Synthesis of Dendritic Polyaniline Nanofibers in a Surfactant Gel

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One-dimensional nanostructures of conducting polymers have attracted intensive interest because of their novel physical properties and potential applications such as chemical sensors or actuators,[1−3] polymeric conducting molecular wires,[4] gas-separation membranes,[5,6] and neuron devices.[7] Among the known conducting polymers, polyaniline is unique due to its oxidation- or protonation-adjustable electrical properties.[8] Recently, considerable efforts have been made on the synthesis of polyaniline or polypyrrole nanofibers or nanotubes by chemical or electrochemical oxidative polymerization of the corresponding monomer. "Hard templates" such as aluminosilicate MCM-41,[4] track-etched polymeric membranes, and porous alumina[9] and "soft templates" such as liquid crystalline phases,[10] reverse microemulsion,[11] and micelles[12−15] were used to prepare polyaniline or polypyrrole nanofibers or nanotubes. Huang et al.[1] reported the synthesis of polyaniline nanofibers using aqueous/organic interfacial polymerization. However, the synthesis of dendritic polyaniline nanofibers or nanotubes has rarely been reported. Wan et al.[16] used anionic surfactants in water to prepare submicrometer-sized dendritic polyaniline tube. In the present work, we report the synthesis of dendritic polyaniline nanofibers with diameters between 60 and 90 nm by chemical oxidative polymerization of aniline in a special surfactant gel, which was formed by a mixture of hexadecyltrimethylammonium chloride (C_{16}TMA), acetic acid, aniline, and water at −7 °C.

The present procedure to prepare the dendritic polyaniline nanofibers is as follows: 0.32 g of C_{16}TMA and 0.093 g of aniline were dissolved in 2 mL of acetic acid (used as the solvent and dopant) at room temperature. This solution was purged with nitrogen for 30 min. Then, 1 mL of 1 mol/L aqueous solution of ammonium peroxydisulfate (used as the oxidant) was added with shaking. The final molar composition of this mixture of C_{16}TMA, aniline, acetic acid, APS, and H_2O was about 1:1:35:1:55. After the reaction was quickly cooled to − 7 °C, a surfactant gel was formed by noncovalent forces. The polymerization reaction was carried out in the gel under static conditions for 36 h at − 7 °C. During the polymerization process, a color change to dark green was observed. The surfactant gel changed into a suspension after holding for 30 min at room temperature. The resulting precipitate was filtered and washed with deionized water and ethanol several times to remove the residual surfactant. Finally, the pure dark green powder was obtained after dried at room temperature for 24 h.

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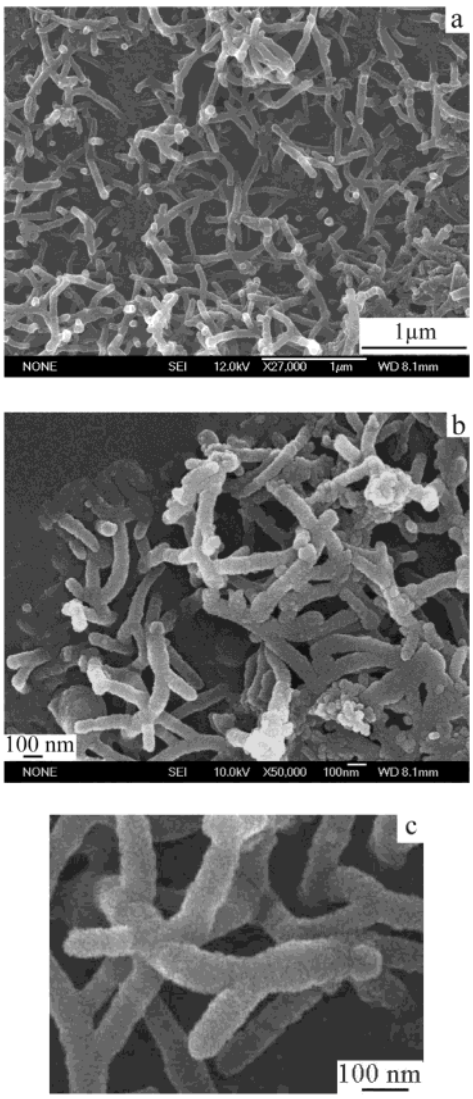

Figure 1. SEM images of dendritic polyaniline nanofibers synthesized with 0.3 mol/L C_{16}TMA at −7 °C in acetic acid: (a, b) at low magnification and (c) at high magnification.

