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Cubic Hybrid Organic−Inorganic Mesoporous Crystal with a Decaoctahedral Shape

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Using the supramolecular templating method, materials with periodic mesopores have been synthesized.[1,2] They have attracted much attention, due to their useful catalytic properties and their potential as adsorbents and hosts for nanocluster synthesis. To generate novel practical applications of these mesoporous materials, especially for separations and optoelectronic devices, the macroscopic morphology of the materials must be controlled. Efforts to control morphology in a variety of mesoporous materials have been reported, such as thin films,[3] spheres,[4] micrometer-scale patterning,[5] hollow tubulars,[6] fibers,[7] and particles with complex forms.[8] However, it is not common for a periodic mesoporous material to show a crystal-like, well-defined, external morphology, in contrast to many microporous zeolites that have been synthesized with well-defined shapes reflecting the crystal symmetries.[9] A rare example of the former is silica mesoporous material with a truncated rhombic dodecahedral shape (cubic *Ia-3d* structure) synthesized by a hydrothermal procedure using alcohol as a additive.[10]

Recently, we reported the synthesis of novel organic−inorganic hybrid mesoporous materials with two- and three-dimensional hexagonal symmetries, which were designated as HMM-1 and HMM-2, from 1,2-bis(trimethoxysilyl)ethane [$(CH_3O)_3Si-CH_2-CH_2-Si(OCH_3)_3$, BTME] in the presence of alkyltrimethylammonium [$C_nH_{2n+1}N^+(CH_3)_3$, ATMA] surfactant.[11] The materials have a homogeneous distribution of ethane fragments ($-CH_2-CH_2-$) and silica moieties (Si_2O_3) fully polymerized within the framework, forming a covalently bonded network. They exhibit quite different pore-wall structure from those of the conventional organic-functionalized "heterogeneous" mesoporous materials, composed of an inorganic main framework, with an organic layer grafted to the framework at one end. HMM-1 and HMM-2 show well-defined external morphologies of hexagonal rod and spherical particle, respectively. They have an unusually well-ordered mesostructure, clearly shown by electron diffraction (ED) patterns and high-resolution transmission electron microscope (HRTEM) images. Incorporation of the organic groups within the inorganic framework produced higher structural order than the silica mesoporous materials reported elsewhere. Following our report, two other groups reported similar hybrid mesoporous materials.[12,13] However, the well-defined morphology of our hybrid materials was not found in those cases and their structural order was less well-defined than that observed in our hybrid mesoporous materials.

Here, we report the synthesis of ethane−silica hybrid mesoporous material with a crystal-like external morphology of decaoctahedron, and uniform particle sizes of 5 μm. The material is a cubic mesophase, which is consistent with the *Pm*-3*n* space group. The hybrid mesoporous material with cubic *Pm*-3*n* symmetry was designated as HMM-3. The synthesis system containing BTME and ATMA is unique to form highly ordered mesoporous materials with a variety of well-defined external morphologies.

In a typical synthesis, BTME was added to a mixture of hexadecyltrimethylammonium chloride (C_{16}TMA), sodium hydroxide (NaOH), and water (H_2O) under vigorous stirring at 25 °C. Heating this clear solution, with a molar ratio of BTME:C_{16}TMA:NaOH:H_2O = 1:0.91:2.28:336, to 95 °C after stirring at 25 °C for 19 h brought about precipitation, and the resulting suspension was maintained at 95 °C for 21 h without stirring. The precipitate was filtered quickly before cooling. The surfactant was removed by stirring 1.0 g of as-synthesized mesoporous material in 150 mL of ethanol with 2.8 g of 36% HCl aqueous solution at 50 °C for 6 h. The extraction process was then repeated. HMM-1 and HMM-2 were synthesized using a C_{18}-TMA surfactant at 95 and 25 °C, respectively.[11] Alkyl-chain length of surfactant and synthesis temperature are crucial parameters to determine the product phase in the BTME−ATMA−NaOH−H_2O system.

Scanning electron microscope (SEM) images reveal that HMM-3 is composed of uniform particles, both in size (~5 μm in diameter) and shape (Figure 1, low magnification (a) and enlarged (b)). In addition, the particles have well-defined external morphology. The shape is a decaoctahedron with 6 squares and 12 hexagons, and is described as a cube whose edges are truncated by hexagons. It is clear from the image that the crystal has four 3-fold axes and exhibits cubic symmetry. The squares and hexagons are indexed as {100} and {110} planes in the cubic structure, respectively. Some particles appear to be different in SEM images due to different projections.

Both electron diffraction (ED) patterns, where 200, 120, 112, 220, 130, 222, 230, and 123 reflections were observed, and powder X-ray diffraction (XRD) pattern suggest that HMM-3 has the cubic *Pm*-3*n* space group, similar to the silica mesoporous

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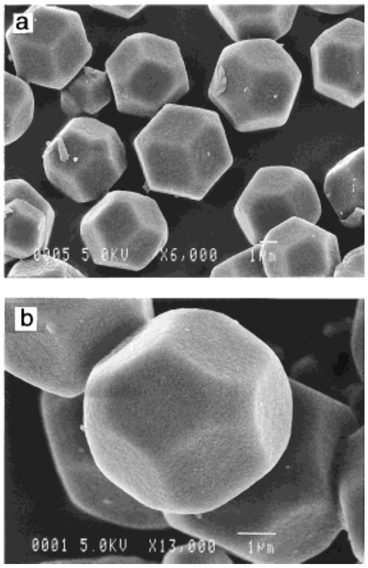

Figure 1. Scanning electron micrographs of ethane−silica hybrid mesoporous material (HMM-3). (a) Low magnification, (b) enlarged. The micrographs were obtained on a JEOL JSM-890 field emission scanning microscope with an acceleration voltage of 5 kV.

