

Electrospinning Combined with Nonsolvent-Induced Phase Separation To Fabricate Highly Porous and Hollow Submicrometer Polymer Fibers

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Supporting Information

ABSTRACT: A simple and efficient method to induce porosity both in the core and on the surface of electrospun submicrometer polymer fibers has been demonstrated by combining nonsolvent-induced phase separation with electrospinning. In this modified electrospinning process, fibers are collected in a bath filled with a nonsolvent for the polymer being electrospun. The presence of residual solvent in the nanofibers causes phase separation once the fibers reach the nonsolvent bath. Poly(acrylonitrile) (PAN) in dimethylformamide (DMF) is chosen as the model polymer/solvent system. The versatility of the approach is demonstrated by extending the technique to poly(styrene)/DMF, poly(styrene)/toluene, and poly(methyl methacrylate)/DMF systems. With a suitable solvent (ethanol) and optimized tip-to-collector distance, the specific surface area of the porous PAN fibers increased to an order of magnitude compared to that of the smooth fibers obtained by the conventional electrospinning. Further, this electrospinning technique is extended to core-shell electrospinning, enabling the fabrication directly in one step of PAN-based hollow fibers having porosity both in the surface and the bulk.

1. INTRODUCTION

Electrospinning is a remarkably simple and versatile technique to generate polymer nanofibers.^{1–4} The rapid whipping motion of the polymer jet during the electrospinning process results in the formation of fibers with diameters that are an order of magnitude lower than those generated by other conventional fiber drawing techniques.^{2–6} Modifications in the electrospinning setup and parameters have been carried out time and again to produce nanofibers suiting a particular requirement and possessing unique characteristics and morphologies.^{7–10} Solution properties and process parameters along with experimental conditions have been exploited to generate porous electrospun nanofibers.^{10–25} Owing to their submicrometer and nanometer dimensions the electrospun fibers have high surface area, which is further enhanced by porosity in these fibers, which makes them useful for various applications.

Conventionally, the template technique has been widely employed to generate the porosity in electrospun fibers.^{11–14} Silica has been commonly used as a template material which on etching with hydrofluoric acid generates porosity in polyacrylonitrile (PAN)¹¹ and PAN-derived carbon^{12,13} fibers. Gupta et al.¹⁴ reported porous nylon-6 fibers using gallium trichloride salt as a template material. Block copolymers have also been used as template materials. Peng et al.¹⁵ carried out blend electrospinning of PAN with a block copolymer poly(AN-co-MMA) with selective dissolution of the polymethyl methacrylate (PMMA) polymer phase to generate highly porous nanofibers. Similar experiments were carried out by electrospinning polymer blends

of two different polymers and then dissolving one of the polymer from the as-spun material to obtain porous PAN and PAN-derived carbon fibers.^{16–18} The effect of volatile solvents leading to the formation of breath figures,²⁶ because of the condensation and subsequent evaporation of water vapor, has also been extensively exploited to generate fibers with porous surface morphologies.^{19,20} Furthermore, ternary systems containing a highly volatile solvent and a less volatile solvent mixed with the polymer have been proposed to create porosity.²¹ The difference in the evaporation rates generates the phase separation in this system. Recently, it has also been shown that the water vapor present in air could also lead to phase separation resulting in porosity in the bulk of the fiber by vapor-induced phase separation (VIPS).²³ The techniques of nonsolvent-induced phase separation (NIPS) and thermally induced phase separation (TIPS) were commonly used in the generation of thin film based porous membranes.^{27–30} In NIPS which is also known as immersion precipitation,³⁰ the phase separation is induced by solvent/nonsolvent exchange, while in TIPS the phase separation is induced by polymer cooling. During NIPS, the polymer precipitates rapidly after immersion in a nonsolvent bath that results in a highly porous

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structure.³⁰ However, these phenomenon have not been widely explored in combination with electrospinning to yield porous electrospun nanofibers. McCann et al.¹⁰ exploited the role of TIPS in the creation of highly porous electrospun nanofibers by using a liquid nitrogen bath as the quenching medium. The fibers were frozen in the liquid nitrogen bath resulting in TIPS. These fibers were then slowly vacuum-dried resulting in porous nanofibers. Wu et al.²⁵ have shown the generation of porosity using poly(ϵ -caprolactone) (PCL) nanofibers using water bath as the collector.