The morphologies of polyaniline nanofibers are characterized by field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Typical SEM images of dendritic polyaniline nanofibers obtained with 0.3 mol/L C_{16}TMA at − 7 °C in acetic acid are shown in Figure 1. It is clear that these polyaniline nanofibers are interconnected to form dendritic or network structures, rather than isolated nanofibers or bundles.[9,10,12−14] The diameters of the polyaniline branches range from 60 to 90 nm, and the lengths are several hundred nanometers. A few polyaniline nanoparticles absorded onto the nanofibers are also found. In a magnified SEM image of the dendritic polyaniline nanofibers (Figure 1c), the crotches of the dendritic polyaniline nanofibers are clearly seen.

The effects of the concentration of C_{16}TMA, dopant, reaction temperature, and solvent on the morphologies of polyaniline were investigated. Figure 2a shows a TEM image of the dendritic polyaniline nanofibers obtained with 0.3 mol/L C_{16}TMA at − 7 °C in acetic acid. The diameters and lengths of the polyaniline branches

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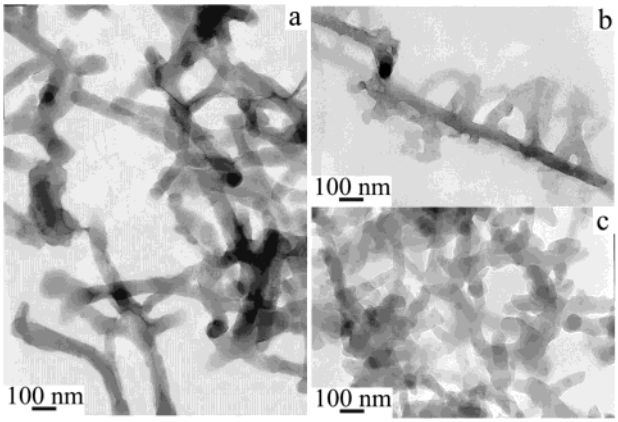

Figure 2. TEM images of dendritic polyaniline nanofibers synthesized with different concentrations of C_{16}TMA at −7 °C in acetic acid: (a) 0.3 mol/L; (b) a typical isolated dendritic polyaniline nanofiber in Figure 2a; (c) 0.1 mol/L.

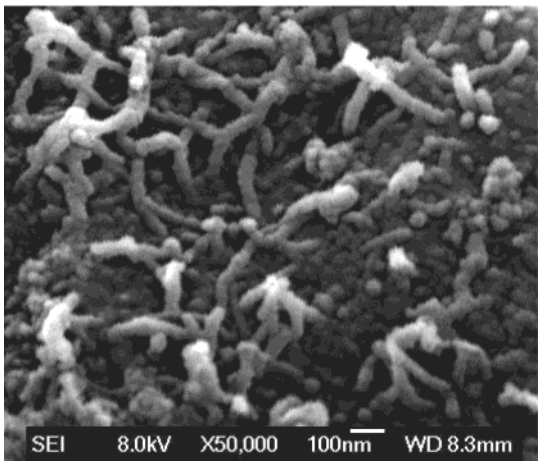

Figure 3. SEM image of dendritic polyaniline nanofibers synthesized with 0.3 mol/L C_{16}TMA at −7 °C in ethanol solution.

