Synthesis of Enantiomorphic Excessive Helical Mesoporous Silicas Using Chiral Molecular Dopants

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Both left-handed and right-handed enantiomorphic excessive helical mesoporous silicas have been selectively synthesized using achiral cationic surfactant cetyltrimethylammonium bromide (CTAB) as a liquid-crystal template and chiral organic dopants as handedness-inducing agents.

Chirality is widely displayed at different scales in nature, varying from macroscopical spiral shells to biological molecules such as DNA and proteins. A molecule can also be chiral, if its image in a plane mirror cannot be brought to coincide with itself. The molecular chiral information can be transmitted to a supramolecular level and presented in another form, such as chiral helical polymer structures.[1]

Recently, the synthesis of chiral helical inorganic materials has attracted increasing attention owing to their potential applications.[2] Chiral mesoporous silica with a twisted rod-like morphology and hexagonally arrayed chiral channels has been first synthesized by using chiral anionic surfactants as templates.[3] The chirality of the surfactant molecules was initially thought to be responsible for the formation of chiral channels.[3,4] Later, the formation of racemic helical mesoporous silicas was successfully achieved by either achiral anionic[5] or cationic[6,7] surfactants. Right- and left-handed excess chiral mesoporous silica nanotubes with chiral mesoporous walls (maximum ee value of 32%) have been prepared using achiral anionic surfactants in the presence of a chiral dopant with a dopant/surfactant molar ratio as high as 0.8.[8] The synthetic conditions[9] (e.g. temperature,[10] stirring rates,[4] concentration[11]) that affected the formation of helical mesoporous silicas have also been studied in details.

Herein, we report the selective synthesis of left-handed and right-handed enantiomorphic excessive helical mesoporous silicas using an achiral cationic surfactant CTAB as a template and only a small amount of chiral organic dopants (dopant/CTAB molar ratio < 0.1) as handedness-inducing agents. Although right- and left-handed excess chiral mesoporous materials have been successfully synthesized by achiral anionic surfactants,[8] our synthesis was carried out in an achiral cationic surfactant-templating system, and only a small portion of left-handed and right-handed chiral molecules are involved.

The chiral dopants utilized in our study include *R*-(−)- and *S*-(+)-mandelic acids (Figures 1a and 1b, respectively). In a typical synthesis, 0.4 g of CTAB was dissolved in 100 mL of aqueous ammonia solution (20 wt %) at 40 °C before the addition of 0.015 g of organic dopant (dopant/CTAB molar ratio = 0.090). To this solution was added 2 mL of tetraethylorthosilicate (TEOS). After stirring for 3 h, the resulting mixture was hydrothermally treated at 100 °C for 24 h. The precipitate was filtered, washed with water, and dried in air. The final products were obtained by calcination at 550 °C for 5 h. The samples obtained in the presence of *R*-(−)- and *S*-(+)-mandelic acids were named R15 and S15, respectively.

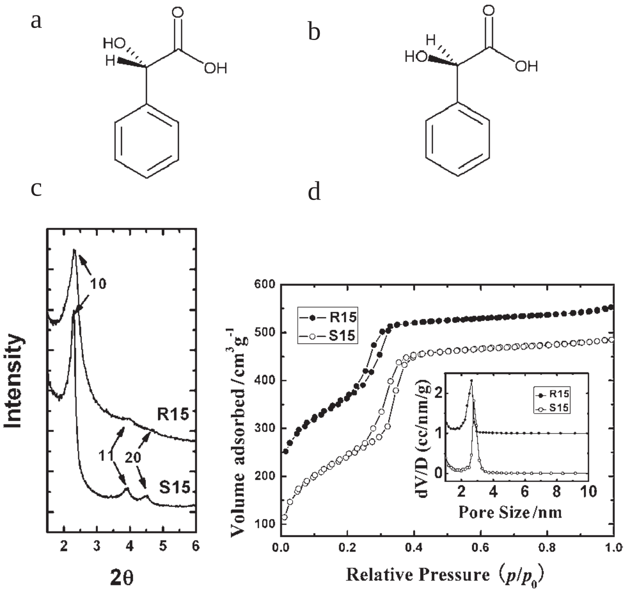

Figure 1. The molecular structures of chiral dopant (a) *R*-(−)-mandelic acid and (b) *S*-(+)-mandelic acid; (c) XRD pattern, and (d) N_2 adsorption–desorption isotherm plots and pore size distribution curves (inset) of calcined samples R15 and S15.

The small angle X-ray diffraction (XRD) patterns of calcined samples R15 and S15 are shown in Figure 1c. The observed three peaks for both samples appear at the same positions ($2\theta = 2.30, 3.96$, and $4.53°$), which can be indexed to the 10, 11, and 20 diffractions of a two-dimensional (2D) hexagonal lattice (space group: *p*6*m*) with a cell parameter (*a*) of 4.43 nm.

The nitrogen adsorption and desorption plots of both calcined samples show a type IV isotherm with hysteresis loops (Figure 1d), which is similar to that of classic MCM-41. Moreover, the pore size distribution (inset of Figure 1d) is quite narrow. The Brunauer–Emmet–Teller (BET) surface area, pore volume and Barret–Joyner–Halenda (BJH) pore size are calculated to be 940 m^2/g, 0.62 cm^3/g, and 2.64 nm for sample R15 and 895 m^2/g, 0.75 cm^3/g, and 2.78 nm for sample S15, respectively.

