Conducting Polyaniline Nanotubes by Template-Free Polymerization

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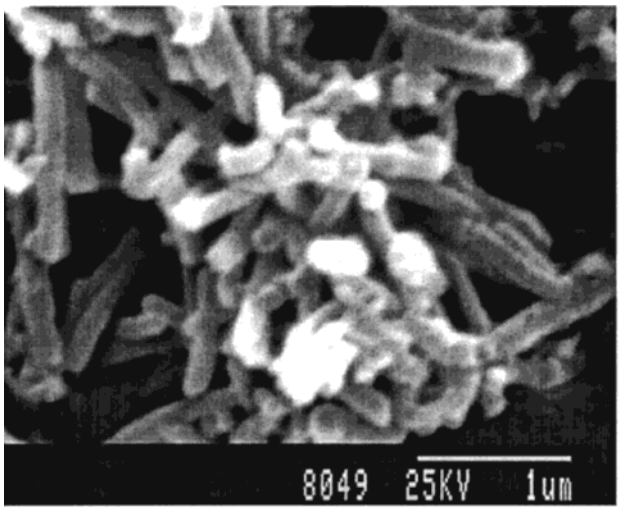
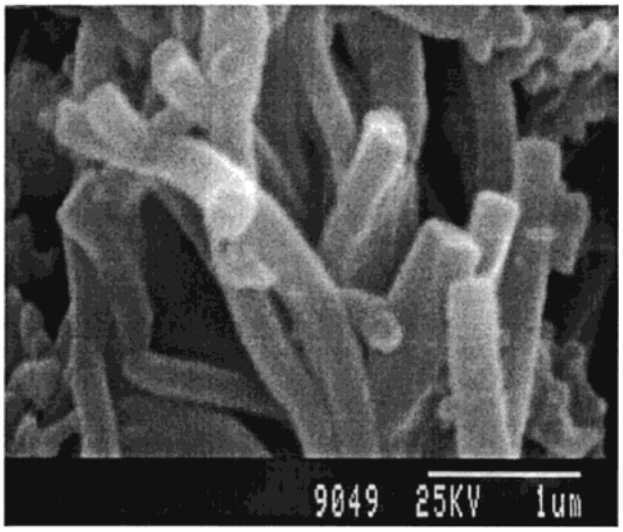
Received August 31, 2000

Nanotubes and/or nanowires are known to play an important role in optoelectronic nanodevices, ranging from single-molecular transistors[1] and electron-emitting flat panel displays[2] to chemical sensors[3] and artificial actuators,[4] both as interconnecting and as active components. Various carbon nanotubes of interesting optoelectronic properties have been synthesized since Iijima's discovery in 1991,[5] whereas the chemical synthesis of nanotubules and/or molecular wires of conducting polymers by a simple process remains a scientific challenge. However, well-defined poly(*p*-phenylene vinylene) (PPV) fibers with a diameter of 4 nm have been prepared within an ordered hexagonal array of hydrophilic channels produced by photo-cross-linking a polymerizable liquid crystal monomer (e.g., acrylate).[6] Although significant fluorescence enhancement was observed, the final products were composite materials consisting of the PPV fibers interspersed within the photo-cross-linked liquid crystal polymer matrices. More generally, conjugated polymer nanofibers and nanotubes have also been synthesized within the pores of a nanoporous membrane[7] or nanochannels of a mesoporous zeolite.[8] These so-called *template* syntheses produce monodispersed polymeric fibers or tubules with controllable diameter, length, and conductivity. However, these cases often require a rather tedious postsynthesis process which is often required in order to remove the template.[9] Furthermore, the polymeric nanofibers and/or nanotubules may form undesirable aggregated structures upon release from the template. This communication reports a simple but effective *template-free* synthesis of conducting polyaniline (PANI) nanotubes.

