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Communications

Fabrication of Zeolite Hollow Fibers by Coaxial Electrospinning

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Microporous materials such as zeolites are widely used in the fields of catalysis, separations, and advanced materials.[1–6] Because of the slow diffusion rate of guest molecules in the micropore of zeolites, hierarchical structures with micro-, meso-, and macropores are attracting increasing attention, and they are expected to open new application opportunities.[7–10] The general strategy for the preparation of such materials has thus far been the desilication/dealuminate of zeolites,[11,12] the modification of mesoporous molecular sieves by zeolite nanoclusters,[13] and self-assembly of zeolite nanoparticles by using macroscopic templates, such as carbon black,[14] latex sphere,[15,16] carbon fibers,[17] polyurethane foams,[18] diatoms,[19] etc. The fabrication of uniform zeolite hollow fibers with hierarchical structures, however, remains a challenge. Zeolite fibers have been finding new applications in areas such as optics, chemical sensing, and biology.[20,21]

In recent decade, a relatively simple and versatile electrospinning method is developed for generating ultrafine fibers of a variety of materials,[22–24] such as polymers,[25] inorganic materials,[26,27] hybrid materials,[28–30] and organic

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compounds.[31] This technique involves the use of a high voltage electric field to induce the ejection of a liquid jet of charged, high viscosity solution through a spinneret. Zribi et al. applied such a technique for the synthesis of micro- and mesoporous nanostructured zeolites;[27] Balkus Jr. et al. prepared molecular sieve SBA-15 and electroluminescent polymer MEH-PPV composite fibers;[29] Botta et al. fabricated poly(ethylene oxide) (PEO) nanofibers embedding dye-loaded zeolite LTL.[30] Loscertales et al. developed a new method of coaxial electrospraying that could produce microcapsules from coaxial cone jet.[32] A similar setup was also adopted by electrospinning, thereby generated a new coaxial electrospinning technique.[33–37] Coaxial electrospinning has proven to be a highly successful technique for the fabrication of microfibers, and it offers unprecedented flexibility and control for tailoring the architecture of microfibers so generated. This method, however, has not been reported to be capable of making zeolite hollow fibers to the best of our knowledge. Such materials with hierarchical pore structures are extremely desirable as catalysts for the refining industry of petroleum.

In this communication, we report the fabrication of uniform hollow fibers with a wall made of zeolite (silicalite-1) nanoparticles by employing the coaxial electrospinning technique. The experimental setup of coelectrospinning is sketched in the Supporting Information, Figure S1, which is similar to that described in the literature.[34] The conductive metallic inner capillary served as the inner fluid vessel and the anode. Two immiscible viscous liquids were fed separately to the inner capillary and the outer syringe with appropriate flow rate.

Here a suspension of silicalite-1 nanoparticles in poly(vinyl pyrrolidone) (PVP)/ethanol solution served as the outer fluid, whereas paraffin oil, which is immiscible with the PVP solution, acted as the inner liquid. Silicalite-1 nanocrystals were prepared by using tetrapropylammonium hydroxide (TPAOH) as the template according to the literature.[38] The product was repeatedly washed and separated by centrifugation. The average particle size was ca. 110 nm based on scanning electron microscopy (SEM) observations.

The content of silicalite-1 and concentration of PVP in the ethanol solution are critical factors for the successful preparation of the hollow fibers. Because silicalite-1 suspension could not be electrospun by itself, a viscous spinnable polymer additive was necessary. A viscous PVP solution was chosen as spinning liquid to make the blend solution feasible for the fluent electrospinning, it also served as an adhesive to bond the silicalite-1 nanoparticles together. However, it should be noted that an excess amount of PVP led to the collapse of the fibers after calcinations because of low solid content. Therefore, an appropriate proportion of PVP and silicalite-1 is necessary. In our experiments, the optimum content of silicalite-1 was 8 wt % and the concentration of PVP was 10 wt %.

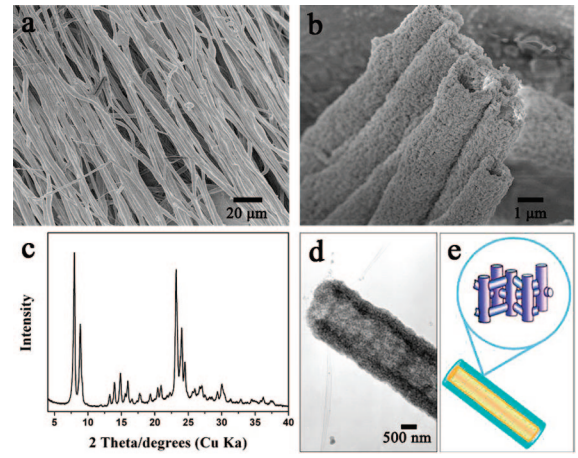

Figure 1. (a) SEM image of the as-spun fibers composed of silicalite-1 and PVP by coelectrospinning. (b) Magnified SEM image of the fibers after removal of the organics by calcinations, showing the circular cross-sections of the hollow fibers. (c) XRD pattern of the fibers corresponding to (b), characteristic of highly crystalline silicalite-1. (d) TEM image of one fiber of (b), revealing the hollow structure of the fibers. (e) Schematic illustration of the hollow fiber made of silicalite-1 with intersecting channels.

After the coaxial electrospinning process, a fibrous film was obtained on the counter electrode. The film was made of ultralong fibers of zeolite/organic composite. These composite fibers were converted to zeolite hollow fibers after removal of the organic materials (paraffin oil, TPAOH, and PVP) by calcinations in air at 550 °C for 6 h.

