNTs resulted in coatings that were not very uniform and were likely to be a result of the irregular density of the current passing through the defect sites in the walls of the MWCNTs.^[10,11,15,16] Similarly, previously described micelle-based synthesis inherently resulted in the formation of a nonuniform coating on the MWCNTs.^[12,13]

The elemental composition of individual PPY-coated MWCNTs was analyzed by means of EELS. A representative EELS spectrum is shown in Figure 3. The π^*

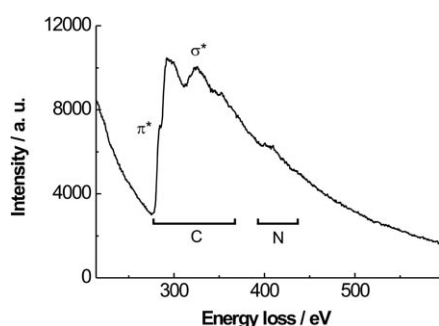


Figure 3. Electron energy loss spectrum of a part of individual PPY-coated MWCNT. Coating conditions: concentration of pyrrole, 15 mM; coating time, 24 h.

(≈ 283.8 eV) and the σ^* band of the K-shell ionization edge of carbon can be observed. The former peak is attributed to the graphite-like sp^2 -bonded network and it indicates that the tube is mainly composed of hexagonal graphitic layers. We also observed an ionization edge at 401 eV, which corresponds to the characteristic K-edge of nitrogen that is present in the PPY coating.

To confirm the presence of the PPY coating on the MWCNTs in a bulk sample and to carry out its quantification, X-ray photoelectron spectroscopy (XPS) measurements were performed on samples of PPY-coated MWCNTs and f-MWCNTs. Figure 4A presents the XPS spectra for

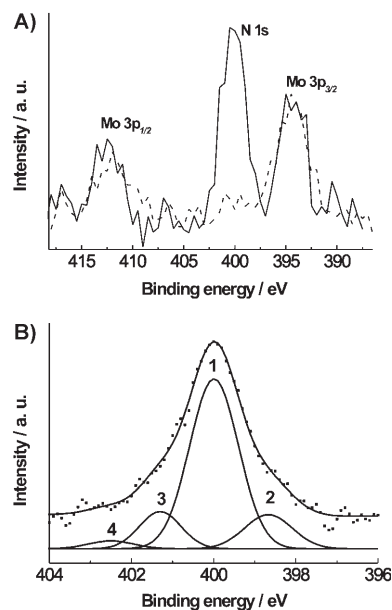


Figure 4. A) X-ray photoelectron spectra of f-MWCNTs (dashed line) and PPY-coated MWCNT (solid line). B) Detailed N 1s spectrum of a sample of PPY-coated MWCNTs with deconvolution results also shown. Peak 1: amine-like $-NH-$, peak 2: imine-like $=N-$, peak 3: polaron $-NH^{+\cdot}$, and peak 4: bipolaron ($=NH^{+\cdot}$) of the PPY layer. Coating conditions: concentration of pyrrole, 15 mM; coating time, 24 h. Note that molybdenum related peaks originate from the specimen holder.

PPY-coated MWCNTs (solid line), which shows a strong nitrogen (N 1s) peak. In contrast, the XPS spectrum of f-MWCNTs (dashed line) shows the absence of the nitrogen N 1s peak. To investigate the doping level of PPY in terms of an N^+/N ratio,^[26] and to gain a deeper insight into the stages of the nitrogen in PPY layer, the detailed spectra of N 1s in the PPY-coated MWCNT sample was measured (Figure 4B). It is clearly visible from Figure 4B that the N 1s peak at ≈ 400 eV is not symmetric and has two shoulders, one at a lower and one at a higher energy level. Careful curve fitting shows that the N 1s spectrum can be quantitatively differentiated into four different nitrogen types, namely, the amine-like $-NH-$ (400 eV, peak 1; peak area of 70.2%), the imine-like $=N-$ (398.7 eV, peak 2; peak area of 13.8%), the positively charged polaron $-NH^{+\cdot}$ (401.3 eV, peak 3; peak area of 13.0%) and the bipolaron $=NH^{+\cdot}$

