Conducting Materials

Fabrication of Polymer Nanofibers and Carbon Nanofibers by Using a Salt-Assisted Microemulsion Polymerization[**]

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Among various types of nanomaterials, nanofibers have attracted much attention because of their intriguing chemical and physical properties.[1] The most widely used method for nanofiber preparation is template synthesis. This method involves the introduction of organic, inorganic, and metallic materials within channels of templates, such as silica,[2] anodic aluminum oxide,[3] zeolites,[4] and track-etched polycarbonates.[5] To date, microemulsion polymerization has been considered to be a facile process to produce polymer nanomaterials as reviewed by Antonietti and co-workers.[6] While nanoparticles,[7] hollow nanospheres,[8] and nanotubes[9] of several polymers were fabricated by using microemulsion polymerization, the synthesis of polymer nanofibers has not yet been performed. Herein, we report that novel polyacrylonitrile (PAN) nanofibers and carbon nanofibers with a high aspect ratio were fabricated by using a salt-assisted microemulsion polymerization. In this work, iron(III) chloride ($FeCl_3$) was employed as a structure-directing agent, it forms a coordination-complex with PAN nanoparticles during polymer nanofiber formation, and it acts as a catalyst for the conversion of the polymer into the carbon nanofibers. Salt-assisted sphere-to-cylinder micelle transformation is the crucial step for nanofiber formation. To the best of our knowledge, this is the first experimental evidence for the fabrication of carbon nanofibers derived from polymer nanofibers by using a salt-assisted microemulsion polymerization.

The overall fabrication procedure is presented in Figure 1. In a typical procedure, a variable amount of dodecyltrimethylammonium bromide (DoTAB) was magnetically stirred in 40 mL of distilled water at room temperature. Monomeric acrylonitrile (AN) was added dropwise to the micelle solution and monomers inside micelles were polymerized by using redox initiators, cerium sulfate and nitrilotriacetic acid (NTA). After 30 min of polymerization, iron(III) chloride was introduced and the polymerization proceeded for an additional 4 h with magnetic stirring. The product was precipitated in methanol to remove surfactants and initiators.

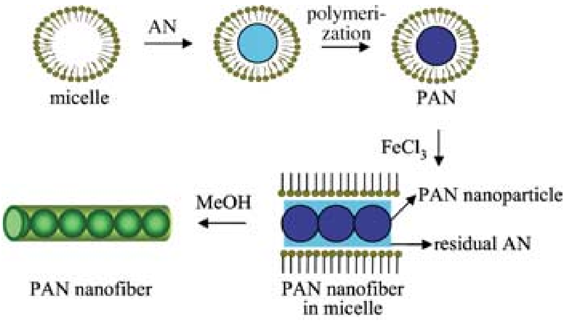

Figure 1. The overall fabrication scheme for PAN nanofibers by using a salt-assisted microemulsion polymerization.

When surfactants are dissolved in water, spherical micelles form between CMC (CMC = critical micelle concentration, 0.016 M for DoTAB) and the concentration of transformation of sphere to cylinder (0.32 M for DoTAB).[10] After 30 min of polymerization, the size of PAN nanoparticles were approximately 20 nm (Figure 2a). It was reported that

