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Self-Doped Polyaniline Nanostructures for Casting Metal Nanorods

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Self-doped polyaniline (SPANI) nanostructures were synthesized using a self-assembly process consisting of an active self-doping monomer (o-aminobenzenesulfonic acid, SAN) and aniline (AN). SAN plays the key roles of a self-doping monomer and a surfactant in the process of forming nanostructures. SAN-AN copolymerizations were carried out using the oxidant ammonium persulfate (APS) dissolved in the aqueous solution. The self-doped polyaniline demonstrates nanotube and nanofibril structures corresponding to the AN/SAN mole ratio of 4 and 1, respectively, through the examination of transmission electron microscopy. Reduction of ionic silver along the nanotubes resulted in the production of nanorod about 140 nm in diam.

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Nanotubular materials have attracted much attention since the discovery of carbon nanotubes.[1] These materials possess diverse potential applications such as nanoelectronics and biomedical devices.[2] Junctions often exist in the nanotube demonstrating a dendritic morphology.[3] Nanotube junctions play an important role in nanoelectronic devices.[4-6]

Polyaniline (PANI) is the simplest linear conjugated macromolecule and a representative of conducting polymers.[7] Pristine polyaniline is a typical semiconductor, but its electrical conductivity can be varied by several orders of magnitude through doping. Recently, conducting polymer nanotube has proven to be a promising material for applications in molecular electronics, molecular wires, and devices.[8,9] Several methods have been used for the preparation of polymer nanostructures, for example, template synthesis,[10-14] charily reaction,[15] and self-assembly.[16] The template method is a common route for preparing micro/nanotubes and nanofibrils of conducting polymers. The advantage of this method is that the length and diameter of the resulting tubes can be controlled by the selected porous membrane. Thus, a regular micro/nanotube can be obtained. In contrast, disadvantages of this method include that a soluble porous membrane as template must be used and then the membrane must be dissolved after preparation and that it is difficult to produce nanostructures in large scale by a template method for practical applications.

More recently, micro/nanotubes of polyaniline[17] have been synthesized using ammonium persulfate as an oxidant in the presence of protonic acid as an external dopant. This self-assembly method is an essential process that the external dopant is used as a template (or a surfactant) in forming a nanotube.[18] Although micro- and nanotubes of conducting polymers have been prepared by template synthesis and self-assembly, the external dopants are not easily controlled in these nanotube materials, especially during the de-doping process with the addition of a base. Here, we report on self-doped polyaniline nanotubes, which have been synthesized using a self-doping monomer as a template without an external dopant (or surfactant) in the process of forming nanotubes. In addition, we show that silver nanoparticles assemble along the nanotubes resulting in the production of nanorod.

In this work, we sought to make the aniline (AN) soluble in an aqueous solution of o-aminobenzenesulfonic acid (SAN) forming micelles. SAN was used as a self-doping monomer and a surfactant. Then, ammonium persulfate (APS) was added as the oxidant. A series of nanostructures were visually observed during the assembly.

Experimental

Chemicals.— Aniline (Merck) was distilled under reduced pressure. o-Aminobenzenesulfonic acid (Acros) was purified by recrystallization two times from distilled water. First, the solution was boiled in the presence of active carbon and filtered through Celite. White needles were obtained. After the second recrystallization, the white needles were washed with dry hexane, dried overnight under vacuum at 80°C, and then stored under nitrogen. Oxidant (ammonium peroxydisulfate (APS), Wako) and silver nitrate ($AgNO_3$, Fwakong) were used as received.

Preparation of nanostructures of SPANI.— Aniline and SAN (total $-NH_2$ concentration kept at 0.057 M) were dissolved in 100 mL distilled water with a desired mole ratio of AN to SAN ranging from 1 to 4. The solution was magnetically stirred under N_2 atmosphere at 4°C. 12.5 mL of an aqueous solution of $(NH_4)_2S_2O_8$ (0.57 g) was added to the above monomer mixture in one portion. The resulting solution was stirred for another 2 min to ensure complete mixing. Then, the reaction was allowed to proceed without agitation for 24 h at 4°C. After that, the resulting product was collected on the surface of reaction solution by filtration and washed several times using water. Finally, it was dried in a dynamic vacuum at room temperature for 24 h.

