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COMMUNICATIONS

Bio-mimic Multichannel Microtubes by a Facile Method

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Envied by many scientists, delicate multichannel (or multichamber) tubular structures have been adopted by a number of animals in long-term evolution. For example, feathers of many birds are of multichannel inner structure. It could reduce weight by increasing friction with air and serve as heat-shields from intense solar radiation.[1] To survive in an extremely formidable polar environment, pelts of some polar homeothermic species (e.g., polar bear) show excellent thermoinsulation properties which also benefit from their hair with multichamber structures.[2] These attractive features of nature are all results from the unique multichannel tubular inner structures.

Partially similar with nature, traditional nanotubes with a single inner channel have attracted considerable interest for their broad applications.[3] Accordingly, various strategies have been proposed for building these materials.[4] Recently, another promising coaxial electrospinning method has been developed for preparing ultralong nanotubes.[5−8] Electrospinning is a versatile top-down method for manufacturing 1-D nanomaterials[9] with various applications.[10,11] Coaxial electrospinning is an evolution of electrospinning, which is based on a spinneret consisting of two coaxial capillaries with different diameters. By co-electrospinning two fluids with such special spinneret, nanotubes or core−shell nanofibers can be prepared.[5−8] Although methods for production of single channel nanotubes have been well established, artificial mimic multichannel tubular structures of nature in micro- to nanometer scale are still a giant challenge. To meet the emerging needs of multifunctional, integrative, and miniature devices, micro/nanomaterials with more complex inner structures are urgently expected.

In this communication, we describe a multifluidic compound-jet electrospinning technique for the first time that could fabricate bio-mimic hierarchical multichannel microtubes in a facile and straightforward way. The experimental setup of the multifluidic compound-jet electrospinning is sketched in Figure 1a, where the three-channel tube (TCT) fabrication system is demonstrated as an example. Three metallic capillaries embedded in a plastic syringe were arranged at three vertexes of an equilateral triangle. These conductive metallic inner capillaries serve as inner fluid vessels and electrode at the same time. Two immiscible viscous liquids were fed separately to the three inner capillaries and an outer syringe in an appropriate flow rate. An ethanol solution of Ti(O*i*Pr)$_4$ and poly(vinyl pyrrolidone)[6] served as outer liquid, while a commercially available innocuous paraffin oil was chosen for inner liquid. After a compound fluidic electrospinning process, a fibrous film was collected on the counter electrode. By removing the organics of as-prepared products through calcination, TiO$_2$ TCT was obtained.

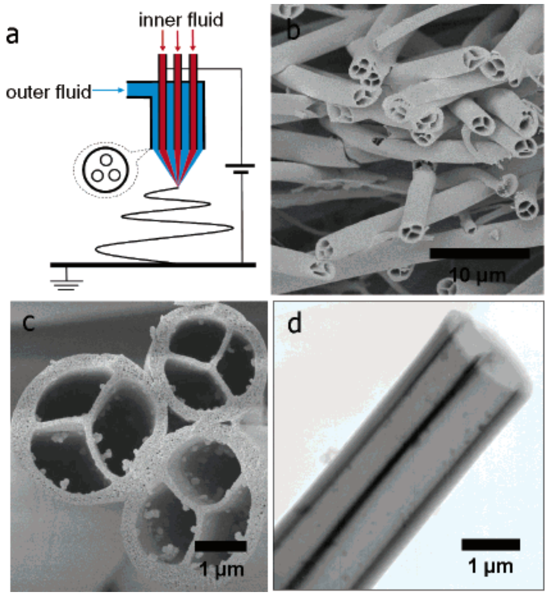

Figure 1. (a) Schematic illustration of the three-channel tube fabrication system. The immiscible inner and outer fluids (red for paraffin oil and blue for Ti(O*i*Pr)$_4$ solution) were issued out separately from individual capillaries. When an appropriate high electric potential was applied, a liquid thread jetted out from the vertex of the compound drop and then formed a fibrous film on the counter electrode. The inset shows the outlet section of the spinneret. (b) Side-view SEM image of sample after the organics have been removed. (c) Magnified SEM image of tubes in which the channels were divided into three independent flabellate parts by a Y-shape inner ridge. (d) TEM image of a three-channel tube; the individual channels of tube are straight and continuous.

Figure 1b is a side-view image of the sample taken by field emission scanning electron microscopy (SEM), which exposes the cross section of the TCT. It can be clearly seen that most of tubes are of hollow structures with three cavums. The diameter distribution of the tubes is relatively uniform with an average value of 2.3 μm. More details of inner structures of TCT are revealed in Figure 1c. A three-pointed star shape trifurcate ridge embeds in the tube shell and partitions the tube into three flabellate parts. The inner channels of the tube correspond to the vacancy of the inner fluids after they were removed. Figure 1d shows the transmission electron microscopy (TEM) image of TCT. It is obvious that the middle wall of the Y-shape ridge in the vertical direction is straight and divides the tube into “two” parallel equal parts without discontinuity (the tube should be divided into three parts actually, but only one ridge can be clearly shown in the TEM image, and the other two ridges are difficult to be seen because of the trifurcate geometry).

