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Highly Porous Fibers by Electrospinning into a Cryogenic Liquid

Jesse T. McCann,[†] Manuel Marquez,[§] and Younan Xia*,[†]

Department of Chemistry, University of Washington, Seattle, Washington 98195-1700, and I'NEST Group, New Technology Research Department, PMUSA, Richmond, Virginia 29238

Received October 5, 2005; E-mail: xia@chem.washington.edu

Electrospinning is a simple, convenient, and versatile technique for generating extremely long fibers with diameters on both the micro- and nanoscales.[1] Recently, there has been much interest in extending this technique to produce uniform fibers with novel compositions and morphologies. For example, modification of the spinneret has facilitated the electrospinning of hollow, core-sheath, and porous fibers.[2] Here we report that, by immersing the collector in a bath of liquid nitrogen, porous polymer fibers can be obtained through thermally induced phase separation (TIPS) between the solvent-rich and solvent-poor regions in the fiber during electrospinning, followed by removal of solvent in vacuo. This method is versatile in that it can be readily used with nonvolatile solvents and does not require selective dissolution of phase-separated polymers. The technique can also be adapted to electrospray to generate hollow or porous colloids in a simple and inexpensive fashion. Unlike the solvent extraction method based on selective dissolution, the fibers do not form interconnections when electrospun into a cryogenic liquid. In addition, the fibers are porous throughout, making them suitable for encapsulation of active substances or catalysts.

Many of the applications of electrospun fibers could be greatly enhanced by increasing the surface area and porosity of the fibers. To this end, reliable production of porous nanofibers in a simple and inexpensive way has been attempted by a number of groups. Previous methods of producing porous polymer fibers relied on either the electrospinning of blends followed by selective removal of one of the phases or phase separation based on the evaporation of solvent or in the presence of vapor. Xia et al. showed that, by using a coaxial spinneret with miscible solvents and immiscible polymers, highly porous fibers could be obtained by selective dissolution (in the case of polymer fibers) or calcination (in the case of composite fibers).[2d] Wendorff et al. reported that porous fibers could be generated by electrospinning polymer blends, followed by selective dissolution.[3] A number of groups have also reported that, when a highly volatile solvent was used in the electrospinning process, porous fibers or fibers with unusual surface structures could be obtained.[4] In addition, it has been observed that rapid evaporation of solvent could lead to the formation of ribbon-like morphologies and collapsed, wrinkled skins on electrospun nanofibers.[5] For inorganic materials, porous fibers have been fabricated by electrospinning sol−gel solutions containing surfactants.[6]

In electrospinning, as the liquid jet is drawn to the collector, rapid evaporation of solvent serves to solidify the fiber and prevent varicose breakup (as in electrospray). In our method, the fibers hit a bath of liquid nitrogen before reaching the collector. The remaining solvent is frozen along with the polymer. In the freezing process, phase separation into solvent-rich and solvent-poor regions is induced.[7] In addition, vitrification of the polymer-rich regions may also occur as the polymer is cooled below its glass transition temperature. By controlling the way the solvent is evaporated, a porous morphology can be easily obtained in a single step.[8]

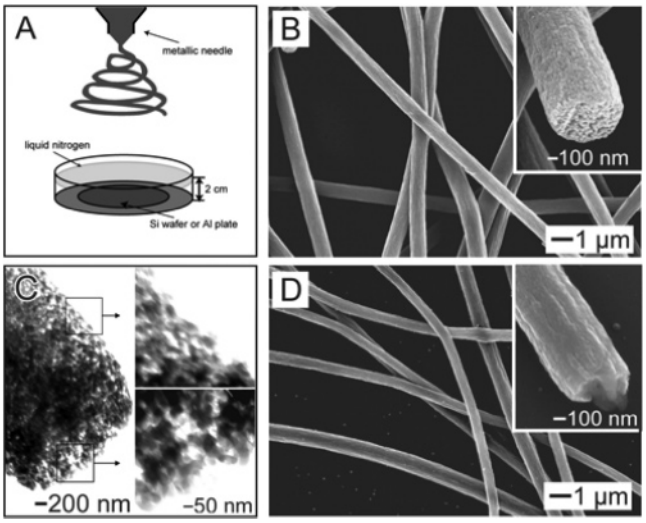

Figure 1. (A) The electrospinning setup with the modified collector used in these experiments. A poly(styrene) dish was used to hold the liquid nitrogen bath, while the rest of the setup was similar to those used in previous studies. (B) SEM images of poly(styrene) porous fibers prepared by electrospinning into liquid nitrogen, followed by drying in vacuo. The inset is an SEM micrograph of the broken end of a fiber at a higher magnification, showing that the fiber was porous throughout. (C) TEM of the porous poly(styrene) fibers shown in (A) with insets at higher magnification. (D) Poly(styrene) fibers electrospun from the same solution into liquid nitrogen but then reheated rapidly to room temperature in air. Note the lack of porosity and lower surface roughness for these fibers.

Figure 1a shows the electrospinning setup that was used in our experiments. It consisted of a syringe pump that was loaded with a plastic syringe. The syringe was tipped with a 24-gauge metallic needle, which was connected to a high voltage power supply. A grounded Si wafer or Al foil was used as the collecting electrode, which was immersed in a bath of liquid nitrogen ~2 cm in depth, with the needle tip placed 10 cm above the liquid nitrogen. The liquid nitrogen was replenished to the 2 cm level every 5 min. Humidity was carefully controlled to avoid the formation of frost on the collector by passing compressed air through a column of desiccant. In this method, the fibers were electrospun directly into the liquid nitrogen bath. The fibers were kept under liquid nitrogen until they were dried in vacuo.