Preparation of silver nanorod.— The self-assembly of silver-polymer composite was carried out by introducing 15 mL $AgNO_3$ aqueous solution into the above monomer solution with AN/SAN mole ratio of 4. This mixture was thoroughly stirred for 10 min under N_2 atmosphere at 4°C. The amount of APS (0.57 g in 12.5 mL H_2O) was added to the above mixture. Then other steps followed the same procedures as the preparation of SPANI nanostructures.

Characterization.— Solid-state ^{13}C magic angle spinning (MAS) nuclear magnetron resonance (NMR) experiments were performed with a Bruker AVANCE-400 spectrometer, equipped with Bruker double-tuned 7 mm probe, with resonance frequencies of 100.6 MHz for ^{13}C nuclei at 298°K. The Hartmann-Hahn condition for $^1H \rightarrow {}^{13}C$ cross-polarization (CP) experiments was determined using admantane. The $\pi/2$ pulse lengths for ^1H and ^{13}C were 4 and 6 s, respectively. A repetition time of 4 s was used. The ^{13}C chemical shifts were externally referenced to tetramethylsilane (TMS). The $^1H \rightarrow {}^{13}C$ CP spectra were recorded as a function of contact time using a single-contact pulse sequence with reversal of spin temperature in the rotating frame and with high-power proton decoupling during the ^{13}C signal acquisition.

Scanning electron microscopy (SEM) was performed on a Philips apparatus (XL-40 FEG or S-3000N), which was operated at low acceleration voltage (V_{acc} = 15 kV) to minimize charging of the as-synthesized samples. For transmission electron microscopy (TEM), the samples were deposited on a holey carbon foil supported on a copper grid. TEM images were recorded on a CM30 microscope (Philips, Eindhoven, V_{acc} = 100 kV, LaB6 cathode). X-ray diffrac-

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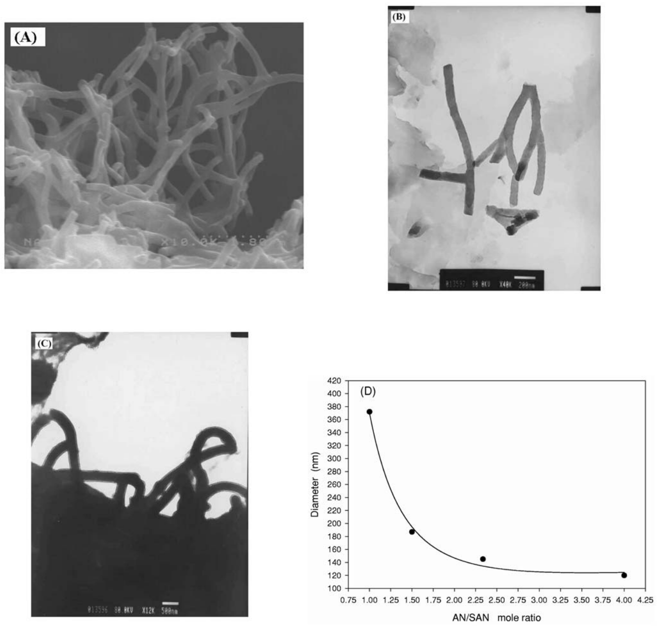

Figure 1. (A) SEM images of self-doped polyaniline with AN/SAN mole ratio of 4. HR-TEM images: (B) Nanotubes were formed by the AN/SAN mole ratio of 4, (C) Nanofibrils were formed by the AN/SAN mole ratio of 1. (D) Dependence of average diameter of the nanostructures on the mole ratio of AN to SAN.

tion (XRD, Riguka Multiflex ZD3609N) was used to characterize the molecular structures of the resulting SPANI nanostructures.