are consistent with the SEM images (Figure 1). A typical isolated polyaniline nanofiber in Figure 2b further reveals that the polyaniline nanofibers form a dendritic structure. Figure 2c presents the polyaniline nanofibers synthesized with 0.1 mol/L C_{16}TMA at − 7 °C in acetic acid. In comparison with Figure 2a, the lengths of the polyaniline branches decrease. Furthermore, when the concentration of C_{16}TMA decreases to 0.05 mol/L, the aggregates of polyaniline nanoparticles are obtained as shown in Figure S1 (Supporting Information). The addition of a small amount of hydrochloride used as dopant (molar ratio aniline:hydrochloride = 1:1) has no noticeable influence on the morphologies of polyaniline. When polymerization proceeded at room temperature, the surfactant gel was not obtained, and only aggregated polyaniline nanoparticles were synthesized with 0.3 mol/L C_{16}TMA in acetic acid, as shown in Figure S2 (Supporting Information). Figure 3 presents a SEM image of the morphologies of polyaniline obtained in a surfactant gel formed by a mixture of C_{16}TMA, ethanol, aniline hydrochloride salt, and water at −7 °C (molar ratio aniline: hydrochloride = 1:1). Rootlike polyaniline nanofibers together with aggregated nanoparticles are obtained. Both polyaniline branches and particles are 30−60 nm in diameter.

A typical Fourier transform infrared (FTIR) spectrum of the dried dendritic polyaniline nanofibers obtained with 0.3 mol/L C_{16}TMA at − 7 °C in acetic acid is shown

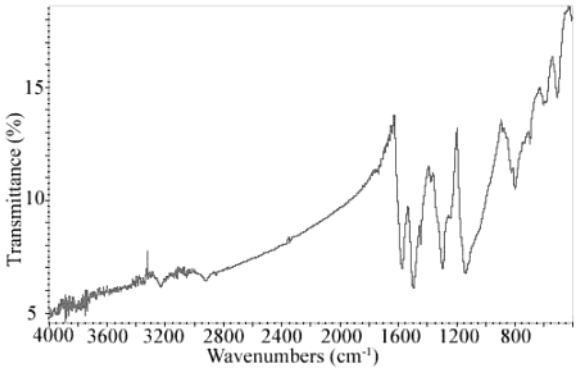

Figure 4. FTIR spectrum of dendritic polyaniline nanofibers synthesized with 0.3 mol/L C_{16}TMA at −7 °C in acetic acid.

in Figure 4. The adsorption peak at 1294 cm^{-1} corresponds to the C−N stretching modes of the leucoemeraldine component.[17] The peak at 1136 cm^{-1} is due to the C−H in-plane bending mode of permigraniline and that at 1242 cm^{-1} is related to the protonated C−N group.[18] The characteristic peaks at 1496 and 1572 cm^{-1} are assigned to the C═C stretching modes of the benzenoid ring and the quinoid ring, respectively,[12−14,19] thereby indicating that the state of the dendritic polyaniline nanofibers is emeraldine rather than solely the leucoemeraldine or permigraniline forms.

On the basis of the morphologies of polyaniline, it can be inferred that the C_{16}TMA/aniline complex can self-assemble into a special superstructure.[20,21] Subsequent oxidative polymerization of aniline is confined by the superstructure in the surfactant gel. Low temperature is the key factor for the formation of the surfactant gel. Polymerization at room temperature results in aggregated particles, possibly because the C_{16}TMA/aniline complex structure is unstable and disrupted by the growth of polyaniline. In addition, the superstructure of the C_{16}TMA/aniline complex is affected by the concentration of C_{16}TMA. The C_{16}TMA/aniline complex with high C_{16}TMA concentration in acetic acid can effectively self-assemble into a sponge phase, which shows a continuous 3D network of interconnected and branched segments. When the concentration of C_{16}TMA decreases, short-branched fiber and aggregated particle are obtained because of the lack of an effective self-assembly. The formation mechanism of the C_{16}TMA/aniline complex superstructure in the surfactant gel needs further investigation. It is expected that this synthetic method may be applicable for the synthesis of other conducting polymer or inorganic nanofibers.