In this work we combined the principle of NIPS to the electrospinning process to fabricate highly porous submicrometer polymeric fibers unlike Wu et al.²⁵ where porosity in the PCL nanofibers was attributed to solvent evaporation and ambient conditions. In this contribution we unequivocally show porosity generated by NIPS for a variety of polymer/solvent systems. Water was used as the nonsolvent for a majority of the experiments. We have also done some preliminary studies to observe how the quench medium could affect the porosity and the specific surface area of the electrospun porous fibers. Furthermore, we have demonstrated a novel way of fabricating hollow submicrometer PAN fibers with porous skin and interior, directly in one step by extending this NIPS phenomenon to core-shell electrospinning. In core-shell electrospinning^{31,32} the collector was filled with a liquid which was a solvent for the core polymer (PMMA) and a nonsolvent for the shell polymer (PAN). This results in the dissolution of the core polymer and simultaneous induction of porosity in the shell polymer due to solvent/nonsolvent exchange. The surface morphology and porosity of the electrospun fibers were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Brunauer-Emmett-Teller (BET) adsorption method was used to characterize the specific surface area of these fibers. Electrospun porous submicrometer fibers fabricated in this work, because of their high surface area and controlled porosity, find potential applications as membranes in filtration systems, cell-scaffolds in tissue engineering, anode materials in energy storage devices, and in sensing devices.^{13,16,33–35}

2. EXPERIMENTAL METHODS

2.1. Chemicals. PAN ($M_w = 140\,000$), PMMA ($M_w = 120\,000$) and polystyrene (PS) ($M_w = 154\,000$) were purchased from Sigma Aldrich Co., India. DMF was purchased from Rankem Chemicals, India. Toluene was purchased from Loba Chemie Pvt. Ltd., India. Acetone was purchased from Fischer Scientific, India, and ethanol was from Merck Chemicals, India.

2.2. Nanofiber Preparation. Figure 1 illustrates the electrospinning setup used in this work. The polymer/solvent system was jetted through a syringe pump (Harvard Apparatus, Holliston, MA) at a flow rate of $3.0\ \mu\text{L}/\text{min}$, maintaining a potential difference of 9 KV (Gamma High Voltage, Inc., High Bridge, NJ) between the needle tip (26 gauge) and collector. A grounded silicon wafer immersed in the nonsolvent was used as the collector. The tip collector distance was optimized at 4.0 cm for these experiments. The polymer/solvent system was prepared by dissolving PAN in DMF at a temperature of $60\ ^\circ\text{C}$ while stirring for 2 h, dissolving PMMA in DMF by strong mechanical stirring, and PS in DMF was prepared by heating at $50\ ^\circ\text{C}$ while stirring for 24 h. The fibers collected on the silicon wafer were removed carefully from the nonsolvent bath in the form of a fibrous mat and were dried at room temperature in open air to complete the

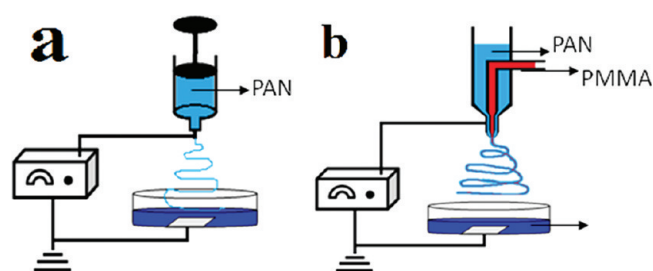


Figure 1. Schematic of the electrospinning setup used for making (a) porous fibers; (b) hollow core-shell fibers.

removal of the solvent. For the coaxial electrospinning (Figure 1b), a 24 wt % solution of PMMA in DMF was used as the core fluid, while the 9.5 wt % solution of PAN in DMF was used as shell polymer. The collector was filled with a 1:1 (v/v) mixture of ethanol and acetone in this case.

2.3. Nanofiber Characterization. Field-emission scanning electron microscopy (FESEM, SUPRA 40VP, Gemini, Zeiss, Germany) was used to characterize the surface morphology of the fibers. The accelerating voltage was maintained at 10 KV. All samples were first sputter-coated with a thin layer of Au-Pd to reduce the surface charging. The BET surface area and pore volumes of the adsorbents were determined by nitrogen adsorption-desorption isotherms, measured at 77 K using Quanta chrome Autosorb 1C system. The porous structure of the PAN nanofibers was also characterized by FEI Technai 20U Twin TEM. For the TEM analysis the fibers were carefully collected on a carbon-coated TEM grid which was kept under the nonsolvent bath.

