

One-step synthesis of ordered mesocomposites with non-ionic amphiphilic block copolymers: implications of isoelectric point, hydrolysis rate and fluoride†

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Highly ordered hexagonal silica/block copolymer mesostructured composites have been prepared using syntheses with fluoride over a wide range of pH conditions (pH 0–9), by controlling the rates of hydrolysis and condensation of the tetramethoxysilane silica source.

Highly ordered mesoporous silica structures have now been well demonstrated through the use of cationic surfactant (S⁺) and anionic silica moieties (I⁻) under basic pH conditions^{1,2} or by using cationic silica (I⁺) assembly through hydrogen bonding mediation with either cationic surfactants (S⁺)² or hydronium ion solvated neutral block copolymers [N⁰(H₃O⁺)].^{3,4} Pinnavaia and coworkers^{5,6} have shown that worm-like mesostructures with monodispersed pore sizes can be obtained using non-ionic surfactants (N⁰) and partially ionized silica [N⁰(H₃O⁺)I⁻] at neutral pH. Prouzet and coworkers⁷ have obtained similar results by starting with a clear [N⁰(H₃O⁺)X⁻I⁰] solution at pH *ca.* 2 and increasing condensation by adding fluoride.

In both the ordered and disordered worm-like structures that have been obtained, a common feature is the independent control of hydrolysis and silica polymerization. For example, highly ordered mesostructures can be created by varying the pH and charge on the silica species at high pH⁸ or alternatively near the isoelectric point⁹ where the rate of silica polymerization can be readily controlled. Hydrogen-bonding interactions, such as occur among polyethylene oxide–polypropylene oxide–polyethylene oxide (PEO–PPO–PEO) triblock copolymers and silica species in acid media, facilitate simultaneous synthesis and processing of ordered mesostructured materials into thin films,¹⁰ fibers¹¹ and monoliths.¹² Features of the inorganic species, such as the isoelectric point, associated cations^{13,14} and the cosolvent generated on hydrolysis of alkoxide,¹⁵ are important factors in these synthesis approaches.

Fluoride is a well known catalyst for hydrolysis and polymerization of silica species¹⁶ and has been used in the synthesis of mesoporous silica materials under various conditions in order to improve structural order.^{5,6,9,17,18} Silva and Pastore¹⁷ first reported the effect of fluoride on synthesis of mesoporous materials with cationic surfactants. Guth and coworkers¹⁸ synthesized mesoporous materials with cationic and non-ionic surfactant species, in the presence of fluoride at a pH between 6.5 and 11. However, use of the non-ionic surfactant species yielded poorly ordered mesostructures compared with those obtained using cationic surfactants. Pinnavaia, Prouzet and their coworkers^{6,7} reported the fluoride-mediated synthesis of MSU-X materials with worm-like disordered channel structures with poorly defined crystallographic symmetry, using non-ionic surfactant species under neutral conditions. Stucky and coworkers⁹ reported synthesis of highly ordered SBA-15 materials using amphiphilic PEO–PPO–PEO triblock copolymer P123 and tetraethoxysilane (TEOS) under

acidic conditions (pH ≤ 3) in the presence of a small amount of fluoride. Here, we report one-step syntheses of well ordered PEO–PPO–PEO/silica mesostructures over a large pH range (0–9), including mild neutral conditions.

The preparation of such materials relies on the control of tetramethoxysilane (TMOS) hydrolysis and silica polymerization in the presence of fluoride and amphiphilic block copolymer, the structure-directing agent. In a typical synthesis batch, 2.0 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀, *M*_{av} = 5800, BASF) was dissolved in 62 g of HCl or NaOH aqueous solution (pH = 0–12) and then 0.3 g of 0.5 M NH₄F solution was added at 313 K with magnetic stirring. To this mixture, 3.2 g of TMOS (98%, Aldrich) was quickly added with vigorous magnetic stirring. The resulting gel mixture was stirred for 1 day at 313 K and aged under static conditions for 1 day at 373 K in an oven. Another set of samples was prepared using P123 and the same procedures, except that NH₄F was not added to the reaction mixtures. The solid products were filtered off and dried at 373 K and subsequently calcined in air at 823 K.

Using these synthesis conditions, clear and homogeneous solutions form first, after which precipitates start to form as the reactions proceed. The times at which precipitates appear are highly dependent on the pH of the reaction mixtures and the presence of fluoride, as shown in Fig. 1. As noted above, the total aqueous solution (TAS) used for the reaction typically consisted of 62 g of HCl or NaOH solution (pH = 0–12). At pH 2 without fluoride, it takes *ca.* 8 h before precipitation begins to occur. This is because pH 2 is near the isoelectric point of silica and the silica polymerization rate is slow under these conditions.¹⁵ Fluoride promotes precipitation, increasing dramatically the rate of silica condensation, for example, more than an order of magnitude at pH 2, due to its catalytic effect on the hydrolysis.¹⁶

Fig. 2 shows powder X-ray diffraction (XRD) patterns for mesoporous silica produced using structure-directing P123 block copolymer surfactant species and TMOS, with and without fluoride. The patterns in Fig. 2(a) all show an intense

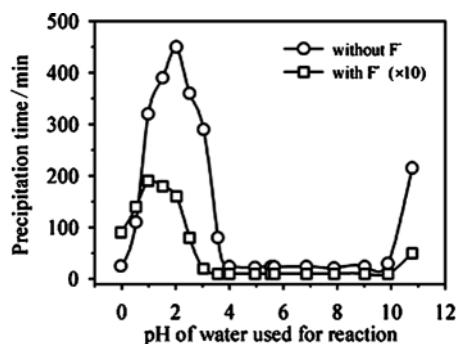


Fig. 1 Silica precipitation time plotted vs. pH of the synthesis solutions in the preparation of PEO–PPO–PEO/silica mesophases. The precipitation time is defined to be the cloud point at which the clear reaction mixture forms colloidal silica particles.

