

Preparation of helical mesoporous ethylene–silica nanofibers with lamellar mesopores on the surfaces

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Helical ethylene–silica nanofibers with chiral pore channels inside and lamellar pores on the surfaces were prepared using cetyltrimethylammonium bromide and (*S*)- β -citronellol as a co-structure-directing agent under basic conditions, the formation mechanism of which was studied by taking field-emission scanning electron microscopy images after different reaction times.

A large number of periodic mesoporous organosilicas (PMOs) have been reported, shortly after the development of mesoporous silicas.^{1–4} Compared with the mesoporous organosilicas obtained by post-synthesis grafting method, PMOs have homogeneously distributed organic bridging groups, high surface area and narrow pore size distribution. Such organic groups play important roles in the crystallinity, mechanical and hydrothermal properties of these materials. The control of the morphologies, pore architectures and wall structures of PMOs is a crucial issue for the future applications. Up to now, a variety of structures, such as spheres,⁵ rods,⁶ hollow shells⁷ and decaoctahedra,⁸ have been prepared.

Helical silica and organic–inorganic hybrid silica nanofibers attracted many research groups because of their potential application for chiral catalysis and separations.^{9–20} Although many approaches for the preparation of helical mesoporous silica nanofibers have been developed, those for the preparation of helical organic–inorganic mesoporous hybrid silica nanofibers are rare.^{19,20} They can be prepared using chiral low-molecular-weight amphiphiles¹⁹ or mixtures of a cationic surfactant and a fluorinated one.²⁰ For the latter case, the reduction of surface free energy was proposed as the driving force of helix formation.¹⁰ Herein, instead of the fluorinated surfactants, a chiral alcohol, (*S*)- β -citronellol, was used as the co-structure-directing agent to prepare helical mesoporous ethylene–silica nanofibers. Ethylene–silica nanofibers with chiral tubular pore channels inside and lamellar mesopores on the surface were obtained. In order to elucidate the mechanism of the formation of the lamellar mesopores, field-emission scanning electron microscopy (FESEM) images were taken after different reaction times.† A phase transition mechanism from hexagonal to lamellar phase is proposed.

A typical synthetic procedure for the helical mesoporous ethylene–silica nanofibers is as follows: 50 mg of CTAB (0.14 mmol) was dissolved in 30.0 mL of deionized water. Then, 0.075 mL of (*S*)- β -citronellol (0.42 mmol) and 0.16 mL of aqueous NaOH (2.0 M) solution were added at a stirring

rate of 1000 rpm. 30 min later, 0.240 mL (0.65 mmol) of bis(triethoxysilyl)ethane (BTEE) was added under stirring at 80 °C. The molar ratio of CTAB/(*S*)- β -citronellol/BTEE/NaOH/H₂O was 1.0/3.0/4.64/2.31/11969. The reaction mixture was then kept at 80 °C for 2.0 h. The resultant white precipitate was filtered off and dried to yield the as-prepared mesoporous ethylene–silica. CTAB was removed by extracting with a mixture of 80 mL of methanol and 10 mL of 36 wt% aqueous HCl solution for 24 h.

Before taking the FESEM images, the sample surface was coated by platinum. Both left- and right-handed helical nanofibers were identified in Fig. 1(a). Although it was reported that the chirality of conjugated polymers can be controlled by adding chiral dopants,²¹ there is no obvious difference between the number of right- and left-handed helical nanofibers. For helical mesoporous silicas and PMOs prepared from achiral surfactants, many groups have tried to reveal the formation mechanism.^{10–14,20} Based on the research of Yu *et al.*, the reduction of surface free energy was proposed to be the driving force for helix formation.¹⁰ Our nanofibers are 0.2–2.0 μm in length and 100–200 nm in diameter with helical pitches about 1.0 μm . The transmission electron microscopy (TEM) image shown in Fig. 1(c) shows several sets of fringes within a single nanofiber, which further indicates the pore channels are chiral and the helical pitches are about 1.0 μm .¹⁶ The TEM image of ends of the nanofibers indicated that the pore channels are arranged in a hexagonal symmetry. Lamellar mesopores were also identified in Fig. 1(a), (c) and (d). Calculated from FESEM images, less than 5% of the nanofibers are straight and seem to be constructed by nanoplates (Fig. 1(b)). Hexagonal and parallel-arranged pore channels wound circularly around and nearly perpendicular to the long axis of the nanorod (Fig. 1(e) and (f)). The mesoporosity of the sample was characterized by using a nitrogen sorption analysis (Fig. 2(a) and (b)). The sample shows type-IV isotherms with capillary-condensation steps occurring at relative pressure (P/P_0) of 0.35–0.5 and 0.9–1.0. It exhibited a nitrogen Brunauer–Emmett–Teller (BET) surface area of 586 $\text{m}^2 \text{g}^{-1}$ and a pore volume of 0.56 $\text{cm}^3 \text{g}^{-1}$. The Barrett–Joyner–Halenda (BJH) pore size distribution plot shows a peak at 2.8 nm. The pore-size distribution curve is narrow and the full-width at half-maximum (FWHM) is 0.34 nm. The small-angle X-ray diffraction (SAXRD) pattern shows three well-resolved diffraction peaks at 2θ of 2.01, 3.45 and 3.95° (Fig. 2(b)), indicating a two-dimensional hexagonal symmetry. The *d*-spacing calculated from the first diffraction peak is 4.4 nm.