3. RESULTS AND DISCUSSION

DMF has a boiling point of $153\ ^\circ\text{C}$ and has a low vapor pressure. In experiments where DMF is the solvent for the polymer, the possibility of porosity generation on the surface of polymer fibers, due to TIPS and the formation of breath figures is minimal.^{19,20} Recently Pai et al.²³ have shown the formation of pores in the interior of PS fibers when DMF was used as the solvent, due to VIPS. Water vapor being highly miscible with DMF, combined with the fact that DMF is a slow evaporating solvent, leads to phase separation in their PS/DMF system. However, there was no porosity observed on the surface of the fibers.²³ Here in this work, with DMF as the solvent we were able to generate fibers with high surface and bulk porosity, demonstrating that NIPS was the main mechanism governing the generation of the porosity. DMF was used as the solvent for the polymers: PAN, PS, PMMA. For phase separation to occur by the technique we propose, it is crucial that the solvent (DMF) does not evaporate completely before the fibers deposit on the collector. Owing to good miscibility of the polymer solvent and nonsolvent, partial replacement of the residual solvent by the nonsolvent in the collected fibers facilitates their precipitation (phase separation) thus generating the porosity. For this purpose the tip to collector distance was optimized to be 4.0 cm. The average diameters of the fibers produced in this work varied from 400 to 700 nm.

Figure 2 shows porous fibers obtained by NIPS for the systems of PAN/DMF, PS/DMF, PS/toluene, PMMA/DMF. Water was used as the nonsolvent for all these cases. As observed from these images (Figure 2a–d) the fibers have high surface porosity. Further to characterize the porosity we performed BET surface area

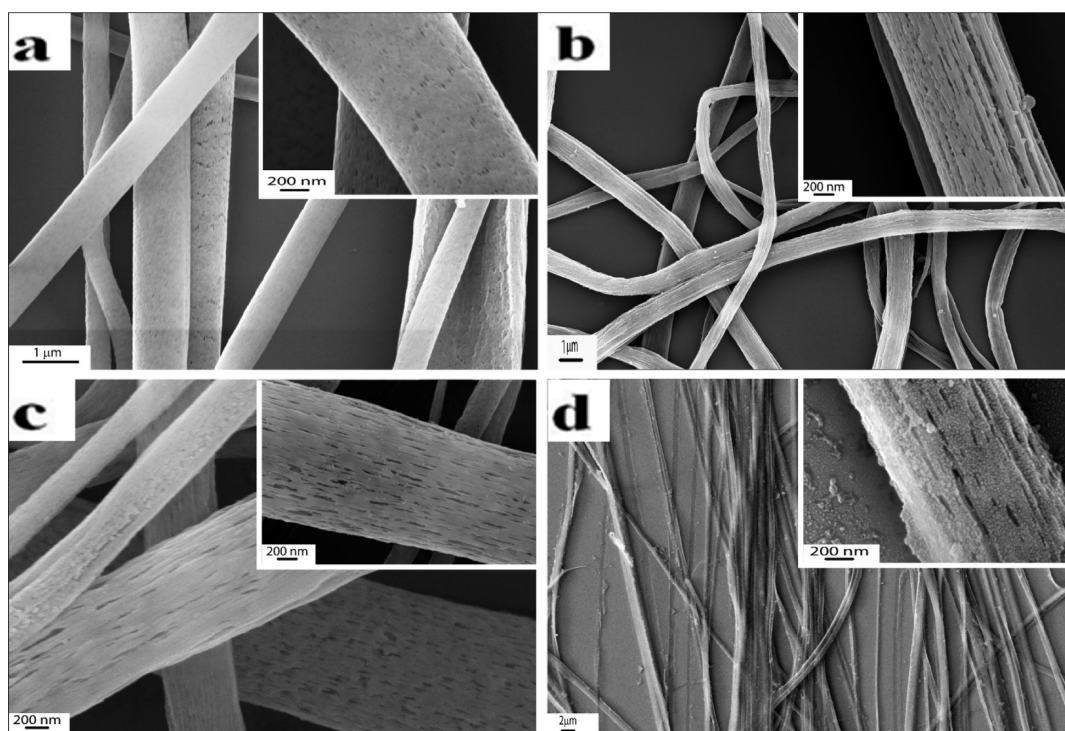


Figure 2. FESEM micrographs of electrospun polymer/solvent systems with a water bath as the nonsolvent: (a) PAN in DMF; (b) PS in DMF; (c) PS in toluene; (d) PMMA in DMF. The insets show the high magnification images, correspondingly.

measurements on the porous PAN fibers (Figure 2a) collected in water. The BET surface area of these fibers was found to be $37.1 \text{ m}^2/\text{g}$. In comparison, the value of smooth PAN fibers electrospun without any collector bath, had a surface area of only $8.0 \text{ m}^2/\text{g}$. In a recent report,²⁴ Yu et al. had mixed a nonsolvent (water), in different proportions, to the solution of PAN/DMF to be electrospun and reported a specific surface area of $46.4 \text{ m}^2/\text{g}$ in their experiments, which is comparable to the value obtained in our experiments.