In summary, we have demonstrated a simple and practical route to the synthesis of polyaniline nanofibers with uniform diameters by chemical oxidative polymerization of aniline in a surfactant gel. These polyaniline nanofibers are interconnected to form dendritic or network structures. The dendritic polyaniline nanofibers may provide potential applications as chemical sensors or actuators, gas-separation membranes and neuron devices.

Experimental Notes. TEM images were obtained on a JEM-2000EX microscope, using an accelerating voltage of 160.0 kV. SEM images were obtained on a JSM-6700F field-emission scanning electron microscope with an accelerating voltage of 10.0 kV. FTIR spectrum was measured on a Nicolet Magna IR-750 spectrophotometer using KBr pressed disk.

Supporting Information Available: Figure S1, TEM image of aggregated polyaniline nanoparticles synthesized with 0.05 mol/L C_{16}TMA at −7 °C in acetic acid, and Figure S2, SEM image of aggregated polyaniline nanoparticles synthesized with 3 mol/L C_{16}TMA at room temperature in acetic acid. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Huang, J.; Virji, S.; Weiller, B. H.; Kaner, R. B. *J. Am. Chem. Soc.* **2003**, *125*, 314.
(2) Gao, J.; Sansinena, J. M.; Wang, H. L. *Chem. Mater.* **2003**, *15*, 2411.
(3) Janata, J.; Josowicz, M. *Nat. Mater.* **2003**, *2*, 19.
(4) Wu, C. G.; Bein, T. *Science* **1994**, *264*, 1757.
(5) Anderson, M. R.; Mattes, B. R.; Reiss, H.; Kaner, R. B. *Science* **1991**, *252*, 1412.
(6) Yang, J.; Burkinshaw, S. M.; Zhou, J.; Monkman, A. P.; Brown, P. J. *Adv. Mater.* **2003**, *15*, 1081.
(7) Baba, A.; Knoll, W. *Adv. Mater.* **2003**, *15*, 1015.
(8) Premamoy, G.; Samir, K. S.; Amit, C. *Eur. Polym. J.* **1999**, *35*, 699.
(9) Martin, C. R. *Science* **1994**, *266*, 1961.
(10) Huang, L.; Wang, Z.; Wang, H.; Cheng, X.; Mitra, A.; Yan, Y. *J. Mater. Chem.* **2002**, *12*, 388.
(11) Jiang, J.; Yoon, H. *Chem. Commun.* **2003**, 720.
(12) Qiu, H.; Wan, M.; Matthews, B.; Dai, L. *Macromolecules* **2001**, *34*, 675.
(13) Yang, J.; Wan, M. *J. Mater. Chem.* **2002**, *12*, 897.
(14) Wei, Z.; Zhang, Z.; Wan, M. *Langmuir* **2002**, *18*, 917.
(15) Yang, Y.; Liu, J.; Wan, M. *Nanotechnology* **2002**, *13*, 771.
(16) Wei, Z.; Zhang, L.; Yu, M.; Yang, Y.; Wan, M. *Adv. Mater.* **2003**, *15*, 1382.
(17) Wang, D.; Caruso, F. *Adv. Mater.* **2001**, *13*, 350.
(18) Lei, Z.; Zhang, H.; Ma, S.; Ke, Y.; Li, J.; Li, F. *Chem. Commun.* **2002**, 676.
(19) Zengin, H.; Zhou, W.; Jin, J.; Czerw, R.; Smith, Jr. D. W.; Echegoyen, L.; Carroll, D. L.; Foulger, S. H.; Ballato, J. *Adv. Mater.* **2002**, *14*, 1480.
(20) Hirst, A. R.; Smith, D. K.; Feiters, M. C.; Geurts, H. P. M.; Wright, A. C. *J. Am. Chem. Soc.* **2003**, *125*, 9010.
(21) Menger, F. M.; Seredyuk, V. A.; Apkarian, R. P.; Wright, E. R. *J. Am. Chem. Soc.* **2002**, *124*, 12408.

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