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Carbon Nanotubes by Electrospinning with a Polyelectrolyte and Vapor Deposition Polymerization

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ABSTRACT

Electrospinning of a polyelectrolyte and vapor deposition polymerization were combined to fabricate nanotubes of oxidatively stabilized poly(acrylonitrile) (PAN∆) with an outer diameter of 100 nm, a wall thickness of 14 nm, and centimeter-scale length. Poly(styrene sulfonate) sodium (PSSNa) nanofibers serves as sacrificial cores while vapor deposition polymerization was used to form smooth PAN sheaths of even thickness. After the PAN sheaths had been oxidatively stabilized, the PSSNa cores were etched away with water to form nanotubes of PAN∆. High-temperature carbonization of these nanotubes at 900 °C under Ar flow yielded carbon nanotubes with an outer diameter of 80 nm and wall thickness of 10 nm. Raman spectroscopy confirms that the carbon nanotubes were composed of highly disordered graphene sheets, consistent with the carbonization of PAN under similar conditions. These carbon nanotubes have many promising applications as catalyst supports, gas absorbents, and as encapsulants for controlled release of active compounds.

Since the discovery of fullerenes and carbon nanotubes, synthesis of carbon nanostructures has attracted a great deal of attention due to the myriad of applications that can be enabled and/or enhanced by these materials. Notable examples of products include supercapacitors, lithium-ion batteries, catalyst supports, gas storage media, fuel cells, and reinforced composite materials.[1] Carbon nanotubes also show great promise for the encapsulation of volatile or reactive organic substances and in drug delivery.[2] The synthesis of well-defined carbon nanotubes with 50−100 nm diameters has been a long-standing goal of materials chemistry. Here we wish to report the fabrication of carbon nanotubes with well-controlled diameters and long lengths by combining polyelectrolyte electrospinning with vapor deposition polymerization. The process relies on the fabrication of poly(styrene sulfonate) sodium (PSSNa) nanofibers by electrospinning, coating of the fibers with poly(acrylonitrile) (PAN) sheaths by vapor deposition polymerization (VDP), and carbonization of the sheaths. This new method is versatile and can be extended to the fabrication of various types of polymeric and carbonaceous nanostructures with hollow interiors.

In the past decade, the technique of electrospinning has undergone a renaissance as it has proved to be quite useful for the fabrication of very long fibers (∼1 km) with diameters from tens of nm to a few μm.[3] Electrospinning is applicable to a wide variety of polymers, composites, sol−gel solutions, and lipids. In this method, a high voltage is applied to a viscoelastic fluid as it is ejected from an orifice.[4] The droplet that forms at the tip of the needle is deformed by the electrostatic force into a conical shape known as the Taylor cone. When the properties of the fluid are properly tuned, the strong repulsion between surface charges leads to a stable jet that undergoes whipping and deformation, which attenuates the jet by several orders of magnitude. The jet then hits the grounded collector, resulting in very long fibers with nanoscale diameters.[5]

Modification to the electrospinning setup has allowed for the fabrication of nanotubes by coaxial electrospinning of sol−gel and composite materials with immiscible cores.[6] Using this technique, inorganic and composite nanotubes such as SiO_2, TiO_2−PVP, and anatase have been successfully fabricated. The inner surface of these fibers could be modified by inclusion of active compounds in the core liquid. Coaxial electrospinning of coagulating solutions has allowed for the fabrication of poly(ϵ-caprolactone) microchannels, which could then be carbonized. Highly porous nanofibers have been obtained by the electrospinning of blends, followed by the selective dissolution or by electrospinning into liquid nitrogen.[7] In addition, several variants of this technique have been developed to fabricate nanofiber assemblies with controllable architectures.[8]

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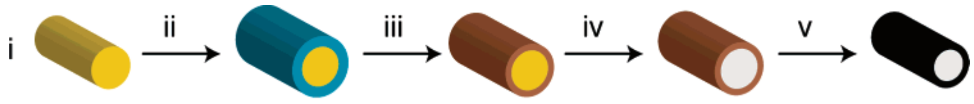

i) Electrospin poly(styrene sulfonate) sodium nanofibers
ii) Vapor deposition polymerization of acrylonitrile
iii) Oxidative stabilization of poly(acrylonitrile) at 250 °C in air
iv) Removal of poly(styrene sulfonate) sodium core with water
v) Carbonization at 900 °C under Ar flow

Figure 1. Schematic showing the fabrication of carbon nanotubes by electrospinning with a polyelectrolyte, followed by vapor deposition polymerization, oxidative stabilization, core removal, and rapid carbonization.