Another feature to note is the porosity generated on the surface of PS fibers with toluene as the solvent (Figure 2c). It has been shown previously that when toluene is used as a solvent for PS, the surface develops porosity due to formation of breath figures.^{19,20} (see Supporting Information for images of PS/toluene system electrospun in humid air, Figure S1) The morphology of the porous fibers in Figure 2c is distinctly different from that obtained by TIPS or breath figures alone, demonstrating that NIPS has an important role in the porosity generation. Another important consideration in the fabrication technique we propose for porosity generation is the miscibility between the solvent and the nonsolvent.²⁴ Water and DMF have excellent miscibility which favors the generation of porosity by NIPS. When ethanol, which is highly miscible with DMF, was used as the nonsolvent bath we obtained porous PAN nanofibers with specific surface area as high as $99.4 \text{ m}^2/\text{g}$ (also see Supporting Information Figure S2 for image of porous PAN fibers collected in ethanol). Further, nearly smooth fibers having no surface porosity were obtained when hexane was used as the nonsolvent bath (see Supporting Information Figure S3 for smooth PAN nanofibers collected in hexane). We have preliminary evidence that the miscibility of the nonsolvent used in collection bath with the solvent strongly affects the porosity and the surface area of the porous fibers. We are further investigating the exact

mechanism which governs the porosity when the miscibility of the solvent/nonsolvent change.

Figure 3 shows SEM image of the cross section and a TEM micrograph of the porous PAN fibers. It is evident from these images (Figure 3a,b) that the porosity is not limited to the surface alone but extends to the bulk of the fiber as well. It is important to note that Pai et al.²³ have shown that the interior of fibers which look smooth on the surface could be porous due to the water vapor in the ambient air acting as a nonsolvent (VIPS). Although we realize that VIPS might also be responsible for the bulk porosity observed in our systems, the morphologies in the two cases is distinctly different. In our system one can clearly observe an interconnected network of pores, characteristic of a spinodal decomposition,²² whereas Pai et al.²³ obtained voids in a continuous polymer matrix. In fact, we observe that there is more roughness in the interior of the fibers as compared to on the outside surface. It may be because of more rapid evaporation of solvent from the surface and therefore entrapment of the solvent in the bulk of the fiber. This leads us to believe that NIPS and henceforth choice of the nonsolvent bath play a significant role in the final morphology and the porosity of the polymer fibers.

3.1. Core–Shell Electrospinning. We have further extended the nonsolvent-based phase separation approach as discussed above for core–shell electrospinning to produce hollow as well as porous fibers. There have been contradictory reports in literature about the miscibility of the core and shell fluids used in electrospinning. McCann et al.³⁶ have suggested that the core and shell fluids must be completely immiscible so that no intermixing takes place at the tip of nozzle. However several other researchers have successfully electrospun core–shell fibers using miscible core and the shell solutions.^{37,38} Yu et al.³⁷ have reported that the use of a common solvent that aids the process of coelectrospinning by reducing the interfacial tension between

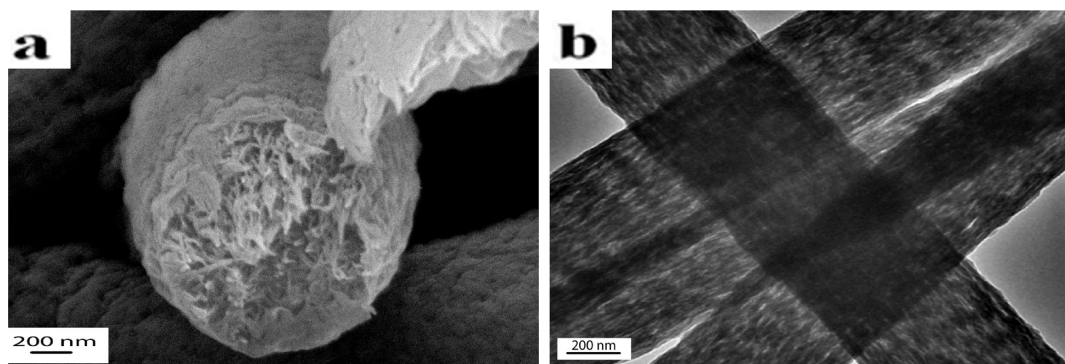


Figure 3. (a) FESEM micrograph showing the cross section of a porous PAN fiber; (b) TEM micrograph of a PAN fiber.

