A facile preparation of transparent and monolithic mesoporous silica materials

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Monolithic mesoporous silica samples of *ca.* 2 × 2 × 1 mm in dimension with large surface areas (> 900 m^2 g^{-1}) and pore volumes (> 0.80 cm^3 g^{-1}) have been readily prepared *via* a sol–gel process in the presence of hydroxy-carboxylic acid compounds as non-surfactant templates, and their pore structure was observed directly by means of atomic force microscopy (AFM).

The synthesis and applications of mesoporous materials prepared using surfactants as templates have attracted great attention since the discovery of the M41S family of mesoporous molecular sieves by scientists at the Mobil Corporation.[1,2] So far, most synthetic methods typically yield products in the form of fine powders resulting from uncontrolled precipitation during the sol–gel synthesis or template removal. Such powder forms hamper their use in catalysis and separation technologies. For example, for potential use in membrane separation, it is important to be able to process mesoporous structures in the form of defect-free, oriented films. Mesostructured silica films with ordered or disordered mesopore channel arrangements have been prepared using surfactants as templates under very carefully controlled conditions.[3–6] Mesoporous silica materials with diverse and remarkable morphologies[7–9] have been prepared under some extreme synthetic conditions to prevent uncontrolled precipitation of the mesostructured silicates. However, the dimensions of the products which occur as hollow spheres, tubules or other shapes is still microscopic. Emulsion biphase chemistry has been demonstrated to yield hollow or hard mesoporous macroscale spheres.[10,11] Recently, Wei *et al.*[12,13] reported a non-surfactant templating route to mesoporous silica materials *via* a sol–gel process. Because of the mild conditions, this process facilitates the preparation of mesoporous silica bulk objects. Here, we present the synthesis of mesoporous silica samples of large size (*e.g.* 2 mm) *via* a non-surfactant sol–gel route with hydroxy-carboxylic acids as templates.

The synthetic procedure was similar to that in the literature.[12] The preparation of colourless, transparent disks (*ca.* 3 cm in diameter) of the template-containing silicas was achieved by HCl-catalyzed sol–gel reactions of tetraethyl orthosilicate (TEOS) in the presence of organic hydroxy-carboxylic acid compounds, *i.e.* citric acid (CA), lactic acid (LA), malic acid (MA) and tartaric acid (TA). In general, TEOS (Acros Organics, 98%) was prehydrolyzed with deionized water in ethanol using HCl as catalyst (at TEOS : HCl : H_2O : EtOH molar ratios of 1 : 0.01 : 4 : 3) at about 70 °C for 5–6 hours. Upon cooling to room temperature, the prehydrolyzed solution (*e.g.* 10.6 ml) was added to a designed volume of aqueous solution (*e.g.* 3 ml of 0.45 g ml^{-1}) of hydroxy-carboxylic acid compound under stirring. The transparent and monolithic template-containing silica disks were obtained after the gel formed and dried within about two months at room temperature. The template-containing silica disks were then broken into smaller pieces instead of being ground into fine powders as reported in the literature.[12] The transparent and monolithic mesoporous silica samples were readily obtained by removing the templates *via* Soxhlet

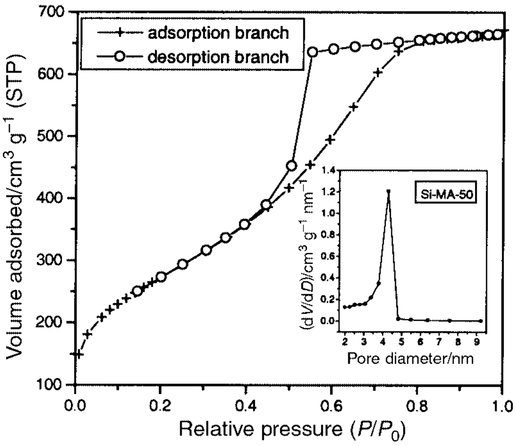

Fig. 1 Nitrogen adsorption–desorption isotherm for the sample Si-MA-50. Inset: BJH pore size distribution curve of the same sample.

Table 1 Physicochemical properties of the monolithic mesoporous silica materials

			Average pore diameter		Micropore data[b]	
Sample code[a]	BET surface area/m^2 g^{-1}	Total pore volume/cm^3 g^{-1}	BET/nm	BJH/nm	Surface area/ m^2 g^{-1}	Pore volume/ cm^3 g^{-1}
Si-CA-50	959	0.888	3.7	3.6	42	0.0079
Si-LA-50	865	0.924	4.3	3.7	10	—
Si-MA-40	1053	0.863	3.3	3.4	24	—
Si-MA-50	991	1.028	4.1	3.8	30	0.0016
Si-MA-60	1030	1.474	5.7	4.8	22	—
Si-TA-50	911	0.977	4.3	3.9	42	0.0087

[a] The two letters in the middle of the sample codes are the abbreviations for the templates: CA = citric acid, LA = lactic acid, MA = malic acid, TA = tartaric acid. The numbers in the codes indicate the template concentrations (wt.%) in the template-containing silicas, as calculated from the feed composition under the assumption that TEOS is completely transformed into SiO_2. [b] The surface area and pore volume of micropores were obtained by t-plot analysis using the Harkins–Jura equation.