† Electronic supplementary information (ESI) available: TEM images and properties for calcined mesoporous silica. See <http://www.rsc.org/suppdata/cc/b0/b005608l/>

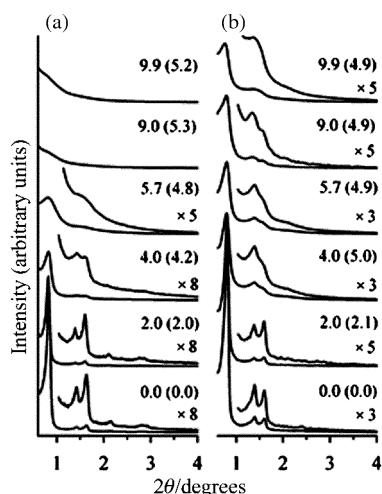


Fig. 2 XRD patterns for calcined mesoporous silica prepared using P123 surfactant species and TMOS: (a) without fluoride and (b) with fluoride. Numbers before parenthesis denote the pH of the precursor HCl or NaOH solution used for the reactions, while the numbers within parenthesis indicate the pH values of the reaction mixture after silica precipitation was complete. The pH of doubly distilled water was 5.7. XRD patterns were collected with a Cu-K α X-ray source using a Scintag X₂ instrument.

XRD diffraction peak and two or more weaker peaks up to pH 4 (TAS), which are characteristics of a 2-d hexagonally ordered (*P6mm*) structure.^{1,3,4} This indicates that hexagonal mesoporous silica materials with high mesoscopic ordering are obtained up to pH 4 (TAS) without fluoride. For materials prepared at pH > 4 without F⁻, disordered products are obtained. XRD patterns in Fig. 2(b) obtained from the mesoporous silica materials synthesized in the presence of fluoride are very similar to those of the materials obtained without fluoride up to pH 4 (TAS) and indicate the persistence of 2-d hexagonal mesostructural ordering up to pH 9 (TAS). Transmission electron microscopic images for calcined materials confirm that the materials obtained up to pH 9 (TAS) have highly ordered 2-d hexagonal structures.[†] Lattice parameters, surface areas, pore volumes, and pore sizes are listed in Table 1 (ESI[†]). It is noteworthy that ordered materials can be obtained from the reaction mixture of P123, doubly distilled water, NH₄F and TMOS without any acid or base catalyst, whereas the absence of fluoride under otherwise identical conditions yields the disordered products [Fig. 2(a)]. A disordered material is obtained at pH 10 (TAS) and there is no precipitation above pH 11 (TAS) with F⁻. Morphologies and XRD peak shapes of the hexagonal mesoporous materials are dependent on the reaction pH. Rod-like morphologies, with bundles of silica fibers aligned coaxially with the rods' long axes,⁹ are obtained in the SBA-synthesis region below the silica isoelectric point, while above the isoelectric point, where anionic silica species are present, particles with more irregular morphologies are observed.

The results above suggest that suitable oligomeric silica species, formed from fully hydrolyzed monomeric silica species, are needed for interaction with the structure-directing block copolymer to obtain ordered mesostructures. This is due to competition between the condensation of partially hydrolyzed silica species and the hydrolysis of alkoxy silane moieties associated with the silica precursors.¹⁶ Above pH 4 (TAS), silica oligomers may contain the organic moieties from incomplete hydrolysis due to relatively rapid condensation compared to the rate of hydrolysis.¹⁶ The presence of such residual organic moieties leads to weaker interactions between hydrophilic block polymer and silica oligomers, resulting in poorly organized mesocomposites. Indeed, the reaction mixtures above pH 4 without fluoride yield gel-like precipitation and disordered or amorphous silica structures.

On the other hand, addition of fluoride results in the formation of white precipitates and well ordered mesostructures

up to pH 9 (TAS). This indicates that hydrolysis of TMOS can be completed before significant condensation of the silica species occurs, which is consistent with the catalytic activity of fluoride for hydrolysis.¹⁶ However, such catalytic activity of fluoride is dependent on the nature of the silica precursors. When TEOS is used as silica source instead of TMOS under the present conditions, ordered mesostructures are obtained up to pH 2.7 with fluoride and disordered mesostructures above pH 2.7⁹ because the hydrolysis rate can compete with the rate of condensation. Hydrolysis of TEOS is slower than that of TMOS, because of steric hindrance at ethoxide moieties and reduced solvation of resulting ethanol.¹⁶ The more rapid hydrolysis of TMOS thus makes it a preferable silica precursor to TEOS for producing ordered mesostructures. Nevertheless, such ordered mesostructures can be produced using TEOS or other precursor species, provided the silica sol is pre-hydrolyzed near pH 2^{12,19,20} where the hydrolysis rate is fast and the condensation rate is slowest.¹⁵

In conclusion, highly ordered PEO-PPO-PEO/silica mesostructures can be prepared over a diverse range of pH (0–9) by controlling the relative rates of hydrolysis and condensation of silica species through the use of fluoride and TMOS. Cubic (*Im3m*) and 3-d hexagonal (*P6₃/mmc*) block copolymer/silica mesostructures can be synthesized using Pluronic F127 (EO₁₀₀PO₇₀EO₁₀₀) and Brij 76 [C₁₈H₃₇(OCH₂CH₂)₁₀OH] structure-directing surfactant species with TMOS and fluoride near the isoelectric point (pH 2) of silica.

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