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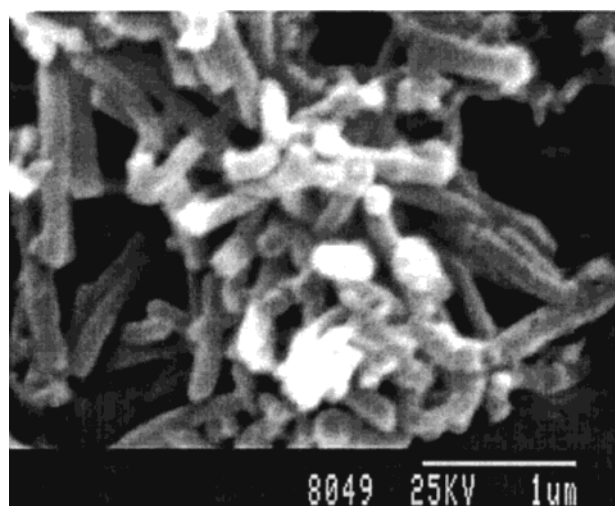
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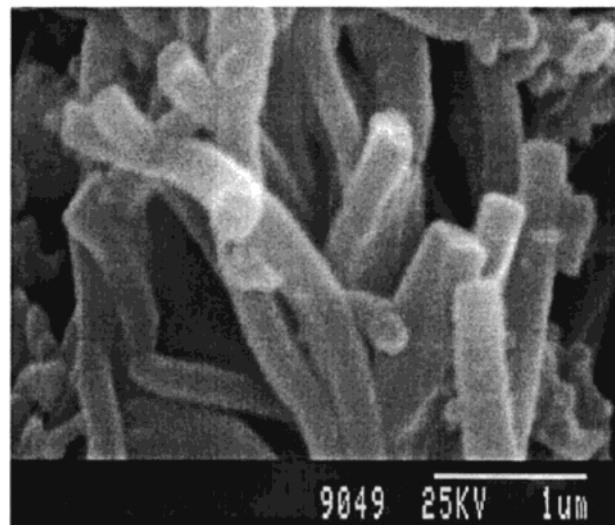
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Nanotubes and/or nanowires are known to play an important role in optoelectronic nanodevices, ranging from single-molecular transistors¹ and electron-emitting flat panel displays² to chemical sensors³ and artificial actuators,⁴ both as interconnecting 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 membrane⁷ 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ 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 template²² and a self-doping reagent. In view of the multidimensional doping of PANI by sulfonated fullerene derivatives and dendrimers with multiple $-(\text{O})\text{SO}_3\text{H}$ 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 $\text{C}_{60}(\text{OSO}_3\text{H})_6$ as a



PANI-PAMAM4.0[naphthyl(SO_3H)₂]₂₄



PANI- $\text{C}_{60}(\text{OSO}_3\text{H})_6$

Figure 1. Typical SEM images of the PANI-PAMAM4.0[naphthyl(SO_3H)₂]₂₄ and PANI- $\text{C}_{60}(\text{OSO}_3\text{H})_6$ nanotubes synthesized by the template-free method. Detailed synthetic conditions are listed in Table 1.

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.

In a typical experiment, we synthesized the hydrogensulfated fullerene of six $-(\text{O})\text{SO}_3\text{H}$ groups (designated as $\text{C}_{60}(\text{OSO}_3\text{H})_6$) 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 $(\text{NH}_4)_2\text{S}_2\text{O}_8$ addition (vide infra), PANI nanotubes were oxidatively polymerized from aniline in the presence of PAMAM4.0[naphthyl(SO_3H)₂]₂₄ or $\text{C}_{60}(\text{OSO}_3\text{H})_6$. In a typical experiment, 0.2 mL of aniline, 1.3 mg of $\text{C}_{60}(\text{OSO}_3\text{H})_6$, 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

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

tubules ^a	size		synthetic conditions				
	diameter (μm)	length (μm)	PAMAM4.0 (mg)	$\text{C}_{60}(\text{OSO}_3\text{H})_6$	aniline (mL)	APS (mmol)	H_2O (mL)
a1	8.0–9.0	~1500	1.0	<i>b</i>	0.2	0.0175	<i>b</i>
a2	2.0–3.0	> 10.0	<i>b</i>	1.3	1.0	0.35	<i>b</i>
b1	0.1–0.3	0.5–1.0	1.0	<i>b</i>	0.2	2.0	1.0
b2	0.1–0.3	~2.0	<i>b</i>	1.3	0.2	2.0	1.0

^a a = microtubules; b = nanotubes; 1 = PANI–PAMAM4.0[naphthyl(SO₃H)₂]₂₄; 2 = PANI–C₆₀(OSO₃H)₆. ^b Absence.