Under high-resolution scanning electron microscopy (HRSEM) observations, a helical rod-like morphology is observed for both R15 and S15 samples (Figures 2a and 2b, respectively). Handedness of the helical porous materials was calculated by counting characteristic morphologies of right-handed and left-handed helices from a cerntain amount of randomly chosen helical rods in the HRSEM images. For sample R15, the left-/

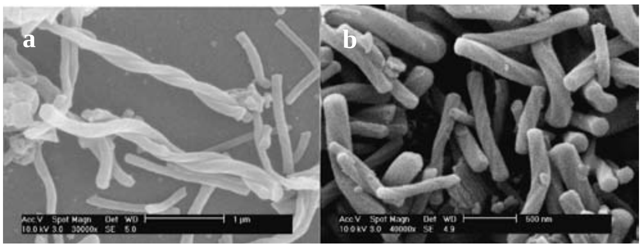

Figure 2. HRSEM images of samples (a) R15 and (b) S15.

right-handed ratio is determined to be 65/35 from 175 rods. While for S15, the left-/right-handed ratio is measured to be 32/68 from 206 rods. Thus, sample R15 and S15 are proved to have left-handed and right-handed enantiomorphic excessive helical structures with an ee value of 30% and 36%, respectively.

To confirm the existence of chiral mesostructure inside the rods, transmission electron microscopy (TEM) technique was employed. The TEM images of sample R15 and S15 are shown in Figures 3a and 3b, respectively. Some fringes corresponding to the (10) plane are observed periodically along the long axis of the rod as indicated by the black arrows. These fringes indicate the existence of chiral helical channels inside the rod, and the pitch (*P*) of the helix can be calculated as being six times the intermittence length between two neighboring (10) fringes.[12]

For a number of helical rods in left-handed and right-handed enantiomorphic excessive samples (R15 and S15, respectively), we have measured *P* as well as the diameter (*D*) of helical rods from TEM images. As shown in Figure 4, *P* shows a linear relationship as a function of $D^{1.5}$. It is noted that the $P \propto D^{1.5}$ function is a straight line passing through the origin, and the slope is similar for two functions corresponding to R15 and S15 samples.

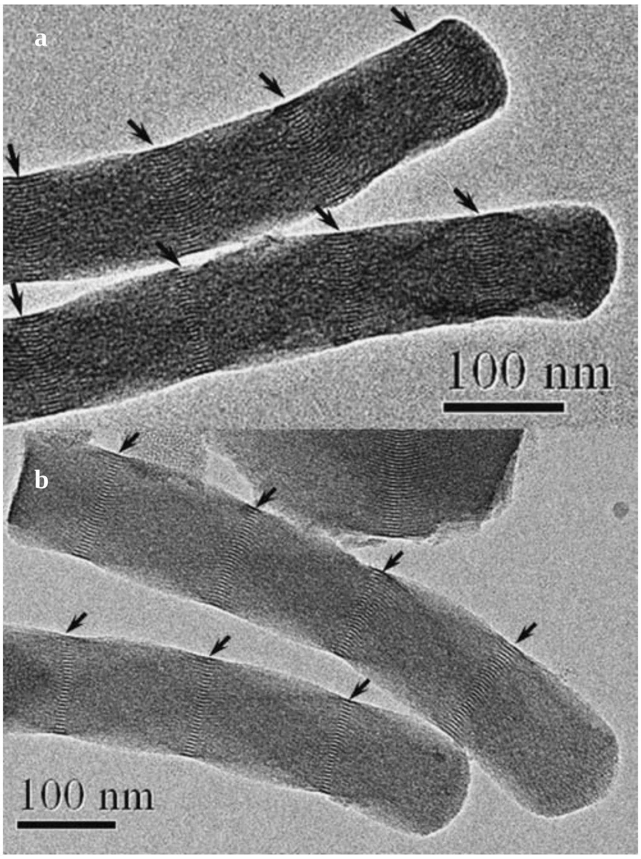

Figure 3. TEM images of calcined samples (a) R15 and (b) S15.

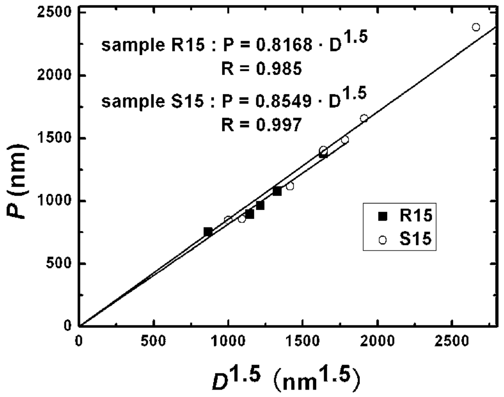

Figure 4. Linear relationship of *P* versus $D^{1.5}$. *R* is the linear regression coefficient.

As shown before, racemic helical silicas can be obtained without any chiral dopant in the presence of achiral surfactant templates.[5,7] Therefore, it is shown that the molecular chirality is responsible for the enantiomorphic excessiveness of helical mesostructures, while the spontaneous formation of the helical morphology itself can be attributed to the reduction in surface free energy.[7]

In general, left-handed and right-handed enantiomorphic excessive helical mesoporous silicas have been selectively synthesized using chiral organic dopants as handedness-inducing agents. Our results are important to further understand the formation of chiral mesoporous materials.

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