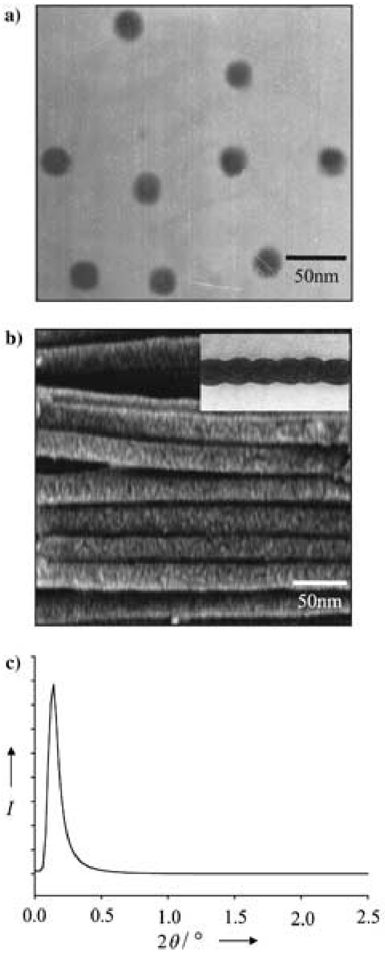

Figure 2. a) TEM image of fabricated PAN nanoparticles. A surfactant, DoTAB was used for micelle formation and acrylonitrile monomer (1 g, 0.02 mol) was polymerized with initiators, cerium sulfate, and nitrilotriacetic acid; b) SEM image of fabricated PAN nanofibers. PAN nanofibers were obtained by addition of iron(III) chloride (1.0 g, 6.2 mmol) in the middle of polymerization reaction. The inset shows the TEM image of the noded nanofiber structure; c) SAXS pattern of the PAN nanofiber.

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the concentration required for the transformation of sphere to cylinder drops significantly with the addition of salt into microemulsion systems.[11] Spherical micelles that contain presynthesized PAN nanoparticles transform into cylindrical micelles after the addition of iron(III) chloride. This salt-assisted sphere-to-cylinder micelle conversion is the crucial step for PAN nanowire formation. Consequently, the self-assembled PAN nanoparticles generated the nodated nanofiber structure (inset in Figure 2b) and the additional polymerization of the residual monomer inside the cylindrical micelles produced the smooth surface of PAN nanofiber (Figure 2b). The average diameter of a PAN nanofiber was about 25 nm and reasonably monodisperse. According to energy dispersive X-ray spectroscopy (EDX) analysis, the PAN nanofiber consisted of carbon (65.2%), nitrogen (19.5%) and iron (3.6%). The atomic ratio of carbon/nitrogen (approximately 3.3) was in good agreement with the theoretical atomic composition of PAN. The presence of Fe atoms demonstrates that iron(III) chloride was embedded in the PAN nanofiber. Control experiments were also performed without $FeCl_3$, consequently, PAN nanoparticles were exclusively synthesized. No polymer nanofibers were formed when the added amount of $FeCl_3$ was below 0.3 g, 1.8 mmol. This means that the cylindrical transformation from spherical micelles does not occur without the presence of salt such as iron(III) chloride under these experimental conditions. In addition, coordination between cyano group in the PAN nanoparticles and iron(III) chloride seems to be a prerequisite for PAN nanofiber formation. FTIR spectra showed that the vibrational band for C≡N stretching that is normally observed at 2244 cm^{-1} for PAN nanoparticles shifted down to 2236 cm^{-1} in the case of PAN nanofiber. This shift is because the vibrational motion of the CN group is restricted by its coordination with embedded iron. EDX and FTIR provide evidence to support the presence of coordination between iron and cyano group in PAN. To verify the coordination complex formation between iron and cyano group, additional experiments were also performed by using 3-ethoxy acrylonitrile, methacrylonitrile, methyl methacrylate, and styrene. CN coordination was substantiated by using AN derivatives, which contained the cyano (C≡N) functional group. In the case of 3-ethoxy acrylonitrile, polymer nanofibers with an average diameter of 30 nm were obtained along with poly(methacrylonitrile) nanofibers (approximately 25 nm in diameter). In contrast, polymer nanospheres were selectively fabricated with methyl methacrylate (approximately 20 nm in diameter) and styrene (approximately 25 nm in diameter), which do not have the cyano functional group. From these results, it is evident that coordination between the cyano group and iron(III) chloride is a prerequisite for the formation of polymer nanofibers. In Figure 2c), the structure of PAN nanofiber was investigated by small angle X-ray scattering (SAXS). A characteristic peak in the SAXS pattern indicated that PAN nanofibers had long-range order. The calculated lattice parameter for PAN nanofibers was approximately 21.5 nm, which was consistent with the average size of PAN nanoparticles. This result revealed that PAN nanoparticles act as lattice crystals for polymer nanofiber formation.[12]

