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Transformation of highly ordered large pore silica mesophases (*Fm*3*m*, *Im*3*m* and *p*6*mm*) in a ternary triblock copolymer–butanol–water system†

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Exceptional control of the phase behavior of highly ordered large pore mesostructured silica (with the choice of *Fm*3*m*, *Im*3*m* or *p*6*mm* symmetry) is achieved using a triblock copolymer ($EO_{106}PO_{70}EO_{106}$) and butanol at low acid concentrations.

Poly(alkylene oxide)-type block copolymers have been shown to be particularly versatile as structure-directing agents for the preparation of ordered large pore (> 5 nm) materials.[1] In principle, the tunable volume ratio of their hydrophilic/hydrophobic blocks and their specific aggregation (self-assembly) behavior may provide supramolecular templating properties with an appreciable degree of control of the resulting porous structures. In other words, pore topology, pore size and pore connectivity may be tailored as a function of copolymer concentration, synthesis temperature, or volume fraction of the different copolymer blocks.[2,3] Structural and textural control is especially desirable for the design of functional porous solids for applications involving selectively tuned adsorption and diffusion, and host–guest interactions within elaborated nanostructured materials. However, directing precisely the formation of ordered large pore silica mesophases[4] still remains a difficult task, because of the fast kinetics of the silica condensation in the strongly acidic media employed. To overcome this, we showed recently that low concentrations of the acid catalyst permit a more thermodynamic and easier control of the synthesis of mesoporous silica,[5] as opposed to the previous conditions that usually favored the kinetically controlled assembly of the inorganic–organic mesophase. We further believe that the phase behavior of the triblock copolymers in water, in the presence of polymerizing silica species, can now be widely enriched since slower silica condensation kinetics allow the use of organic co-surfactants to modify 'thermodynamically' the mesophase behavior.[6] To demonstrate this, we describe herein a simple and systematic preparation of mesoporous silicas with tailored structural arrangement of the pores. Butanol is used as a co-surfactant[6,7] in combination with a commercially available triblock copolymer ($EO_{106}PO_{70}EO_{106}$) for the structure-direction in aqueous solution. In our system, the butanol/triblock copolymer mass ratio only is utilized to direct specifically the formation of high quality silica mesophases with cubic *Fm*3*m*, cubic *Im*3*m* or 2-D hexagonal *p*6*mm* structures, with all other synthetic parameters and molar ratios remaining constant.

Details of the synthesis procedure using butanol are briefly as follows: 5.00 g of Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, Sigma) is dissolved in 240 g of distilled water and 10.5 g of conc. hydrochloric acid (35wt%). To this mixture, different amounts of butanol (BuOH, Aldrich 99%) are added at 45 °C, with BuOH : F127 mass ratios = 0 : 1, 1 : 1, 2 : 1, 3 : 1 and 4 : 1. After one hour stirring, 24.0 g of tetraethoxysilicon (TEOS, ACROS 98%) is added. The molar composition of the resultant reaction mixture TEOS/F127/BuOH/HCl/H_2O is 1.00/0.0035/*x*/0.88/119 (*x* = 0.59–2.34). The mixture is further stirred vigorously for 24 h and subsequently heated for 24 h at 100 °C under static conditions for hydrothermal treatment. The solid product is then filtered and dried at 100 °C. The template is removed by extraction in ethanol–HCl mixture followed by calcination at 550 °C.

The lattice type and the symmetry of the mesoporous materials were accurately determined by a combination of powder X-ray diffraction (XRD) investigations (Fig. 1) and transmission electron microscopy (TEM) analyses, (see ESI†). The synchrotron XRD powder patterns (collected using BL 8C2 at Pohang Light Source in reflection mode; $\lambda = 0.14923$ nm) of the samples as-synthesized with mass ratios, BuOH : F127 = 0, 1, 2, 3, and 4 (denoted S0, S1, S2, S3, and S4), are shown in Fig. 1. In the absence of butanol, the highly resolved diffraction peaks are indexed to a lattice with face-centered cubic (*fcc*) *Fm*3*m* symmetry. As shown recently, this silica consists of large cage-like pores or cavities arranged in a cubic-close packed mesostructure.[8] Addition of increasing amounts of butanol to the starting mixture up to BuOH : F127 = 2 does not alter the symmetry of the mesophase, but clear differences in relative intensities of the diffraction peaks are observed. At BuOH : F127 = 3, a transition to the body-centered cubic (*bcc*) *Im*3*m* symmetry has apparently occurred, the material being hence analogous to SBA-16.[9] This is also confirmed for the sample after calcination by the nitrogen physisorption isotherm being a type IV (ESI†) and a broad H2 hysteresis loop indicative of large uniform cage-like pores.[3,10] A further increase in the amount of butanol added (up to BuOH : F127 = 4) induced the formation of a phase that could be assigned to a SBA-15-type 2-D hexagonal structure.[1,5]

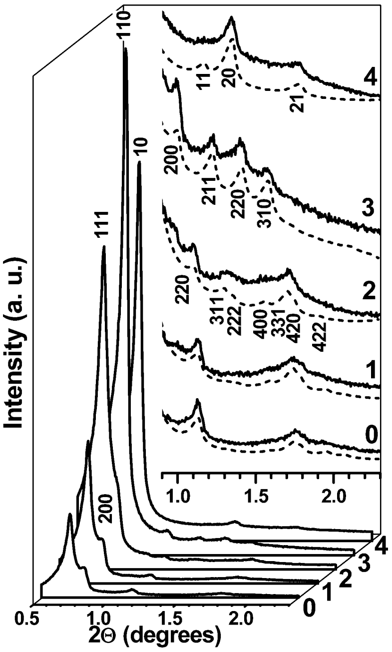

Fig. 1 Experimental (solid line) and simulated (dashed line) XRD powder patterns of samples with mass ratio BuOH : F127 = 0, 1, 2, 3, and 4.

