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Rapid synthesis of mesoporous silica with micrometer sized hexagonal prism structure

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Mesoporous silica MCM-41 material with hexagonal prism structure is rapidly synthesized under strongly acidic condition; accretion of surfactant micellae combined with silica oligomers according to the geometric symmetry of liquid-crystal structure leads to the morphogenesis of the hexagonal structure.

The biomimetic templating approach to the synthesis of inorganic materials has attracted considerable attention in recent years.[1–5] This process offers new opportunities for the design and fabrication of inorganic frameworks with specified and organized networks, which has potential applications as catalysts, adsorbents, biomaterials, nanoscale devices, *etc*. The understanding of the biomineralization processes can help to formulate the strategy of manipulating macroscopic materials properties through hierarchical design of the microstructure. However, the mechanisms of inorganic morphosynthesis are complex and poorly understood up to now.

The synthesis of novel silica-based mesoporous MCM-41 materials by using supramolecular assemblies of surfactant molecules to template the inorganic species was a good example as a biomimetic approach to the fabrication of inorganic–organic nanocomposites.[6,7] A great deal of earlier work has dealt with the synthetic method and mechanism of forming mesoporous silica.[6–9] However, the morphology of most MCM-41 materials reported in the literature was in the form of microparticles. Recently, more complex organization of hierarchical order of mesoporous silica has been reported by several research groups.[10–14] Yang *et al.* obtained a rich diversity of morphology of mesoporous silica with discoid, ropes, shell and other morphologies under quiescent aqueous acidic condition.[10] Lin *et al.* reported mesoporous silica with a hollow tubules-within-tubule hierarchical structure in highly alkaline conditions[11,12] while micrometer sized mesoporous silica spheres were described by Qi *et al.*[13] and Yang *et al.*[14] These rich morphologies were obtained from the complex interplay of curvature changes in the nanostructure of surfactant and silica condensation. Therefore, the morphologies of MCM-41 materials might be varied by making use of changing the reaction compositions, inorganic/organic interface and synthetic process. However, although it is well known that mesoporous silica can be templated by hexagonal accumulation of surfactant rods, the formation of MCM-41 with a regular hexagonal prism structure at the macroscopic scale has not yet been reported. Here we present an example for the rapid synthesis of micrometer scale hexagonal mesoporous silica.

To prepare MCM-41 materials, aqueous solutions of cetyltrimethylammonium bromide (C_{16}TMABr) and hydrochloric acid (HCl) were well mixed with tetraethyl orthosilicate (TEOS) under stirring, and a gel mixture was formed at room temperature. Two MCM-41 materials were synthesized: one was synthesized according to the general synthetic procedure,[8] the molar ratio of the resultant gel being $0.12C_{16}TMABr:1TEOS:14.6HCl:100H_2O$ while the other sample was obtained by using much less TEOS with a gel of molar ratio $0.12C_{16}TMABr:0.12TEOS:14.6HCl:100H_2O$. The gels was stirred for 5 min with a stirring speed of *ca.* 200 rpm and then loaded in a water bath at 75 °C for 15 min. Both precipitates were filtered off, washed with distilled water and dried at 80 °C and calcined in air at 540 °C for 6 h. The obtained materials are designated as G1(general synthetic procedure) and S1, respectively.

The X-ray powder diffraction data of sample S1 (Fig. 1) shows an intense diffraction peak between $2\theta = 2–3°$ (d_{100} spacing *ca.* 3.84 nm) and characteristic of mesoporous silica material. From the N_2 adsorption isotherm of sample S1 (Fig. 2), it can be seen that a jump of adsorbed N_2 volume occurs at P/P_0 (N_2 relative pressure) of *ca.* 0.2–0.3, which is indicative of the filling of framework confined uniform mesopores. The gradual increase of adsorption curves in the high P/P_0 region of the N_2 isotherm could be due to the interparticle porosity; some of the hexagonal prismatic mesoporous silica materials may be damaged and lead to irregular structured particles during the processes of synthesis and characterization (*e.g.* the effect of the mechanical press). The specific surface area of the material S1 was calculated based on the adsorption curve, and a high S_{BET} value of 851 $m^2\ g^{-1}$ was obtained.