The rational design of spinneret is utmost important to the successful fabrication of TCT. To ensure outer fluid could surround three inner fluids effectively, each inner capillary is isolated from the other two capillaries and the outer nozzle. The gaps between each capillary and the capillary to the inner wall of the outer nozzle are equal. Such spinneret makes inner liquids flow out independently and do not mix with each other. In the multifluidic compound-jet electrospinning process, the outer Ti(O*i*Pr)$_4$ solution

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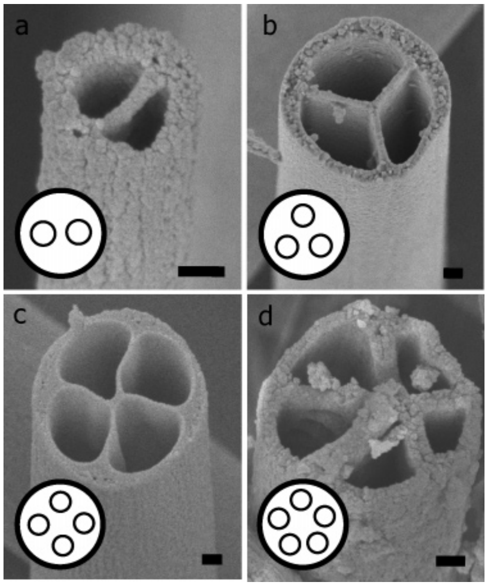

Figure 2. SEM images of multichannel tubes with variable diameter and channel number. (a−d) Corresponding to tube with channel number from two to five. The inset in each figure shows the cross section illustration of spinneret that was used to fabricate the tube. The as-prepared tubes accord very well with the corresponding spinneret. Scale bars are 100 nm.

and inner paraffin oil were co-issued from respective nozzles, and the outer liquid flowed through the gaps between three capillaries and formed a liquid jacket envelope for the three inner fluids. When the high voltage was applied, the conductive outer solution (75.0 μS·cm^{-1}) was charged and the compound liquid was stretched and whipped to a thin liquid thread in order to release the static electric repulse by dispersing electric charge.[9] However, this repulsive force could not act on the three inner fluids directly because of the insulation of paraffin oil (0.05 μS·cm^{-1}). This means that the paraffin oil cannot be electrospun on its own. As a result, the inner fluids were subjected to the pressure transferred from the outer fluid and were compressed to a thin liquid thread accompanied with an outer liquid. At the same time, with the evaporation of solvent and gelation of $Ti(OiPr)_4$, the outer liquid shell solidified very quickly and suppressed the Reyleigh instability of the whipping jet.[9] Consequently, solid tubes with three independent channels formed in which paraffin oil was enveloped.

There were two great progresses in the evolution of electrospinning: coaxial electrospinning[5−8] and dual nozzle side-by-side electrospinning.[12] A number of biphase core−shell or anisotropic Janus materials were obtained by these two methods. However, both of them were limited to two fluid systems and cannot be applied for producing multicomponent materials. The multifluidic compound-jet electrospinning technique breaks through the limit that could generate programmable multichannel or multicomponent 1-D micro/nanomaterials in a simple and promising way. As a matter of fact, tubes with two to five channels have been successfully fabricated. Figure 2a−d exhibits the cross section of these tubes. The insets describe the corresponding schematic diagram of spinneret. All of the multichannel tubes show good fidelity to the respective spinneret. It validates the effectiveness of this multifluidic compound-jet electrospinning technique. We do believe that tubes with six or even more inner channels could be fabricated by adjusting the parameters of the experiments. Besides channel number, the tube diameter, surface roughness, wall thickness, and inner ridge morphology are also easily controllable. For instance, the diameter of TCT could vary from several micron (Figure 1c) to micron (Figure 2b) to hundreds of nanometers by adjusting the experimental conditions (see Supporting Information).

In summary, we developed a very simple and powerful multifluidic compound-jet electrospinning technique for fabricating biomimic multichannel microtubes that have been seldom obtained by other means. Compared with single channel, multichannel structures may possess considerable advantages such as independent addressable channels, better mechanic stability, and larger surface-to-volume area. Furthermore, by replacing inner fluids with other functional materials, multicore−shell nanofibers would be created and different components could be integrated in the nanodomain without interaction. Such compound nanofibers should be of novel and improved properties that do not exist in each component. It is a promising candidate for a wide range of applications, such as for bio-mimic super-lightweight thermoinsulated textiles, vessels for macro/nanofluidic devices, multicomponent drug delivery, and high efficient catalysts.