Figure 1a shows the SEM image of as-spun sample, which exhibits the uniform ultralong fibrous structures of the products. Figure 1b exposes the cross section of the fibers after the organic materials have been removed by calcination, and the fibrous morphology was clearly revealed. The wall of the hollow fiber is composed of nanoparticles of zeolite. Moreover, the film made up of zeolite hollow fibers had good mechanical strength so that it could be self-supporting easily (see the Supporting Information, Figure S2). X-ray powder diffraction (XRD) analysis (Figure 1c) confirmed that the zeolite phase in the hollow fibers was crystalline silicalite-1. The tubular structure is further confirmed by transmission electron microscopy (TEM), as given in Figure 1d. It clearly exhibits the continuous channel and the rough wall constructed by nanoparticles. Figure 1e schematically displays the intersecting channel structure in silicalite-1.

N_2 adsorption measurements of the zeolite hollow fibers calcinated at 550 °C for 6 h in the air (Figure 2) give a Brunauer−Emmett−Teller (BET) surface area of 468 $m^2\ g^{-1}$ and show a characteristic hysteresis loop at higher relative pressure, indicative of the presence of mesopores, likely due to the intraparticle voids of zeolite nanoparticles. The

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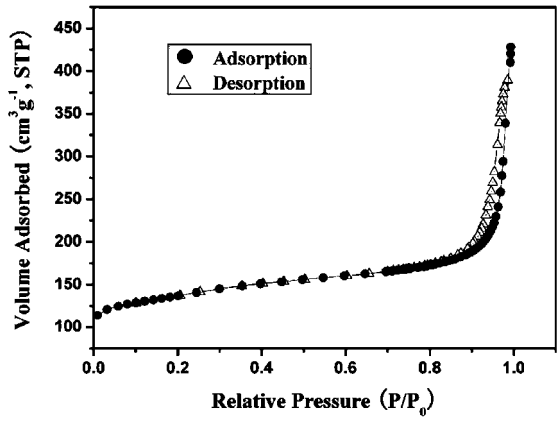

Figure 2. Nitrogen adsorption−desorption isotherms of the zeolite hollow fibers after calcination at 550 °C.

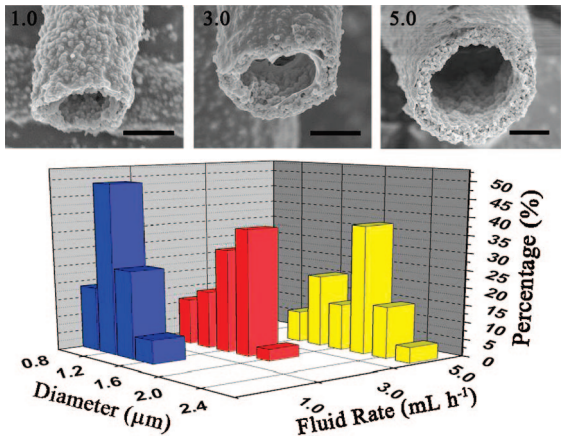

Figure 3. Three-dimensional plot showing the diametric distribution of the hollow fibers with inner fluid rates of 1.0, 3.0, and 5.0 mL h^{-1}, respectively. SEM images above the chart represent the cross-section of the fibers with corresponding fluid rate. The scale bar is 1 μm. All the samples were calcined at 550 °C with the removal of occluded organic materials.

maximum pore size distribution of the mesopore is around 41 nm. The distribution of the mesopore is affected by the calcination temperature. When the temperature of calcination is increased to 800 °C, the maximum pore size distribution of the mesopore is around 10 nm.

Compared to the conventional methods for the preparation of zeolite fibers, the coelectrospinning method of this work offers much more ease with which the morphology of the fibers is controlled. Zussman et al. discussed in detail the factors affecting the coelectrospinning process.[39] Herein, the channel diameter of the fibers can be controlled by simply changing the feed rate of inner liquid. When the inner liquid flow rate is 0 mL h^{-1}, ultralong uniform solid zeolite fibers are formed. Figure S3 in the Supporting Information shows the as-spun solid fibers and fibers after the removal of the organics. Figure 3 reveals the inner-diameter distribution of these fibers prepared with inner liquid flow rate of 1.0, 3.0, and 5.0 mL h^{-1}. When the inner flow rate is 1.0 mL h^{-1}, the inner-diameter distribution centered around 0.9−1.1 μm, and the average diameter of total fibers is 1.06 μm. By increasing the flow rate from 3.0 to 5.0 mL h^{-1}, the average inner-diameter of the fibers increased from 1.42 to 1.90 μm. Flow rate of the inner liquid above 7.0 mL h^{-1}, however, did not favor the formation of the uniform hollow zeolite fibers, presumably because there was insufficient amount of the outer solution to enclose the inner fluid continuously (see the Supporting Information, Figure S4).

In conclusion, zeolite hollow fibers with hierarchical structure have been fabricated by coaxial electrospinning. The fiberous structure can be straightforwardly manipulated and the continuous method is amenable to relatively large scale fabrication. The method should also be applicable to zeolites of other structure types. These materials may find application in many practical processes, such as catalysis, optics, chemical sensing, and biology, and will be particularly useful in the refining industry of petroleum.

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Supporting Information Available: Detailed experimental procedures and characteristics of materials (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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