Representative scanning electron micrographs (SEM) of samples G1 [Fig. 3(c)] and S1 [Fig. 3(a) and (b)] reveal that the morphologies are very different. It can be seen from Fig. 3(a) that sample S1 consists almost entirely of a wormlike microstructure. The higher magnification photograph [Fig. 3(b)] clearly indicates that each individual elongated

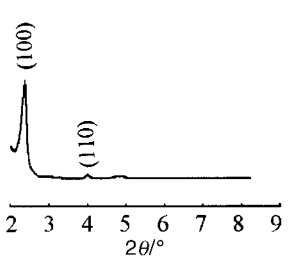

Fig. 1 X-Ray powder diffraction pattern of sample S1.

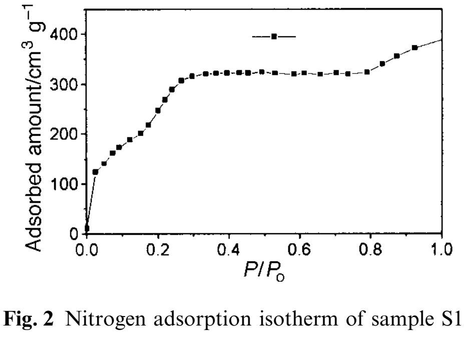

Fig. 2 Nitrogen adsorption isotherm of sample S1.

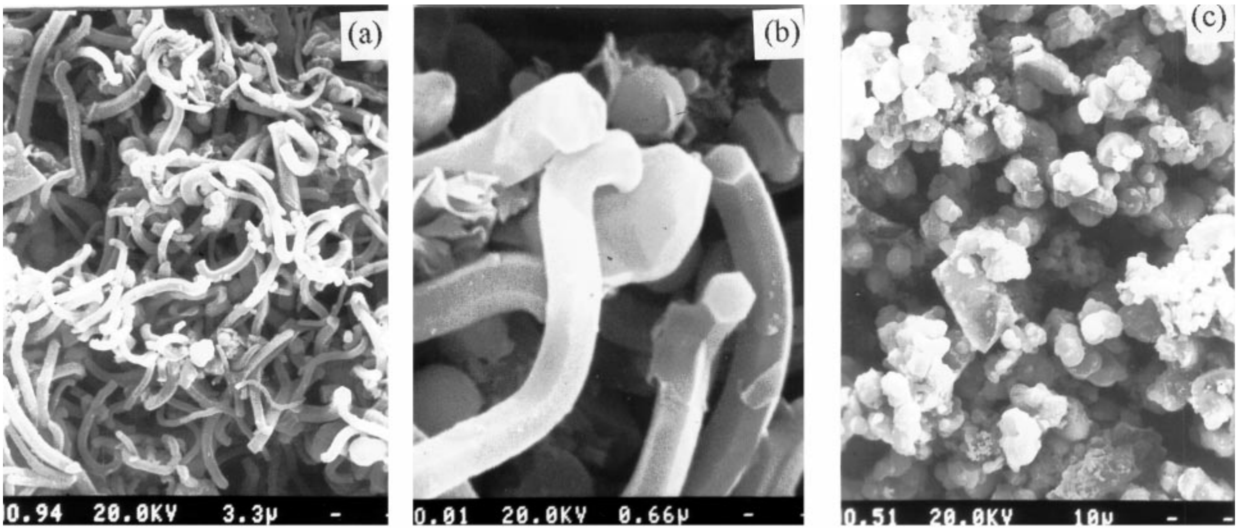

Fig. 3 Scanning electron micrographs of MCM-41 samples. (a), (b) sample S1; (c) sample G1.

particle has an obvious hexagonal prism shape while the morphology of sample G1 showed the ordinary microstructure of an assembly of microparticles. Fig. 4 shows transmission electron micrographs of sample S1. It can be seen from Fig. 4(b) [higher magnification of Fig. 4(a)] that the regular hexagonal head of the wormlike particle consists of thousands of dark dots (dark field image) in a regular array, indicating the characteristic nanostructure of mesoporous silica. Some dark parallel lines, the meso-channels, could be observed in the body region of the particle. The d_{100} spacing based on the diffraction measurement was calculated to be 3.71 nm, consistent with the results of XRD. Therefore, this MCM-41 material with micrometer-sized hexagonal prismatic structure contains a huge number of coaxial cylindrical nanometer channels. The SEM and TEM photographs show that the 'hexagonal prism' is 'solid', different from MCM-41 materials having a hollow tubules-within-tubule morphology.[12]