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Supporting Information Available: Detailed experimental procedures, characteristics of materials, and control of multichannel tube structures. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Dyck, J. *Zool. Scr.* **1985**, *14*, 137−154.
(2) Grojean, R. E.; Sousa, J. A.; Henry, M. C. *Appl. Opt.* **1980**, *19*, 339−346.
(3) (a) Hu, J. T.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435−445. (b) Law, M.; Goldberger, J.; Yang, P. D. *Annu. Rev. Mater. Sci.* **2004**, *34*, 83−122.
(4) (a) Steinhart, M.; Wendorff, J. H.; Greiner, A.; Wehrspohn, R. B.; Nielsch, K.; Schilling, J.; Choi, J.; Gösele, U. *Science* **2002**, *296*, 1997−1997. (b) Schmidt, O. G.; Eberl, K. *Nature* **2001**, *410*, 168−168.
(5) (a) Loscertales, I. G.; Barrero, A.; Guerrero, I.; Cortijo, R.; Marquez, M.; Gañán-Calvo, A. M. *Science* **2002**, *295*, 1695−1698. (b) Larsen, G.; Velarde-Ortiz, R.; Minchow, K.; Barrero, A.; Loscertales, I. G. *J. Am. Chem. Soc.* **2003**, *125*, 1154−1155. (c) Loscertales, I. G.; Barrero, A.; Márquez, M.; Spretz, R.; Velarde-Ortiz, R.; Larsen, G. *J. Am. Chem. Soc.* **2004**, *126*, 5376−5377.
(6) (a) Li, D.; Xia, Y. N. *Nano Lett.* **2004**, *4*, 933−938. (b) Li, D.; McCann, J. T.; Xia, Y. N. *Small* **2005**, *1*, 83−86. (c) McCann, J. T.; Li, D.; Xia, Y. N. *J. Mater. Chem.* **2005**, *15*, 735−738.
(7) Sun, Z. C.; Zussman, E.; Yarin, A. L.; Wendorff, J. H.; Greiner, A. *Adv. Mater.* **2003**, *15*, 1929−1932.
(8) (a) Yu, J. H.; Fridrikh, S. V.; Rutledge, G. C. *Adv. Mater.* **2004**, *16*, 1562−1566. (b) Wang, M.; Yu, J. H.; Kaplan, D. L.; Rutledge, G. C. *Macromolecules* **2006**, *39*, 1102−1107.
(9) (a) Reneker, D. H.; Chun, I. *Nanotechnology* **1996**, *7*, 216−223. (b) Reneker, D. H.; Yarin, A. L.; Fong, H.; Koombhongse, S. *J. Appl. Phys.* **2000**, *87*, 4531−4547. (c) Li, D.; Xia, Y. N. *Adv. Mater.* **2004**, *16*, 1151−1170. (d) Huang, Z. M.; Zhang, Y. Z.; Kotaki, M.; Ramakrishna, S. *Compos. Sci. Technol.* **2003**, *63*, 2223−2253.
(10) (a) Patel, A. C.; Li, S. X.; Yuan, J. M.; Wei, Y. *Nano Lett.* **2006**, *6*, 1042−1046. (b) Matthews, J. A.; Wnek, G. E.; Simpson, D. G.; Bowlin, G. L. *Biomacromolecules* **2002**, *3*, 232−238. (c) Caruso, R. A.; Schattka, J. H.; Greiner, A. *Adv. Mater.* **2000**, *13*, 1577−1579.
(11) (a) Jiang, L.; Zhao, Y.; Zhai, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 4338−4341. (b) Zhu, Y.; Zhang, J. C.; Zheng, Y. M.; Huang, Z. B.; Feng, L.; Jiang, L. *Adv. Funct. Mater.* **2006**, *16*, 568−574. (c) Zhu, Y.; Zhang, J. C.; Zhai, J.; Zheng, Y. M.; Feng, L.; Jiang, L. *Chem. Phys. Chem.* **2006**, *7*, 336−341. (d) Zhao, Y.; Zhai, J.; Tan, S. X.; Wang, L. F.; Jiang, L.; Zhu, D. B. *Nanotechnology* **2006**, *17*, 2090−2097.
(12) (a) Madhugiri, S.; Dalton, A.; Gutierrez, J.; Ferraris, J. P.; Balkus, K. J., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 14531−14538. (b) Roh, K. H.; Martin, D. C.; Lahann, J. *Nat. Mater.* **2005**, *4*, 759−763.

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