(402.5 eV, peak 4; peak area of 3.0%) stages.^[27,28] The presence of a polaron ($-\text{NH}^{+\cdot}$) and a bipolaron ($=\text{NH}^{+\cdot}$) and an N^+/N ratio of 16:84 suggests that the PPy layer is partly doped by f-MWCNTs that contain carboxylic acid groups. Elemental quantification of the XPS spectra based on detailed C 1s and N 1s XPS scans of PPy-coated MWCNT gives carbon and nitrogen atomic percentages of 94.6 and 5.4%, respectively.

Figure 5 shows the influence of pyrrole concentration upon the thickness of the PPy layer on the MWCNT. When the pyrrole concentration in the coating solution was low, in

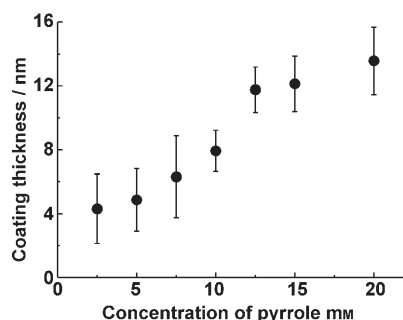


Figure 5. Influence of pyrrole concentration upon the thickness of the PPy layer.

range of 2.5 to 7.5 mm, the average thickness of the PPy layer on the MWCNT was in range of 4 to 6 nm. However, the PPy layer on the MWCNTs at such low pyrrole concentrations was not uniform, which is shown by the large error margins observed (40–50%; note standard deviation bars in Figure 5). When the pyrrole concentration was 10 mm, the PPy layer formed uniformly with an average thickness of 7.9 nm (relative standard deviation (RSD) of 11% for different PPy-coated nanotubes in the same batch in which $n=8$, RSD of 16% for PPy-coated MWCNT in two different batches in which $n=15$); all observed MWCNTs in the sample were covered by an ultrathin PPy coating. Further increasing the pyrrole concentration to 12.5, 15.0, and 20.0 mm resulted in an increase in the PPy-layer thickness to 14 nm, with similar variations in the thickness of the PPy layer (RSD of 12, 14, and 16%, respectively; for more data on the PPy-coating thickness, see Table S1 in the Supporting Information). The influence of coating time upon the thickness of the PPy layer was also studied, but it was found to be negligible. The thickness of the PPy coating increased from 7.9 to 10.2 nm upon increasing the coating time from 24 to 336 h (other conditions, as in Figure 2).

SEM images demonstrate that the uniformly PPy-coated MWCNTs do not aggregate. The morphology of the sample of f-MWCNTs (Figure 6A and B) is very similar to the morphology of the sample of PPy-coated MWCNTs (Figure 6C and D).

We measured the electrical conductivity of the f-MWCNT film and the PPy-coated MWCNT film. The films were formed by dispersing f-MWCNTs (1.5 mg) or PPy-coated

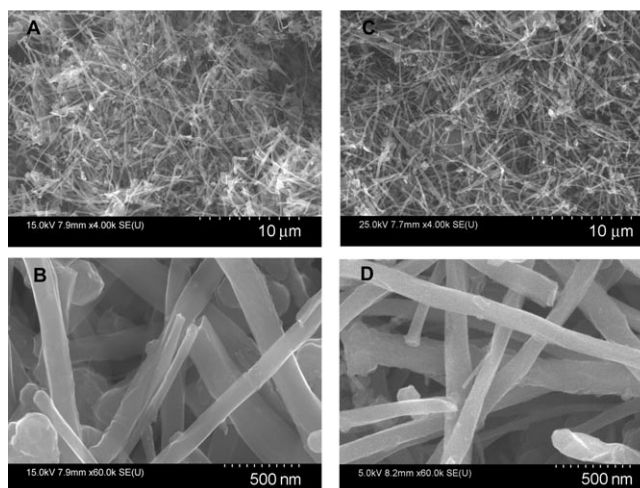


Figure 6. SEM images of f-MWCNT at magnifications of A) 4000 \times and B) 60000 \times . SEM images of PPy-coated MWCNTs at magnifications of C) 4000 \times and D) 60000 \times . Coating conditions: concentration of pyrrole, 10 mm; coating time, 24 h.