VDP is a versatile method for the formation of smooth polymeric coatings on hydrophilic surfaces.[9] This technique has been used for the fabrication of inorganic−organic core−shell colloids and mesoporous carbons and the formation of conducting polymeric nanotubes from anodic alumina templates.[10] VDP involves the exposure of a substrate to monomer vapor at low pressure (∼0.1 Torr) in the presence of radical initiator. The monomer vapor wets the surface of the substrate, and the polymerization is initiated by thermal decomposition of a radical initiator at an elevated temperature. The technique has been successfully applied to a wide range of organic polymers, including PAN, poly(styrene), poly(divinylbenzene), and poly(methyl methacrylate) (PMMA). Inorganic substrates such as silica and titania colloids have been successfully used as the core materials for vapor deposition polymerization. A polyelectrolyte such as PSSNa would be an ideal substrate for VDP, as its hydrophilic surface allows for homogeneous wetting by the monomer vapor. PSSNa also has a very high decomposition temperature and can endure temperatures above 300 °C for multiple hours without change in either morphology or solubility. If necessary, ion exchange can also be utilized to readily incorporate various cations into the poly(styrene sulfonate) matrix.

PAN is a commercial precursor for the fabrication of carbon fibers. The fabrication process relies on the oxidative stabilization of PAN by intramolecular cyclization to form a ladder polymer precursor. These ladder polymers bond together into graphitic sheets. Finally, pyrolysis at high temperatures (850−1300 °C) under an inert condition yields graphitic carbon fibers.[11] PAN has been electrospun from solution in DMF by several groups to form 40 nm carbon fibers.[12] Porous carbon fibers have been fabricated by electrospinning PAN into liquid nitrogen followed by drying in vacuo.[5h] Carbon materials with cylindrical pores have been fabricated by backfilling a network of silica nanofibers.[13] However, it is difficult or impossible to directly fabricate carbon nanotubes by coaxial electrospinning of PAN due to the tendency of the PAN nanotubes to collapse by capillary forces upon removal of the liquid cores.

Recent advances in the understanding of the effects of rheology on electrospinning have enabled the fabrication of nanofibers from nontraditional materials such as polyelectrolytes and phospholipids.[14,15−17] By tuning the entanglement of polymer chains or lipid micelles though counterion concentration, we have fabricated well-defined nanofibers of PSSNa from formic acid solutions. These resultant fibers have hydrophilic surfaces and thermostability up to 300 °C. The charged surfaces of these fibers mimic the charged surfaces of inorganic oxide colloids such as silica and enable a homogeneous coating by the monomer vapor. Their shape does not change appreciably during heat treatment and oxidative cross-linking of the sheath, allowing for the core morphology to be maintained.[17] Unlike silica, these polymer cores can be removed easily and rapidly following heat treatment under mild conditions by immersion in water.

Figure 1 shows the schematic used to fabricate carbon nanotubes. It involves electrospinning of a PSSNa nanofiber core, followed by VDP of acrylonitrile, oxidative stabilization of the PAN sheath, selective removal of the core with water, and high-temperature carbonization under Ar flow. This technique leverages the low-aggregation and smooth coating of a hydrophilic surface that is characteristic of VDP, the thermostability of PSSNa, the facile etching of PSSNa with water, and the morphologically stable carbonization of PAN to fabricate carbon nanotubes of 80 nm in diameter and 10−20 nm in wall thickness.

Figure 2A shows SEM image of the PSSNa nanofibers obtained by electrospinning from a solution in formic acid. The nanofibers had an average diameter of ∼120 nm with circular cross-sections. Figure 2B shows the result of VDP of PAN on the PSSNa nanofibers to form PSSNa@PAN nanocables. The nanocables have an outer diameter of ∼180 nm, indicating a 30 nm thick coating of PAN on the surface of the fiber. The surface of PAN coating is smooth and there are few interconnections between the nanocables, thanks to the electrostatic repulsion between the negatively charged fibers.