Results and Discussion

To obtain nanostructures (tubes or fibrils), the reactions were performed without stirring in the self-assembly process. SEM was used to study the nanostructures (Fig. 1A). The nanostructures were applied on a conductive tape and imaged by SEM. SEM analysis indicated that the SPANI might form tubular or fibril appearance and elongated assemblies. The micrographs demonstrate that the structures are relatively homogeneous with a persistence length on the order of micrometers. Two tubes (or fibrils) are often linked together to form branched junctions, which in turn construct more junctions composed of tube or fibril branches. These results are similar to the vessels in the bodies of animals and peptide nanotubes.[19] The formation of the nanostructures was very efficient, with the molar ratio of AN to SAN ranging from 1 to 4.

Almost all the assemblies as observed by TEM had tubular or fibril structures. The cations of AN and SAN first form micelles spontaneously in aqueous solution, owing to their hydrophilic and hydrophobic properties. With the addition of oxidant $(NH_4)S_2O_8$, the polymerization performed on the surface of the micelles. The micelles are inclined to fuse along the extension of polymer chain during the polymerization process. Thus, the polymer chain acted as a template in the self-assembly of SPANI nanostructure because SPANI is a rigid molecule. This is similar to our previous study in the preparation of conducting polymer fibers.[20] Micelles can aggregate to form branched structures. In this case, the micelles are regarded as templates for nanostructural junctions. The interactions, hydrogen bonds, and ionic bonds among these polymer chains might lead to this aggregation.[21] Based on the above discussion, we can deduce that the nanostructures are related to the relative concentrations of AN and SAN at the same synthesis conditions.

In fact, we found that the morphologies of conducting polymer nanostructures could be adjusted by changing the molar ratio of AN to SAN. TEM was employed to further study the nanostructures. Figures 1B and C show TEM images of these self-doped polyanilines as a typical tubular or fibril structures. Note that the composition of AN/SAN ratio of 4 will be converted into tubes (Fig. 1B). The light center matrix, as observed in this micrograph, suggests hollow tubular structures. The outer diameter of the tubes is about 120 nm in average along the length of the tube, and wall thickness becomes relatively thin. In general, anilinium cations can be solubilized in the micelle-water interface to form micelle. At high AN/SAN ratio of 4, the amount of sulfonate (on SAN) is relatively small within the micelles, the interaction through doping action between AN and SAN is weak. Thus, solubilized aniline and anilinium molecules are oxidatively polymerized by APS existing in the aqueous phase. This reaction takes place mainly in the micelle-water interface adjacent to the surfactant (SAN) head groups. This leads to a nanotube structure. In contrast, at AN/SAN ratio of 1, the amount of sulfonate (on SAN) is relatively large within the micelles, the interaction through doping action between AN and SAN is significant. Therefore, solubilized aniline and anilinium molecules are polymerized within the micelles. This resulted in a nanofibril structure (Fig. 1C) with the average diameter of ca. 370 nm. When the molar ratio of AN to SAN was increased from 1 to 4, the average diameter of these nanostruatures decreased from 370 to 120 nm based on SEM results (Fig. 1D).

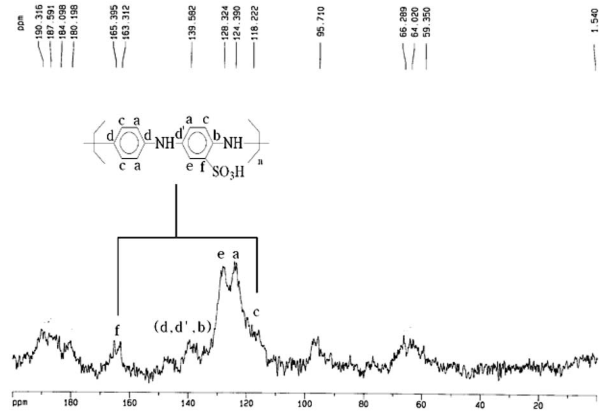

Figure 2. Aromatic region of the ^{13}C-NMR spectrum of SPANI with AN/SAN mole ratio of 4 at 298°K.

NMR was used to characterize the molecular structure of the resulting nanostructures of SPANI. NMR analyses indicated that well-defined SPANI had been obtained. As an example with its simple repeat unit, we show here the ^{13}C-NMR spectra (Fig. 2) of this SPANI. The aromatic region of the ^{13}C-NMR spectrum of SPANI supports the regiochemical structure of the polymer. Only five obvious peaks appear in the aromatic region, related to the 12 aromatic carbon atoms of the partial symmetric repeating unit (AN and SAN). In addition, this ^{13}C-NMR spectrum shows some additional small peaks, suggesting that the distortion on polymer chains occurs in these SPANI nanostructures. This information confirms that the polymer nanostructures prepared from a self-assembly process are region-irregular.