Figure 1b shows the SEM image of porous poly(styrene) fibers prepared by electrospinning the solution into a liquid nitrogen bath followed by drying in vacuo. The fibers were ~1 μm in diameter. Examination of the end of a broken fiber (inset) indicates that the fiber is porous throughout. The role of residual solvent can be observed by increasing the collection distance. At a distance of 20 cm, the fibers had a smooth surface and solid morphology, as the solvent evaporated completely by the time the fibers reached the

[†] University of Washington.
[§] PMUSA.

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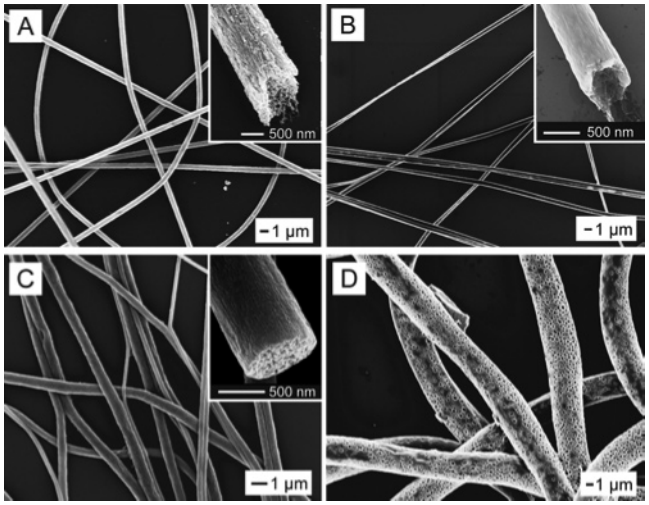

Figure 2. (A) Poly(acrylonitrile) fibers electrospun into liquid nitrogen from DMF. The inset shows the end of a broken fiber, clearly indicating a highly porous structure. (B) Porous carbon fibers obtained by carbonization of the poly(acrylonitrile) fibers. (C) Poly(vinylidene fluoride) fibers obtained by electrospinning into liquid nitrogen followed by drying in vacuo. (D) Poly(ϵ-caprolactone) fibers obtained by electrospinning into liquid nitrogen followed by drying in vacuo.

liquid nitrogen bath. It is worth pointing out that the fibers collected by this method have larger diameters than those collected without the use of a liquid nitrogen bath. Since the fibers are collected in an earlier stage of the electrospinning process, the size reduction caused by whipping and solvent evaporation is greatly reduced. The SEM image shows that the fibers are not interconnected, and that the morphology of individual fibers is not degraded by this method, unlike porous fibers generated using solvent extraction.[3] Figure 1c shows a TEM image of the same batch of poly(styrene) fibers, where the bright spots correspond to the pores. Figure 1d demonstrates that thermally induced phase separation is the driving force that leads to the formation of porous fibers. In this case, the electrospun fibers were removed from the liquid nitrogen bath and warmed rapidly in air. The result is that the polymer-rich and polymer-poor regions of the fiber remixed, only yielding fibers with a slightly roughened surface texture rather than high porosity.

This method can be extended to prepare porous fibers from a variety of different polymers. Poly(acrylonitrile) (PAN) is an important commodity polymer as it is a precursor for producing graphitic carbon fibers. Figure 2a shows PAN fibers that were prepared by electrospinning a solution in DMF (7% w/v) into liquid nitrogen, followed by drying in vacuo. Specific surface area of these 1 μm fibers was found to be 9.497 m^2/g by BET nitrogen absorption, which is significantly higher than the theoretical surface area of smooth 1 μm PAN fibers (3.419 m^2/g). Figure 2b shows carbon fibers obtained by thermally stabilizing the PAN fibers at 250 °C in air for 5 h, followed by carbonization at 1100 °C under Ar flow for 4 h.[9] Note the surface roughness has decreased, yet the fibers remain porous in the core. These porous carbon fibers are promising as lightweight reinforcement material and as catalyst supports.

Figure 2c shows porous electrospun fibers of poly(vinylidene fluoride) (PVDF) that were prepared by electrospinning into liquid nitrogen from *N*,*N*′-dimethylacetamide. PVDF has a very low coefficient of adhesion. In addition, PVDF is a piezoelectric material attractive for fabricating sensors and electroacoustic transducers.[10] By increasing the surface roughness of PVDF nanofibers, it should be possible to increase the hydrophobicity of their surfaces.[11] In preliminary testing using the sessile drop method, the advancing contact angle of water on a nonwoven mat of porous PVDF fibers was found to be 135°, compared to 110° for PVDF film and 130° for a mat of nonporous PVDF fibers.

Fiber-based scaffolds have been widely employed for tissue engineering and controlled release of drugs.[12] Previous methods for porogenesis in these materials are based on salt leaching or selective dissolution, which often cause significant degradation to the morphology of individual fibers. As a proof-of-concept experiment, poly(ϵ-caprolactone) was electrospun as nonwoven mats of porous fibers using our method. Figure 2d shows the SEM image of the fibers prepared by electrospinning of a solution of this polymer in chloroform, followed by drying in vacuo. The surface of each fiber contains a high density of pores 30−50 nm in diameter. The difference of morphology can be explained by the highly crystalline nature of poly(ϵ-caprolactone) and the volatility of chloroform. Crystalline polymers have been found to phase separate into closed pore structures by thermally induced phase separation.[12d]

In summary, the immersion of a collector in a cryogenic liquid further extends the capability of the electrospinning process. By taking advantage of the phase separation between residual solvent and polymer, we could directly generate highly porous fibers with increased surface areas. These porous fibers are promising for use in the encapsulation of active substances, as supports of catalysts, as lightweight reinforcement, and as hydrophobic coatings.

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Supporting Information Available: Experimental procedure; large, high-resolution SEM images showing the morphology of the electrospun porous fibers; and enlarged TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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