The PSSNa@PAN nanocables were heated in air for 5 h at 250 °C to oxidatively stabilize the sheath to PANΔ. Following heat treatment, the nanocables displayed the characteristic brown color. The PSSNa cores were then removed by immersion in water for 24 h. Figure 3A shows the result of dissolving the PSSNa cores from the nanocables. TEM imaging reveals nanotubes of PANΔ with smooth, continuous sidewalls and ∼100 nm in outer diameter, and the shrinkage could be attributed to oxidative stabilization. Figure 3B shows a high magnification image of the broken end of a nanotube shown in 3A. Figure 3C shows a collection of the PANΔ nanotubes, demonstrating that there were few

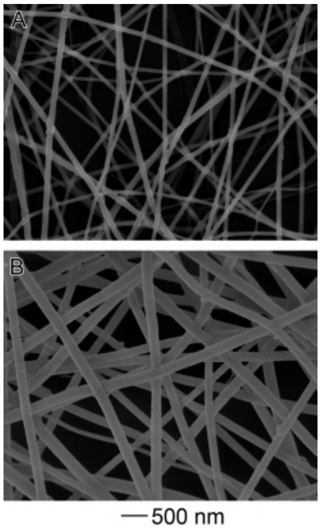

Figure 2. (A) SEM image of PSSNa nanofibers electrospun from 88% formic acid. (B) SEM image of PSSNa@PAN core−sheath nanofibers formed through vapor deposition polymerization of acrylonitrile onto the PSSNa nanofibers.

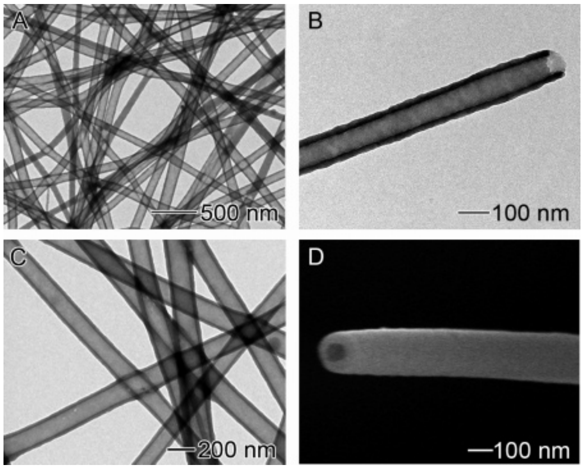

Figure 3. (A) TEM image of PAN ladder polymer (PANΔ) nanotubes. (B) TEM image of the broken end of a PANΔ nanotube. (C) TEM image of a number of PANΔ nanotubes showing that they are disconnected when they cross. (D) SEM image of a broken end of a PANΔ nanotube.

interconnects and the sidewall thickness remains uniform over the entire length of the tubes. As this technique is dependent on the dimensions of the core and not the length-based growth, there are few practical limitations to the length of the nanotubes.

Figure 4A shows the result of carbonization of the PANΔ nanotubes by heating to 900 °C for 1 h under Ar flow and 25 °C/min heating profile. The nanotubes were fully carbonized and experienced another shrinkage for the outer diameter from ∼100 to ∼80 nm. The SEM image was taken with 15° tilt, and the broken ends demonstrate that the nanotubes did not collapse and that the morphology of these nanotubes remained intact through the carbonization process. Figure 4B shows the TEM image of one of the nanotubes. The tubes were found to be 80 nm in diameter with 10 nm sidewalls.

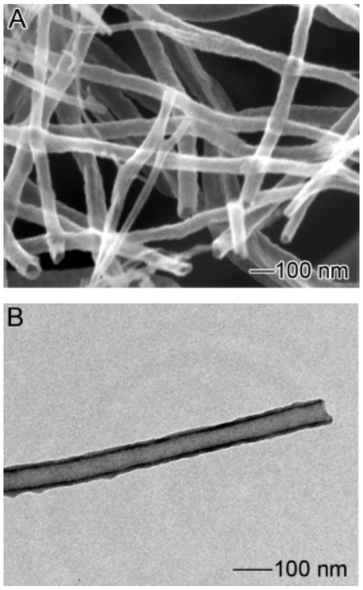

Figure 4. (A) SEM image of carbon nanotubes fabricated by carbonizing the PANΔ nanotubes at 900 °C under Ar flow. (B) TEM image of the broken end of one of the amorphous carbon nanotubes shown in (A).

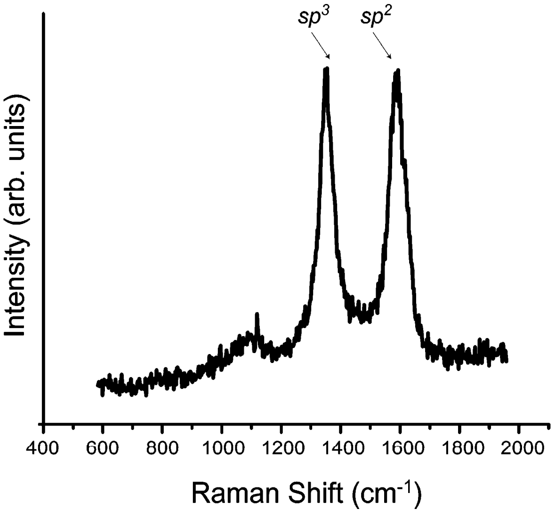

Figure 5. Raman spectra obtained for the carbon nanotubes carbonized at 900 °C. The Raman bands at 1593 cm^{-1} (G band, sp^2) and 1339 (D band, sp^3) are consistent with nanocrystalline graphitic material with 4.3 nm crystallite size.