It was reported that the addition of organic dopants would decrease the critical micelle concentration of CTAB and enhance the formation of rod- or worm-like micelles. With

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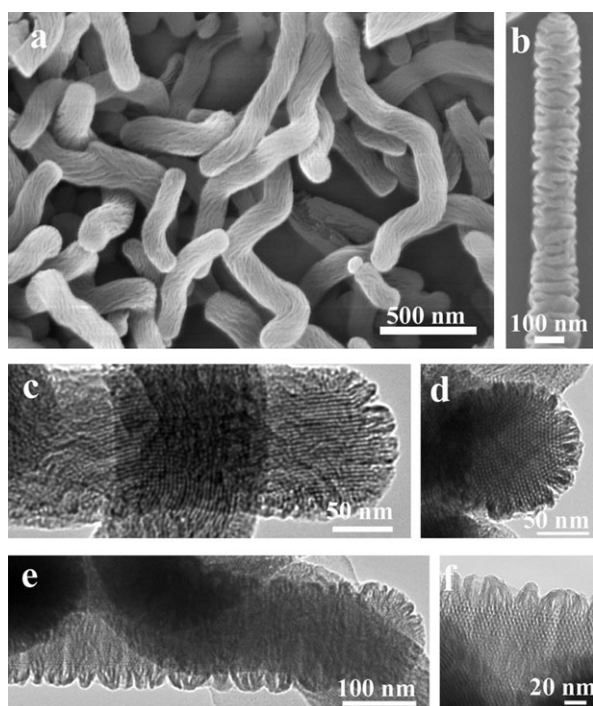


Fig. 1 FESEM (a and b) and TEM (c, d, e and f) images of the ethylene-silica nanofibers with chiral and concentric circular pore channels.

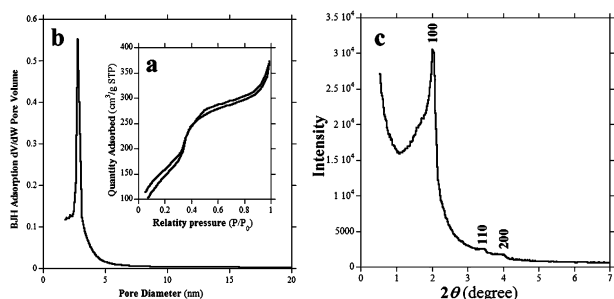


Fig. 2 N_2 adsorption-desorption measurements of the mesoporous silica nanofibers. Sorption isotherms (a) and BJH pore size distribution plot (b) from the adsorption branch; SAXRD pattern (c) of the mesoporous silica nanofibers.

the increase of the molarity of organic dopants, lamellar structures are formed.¹⁵ Herein, (*S*)- β -citronellol was used to change the morphologies of CTAB micelles in the reaction mixture. The morphologies of the obtained ethylene-silica structures are sensitive to the molar ratios of CTAB to (*S*)- β -citronellol. Mesoporous hexagonal particles, helical mesoporous nanofibers and shrunk vesicles were obtained at molar ratios of 1:2, 1:2.5 and 1:4, respectively (Fig. 3). The helical nanofibers at 1:2.5 ratio (Fig. 3(c) and (d)) are shorter than those prepared at the molar ratio of 1:3 (Fig. 1) and lamellar mesopores were also identified (Fig. 3(c)). However, no nanofibers with concentric circular mesopores were identified. It should be noted here that the helical nanofibers were only obtained within a narrow molar ratio range. Although much research has been carried out to study the morphological change by adding organic dopants in the reaction mixtures,²³ to the best of our knowledge, this is the first report on helical

PMO nanofibers with lamellar mesopores on the surfaces. Phase transformations in mesostructured silica/surfactant composites have been well illustrated.²⁴ The lamellar mesopores on the surface of nanofibers should be formed by merging the hexagonally arranged cylinder-like micelles.