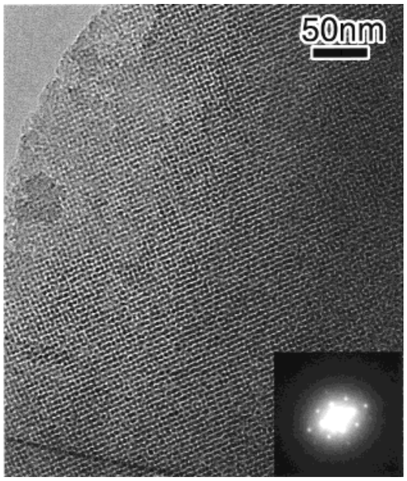

Figure 2. Transmission electron microscope image and electron diffraction pattern (inset) of ethane−silica hybrid mesoporous material (HMM-3). They were recorded on a JEM-4000EX microscope operating at an accelerating voltage of 400kV.

material, previously reported as SBA-1.[14] Unit cell constant of 111 Å is determined from the XRD pattern. The EM experiments indicate that the mesoporous particles are single crystals (Figure 2). Nitrogen adsorption isotherm shows a type-IV isotherm, with a sharp increase in adsorption at $P/P_0 = 0.32-0.37$, indicating that this material had uniform mesopores (Figure 3). The BJH (Barrett−Joyner−Halenda) pore diameter and BET (Brunanuer−Emmett−Teller) surface area were 29 Å and 770 m^2 g^{-1}, respectively.

The framework of this mesoporous material consists of an organic−inorganic covalently bonded network, confirmed by ^{29}Si and ^{13}C magic angle spinning (MAS) nuclear magnetic resonance (NMR) measurements. The ^{29}Si MAS NMR spectrum shows two signals at −57.9 and −66.6 ppm which are assigned to $\underline{Si}C(OH)(OSi)_2$ (T^2) and $\underline{Si}C(OSi)_3$ (T^3). No signals due to SiO_4 species (Q^n, $n = 1-4$) indicates that all of Si in the material are bonded covalently to carbon atoms in the framework. The ^{13}C cross-polarization (CP) MAS NMR spectrum shows a strong signal at 5.6 ppm. The signal at 5.6 ppm is due to an ethane fragment sandwiched by Si ($Si-CH_2CH_2-Si$). These NMR measurements indicate that the mesoporous material has a $SiO_{1.5}-CH_2CH_2-SiO_{1.5}$ unit in the framework. That fragment is also found in the HMM-1 and HMM-2 mesoporous materials, reported previously.[11] No carbon signal due to C_{16}TMA surfactant is observed, suggesting complete removal of surfactant from the as-synthesized mesoporous material.

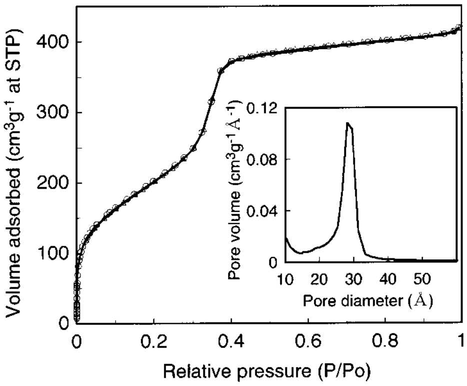

Figure 3. Nitrogen adsorption (○)-desorption (△) isotherms and pore-size distribution plots (inset) for ethane−silica hybrid mesoporous material (HMM-3). The isotherms were measured at the temperature of liquid nitrogen using a Quantachrome Autosorb-1 system. The sample was vacuum-dried in 10^{-2} Torr for 2 h at room temperature before measurement. The pore-size distribution was calculated using the Barrett−Joyner−Halendan (BJH) method from the adsorption branch.

This is the first synthesis of periodic mesoporous material possessing well-defined external morphology of the decaoctahedron commensurate with the point group *Pm*-3*n* symmetry. It is interesting that the well-defined external morphology has been formed by incorporation of organic fragments within the inorganic framework of mesoporous material. This phenomenon would be related to a biomineralization, in which organic materials play an important role for organization of inorganic material. The synthesis system of BTME−ATMA−NaOH−H_2O is unique because the system has formed a variety of highly ordered mesoporous materials with well-defined external morphologies of hexagonal rod (two-dimensional hexagonal), spherical particle (three-dimensional hexagonal), and decaoctahedron (cubic *Pm*-3*n*). The formation of periodic mesoporous material with cubic *Pm*-3*n* symmetry is the first case in a system using ATMA as a surfactant. ATMA usually forms hexagonal (2*d*, *p*6mm), cubic (*Ia*-*3d*) and lamellar mesophases in ATMA−water binary system[15] and also in inorganic−ATMA−water ternary system.[16]

The hybrid organic−inorganic mesoporous material with an ideal crystal form reflecting underlying mesostructure is unique. The formation of well-defined polyhedral particles of uniform size will allow new applications for periodic mesoporous materials. For example, the mesoporous particles can be packed into an aligned monolayer on a flat plate, with identical orientation of each particle. Such a material offers unique capabilities for optical filters and separation membranes. As this mesoporous material has a unique hybrid organic−inorganic framework, it is also expected to show unique separation and inclusion properties.

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Supporting Information Available: Figures of X-ray powder diffraction pattern and ^{29}Si and ^{13}C MAS NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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