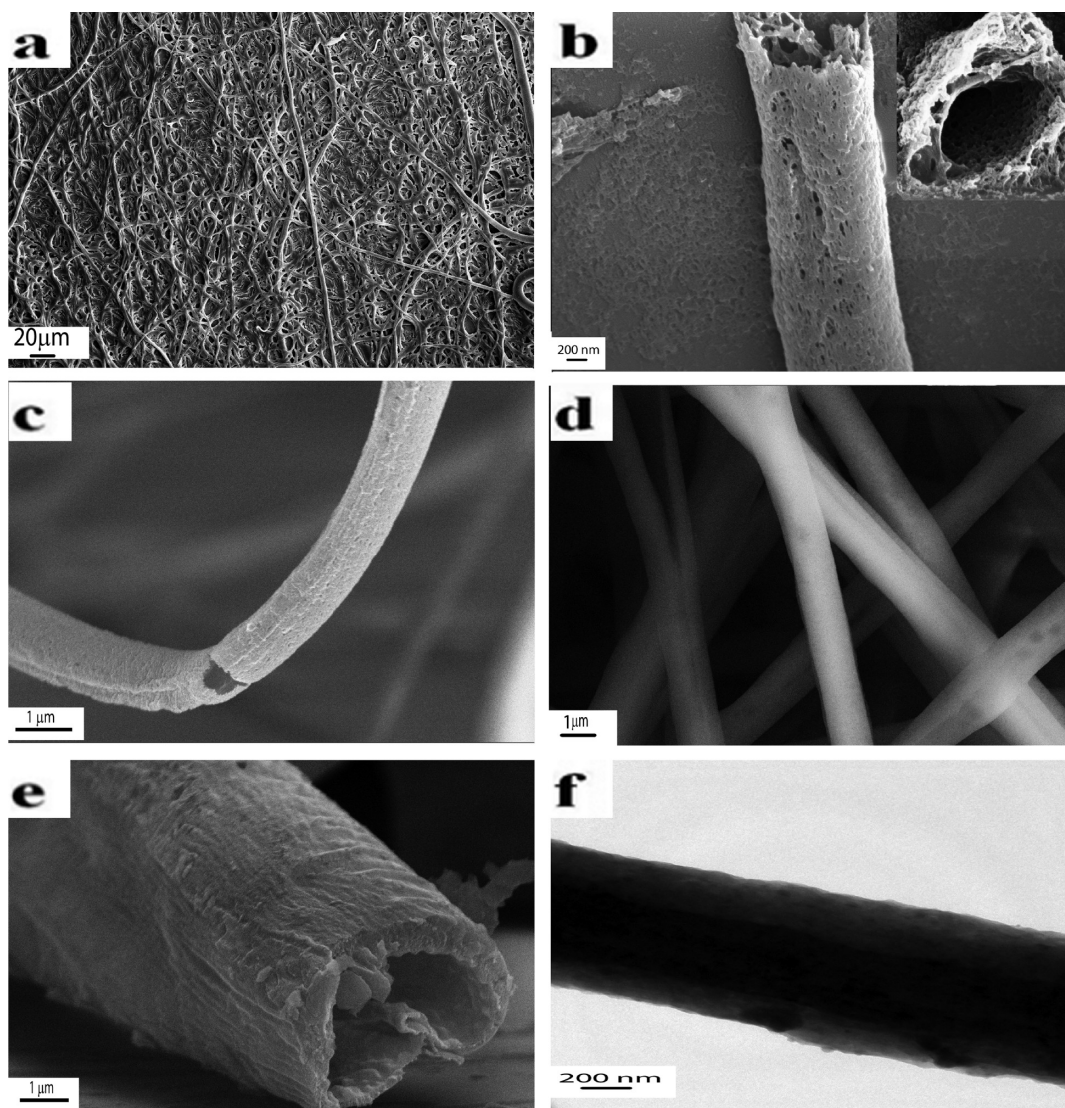


Figure 4. (a) FESEM image of porous hollow fibers collected in ethanol/acetone; (b) high magnification FESEM image of a single porous and hollow PAN fibers collected in ethanol/acetone mixture as shown in panel a. Inset shows cross-section of one of these fibers; (c) FESEM image of a single PAN fiber clearly showing the hollow nature of these fibers; (d) FESEM image of the PAN fibers collected on Si wafer and then dissolved in ethanol/acetone mixture; (e) image of a hollow PAN fiber collected with MEK as a collecting bath; (f) TEM image of core-shell PAN/PMMA fibers.