To obtain carbon nanofiber (CNF), the PAN nanofibers were heated up to 900 °C. The diameter of the carbonized PAN nanofiber was approximately 20 nm, which is smaller than PAN nanofiber; the reduction in size is due to mass transfer during carbonization (Figure 3a).[7] Raman spectrum of CNF is displayed in Figure 3b. The band at 1580 cm^{-1}, assigned to the E_{2g} vibration of the infinite crystal, is associated with graphitic carbon atoms with sp^2 electronic configuration. Polycrystalline graphite has a distinct peak in its Raman spectrum at 1360 cm^{-1} arising from the A_{1g} mode, which is attributed to diamondlike carbon atoms with sp^3 configuration.[13] The integrated intensity ratio of A_{sp^2}/A_{sp^3} for carbonized PAN nanofibers is 0.80, which indicates a higher degree of graphitization compared with pristine PAN carbon (approximately 0.30). It was reported that the presence of transition metal atoms boost the formation of graphite during the carbonization process.[14] The powder XRD pattern of CNF also confirmed the presence of characteristic 002 and 110

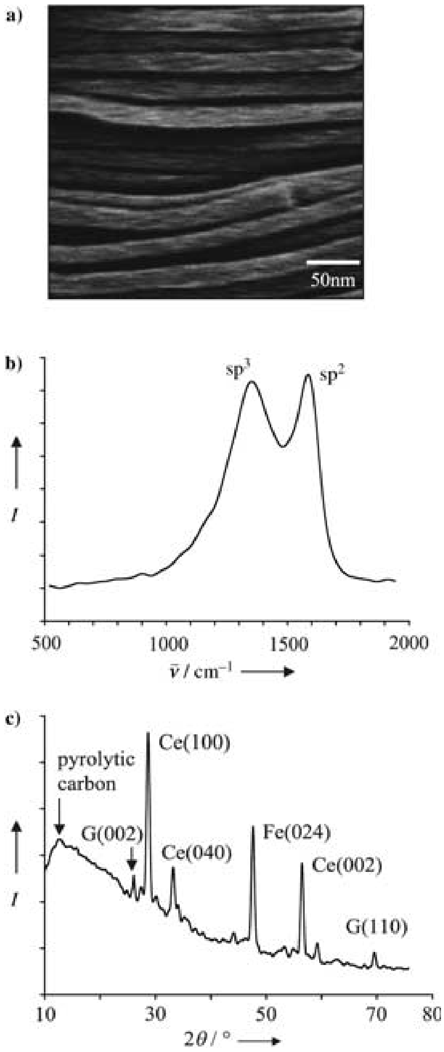

Figure 3. a) SEM image of carbon nanofibers obtained by heating the PAN nanofibers at a heating ratio of 1 °C min^{-1} to 300 °C then continuously 3 °C min^{-1} to 900 °C, and holding it at that temperature for 4 h under an N_2 atmosphere; b) Raman spectrum; and c) X-ray diffraction pattern of the carbon nanofibers.

Bragg reflections of graphite(Figure 3c). The weight ratios of the Ce and Fe atoms within the carbon nanofiber increased after carbonization process compared with pristine PAN nanofiber due to degradation and loss of PAN during cyclization, dehydrogenation, and decomposition.[15] The residual cerium-based products originated from the presence of initiators. Iron centers embedded in the PAN nanofiber catalyze the carbonization. Therefore, strong peaks associated with Ce and Fe atoms were observed at 28° and 48°, respectively.