PANI- PAMAM4.0[Naphthyl(SO₃H)₂]₂₄



PANI- C₆₀(OSO₃H)₆

Figure 2. Typical TEM images of the PANI–PAMAM4.0-[naphthyl(SO₃H)₂]₂₄ ($\times 33.0$ K) and PANI–C₆₀(OSO₃H)₆ ($\times 17.0$ 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(SO₃H)₂]₂₄ and PANI–C₆₀(OSO₃H)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

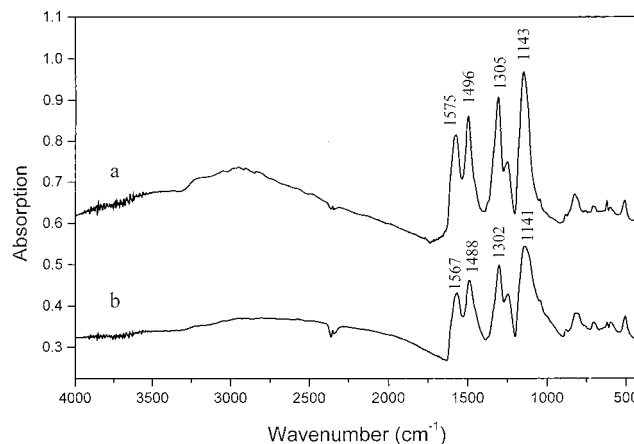


Figure 3. Typical FTIR spectra of the PANI–PAMAM4.0-[naphthyl(SO₃H)₂]₂₄ (a) and PANI–C₆₀(OSO₃H)₆ (b) nanotubes synthesized by the template-free method.

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 H₂O to both the aniline/PAMAM4.0[naphthyl(SO₃H)₂]₂₄ and aniline/C₆₀(OSO₃H)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 H₂O. It is most likely, therefore, that the addition of H₂O at this stage causes the aniline/PAMAM4.0[naphthyl(SO₃H)₂]₂₄ or aniline/C₆₀(OSO₃H)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(SO₃H)₂]₂₄ and 1567 and 1488 cm^{−1} for PANI–C₆₀(OSO₃H)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(SO₃H)₂]₂₄ and PANI–C₆₀(OSO₃H)₆ nanotubes revealed a partial crystalline structure, suggesting a molecular ordering.²⁹

The electronic structure of the PANI–PAMAM4.0-[naphthyl(SO₃H)₂]₂₄ and PANI–C₆₀(OSO₃H)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 base³⁰ have been observed for PANI-C₆₀-(OSO₃H)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 C₆₀(OSO₃H)₆-doped PANI,²³ indicating a conducting state. The conductivity for a PANI-C₆₀(OSO₃H)₆ nanotube pellet was measured by the standard Van Der Pauwe DC four-probe method.³¹ Its room-temperature conductivity ($\sigma_{20^\circ\text{C}}$) 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)SO₃H 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-C₆₀(OSO₃H)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 (NH₄)₂S₂O₈ as an oxidant in the presence of a hydrogensulfated fullerene with six -(O)SO₃H groups (C₆₀-(OSO₃H)₆) or sulfonated dendrimer containing 24 terminal groups of 3,6-disulfonaphthylthiourea (PAMAM4.0-[naphthyl(SO₃H)₂]₂₄) as the protonic acid dopant. Water likely plays an important role in regulating the self-assembled structure of aniline/PAMAM4.0[naphthyl-(SO₃H)₂]₂₄ and aniline/C₆₀(OSO₃H)₆ and hence the tubular morphology and properties of the resulting materials. The resulting PANI-PAMAM4.0[naphthyl-(SO₃H)₂]₂₄ and PANI-C₆₀(OSO₃H)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.

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