the two fluids. On the basis of this fact, we have used DMF as the common solvent for PAN, the shell polymer, and PMMA, the

core polymer. Figure 4 summarizes the results for electrospun PAN hollow fibers with a porous exterior obtained by core-shell

electrospinning. The electrospinning conditions such as core and shell polymer flow rates of 6.0 and 7.0 $\mu\text{L}/\text{min}$, accelerating voltage of 10 KV, and tip collector distance of 4.0 cm were optimized to ensure the core-shell structure of electrospun fiber as also confirmed by the TEM image shown in Figure 4f. A custom-made nozzle was used for the core-shell electrospinning, with the inner diameters for the core fluid opening and the shell fluid opening being 0.30 mm and 0.80 mm, respectively. Fibers were collected directly in a bath containing a 1:1 (v/v) mixture of ethanol and acetone. It is the mixture of acetone and ethanol which dissolves PMMA. Although acetone itself can dissolve PMMA, ethanol was added because high porosity was observed when ethanol was used as the nonsolvent bath in the prior experiments on electrospun pure PAN fibers (without the core-shell setup).

Figure 4a–c shows the electrospun PAN hollow and porous fibers collected in ethanol/acetone mixture. It is clearly observed from Figure 4b,c that the PMMA core was completely dissolved to produce hollow PAN fibers with a porous exterior. Porosity was generated in these fibers because of solvent (DMF)/nonsolvent (mixture of ethanol and acetone) exchange resulting in NIPS. To test the hypothesis that it is NIPS that generates the porosity in the hollow fibers, and not the intermixing of the two solutions at the tip, the following experiment was carried out. The fibers were first collected directly on a silicon wafer (without collecting bath), dried in the open air, and then dissolved in the ethanol/acetone mixture to dissolve the core polymer. As the FE-SEM image in Figure 4d shows, the fibers obtained by this method have a smooth surface morphology, which establishes that the porosity is indeed generated by NIPS. For a further confirmation of NIPS generated porosity, methyl ethyl ketone (MEK) was used as the collecting bath. MEK is a solvent for PMMA and a nonsolvent for PAN. MEK is immiscible with DMF. The image in Figure 4e shows the rough surface of the hollow fibers when MEK was used as the collecting bath, but there was no porosity observed. As we have also observed earlier in the case of hexane no phase separation and thus no porosity was generated when the nonsolvent/diluent pair was immiscible. Both these observations confirmed that porosity in the hollow fibers collected in the ethanol/acetone system was indeed generated by the NIPS mechanism. These hollow fibers have extremely porous morphology on the surface as well as the interior having a very high surface area. These features may be exploited for a wide range of applications such as drug delivery, biosensing, microfluidics, photonics, and energy storage.

CONCLUSIONS

A modified electrospinning technique by combining nonsolvent phase separation phenomenon with electrospinning has been proposed to fabricate highly porous submicrometer size polymeric fibers. As compared to conventional electrospinning, polymeric fibers fabricated in this work have almost an order of magnitude increased specific surface area owing to the porosity generated on the surface as well as interior of these fibers. To ensure the robustness of the approach, we have used many polymer/solvent systems and successfully demonstrated the general acceptability of the method reported here. Further, this modified electrospinning technique was extended to core-shell electrospinning in order to fabricate hollow fibers having a highly porous sheath directly in one step. The methodology proposed here to produce highly porous as well as hollow electrospun PAN

fibers is rather simple, novel, and versatile and can be employed for any polymer which can be electrospun as long as we choose the right solvent/nonsolvent pair. A variety of polymeric fibers fabricated in this work with characteristic porosity and hollow porous interior may find potential applications as filtration membranes, bioscaffolds, electrode materials for MEMS, and sensing devices.