For a better understanding of the formation of the lamellar pores, FESEM images of the reaction mixture were taken after different reaction times. Shrunk hollow shells, of 0.5–1.5 μm diameter, were identified after 40 s (Fig. 4(a)), which indicated that the BTEE droplets was covered by CTAB, after BTEE was dropped into the reaction mixture. After 80 s, both shrunk hollow shells and nanotubes were identified (Fig. 4(b)). Pore architecture transitions of the silica/surfactant composites from multilamellar vesicles to hexagonal phase might occur. Because both chiral and concentric circular pore architectures were found in the final products, two kinds of hexagonal phases should exist in the reaction system. After 2.0 min, helical nanofibers were identified (Fig. 4(c)) and their morphology did not change much after 5.0 min (Fig. 4(d)). The helical morphology should be driven by the reduction of surface free energy.¹⁰ The diameters of these nanofibers are about 100 nm. After 14 min, both helical nanofibers with chiral pore channels and straight nanofibers with concentric circular pore channels were identified (Fig. 4(e)). Lamellar mesopores were identified on the surface of the nanofibers, which should be formed by merging the hexagonally arranged

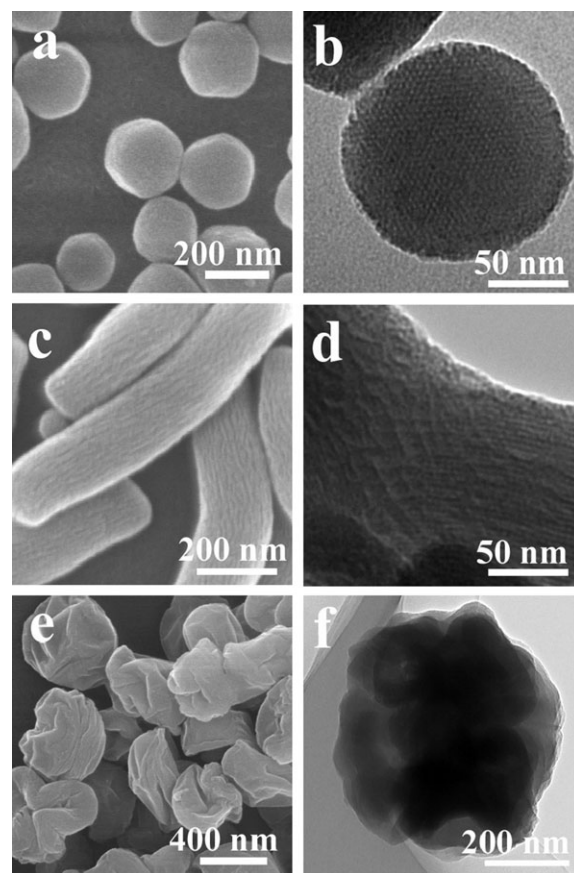


Fig. 3 FESEM (a, c and e) and TEM (b, d and f) images of ethylene-silicas prepared at different CTAB:(*S*)- β -citronellol molar ratios: (a, b) 1:2; (c, d) 1:2.5; (e, f) 1:4.

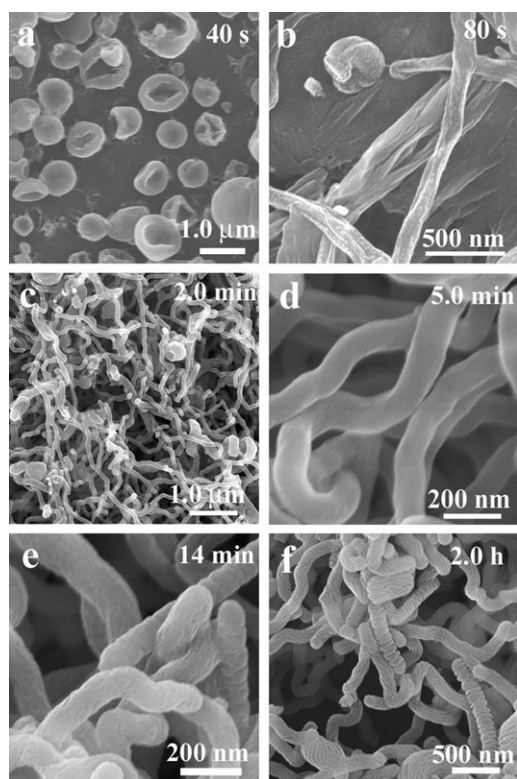


Fig. 4 FESEM images of reaction mixtures after different reaction times: (a) 40 s; (b) 80 s; (c) 2.0 min; (d) 5.0 min; (e) 14 min; (f) 2.0 h.

cylinder-like micelles. The diameters increased to about 150–200 nm, the increase of which might originate from this hexagonal to lamellar phase transition. After 2.0 h, the size of the lamellar mesopores on the surface of the nanofibers became larger (Fig. 4(f)).

In summary, ethylene-silica nanofibers with chiral or concentric circular pore channels inside and lamellar mesopores on the surfaces were prepared using CTAB and (*S*)- β -citronellol as a co-structure-directing agent under basic conditions. The formation of the lamellar pores is formed by merging the hexagonally arranged cylinder-like silica/surfactant micelles. By trapping the phase transformations, a variety of interesting morphologies and pore architectures of silica or PMOs are proposed to be obtained. Multi-functional materials are also possible to be designed and prepared.

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Notes and references

† TEM images were obtained using a TecnaiG220. FESEM images were taken on a Hitachi S-4700. Specific surface area and pore-size distribution were determined by the BET and BJH methods using the N_2 adsorption isotherm measured by a Micromeritics ASAP 2020M + C instrument. SAXRD patterns were taken on an X' Pert-Pro MPD X-ray diffractometer.

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