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† Electronic supplementary information (ESI) available: Figures S1 and S2. See http://www.rsc.org/suppdata/cc/b4/b403903c/

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To monitor the structure changes, XRD structure modeling was performed using the continuous density function (CDF) approach[11] and the derivative difference minimization full-profile refinement.[12] The density distribution in *fcc* and *bcc* materials was simulated by a three-dimensional array of spherical cavities arranged in accordance with the face-centered cubic and the body-centered cubic packing respectively. For the 2-D hexagonal phase the density distribution function described in ref. 11 was applied assuming the cylindrical pore model. The cavity (or pore) diameters and the lattice parameters were varied to obtain the best agreement between the experimental and calculated XRD profiles. As shown in Fig. 1, the structure models provided full matching between the experimental and calculated XRD peak positions and intensities for all the samples. The structure parameters are summarized in Table 1. The addition of butanol induced prominent increase of the cavity diameter, while the lattice parameter expansion was minor. The lattice parameter of *bcc* structure cannot be directly compared to that of *fcc*. Instead, we can compare the unit cell volumes normalized to the number of cavities per unit cell. For samples S0, S1, S2, and S3 these specific volume values are 2488, 2502, 2666, and 2513 nm^3 respectively. The specific volumes per cavity for sample S0 and S3 differ only by 1%, which suggests negligible lattice expansion. On the other hand, the nearest distance between the cavity surfaces, which is given by $a\sqrt{2}/2 - D$ for *fcc* and $a\sqrt{3}/2 - D$ for *bcc* and can be used as a measure of the silica wall thickness, decreased from 6.2 nm for sample S0 to 3.8 nm for sample S3. From the above considerations we may conclude that butanol causes minor swelling of the mesostructure lattice but major decrease of the silica wall thickness, presumably due to the dehydration of the PEO blocks.[6b] The XRD pore diameter for sample S4 appeared to be smaller than those of S3 and S2. However, the nitrogen physisorption analysis for this sample suggested an intermediate pore shape between cage-type and cylindrical (ESI†). In this respect, the pore diameter 9.7 nm for S4 should be considered as an effective value since the XRD modeling for this sample was done applying a simplified cylindrical pore model.

The present study demonstrates unambiguously that the introduction of butanol to a triblock copolymer-based mesoporous silica synthesis provides an extremely efficient means of tuning the material structure. Such straightforward tailoring of the phase behaviour is made possible under the low HCl concentrations conditions utilized. Butanol is known to act as a co-surfactant participating together with the block copolymer in forming the polar/apolar interfaces. Specifically, it is believed that butanol is mainly located at the hydrophilic–hydrophobic interface (EO/PO) stabilizing the micellar aggregates and determining the surface curvature.[6] We could speculate that the evolution of the mesophase from the cage-type *fcc* and *bcc* to the near-cylindrical pore 2-D hexagonal structure may, therefore, originate from changes in the interfacial curvature and the hydrophobic to hydrophilic volume fractions. Similar transition between *Im*3*m* and *p*6*mm* phases resulting from the reduced hydration of the polar headgroups and lowering curvature has been observed, for example, in a polyalkylene oxide-based surfactant–water system where, besides, an epitaxial relationship between both phases was evidenced.[13] In our case, it is possible that the curvature of the micellar aggregates could be reduced due to the combined swelling of the micelles and decrease in hydration of the polyethylene oxide groups caused by increasing amounts of butanol.[6c] In addition, the location of butanol at the hydrophilic–hydrophobic interface may be responsible for the shift of the silica region in the micelles, which resulted in reducing the silica wall thickness and, consequently, in the pore opening.

Table 1 Structure characteristics of samples synthesized with different amounts of butanol[a]

Sample	Lattice type	*a*(nm)	*D* (nm)
S0	*Fm*3*m*	21.51	9.0
S1	*Fm*3*m*	21.55	9.6
S2	*Fm*3*m*	22.01	10.2
S3	*Im*3*m*	17.13	11.0
S4	*p*6*mm*	14.52	9.7

[a] *a*, the lattice parameter; *D*, the cavity (or pore for *p*6*mm*) diameter determined from XRD modeling.

In conclusion, we demonstrated a facile and systematic control over the formation of mesoporous silica with tailored pore architecture. The structural evolution is exclusively due to the addition of different amounts of butanol as the unique phase-controlling agent. Phase transitions from face-centered cubic *Fm*3*m*, to body-centered cubic *Im*3*m* (SBA-16) to, finally, 2-D hexagonal *p*6*mm* (SBA-15-like) mesostructures accompanied by pore widening and opening were observed upon increasing the amount of the co-surfactant. With regard to this, we stressed that combining experimental and simulated powder XRD patterns and TEM could ensure the precise structure characterization. Furthermore, it is reasonable to consider synthesis of mesostructured materials using other organic additives that can affect the hydrophilic–hydrophobic interface of the triblock copolymers. Therefore, we expect this particular synthesis route and the principle described herein to be readily and widely adopted.

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