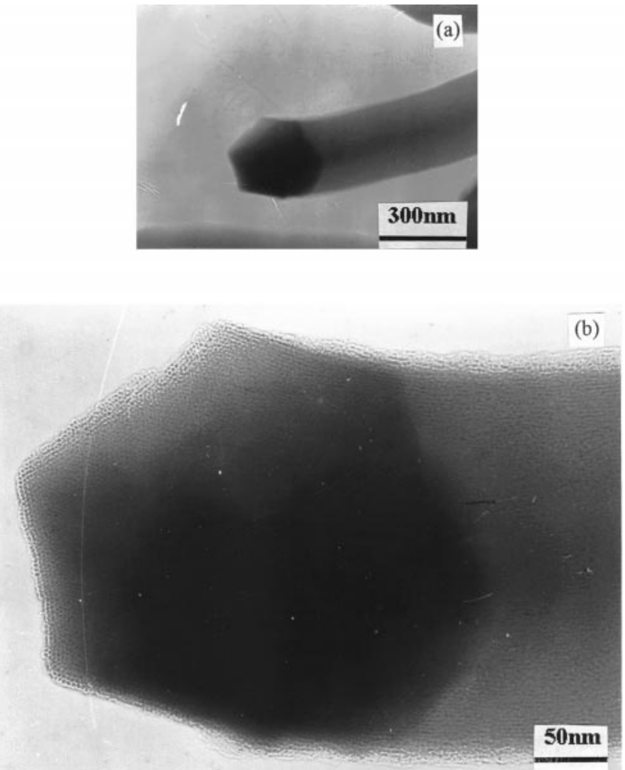

Fig. 4 Transmission electron micrographs of sample S1. (a) low magnification; (b) high magnification.

Both samples G1 and S1 were synthesized in the same strongly acidic medium (pH$<$1) in a aqueous surfactant solution (wt%$<$2), however, one significant difference was that much less TEOS was used in the synthesis of sample S1. Therefore, the different morphologies of the products formed can be attributed to the concentration and condensation of TEOS in solution. Hydrolysis and condensation of TEOS will take place rapidly when added to a strongly acidic reaction solution with the immediate formation of multiply charged silicate oligomers. According to the cooperative templating model for mesoporous silica synthesis,[8] polydentate inorganic ions in solution can play an important role in determining the morphology of the organic array through multidentate bonding and charge density matching of surfactant with inorganic ions.

In the ordinary synthesis method of mesoporous silica, the mole ratio of TEOS/surfactant is high, leading to a high concentration of inorganic silicate ions upon hydrolysis and condensation of TEOS in solution. Thus, the charge density of silicate oligomers is high and they readily associate with the surfactant molecules by cooperative interaction. Then homogeneous nucleation and rapid precipitation of the organized surfactant arrays adhered with inorganic ions can take place. Therefore, only MCM-41 material with ordinary microparticular morphology is formed. However, when much less TEOS was employed (sample S1), the concentration of silicate oligomers is considerably lower. The low charge density of inorganic ions would have a weak effect on the organic array configuration, and fewer organic arrays would be formed. Therefore, when self-assembling among the inorganic/organic nanocomposite takes place, there is enough open space for the organization of a hexagonal mesophase. The accretion of surfactant–silicate biphase arrays could continue on every basal plane according to the geometric symmetry of the liquid-crystal structure over short times without interference, thus leading to the formation of a micrometer sized regular hexagonal prism structure.

In summary, we have succeeded in preparing micrometer sized mesoporous silica materials with regular hexagonal prism structure under strongly acidic conditions. An oriented aggregation process at a low concentration of inorganic ion species has been proposed for the formation of a hexagonal prism structure. The freedom of accretion of the inorganic/organic biphase according to the symmetry of hexagonal structural plane provides another example toward the understanding of biomineralization. The material would provide a perfect host in which conductive carbon wire or polyaniline can be encapsulated in the oriented mesopore, and plays a role in the development of nanometer-sized electronic devices. One might further explore the supramolecular templating process of inorganic materials exhibiting complex forms over an array of length scales and their potential applications in nanotechnology.

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