Based on TEM observations, the SPANI nanotubes were further employed to cast metal nanorods. The formation of SPANI nanotubes by coplymerization of AN and SAN is interesting when viewed in the context of mechanism of assembly. To study whether the metal nanorods can be simultaneously formed by the reduction of metal ions within or along the tubes, we introduced ionic silver to the aqueous solution of AN and SAN (at the AN/SAN ratio of 4) with the addition of oxidant APS. TEM visualization was monitored in the assembly process. We examined the ability of the assembling SPANI nanotube to serve as molds for casting metal nanorods. The ionic silver was first added to the mixture of AN-SAN aqueous solution, and the silver was then reduced by AN and SAN molecules. Thereafter SAN-AN copolymerization was performed using

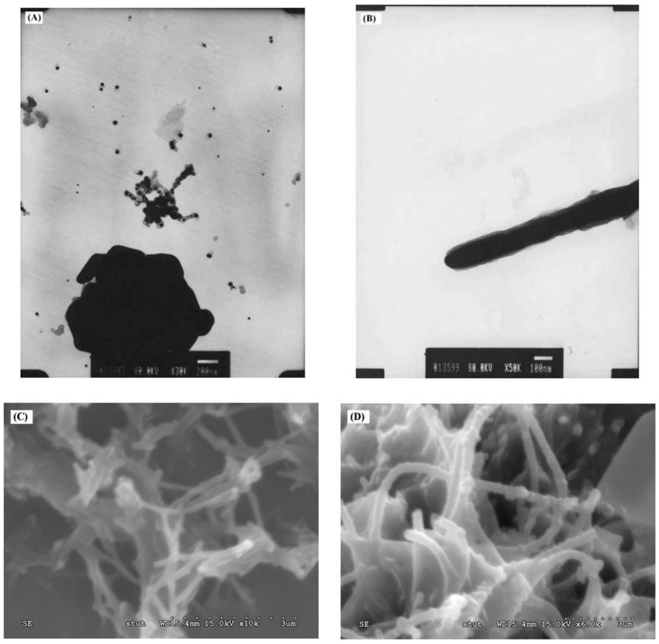

Figure 3. Silver nanorods were cast with the assembling polyaniline nanotubes. (A) TEM images of the silver nanoparticles by the introduction of silver ions (0.42 g $AgNO_3$) in the assembly solution. (B) TEM images of silver nanorods with the addition of $AgNO_3$ (0.85 g) in the assembly solution. (C) SEM images of silver nanorods along the SPANI tubes under the same experimental conditions in (B). (D) SEM images of silver clusters along both inner and outer the SPANI tubes (1.20 g $AgNO_3$).

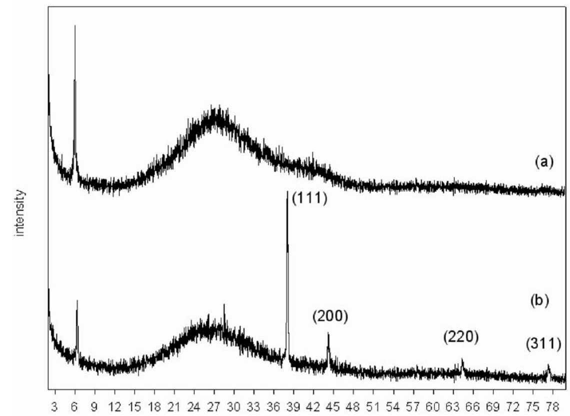

Figure 4. XRD patterns of (a) SPANI nanotubes and (b) the complex assembly of silver nanorods and SPANI tubes.