Owing to its excellent electronic and environmental stability, PANI has attracted considerable scientific interest in the development toward polymeric conducting molecular wires.[10] Although polyaniline materials synthesized by most conventional methods show a granular/spherical morphology,[11−14] needlelike[15−17] and fibrous[18,19] structures have recently been reported. In particular, Wan et al.[20] have polymerized *microtubules* of PANI using $(NH_4)_2S_2O_8$ oxidant in the presence of naphthalenesulfonic acid (NSA) as a dopant without involving any template(s). The "*template-free*" formation of these PANI microtubules can be attributed to self-assembling of NSA molecules and/or their aniline salts into a microstructured intermediate[20,21] that acts as both a supramolecular template[22] and a self-doping reagent. In view of the multidimensional doping of PANI by sulfonated fullerene derivatives and dendrimers with multiple $-(O)SO_3H$ groups reported recently by one of our groups (Dai et al.),[23] we carried out the template-free synthesis of polyaniline tubules in the presence of PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$ or $C_{60}(OSO_3H)_6$ as a protonic acid dopant. By doing so, we obtained conducting PANI *nanotubes* with a diameter on the order of hundreds of nanometers and a length up to several micrometers, as described below.



PANI- PAMAM4.0[Naphthyl$(SO_3H)_2]_{24}$



PANI-$C_{60}(OSO_3H)_6$

Figure 1. Typical SEM images of the PANI−PAMAM4.0-[naphthyl$(SO_3H)_2]_{24}$ and PANI−$C_{60}(OSO_3H)_6$ nanotubes synthesized by the template-free method. Detailed synthetic conditions are listed in Table 1.

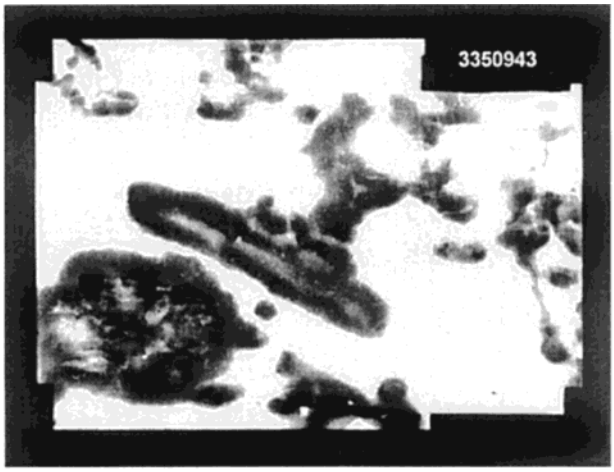
In a typical experiment, we synthesized the hydrogensulfated fullerenol of six $-(O)SO_3H$ groups (designated as $C_{60}(OSO_3H)_6$) and sulfonated dendrimer with 24 terminal groups of 3,6-disulfonaphthylthiourea (designated as PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$) according to the reported procedures.[24,25] With slight modification of the template-free method[21,26] using an additional amount of H_2O prior to the $(NH_4)_2S_2O_8$ addition (vide infra), PANI nanotubes were oxidatively polymerized from aniline in the presence of PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$ or $C_{60}(OSO_3H)_6$. In a typical experiment, 0.2 mL of aniline, 1.3 mg of $C_{60}(OSO_3H)_6$, and 1.0 mL of deionized water were mixed by ultrasonic stirring at room temperature for over 0.5 h. A 1.0 mL aliquot of ammonium

10.1021/ma001525e CCC: $20.00
Published on Web 01/11/2001

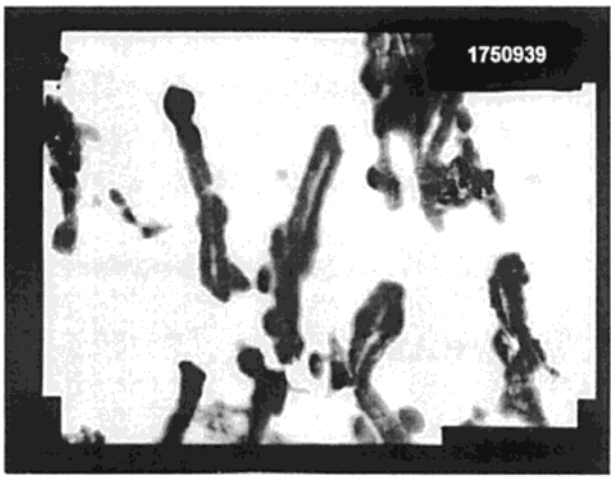
Table 1. Influence of Synthetic Conditions on the Morphology of Tubular PANI