ASSOCIATED CONTENT

S Supporting Information. SEM images for the cases (a) PS/toluene system when electrospun in humid air; (b) PAN nanofibers electrospun in ethanol as nonsolvent bath; (c) smooth PAN nanofibers collected in hexane. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) Formulas, A. U.S. Patent 1,975,504, 1934.
- (2) Doshi, J.; Reneker, D. H. Electrospinning process and application of electrospun fibers. *J. Electrostat.* **1995**, *35*, 151–160.
- (3) Dzenis, Y. Spinning continuous fibers for nanotechnology. *Science*. **2004**, *304*, 1917–1919.
- (4) Li, D.; Xia, Y. Electrospinning of nanofibers: Reinventing the wheel? *Adv. Mater.* **2004**, *16*, 1151–1170.
- (5) Ramakrishna, S.; Fujihara, K.; Teo, W. E.; Lim, T. C.; Ma, Z. *An Introduction to Electrospinning and Nanofibers*; World Scientific: Singapore, 2005.
- (6) Shin, Y. M.; Hohman, M. M.; Brenner, M. P.; Rutledge, G. C. Electrospinning: A whipping fluid jet generates submicron polymer fibers. *Appl. Phys. Lett.* **2001**, *78*, 1149–1151.
- (7) Teo, W. E.; Gopal, R.; Ramaseshan, R.; Fujihara, K.; Ramakrishna, S. A dynamic liquid support system for continuous electrospun yarn fabrication. *Polymer*. **2007**, *48*, 3400–3405.
- (8) Zhang, D.; Chang, J. Patterning of electrospun fibers using electroconductive templates. *Adv. Mater.* **2007**, *19*, 3664–3667.
- (9) Sharma, C. S.; Sharma, A.; Madou, M. Multiscale carbon structures fabricated by direct micropatterning of electrospun mats of SU-8 photoresist nanofibers. *Langmuir* **2010**, *4*, 2218–2222.
- (10) McCann, J. T.; Marquez, M.; Xia, Y. N. Highly porous fibers by electrospinning into a cryogenic liquid. *J. Am. Chem. Soc.* **2006**, *128*, 1436–1437.
- (11) Ji, L.; Saquing, C.; Khan, S. A.; Zhang, X. W. Preparation and characterization of silica nanoparticulate – polyacrylonitrile composite and porous nanofibers. *Nanotechnology* **2008**, *19*, 085605–085614.
- (12) Im, J. S.; Jang, J. S.; Lee, Y. S. Synthesis and characterization of mesoporous electrospun carbon fibers derived from silica template. *J. Ind. Eng. Chem.* **2009**, *15*, 914–918.
- (13) Ji, L.; Lin, Z.; Medford, A. J.; Zhang, X. Porous carbon nanofibers from electrospun polyacrylonitrile/SiO₂ composites as an energy storage material. *Carbon* **2009**, *47*, 3346–3354.
- (14) Gupta, A.; Saquing, C.; Afshari, M.; Tonelli, A.; Khan, S. A.; Kotek, R. Porous nylon-6 fibers via novel salt-induced electrospinning method. *Macromolecules* **2009**, *42*, 709–715.

