Crystallization of hollow mesoporous silica nanoparticles

Glenna L. Drisko, Adrian Carretero-Genevrier, Alexandre Perrot, Martí Gich, Jaume Gàzquez, Juan Rodriguez-Carvajal, Luc Favre, David Grosso, Cédric Boissière, Clément Sanchez

Experimental Procedures and Materials

Materials. All chemicals were obtained from Aldrich and used as received. X-ray diffraction (XRD) was used to probe the crystalline texture of films using a Bruker D8 diffractometer: 3s acquisition every 0.02° in Bragg-Brentano geometry. A Su-70 Hitachi field emission gun scanning electron microscope (FEG-SEM) was employed. Transmission electron microscope (TEM) was used to observe the microstructure of the films using a FEI Technai G2 F20 operated at 200 kV, and equipped with a high angle annular dark field detector, with which the Z-contrast images were acquired. And a FEI TITAN³ operated at 80KV and equipped with a SuperTwin® objective lens and CETOR C₅-Objective corrector from CEOS company. Scanning TEM with high EDX resolution was performed on a Jeol 2010 F. Porosimetry measurements were performed with micrometrics ASAP 2000 model at 77 K.

Preparation of polystyrene particles. Anionic polystyrene particles were prepared using an anionic initiator, as described in a recent publication.¹ dihexylsulfosuccinate sodium salt (2.63 g, 5.92 mmol), MilliQ H₂O (200 g, 11.1 mol), sodium hydrogen carbonate (0.43 g, 5.14 mmol) and styrene (30.2 g, 0.290 mol) were mixed together in a round bottom flask. The solution was degassed over 45 min by bubbling with argon. The initiator, potassium persulfate (0.43 g, 1.60 mmol) in MilliQ H₂O (14.8 g, 0.821 mol) was added via syringe and then the solution was immediately placed in a pre-heated 90 °C oil bath. The reaction was performed under slightly positive Ar pressure. After 6 h the reaction was exposed to air and removed from heat. The particles were dialyzed over one week producing an 11.8 wt% polystyrene (PS) dispersion of particles 83 ± 6 nm. Cationic polystyrene particles were produced by changing the initiator to 2,2’-azobis(2-methylpropionamidine) dihydrochloride as reported in the same reference,¹ to produce latexes compatible with the aerosol process. The synthesis protocol was otherwise identical to that for anionic polystyrene particles.
Preparation of mesoporous silica shells. \(^1\) Hexadecyltrimethylammonium bromide (CTAB, 3.2 g) was dissolved in MilliQ water (100 g) at 35 °C. The anionic polystyrene particle solution (10.0 g) was diluted with 500 mL MilliQ water, 200 mL of ethanol and basified with 7.5 g of 28% ammonium hydroxide solution. The CTAB/H\(_2\)O solution was added to the latex solution and allowed to equilibrate for 1 h. TEOS (5.4 g) was added dropwise to the latex/CTAB solution, which was subsequently allowed to react for 24 h. To collect the material, the solution was centrifuged at 8,000 rpm for 1 h. The block of collected solid material was calcined using the following program: 25 to 250 °C at a rate of 5 °C min\(^{-1}\), held at 250 °C for 2 h, 250 to 550 °C at a rate of 2 °C min\(^{-1}\), held at 550 °C for 5 h. These particles were then infiltrated with a 1 M salt solution containing either SrCl\(_2\) or Sr(NO\(_3\))\(_2\), Ca(NO\(_3\))\(_2\), Mg(NO\(_3\))\(_2\), or BaCl\(_2\), by placing a monolith of tightly packed hollow silica spheres in the solution for a period of several hours and then drying excess solution from the monolith with a kimwipe. The monolith was then heat treated at 800-1000 °C for 5 h with a 10 °C min\(^{-1}\) heating ramp.