Liquid-crystalline epoxy (LCE, diglycidyl ether of 4,4′-dihydroxy α-methyl stilbene[16]) is a typical matrix for display media, adhesives, antistatic coatings, and highly conductive composites. A typical LCE is composed of an aromatic mesogenic unit and a reactive oxirane ring, which takes part in the crosslinking reaction with an amine. The balanced properties between a liquid-crystalline polymer and a cured epoxy indicate that LCE can be used as a matrix for high performance polymer composites. To fabricate the conducting polymer composite, carbonized PAN nanofibers were used as a conducting filler and blended with LCE matrix. Figure 4 displays the electrical conductivity of LCE/CNF composites as a function of filler content. The electrical conductivity of CNF filled LCE composite was measured by a standard four-probe method.[17] As the amount of CNF increased, the electrical conductivity of CNF/LCE composite increased drastically. The conductivity pattern represented that the CNF/LCE composite shows percolation threshold behavior, which means that more electrical paths are generated with an increasing number of carbonized PAN nanofibers. Besides, LCE/CNF composites have enhanced electrical conductivity (ca. $10^{-4}\,\mathrm{S\,cm^{-1}}$) compared with conventional epoxy composites.[18]

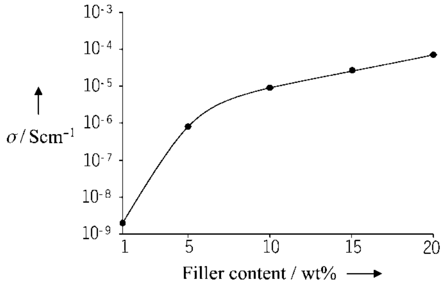

Figure 4. The electrical conductivity of LCE/CNF composite as a function of CNF content. The LCE/CNF sample was cured at 150 °C for 4 h and postcured at 175 °C for 1 h. The electrical conductivity of LCE/CNF sample was measured by a standard four-probe method.

In summary, we have demonstrated a salt-assisted microemulsion polymerization for the novel synthesis of polymer and carbon nanofibers. Salt-assisted sphere-to-cylinder micelle transformation is the crucial step for nanofiber formation. Iron(III) chloride is coordinated by PAN nanoparticles, it acts as a structure-directing agent for the formation of polymer nanofibers, and it is the catalyst for the production of carbon nanofibers. The carbonized PAN nanofibers can be applied as a conducting filler for polymer composites and has enhanced conductivity in liquid-crystalline epoxy medium.

Experimental Section

General procedure: Variable quantities of cationic surfactants (DoTAB, 3–6 g, 0.01–0.02 mol; docyltrimethylammonium bromide (DeTAB), 3–6 g, 0.011–0.022 mol) were dissolved in distilled water (40 mL) and AN monomer (1–2 g, 0.02–0.04 mol) was added dropwise to the surfactant solution and stirred for 2 h. The initiators, cerium(IV) sulfate (0.4 g, 1.2 mmol) and nitrilotriacetic acid (0.1 g, 0.5 mmol), were added for the polymerization of AN. After AN was polymerized for 30 min, iron(III) chloride (0.3–1.5 g, 1.8–9.2 mmol) was added into the polymer solution consecutively and the resulting solution was stirred for additional 4 h at ambient condition. The product was precipitated in methanol to remove surfactants and initiators. The carbonization process was performed by heating the PAN nanofibers at a heating rate of $1\,^{\circ}\mathrm{C\,min^{-1}}$ to 300 °C then continuously at $3\,^{\circ}\mathrm{C\,min^{-1}}$ to 900 °C, and holding it at that temperature for 4 h under an N_2 atmosphere. The LCE/CNF composites were cured at 150 °C for 4 h and postcured at 175 °C for 1 h. Sulfanilamide was used as curing agent. The electrical conductivity of LCE/CNF composite was measured by standard four-probe method.[17]

FTIR spectra were recorded on a Bomem MB 100 spectroscope (Quebec, Canada) in the absorption mode. The EDX was carried out on a JEOL JSM 5410 LV. Photographs of SEM were taken with a JEOL 6700. TEM analysis was performed with a JEOL JEM-200CX. Raman spectrum was obtained on a Jobin-Yvon T64000 spectrometer. XRD patterns were recorded on a Rigaku D-max/3C X-ray diffractometer. SAXS pattern was obtained with a Bruker AXS Nanostar small angle X-ray scattering spectrometer with a generator voltage of 40 KV and a current of 35 mA.

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