MWCNTs (1.5 mg) in distilled water (3 mL) and filtering this suspension through a 0.2 μm Teflon membrane. Such films were subsequently vacuum dried. The resistance of the f-MWCNT film was found to be $(2.25 \pm 0.19) \text{ k}\Omega \text{ sq}^{-1}$ ($n=13$; film thickness of 5.22 μm) and the resistance of the PPy-coated MWCNT film was found to be $(197.37 \pm 20.54) \text{ k}\Omega \text{ sq}^{-1}$ ($n=13$; film thickness of 4.57 μm). As SEM images confirm that the f-MWCNT and the PPy-coated MWCNT films have similar morphologies, a resistivity value that is about two orders of magnitude higher for the PPy-coated MWCNT film than that of the f-MWCNT film can be attributed to the insulating properties of the PPy layer. Figure 7 displays the current–voltage (I – V) traces of the f-MWCNT (Figure 7a) and PPy-coated MWCNT (Figure 7b) films ($n=10$; thickness of films as in conductivity measurements). The characteristics of the I – V slopes are significantly different. The slope of the I – V curve for the f-MWCNT film has a value of 23.6 mA V^{-1} , whereas the slope of the I – V curve for the PPy-coated MWCNT film has a value of

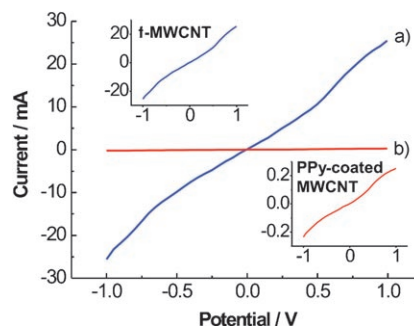


Figure 7. Current–voltage curves of f-MWCNTs (blue) and PPy-coated MWCNTs (red) films. The insets separately show the I – V characteristics of the f-MWCNTs and the PPy-coated MWCNTs. Coating conditions: concentration of pyrrole, 10 mm; coating time, 24 h.

0.235 mAV⁻¹. Such a difference reflects the fact that the PPy-coating layer effectively insulates the MWCNTs. The differences in the *I*-*V* characteristics of f-MWCNTs and PPy-coated MWCNTs are consistent with conductivity measurements.

Conclusion

We have described the chemical approach to facilitate an ultrathin coating of conjugated polymers on MWCNTs. The PPy layer forms spontaneously on the walls of the MWCNTs and its thickness can be controlled by controlling the concentration of pyrrole in the solution. PPy-coated MWCNTs have dramatically different electronic properties compared with f-MWCNTs. The PPy coating effectively prevents electron transfer between the individual carbon nanotubes. This coating technique opens doors for many applications, which range from chemical sensing to nanoelectronics.

Experimental Section

Materials: MWCNTs (length, 7 μm; o.d. 90 nm; MWCNT content >90%; metal catalyst (Fe) content, <0.1% (w/w)), pyrrole, APS, and 2-propanol were purchased from Sigma-Aldrich (Japan).