	size		synthetic conditions				
tubules[a]	diameter (μm)	length (μm)	PAMAM4.0 (mg)	$C_{60}(OSO_3H)_6$	aniline (mL)	APS (mmol)	H_2O (mL)
a1	8.0−9.0	∼1500	1.0	*b*	0.2	0.0175	*b*
a2	2.0−3.0	>10.0	*b*	1.3	1.0	0.35	*b*
b1	0.1−0.3	0.5−1.0	1.0	*b*	0.2	2.0	1.0
b2	0.1−0.3	∼2.0	*b*	1.3	0.2	2.0	1.0

[a] a = microtubules; b = nanotubes; 1 = PANI−PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$; 2 = PANI−$C_{60}(OSO_3H)_6$. [b] Absence.



PANI- PAMAM4.0[Naphthyl$(SO_3H)_2]_{24}$



PANI- C60$(OSO_3H)_6$

Figure 2. Typical TEM images of the PANI−PAMAM4.0-[naphthyl$(SO_3H)_2]_{24}$ (×33.0 K) and PANI−$C_{60}(OSO_3H)_6$ (×17.0 K) nanotubes synthesized by the template-free method under the same synthetic conditions as Figure 1.

peroxide sulfate (APS: 2.0 mol/L) predissolved in deionized water was then rapidly added to the above mixture under ultrasonic stirring. The ultrasonication was continued for about 1.0 h to allow the polymerization to be completed. Finally, the precipitate was washed with deionized water and dried under a vacuum atmosphere for 24 h. Figure 1 represents SEM micrographs for the resulting tubular PANI−PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$ and PANI−$C_{60}(OSO_3H)_6$, respectively, which clearly show the formation of polymeric tubules with about 100−300 nm in diameter and several micrometers in length. TEM examination reveals the opened hollow structure for the PANI nanotubes (Figure 2), as is the case for carbon nanotubes.[5]

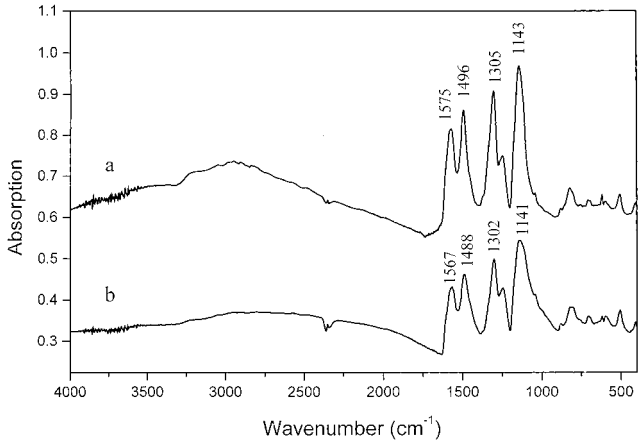


Figure 3. Typical FTIR spectra of the PANI−PAMAM4.0-[naphthyl$(SO_3H)_2]_{24}$ (a) and PANI−$C_{60}(OSO_3H)_6$ (b) nanotubes synthesized by the template-free method.

As seen in Table 1, the synthetic conditions have a profound influence on the diameter and length of PANI tubules formed by the template-free synthesis. For instance, the addition of H_2O to both the aniline/PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$ and aniline/C_{60}-$(OSO_3H)_6$ systems prior to the oxidation polymerization significantly decreases the tubular diameter from micrometers down to nanometers. Particularly, granular PANI were obtained in the absence of H_2O. It is most likely, therefore, that the addition of H_2O at this stage causes the aniline/PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$ or aniline/$C_{60}(OSO_3H)_6$ to form self-assembled nanostructures,[27] which act as a nanometer-sized template for aniline polymerization. This is also supported by the nontubular morphology produced by prolonged powerful ultrasonication during the template-free polymerization. The detailed structure of the self-assembled supramolecular template is currently under investigation.