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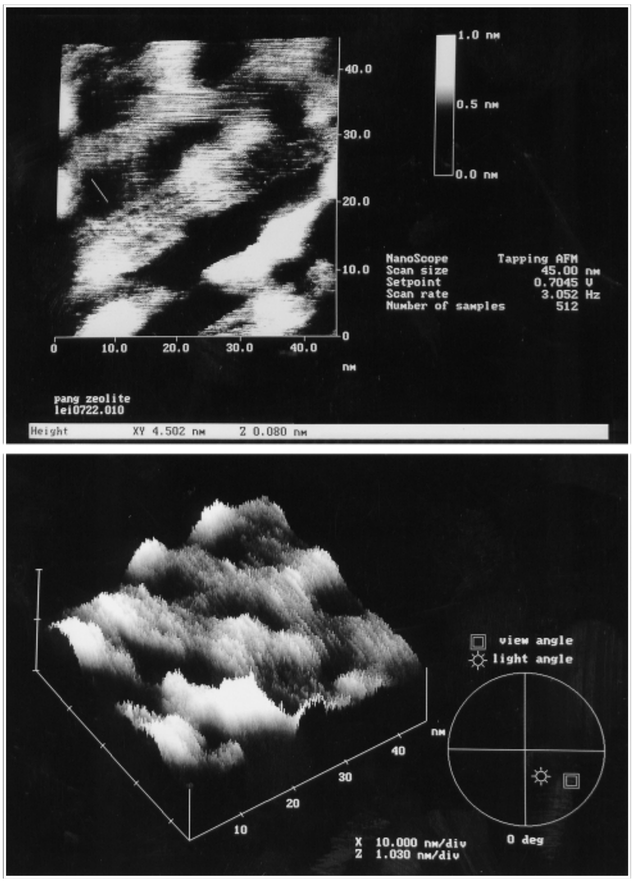

Fig. 2 AFM images of the surface of the sample Si-LA-50 (the scale bar in the top-view image is 4.50 nm).

extraction with ethanol for 3–4 days followed by drying. The samples before and after extraction were monitored by FTIR using a Bruker Vector22 FTIR spectrometer. Disappearance of the characteristic absorption band at *ca.* 1734 cm^{-1} for the carbonyl of the hydroxy-carboxylic acids indicated the completion of template removal. The Brunauer–Emmett–Teller (BET) surface area and pore parameters of the samples as small pieces after the removal of templates were determined by nitrogen adsorption–desorption isotherm measurements at 77 K on a Micromeritics ASAP2100 analyzer. Mesopore size distributions were calculated from the desorption branch of the isotherm by the Barrett–Joyner–Halenda (BJH) method using the Halsey equation. The AFM images were obtained on a Digital Instruments Nanoscope IIIa SPM by tapping mode AFM.

The BET surface area data and pore parameters of the silica samples after the removal of the templates are summarized in Table 1. Mesoporous materials with large surface areas (> 900 $m^2\ g^{-1}$) and pore volumes (> 0.80 $cm^3\ g^{-1}$) were obtained with CA, LA, MA or TA as template. As shown in the MA-templated synthesis, the pore diameter and volume tend to increase with the MA concentration. From the t-plot analysis with the Harkins–Jura equation, we conclude that the contributions from micropores to the measured surface areas and pore volumes are negligible.

The nitrogen adsorption–desorption isotherms of all the samples exhibit type IV-like isotherms with a sharp inflection at $P/P_0 \approx 0.5$ (type H2 hysteresis), as shown in Fig. 1. The pore size distributions are quite narrow in all the samples. As shown in the inset of Fig. 1, the pore size distribution has a peak pore diameter at *ca.* 4.3 nm with a peak width of *ca.* 0.6 nm at half-maximum. In contrast, the silica sample prepared in the absence of template under otherwise identical conditions shows a type I isotherm and a BET surface area of *ca.* 50 $m^2\ g^{-1}$.

Most reported mesoporous materials have been characterized with established techniques, such as transmission electron microscopy (TEM) or scanning electron microscopy (SEM).[1,2] Atomic force microscopy (AFM) enables resolution at the atomic level[14] and can be used to obtain nanoscale images of the surface of bulk materials and recently, AFM images of nanoporous ceramic films have appeared in a report.[15] The mesoporous silica samples obtained in this work are relatively easily characterized by AFM, as long as a smooth surface on freshly prepared samples could be identified. Fig. 2 shows AFM images (top-view and topographic view) of the sample Si-LA-50. From the images, we can readily identify the mesopores of *ca.* 4.5 nm diameter. Some channels are vertical to the observed surface and two are slanted to the surface, suggesting that the channel axes are largely disordered and three-dimensionally interconnected as reported in the literatures using TEM.[12] Although the images only reflect the surface pattern of the mesoporous materials, the inner mesostructures can be inferred from the large surface area, large pore volume and narrow pore size distribution as measured with the BET method.

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