Apparatus: A scanning electron microscope (field emission type, Hitachi S-4800) was used to study the morphology of the f-MWCNT and the PPy-coated MWCNT samples. A JEM 2100F field emission transmission electron microscope (JEOL, Japan) working at 200 kV was employed to acquire electron diffraction (ED) patterns and to obtain high-resolution TEM (HR-TEM) images in a scanning TEM mode (spot size, 0.4 nm; 200 kV). EELS was carried out to analyze the PPy layer that coated the MWCNT by using a JEM 3000F field emission high-resolution transmission electron microscope equipped with a Gatan-766 electron energy loss spectrometer (2D-DigiPEELS). A laser microscope/profilometer (Lasertec VL2000, Japan) was used to obtain information on the thickness of the f-MWCNT and the PPy-coated MWCNT films. Raman spectra were collected by using λ = 514.5 nm excitation from an Ar ion laser beam in a backscattering geometry (BeamLok 2060-RS/T64000, Spectro-Physics, Mountain View, CA/Jobin Yvon, Horiba, France). XPS was performed in an ultra high vacuum chamber equipped with a hemispherical energy analyzer Phoibos-HSA 3500 with a nine-channel charged particle detector and a dual (Al/Mg) X-ray source. In our experiments we used an Al source (Al_{Kα} line, 1486.6 eV) operating at 12.5 kV and 20 mA. The typical background pressure during the measurements was about 3 × 10⁻⁸ Pa. For analysis, the samples were pressed into indium foil (Goodfellow, 99.999% purity). Aside from the overall-wide spectrum, C 1s, O 1s, and N 1s photoelectron peaks were recorded in detail. After subtraction of a Shirley background,^[29] the N 1s peak was fitted by using mixed Gaussian-Lorentzian component profiles. The values of resistance were obtained by using a four-point probe sheet resistance measurement system (RT-70/RG-7B) manufactured by Napson Corporation (Japan). This system has a probe head in which four tungsten carbide electrodes are aligned at a distance of 0.5 mm. The upper limit of the applied voltage of RT-70/RG-7B system is 1.0 V and the lowest current is 1.0 μA. Current-voltage experiments were performed by using an μAutolabIII (Ecochemie) connected to a personal computer.

Coating: MWCNTs were functionalized in concentrated nitric acid (6M) at 80 °C for 24 h.^[20-22] The acid/MWCNT mixture was subsequently washed with distilled water and centrifuged several times until the aqueous solution reached a neutral pH. Subsequently, carboxylic acid-functionalized MWCNTs were filtered through a 0.2 μm membrane (Nuclepore Track-Etch Membrane, Whatman) and left to dry in air. The PPy

coating step involved dispersion of f-MWCNT in distilled water (concentration of 0.5 mg mL⁻¹; typically 2 mg of f-MWCNT in 4 mL of distilled water) followed by 5 min ultrasonication. Subsequently, a pyrrole solution in 2-propanol was added to reach required pyrrole concentration in the final solution (typically 10 mM, which required the addition of 100 μL of 451 mM stock solution of pyrrole in 2-propanol) and consequently APS (typically 410 μL of 10 mM stock solution of (NH₄)₂S₂O₈ in water). This mixture was stirred by magnetic stirring (at 550 rpm) for 24 h (if not stated otherwise) and finally filtered through a 0.2 μm Nuclepore membrane, thoroughly washed with distilled water, and left to dry in air.

Current-voltage measurements: For *I*-*V* measurements of the nanowire films, nanoscale material (1.5 mg) (f-MWCNT or PPy coated MWCNT) was dispersed in distilled water (3 mL) and filtered through a 0.2 μm Teflon membrane (Nuclepore Track-Etch Membrane, Whatman, UK). Such films were vacuum dried and their thickness was measured by using a laser profilometer. Electrical contact was achieved by using a conducting silver epoxy (D-550, Fujikura Kasei, Japan). Current-voltage curves were obtained by a linear sweep at a rate of 50 mV s⁻¹. The displayed data are average from ten measurements.