Figure 5 shows the result of Raman spectroscopy on the carbon nanotubes shown in Figure 4. Raman spectroscopy can be used to characterize the bonding, order, and crystallite size in carbon samples.[18] The Raman spectrum of the carbon nanotubes prepared by the electrospinning-VDP method is consistent with disordered graphitic material obtained from the carbonization of PAN at 900 °C. The Raman band at 1593 cm^{-1} (the "G" band) is due to the in-plane phonon modes of graphene, which indicates sp^2 bonding. The band at 1339 cm^{-1} is due to disorder in the graphene layers caused by sp^3 bonding (the "D" band). By comparing the ratio of the intensity of these two bands, it can be determined that the fibers consist of disordered graphene nanosheets ∼4 nm in size.[17]

The carbon nanotubes fabricated using our technique are distinct from SWNT and MWNT generated by HiPCO, CVD, and laser ablation in that they have bigger diameters and thicker walls (at least an order of magnitude larger than those of SWNT and MWNT). The relatively larger openings should allow one to more easily fill these nanotubes with functional materials for various applications. These large carbon nanotubes may also find use as liquid conducts in nanofluidics. For potential applications in composites, these carbon nanotubes have distinct advantages over SWNT and MWNT, as they can be dispersed and processed without the use of surfactants. The carbon fiber industry is very large and the PAN-based processing techniques have been extensively developed, allowing for rapid advancement of this technology. Finally, carbon nanotubes made from electrospun templates could be extremely long due to the long length of electrospun nanofibers ($\sim$1 km under controlled conditions).[5]

In summary, we have demonstrated a simple and convenient method for the fabrication of polymeric core−sheath nanofibers and carbon nanotubes by combining electrospinning with polyelectrolyte and vapor deposition polymerization. Raman spectroscopy revealed that the nanotubes were made of disordered graphitic carbon, consistent with the carbonization of PAN. This new method is promising, as it is applicable to a wide range of monomers to generate polymeric nanotubes. The nanotubes generated by this method may have a number of potential applications in controlled release, catalyst support, and lightweight reinforcement.

Experimental. *Electrospinning PSSNa.* In a typical procedure for electrospinning PSSNa nanofibers, a solution of 20% w/v PSSNa (1 000 000 g/mol, Aldrich) in 88% formic acid (FA, J. T. Baker) was utilized. The fibers were spun at 15 kV with a feed rate of 0.2 mL/hr from a 25 gauge needle. A stainless steel frame was used as the collector with a 1 cm × 5 cm void gap.

Vapor Deposition Polymerization of Poly(acrylonitrile). To a specialized pressure vessel, 1 mL of acrylonitrile (Aldrich) and 0.02 g of AIBN (Aldrich) were added in separate vials. The stainless steel collector with PSSNa nanofibers was then attached to the top of the vessel. The apparatus was pumped down for 30 s using a Schlenk line to 0.1 Torr. The apparatus was then placed in a 90 °C furnace for 12 h.

Heat Treatment and Carbonization. PSSNa@PAN nanocables were treated in air at 250 °C for 5 h. The PSSNa@PANΔ nanocables were soaked in 18 mΩ water for 24 h to remove PSSNa. The water was changed twice during the soaking process. The PANΔ nanotubes were carbonized at 900 °C under Ar flow for 1 h with 25 °C/min ramping.

Characterization. Scanning electron microscopy (SEM) images were obtained by imaging a sample of fibers on a Si wafer with an FEI Sirion microscope at an accelerating voltage of 5 kV. Polymeric nanofibers were sputtered with Au/Pd for 30 s before imaging. Transmission electron microscopy (TEM) images of the heat-treated and carbonized samples were obtained on carbon-coated copper grids using a Philips CM100 TEM microscope with a Gatan 689 digital camera.

The Raman spectra were collected using a Reinshaw inVia Raman spectrometer (HPNIR785) attached to a Leica DM IRBE optical microscope. The samples were irradiated using a 415.4 nm laser with a spot size $\sim$1.6 μm in diameter. The Raman scattering signals were collected on a thermoelectrically cooled (−60 °C) CCD detector. The carbon nanotubes were transferred onto Si wafers coated with 50 nm of gold in order to reduce the signal from Si.

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