Preparation of aerosols. Aerosol particles templated by sacrificial latex beads were prepared by mixing 33.95 g distilled water with 8.15 g of 0.01 M HCl solution (pH = 2). TEOS (7.85 g) was then added to the solution, which was subsequently left under magnetic stirring for 3 h to let hydrolysis and condensation proceed. After the hydrolysis step, 0.046 g of barium chloride dihydrate (Aldrich, 99%) was added. Finally 34.66 g of a colloidal solution (\(\phi_w = 0.12\)) of monodisperse (\(d_p \approx 50\) nm) cationic latexes were added just before spraying. Final molar ratios versus TEOS of all molecular species involved were 102.6:2.2:1:0.005 for H\(_2\)O:HCl:TEOS:BaCl\(_2\)2H\(_2\)O with the polystyrene latexes composing approximately 0.64 in mass fraction of the final dried product. This solution was subsequently sprayed on a home built nebulizer coupled with a tubular furnace. The following parameters were used to produce the aerosol particles: input temperature: 300 °C, atomization gas pressure: 40 psi, atomization flow: 600 L/h, suction flow: 35 m\(^3\)/h, and pump flow: 9 cm\(^3\)/min. The powder was recovered in a filter and then was calcined under static air at 1000 °C for 15 h (10 °C min\(^{-1}\)).

Reference

**Figure S1.** (a) FEG-SEM image, (b) low magnification TEM image, and (c) electron diffraction pattern (SAED) of crystalline silica nanoparticles calcined for 5 h under air at 900 °C.

**Figure S2.** (a) Wide-angle diffraction pattern (card no. 09-8780 corresponding to α-quartz *; and card no. 46-1045 corresponding to monoclinic lithium silicon oxide °. The peaks were indexed
according to the International Centre for Diffraction Data.) and (b) TEM image of amorphous particles infiltrated with a 1 M LiCl solution, then heat treated at 650 °C for 5 h.

Figure S3. (a) FEG-SEM image, (b) TEM image and (c) X-ray diffraction pattern corresponding to non-infiltrated particles treated at 900 °C for 5 h in air. The mesoporosity and amorphous character are maintained after the thermal treatment.
Figure S4. (a) Rietveld refinement and pattern matching analyses of crystallized nanoparticles at 1000 °C using the Fullprof software after infiltration with a 1 M solution of Sr(NO₃)₂. The figure shows the observed (in red) and calculated (in black) patterns. The difference between the observed and calculated intensities is shown below the vertical lines (blue line). (b) Rietveld refinement and pattern matching analyses of crystallized nanoparticles at 1000 °C. In colors are indicated the four phases found: Total observed pattern (red), total calculated pattern (black), Cristobalite (blue), Quartz (brown), Tridymite (green) and unknown monoclinic phase (magenta). Apparent crystallite size of different phases: Cristobalite (15.2 nm), Quartz (43.8 nm), Tridymite (13.1 nm) unknown monoclinic phase (24.1 nm). Relative amount of known phases at 1000 °C: Cristobalite (65.2%), Quartz (20.5%), Tridymite (14.4%). (c) Effect of calcination temperature on the crystallite size of quartz.
Figure S5. Wide-angle diffraction patterns of particles infiltrated with 1 M solutions of Ba\(^{2+}\) (orange pattern, all peaks matching to card no. 26-0176 corresponding to orthorhombic sanbornite), and Ca\(^{2+}\) (green pattern, card no. 46-1045 corresponding to α-quartz *; card no. 07-2134 corresponding to cristobalite #; and card no. 11-2265 corresponding to monoclinic wollastonite CaSiO\(_3\) °). The samples were calcined at 900 °C for 5 h in air.
**Figure S6.** Wide-angle diffraction patterns of particles infiltrated with strontium chloride solutions of the following concentration: 3 M (orange pattern, unknown crystal phase), 2 M (green pattern, unknown crystal phase), 1 M (yellow pattern, unknown crystal phase), 0.5 M (purple pattern, unknown crystal phase) and 0.18 M (blue pattern, card no. 46-1045 corresponding to α-quartz *).
Figure S7. TEM (upper panel) and SEM (lower panel) micrographs of thin walled (a) amorphous and (b) crystalline particles produced from latex templating of an aerosol. Scale bars represent 100 nm.

Figure S8. The alkaline earth metal (blue) is distributed in the mesopores, in the central cavity and at the exterior of the particle before heat treatment. The alkaline earth metal devitrifies the silica, inducing crystallization, while migrating to the crystal boundaries.