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- [1] M. Panhuis, *J. Mater. Chem.* **2006**, *16*, 3598.
- [2] C. Downs, J. Nugent, P. M. Ajayan, D. J. Duquette, S. V. Santhanam, *Adv. Mater.* **1999**, *11*, 1028.
- [3] A. Merkoci, M. Pumera, X. Llopis, B. Perez, M. Valle, S. Alegret, *TrAC Trends Anal. Chem.* **2005**, *24*, 826.
- [4] M. J. Esplandiu, V. G. Bittner, K. P. Giapis, C. P. Collier, *Nano Lett.* **2004**, *4*, 1873.
- [5] J. K. Campbell, L. Sun, R. M. Crooks, *J. Am. Chem. Soc.* **1999**, *121*, 3779.
- [6] A. Star, J.-C. P. Gabriel, K. Bradley, G. Gruner, *Nano Lett.* **2003**, *3*, 459.
- [7] G. B. Blanchet, S. Subramoney, R. K. Bailey, G. D. Jaycox, *Appl. Phys. Lett.* **2004**, *85*, 828.
- [8] G. G. Wallace, G. M. Spinks, L. A. P. Kane-Maguire, P. R. Teasdale, *Conductive Electroactive Polymers: Intelligent Materials Systems*, CRC press, Florida, **2003**.
- [9] J. Wang, J. Dai, T. Yarlagadda, *Langmuir* **2005**, *21*, 9.
- [10] G. Z. Chen, M. P. S. Shaffer, D. Coleby, G. Dixon, W. Zhou, D. J. Fray, A. H. Windle, *Adv. Mater.* **2000**, *12*, 522.
- [11] M. Hughes, M. S. P. Shaffer, A. C. Renouf, C. Singh, G. Z. Chen, D. J. Fray, A. H. Windle, *Adv. Mater.* **2002**, *14*, 382.
- [12] Y. Yu, C. Ouyang, Y. Gao, Z. Si, W. Chen, Z. Wang, G. Xue, *J. Polym. Sci., A: Polym. Chem.* **2005**, *43*, 6105.
- [13] T.-M. Wu, S.-H. Lin, *J. Polym. Sci., B: Polym. Phys.* **2006**, *44*, 1413.
- [14] J. Fan, M. Wan, D. Zhu, B. Chang, Z. Pan, S. Xie, *Synth. Met.* **1999**, *102*, 1266.
- [15] J. H. Chen, Z. P. Huang, D. Z. Wang, S. X. Yang, W. Z. Li, J. G. Wen, Z. F. Ren, *Appl. Phys. A* **2001**, *73*, 129.
- [16] J. H. Chen, Z. P. Huang, D. Z. Wang, S. X. Yang, W. Z. Li, J. G. Wen, Z. F. Ren, *Synth. Met.* **2002**, *125*, 289.
- [17] I. Ichinose, T. Kunitake, *Adv. Mater.* **1999**, *11*, 413.
- [18] I. Ichinose, H. Miyauchi, M. Tanaka, T. Kunitake, *Chem. Lett.* **1998**, 19.
- [19] J. Huang, I. Ichinose, T. Kunitake, *Chem. Commun.* **2005**, 1717.
- [20] K. Kordas, T. Mustonen, G. Toth, H. Jantunen, M. Lajunen, C. Soldano, S. Talapatra, S. Kar, R. Vajtai, P. M. Ajayan, *Small* **2006**, *2*, 1021.

- [21] A. Gomathi, S. R. C. Vivekchand, A. Govindaraj, C. N. R. Rao, *Adv. Mater.* **2005**, *17*, 2757.
- [22] X. Yu, B. Munge, V. Patel, G. Jensen, A. Bhirde, J. D. Gong, S. N. Kim, J. Gillespie, J. S. Gutkind, F. Papadimitrakopoulos, J. F. Rusling, *J. Am. Chem. Soc.* **2006**, *128*, 11199.
- [23] P. H. Tan, C. Y. Hu, J. Dong, W. C. Shen, B. F. Zhang, *Phys. Rev. B* **2001**, *64*, 214301.
- [24] W. E. Alvarez, F. Pompeo, J. E. Herrera, L. Balzano, D. E. Resasco, *Chem. Mater.* **2002**, *14*, 1853.
- [25] P. M. Ajayan, *Chem. Rev.* **1999**, *99*, 1787.
- [26] J. G. Eaves, H. S. Munro, D. Parker, *Polym. Commun.* **1987**, *28*, 39.
- [27] L. Ruangchuay, J. Schwank, A. Sirivat, *Appl. Surf. Sci.* **2002**, *199*, 128.
- [28] V. W. L. Lim, S. Li, E. T. Kang, K. G. Neoh, K. L. Tan, *Synth. Met.* **1999**, *106*, 1.
- [29] D. A. Shirley, *Phys. Rev.* **1972**, *55*, 4709.

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