the oxidant ammonium persulfate (APS) dissolved in the above solution to ensure an uniform assembly of the silver nanorods. A series of $AgNO_3$ amounts have been introduced into this reaction system. At the addition of 0.42 g $AgNO_3$, TEM analysis indicated the formation of dispersing silver nanoparticles ranging from 20 to 40 nm in the assembly process (Fig. 3A). With the increase of $AgNO_3$, the silver nanoparticles show a tendency to aggregate closely together to form a cluster. Particularly, the complex assembly of silver and SPANI, by adding 0.85 g $AgNO_3$, resulted in the attainment of a silver nanorods ~140 nm in diameter as seen by TEM (Fig. 3B). The diameter of the nanorods is slightly larger than that of the polymer tubes, suggesting that casting was done within/along the tubular structure. This result can be further supported by the examination of SEM (Fig. 3C). The assembling SPANI nanotubes serve as a mold, providing a driving force for casting metal nanorods, leading to these silver nanoparticles in dense alignment along the SPANI tubes. When the addition of $AgNO_3$ is higher than 1.20 g, the SPANI tubes were overloaded by silver nanoparticles and showed aggregation of particles along outer tubes (Fig. 3D).

The crystalline identity of the complex assembly of silver nanorods and SPANI was confirmed by XRD analysis. X-ray diffraction patterns of SPANI nanotubes and its silver composite are shown in Fig. 4. A broad peak centered at $2\theta = 27°$ was observed for SPANI nanotubes, showing the resulting nanotubes are amorphous. The peak around $2\theta = 27°$ may be caused by the periodicity perpendicular to the polymer chain.[18] Particularly, the unusually sharp peak centered at $2\theta = 6°$ assigned to the scattering along the orientation parallel to the SPANI chain corresponding to a crystallographic spacing (d), suggesting that the nanotubes are formed by a layer-assembly pattern. This sharp peak is absent from PANI-external dopant synthesized by a common method.[18] Bragg's law, $n = 2d \sin \theta$, was used to calculate the crystallographic spacing. The basal spacing of 1.47 nm was obtained in the SPANI nanotubes. On the other hand, a typical silver nanorod was synthesized by reducing silver nitrate in the AN-SAN solution and the SPANI was used as a structure-directing reagent. The crystalline identity of the complex assembly of silver nanorod and SPANI was also confirmed by XRD analysis, revealing that the silver crystal is present in the composite matrix corresponding to (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes. All of the peaks can be readily indexed to face-centered cubic silver belonging to the spacing group of Fm3m [225] (JCPDS file no. 04-0783). The calculated lattice constants according to the spacing distance (d_g) of the (1 1 1) planes and the equation of $1/d_g^2 = (h^2 + k^2 + l^2)/a^2$ are 4.079 Å, which is in agreement with the literature value of 4.086 Å. Moreover, this material tends to grow as crystals at (1 1 1) planes. Similar orientations are also obtained from silver plating based on ammonium hydroxide[22] and poly(vinyl pyrrolidone)-directed polyol process.[23] In contrast, the peak around $2\theta = 6°$ in the SPANI tubes is more obvious than that in the SPANI-silver composite, whereas it shifts to higher angle (2θ) with the basal spacing of 1.41 nm. This result indicates that the crystallographic spacing was slightly depressed during the complex assembly due to the incorporation of silver crystal in the SPANI matrix. In addition, the peak arising from the periodicity perpendicular to the polymer chain shows more obvious and shifts to higher angle ($2\theta = 28.5°$). Thus, silver crystal can be considered to act as a template for forming the plane of the periodicity perpendicular to the polymer chain.

In light of the formation of SPANI nanostructures by such uni-amino compound (SAN) as a self-doping monomer, we also tested the ability of other di-amino derivatives (for instance, 2, 5-diaminobenzenesulfonic acid) under same conditions. No nanoscale structures were observed by electron microscopy examination (as compared with hundreds of tubular or fibril structures observed in the case of uni-amino SAN). However, substantial amounts of amorphous aggregates were obtained. This result differs markedly from the case of uni-amino SAN in which tubular or fibril structures were primarily dominated.

Conclusion

Our studies present the synthesis of SPANI nanostructures that consist of nanotubes and nanofibrils. The unique reduced properties of the tubes allow their use as nanoscale molds for the casting of silver nanorods.

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