- (15) Peng, M.; Li, D.; Shen, L.; Chen, Y.; Zheng, Q.; Wang, H. Nanoporous structured submicrometer carbon fibers prepared via solution electrospinning of polymer blends. *Langmuir* **2006**, *22*, 9368–9374.
- (16) Lin, J.; Ding, B.; Yu, J.; Hsieh, Y. Polyacrylonitrile and carbon nanofibers with controllable nanoporous structure by electrospinning. *Macromol. Mater. Eng.* **2009**, *294*, 673–678.
- (17) Zhang, L.; Hsieh, Y. L. Nanoporous ultrahigh specific surface polyacrylonitrile fibers. *Nanotechnology* **2006**, *17*, 4416–4423.
- (18) Bognitzki, M.; Frese, T.; Steinhart, M.; Greiner, A.; Schaper, A.; Hellwig, M.; Wendorff, J. H. Preparation of fibers with nanoscaled morphologies: Electrospinning of polymer blends. *Polym. Eng. Sci.* **2001**, *41*, 982–989.
- (19) Casper, C. L.; Stephens, J. S.; Tassi, N. G.; Chase, D. B.; Rabolt, J. F. Controlling surface morphologies of electrospun polystyrene fibers: Effect of humidity and molecular weight on electrospinning process. *Macromolecules* **2004**, *37*, 573–578.
- (20) Megelski, S.; Stephens, J. S.; Chase, D. B.; Rabolt, J. F. Micro- and nanostructured surface morphology on electrospun polymer fibers. *Macromolecules* **2002**, *35*, 8456–8466.
- (21) Qi, Z.; Yu, H.; Chen, Y.; Zhu, M. Highly porous fibers prepared by electrospinning a ternary system of non-solvent/solvent/poly(L-lactic acid). *Mater. Lett.* **2009**, *63*, 415–418.
- (22) Pai, C. L.; Boyce, M. C.; Rutledge, G. C. Morphology of porous and wrinkled fibers of polystyrene electrospun from dimethylformamide. *Macromolecules* **2009**, *42*, 2102–2114.
- (23) Dayal, P.; Liu, J.; Kumar, S.; Kyu, T. Experimental and theoretical investigation of porous structure formation in electrospun fibers. *Macromolecules* **2007**, *40*, 7689–7694.
- (24) Yu, X.; Xiang, H.; Long, Y.; Zhao, N.; Zhang, X.; Xu, J. Preparation of polyacrylonitrile fibers by electrospinning a ternary system of PAN/DMF/H₂O. *Mater. Lett.* **2010**, *64*, 2407–2409.
- (25) Wu, Y.; Clark, R. L. Controllable porous polymer particles generated by electrospraying. *J. Colloid Interface Sci.* **2007**, *310*, 529–535.
- (26) Srinivasarao, M.; Collings, D.; Philips, A.; Patel, S. Three-dimensionally ordered array of air bubbles in a polymer film. *Science* **2001**, *292*, 79–83.
- (27) Matsuyama, H.; Takida, Y.; Maki, T.; Teramoto, M. Preparation of porous membrane by combined use of thermally induced phase separation and immersion precipitation. *Polymer* **2002**, *43*, 5243–5248.
- (28) Kuoa, C. Y.; Lina, H. L.; Tsai, H. N.; Wang, D. M.; Lai, J. Y. Fabrication of highly hydrophobic PVDC membrane via non-solvent induced phase separation. *Desalination* **2008**, *233*, 40–47.
- (29) Lee, H. J.; Jung, B.; Kang, Y. S.; Lee, H. Phase separation of polymer casting solution by non-solvent vapor. *J. Membr. Sci.* **2004**, *245*, 103–112.
- (30) Guillen, G. R.; Pan, Y.; Li, M.; Hoek, E. M. V. Preparation and characterization of membranes formed by nonsolvent induced phase separation: A review. *Ind. Eng. Chem. Res.* **2011**, *50*, 3798–3817.
- (31) Sun, Z.; Zussman, E.; Yarin, A. L.; Wendorff, J. H.; Greiner, A. Compound core-shell polymer nanofibers by co-electrospinning. *Adv. Mater.* **2003**, *15*, 1929–1932.
- (32) Loscertales, I. G.; Barrero, A.; Marquez, M.; Spertz, R.; Ortiz, R. V.; Larsen, G. Electrically forced coaxial nanojets for onestep hollow nanofiber design. *J. Am. Chem. Soc.* **2004**, *126*, 5376–5377.
- (33) Yu, Y.; Gu, L.; Zhu, C.; Aken, P. A. V.; Maier, J. Tin nanoparticles encapsulated in porous multichannel carbon microtubes: Preparation by single-nozzle electrospinning and application as anode material for high-performance Li-based batteries. *J. Am. Chem. Soc.* **2009**, *131*, 15984–15985.
- (34) Gopal, R.; Kaur, S.; Feng, C. Y.; Chan, C.; Ramakrishna, S.; Tabe, S.; Matsuura, T. Electrospun nanofibrous polysulfone membranes as pre-filters: Particulate removal. *J. Membr. Sci.* **2007**, *289*, 210–219.
- (35) Bjorge, D.; Daels, N.; Vrieze, S. D.; Dejang, P.; Camp, T. V.; Audenaert, W.; Hogie, J.; Westbroek, P.; Clerck, K. D.; Stijn, W. H.; Hulle, V. Performance assessment of electrospun nanofibers for filter applications. *Desalination* **2009**, *249*, 942–948.
- (36) McCann, J. T.; Li, D.; Xia, Y. Electrospinning of nanofibers with core-sheath, hollow, or porous structure. *J. Mater. Chem.* **2005**, *15*, 735–738.
- (37) Yu, J. H.; Fridrikh, S. V.; Rutledge, G. C. Production of submicrometer diameter fibers by two-fluid electrospinning. *Adv. Mater.* **2004**, *16*, 1562–1566.
- (38) Jiang, H.; Hu, Y.; Li, Y.; Zhao, P.; Zhu, K.; Chen, W. A facile technique to prepare biodegradable coaxial electrospun nanofibers for controlled release of bioactive agents. *J. Controlled Release* **2005**, *108*, 237–243.