The molecular structures of the PANI nanotubes were investigated by Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) measurements. The FTIR measurements showed bands at 1575 and 1496 cm^{-1} for PANI−PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$ and 1567 and 1488 cm^{-1} for PANI−$C_{60}(OSO_3H)_6$, characteristic of C═C stretching of the quinoid and benzenoid rings in the doped PANI (Figure 3).[28] The C−N stretching mode at ca.1300 cm^{-1} and the absorption peak of N═Q═N (Q representing the quinoid ring) at ca. 1140 cm^{-1} were observed in both cases. Unlike the highly crystalline PANI−NSA microtubules[21,26] and amorphous PANI granules,[11] the XRD data obtained from the PANI−PAMAM4.0[naphthyl$(SO_3H)_2]_{24}$ and PANI−$C_{60}(OSO_3H)_6$ nanotubes revealed a partial crystalline structure, suggesting a molecular ordering.[29]

The electronic structure of the PANI−PAMAM4.0-[naphthyl$(SO_3H)_2]_{24}$ and PANI−$C_{60}(OSO_3H)_6$ nanotubes dissolved in organic solvents was studied by an ultraviolet/visible (UV/vis) spectrophotometer, which de-

pended strongly on the solvent acidity. For instance, absorption peaks at 320 and 620 nm attributable to the emeraldine base[30] have been observed for PANI−C_{60}-$(OSO_3H)_6$ in the *N*-methylpyrrolidinone (NMP) due to the dedoping effect associated with NMP. On the other hand, the corresponding UV/vis absorption spectrum from *m*-cresol showed two absorption peaks at ca. 400 and 880 nm with a free carrier tail extending into the near-infrared region, typical for the $C_{60}(OSO_3H)_6$-doped PANI,[23] indicating a conducting state. The conductivity for a PANI−$C_{60}(OSO_3H)_6$ nanotube pellet was measured by the standard Van Der Pauwe DC four-probe method.[31] Its room-temperature conductivity ($\sigma_{20°C}$) was ca. 0.1 S/cm. This is slightly lower than the conductivity reported for pure PANI films after being doped with the corresponding acid.[23] The relatively low conductivity can be attributed to a relatively low doping level of [S]/[N] $\approx$ 0.25 as determined by X-ray photoelectron spectroscopy (some of the XPS probed $-(O)SO_3H$ groups may be ineffective for the protonic doping due to self-assembling into the supramolecular template) for the *as-synthesized* PANI nanotubes. Temperature-dependent measurements revealed a $\ln \sigma(T) \sim T^{-1/4}$ relationship for PANI−$C_{60}(OSO_3H)_6$, consistent with a variable range hopping (3D-VRH) model.[32]

In summary, we have synthesized the first polyaniline nanotubes through a template-free polymerization using $(NH_4)_2S_2O_8$ as an oxidant in the presence of a hydrogensulfated fullerenol with six $-(O)SO_3H$ groups (C_{60}-$(OSO_3H)_6$) or sulfonated dendrimer containing 24 terminal groups of 3,6-disulfonaphthylthiourea (PAMAM4.0-[naphthyl$(SO_3H)_2]_{24}$) as the protonic acid dopant. Water likely plays an important role in regulating the self-assembled structure of aniline/PAMAM4.0[naphthyl-$(SO_3H)_2]_{24}$ and aniline/$C_{60}(OSO_3H)_6$ and hence the tubular morphology and properties of the resulting materials. The resulting PANI−PAMAM4.0[naphthyl-$(SO_3H)_2]_{24}$ and PANI−$C_{60}(OSO_3H)_6$ nanotubes having diameters in the range 100−300 nm and up to 2 μm in length showed a 3-dimensional-hopping semiconducting behavior with a room-temperature conductivity of ca. 0.1 S/cm.

Acknowledgment. This project was supported by National Natural Science Foundation of China (No. 29634020-2; No. 29974037), 973 Program of China (No. G1999064504), and Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences.

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