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One-Pot Synthesis of Hierarchically Ordered Porous-Silica Materials with Three Orders of Length Scale

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Porous, solid materials occur widely in nature and are the subject of intense study owing to their unique properties. The pore sizes can vary from Ångstroms in zeolite minerals to nanometers in leaf cellular structures to microns in diatom skeletons. The pores can be very uniform in shape and size with near delta function for the pore size distribution or can cover a wide range of pore sizes. The wall structure can be highly organized (crystalline) or highly disorganized (amorphous). Finally, the chemistry (composition) of the wall can vary enormously from oxide structures to functionalized polymers. In synthetic inorganic porous materials a Rubicon was crossed in 1992 by researchers at Mobil[1] who devised a method by using molecular self-association templating to synthesize materials with well defined pores on a nanometer scale. That is, they used the well-known phenomenon of self-organization of surfactant molecules into mesostructures such that the combined assembly of organic molecules acted as a template around which an inorganic material could be formed. Previously, in zeolite synthesis in which pores are formed on an Ångstrom scale, individual organic molecules rather than collections of organic molecules were used. Such a macromolecular templating is almost certainly the root of many complex inorganic porous structures in nature. However, the work of the Mobil researchers demonstrated, for the first time, that such a general synthetic philosophy could be used to control the porosity and chemistry of a multitude of porous materials. Since 1992 several thousand publications have reported extensions of the Mobil work.

Armed with this knowledge one important avenue that can be pursued is the creation of hierarchically ordered porous materials. That is, materials with several different degrees of porosity incorporated into one composite material. Nature produces such hierarchically ordered porous structures for example, diatoms, lumbar vertebra, lungs for optimal transport of fluids and gases. There are a number of reasons why this is important. For a porous material to be used in

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bulk-chemistry applications such as catalysis, in which reactant molecules need to readily access the interior pore structure but at the same time the internal surface area is maximized, a ramified pore structure with large pores leading to smaller and then smaller pores is desired (similar to the structure of lungs). Indeed it can be shown that the largest pores should form a 3D grid with the grid sections subdivided by a subgrid of smaller pores, and so on.[2] Consequently, there is a desire to have complete control not only of the pore sizes at each dimension but also the interconnectivity of these pores. Furthermore for bulk applications it is important that the preparation of such materials is facile, scalable and ultimately fairly inexpensive. In a recent paper,[3] we showed how some of these criteria could be met through a combination of using natural, inexpensive macroporous diatomaceous earth that is coated with a microporous zeolite. Herein, we adopt a different strategy that is entirely synthetic to achieve porosity with 3D interconnectivity of pores controlled on three length scales in a one-pot synthesis. Furthermore, at the macro- and mesoscale both ordering and size is controlled whilst at the microscale only the interconnectivity is controlled. We draw upon a number of different methodologies developed by others (most importantly the Mobil researchers) but also on the efforts to use a variety of templates such as synthetic opals,[4] latex spheres,[5] block copolymers,[6] emulsion droplets,[7] foams,[8] vesicles,[9] and bacteria.[10] Most of these papers report materials with a porous structure on one scale. However, Stein and co-workers[11] reported an ordered macroporous material with a crystalline microporous (silicalite-1) wall structure or disordered mesoporous structure.[12] Also, recently Danumah et al.[13] reported the synthesis of materials containing ordered macropores with cubic mesoporous (MCM-48) wall structure. Neither report demonstrated 3D interconnectivity between the pores. Stucky, Whitesides and co-workers[14] have concentrated on an approach, which involves stamping a sol–gel designed to produce mesopores with a 2D macroporous architecture. This process is tailored to produce films for optoelectronic applications but is not suitable for bulk chemical applications. Our strategy uses synthetic latex spheres to produce a controlled three-dimensionally interconnected macroporosity (300 nm–1 µm), block copolymer macromolecular templating to produce a mesoscale porosity (≈10 nm) and individual polymer templating to produce micropores (≈1 nm). These materials which are the subject of a recent patent[15] could be potential candidates as supports for heterogeneous catalysis with bulky molecules.

Monodispersity, sphere packing, and void size of the polystyrene sphere monoliths were determined by SEM and Hg-porosimetry experiments and are presented in Figure 1. Two distinct voids (Figure 1b) are present in the monoliths owing to octahedral (O_h; left peak) and tetrahedral interstitial sites (T_d; right peak). The position of the peaks due to the O_h and T_d interstitial sites are well matched with the theoretically calculated values from radius-ratio rules for a cubic close-packed arrangement.

The ordering of macropore structure of the silica materials is evidenced from SEM (Figure 2a) This shows a material where the latex spheres have been removed by toluene

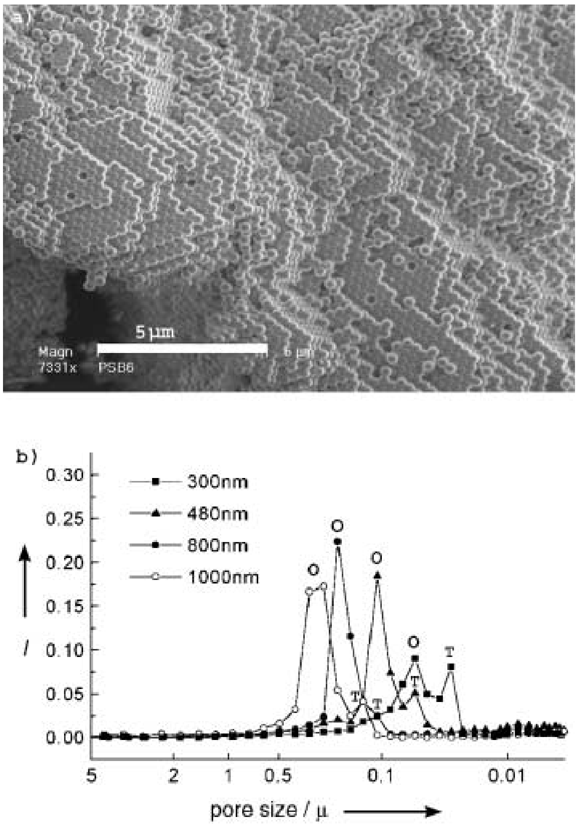

Figure 1. a) SEM of polystyrene latex sphere monolith, b) Hg intrusion curves over polystyrene latex spheres of various sizes. O = octahedral, T = tetrahedral, *I* = intensity (arbitrary units).

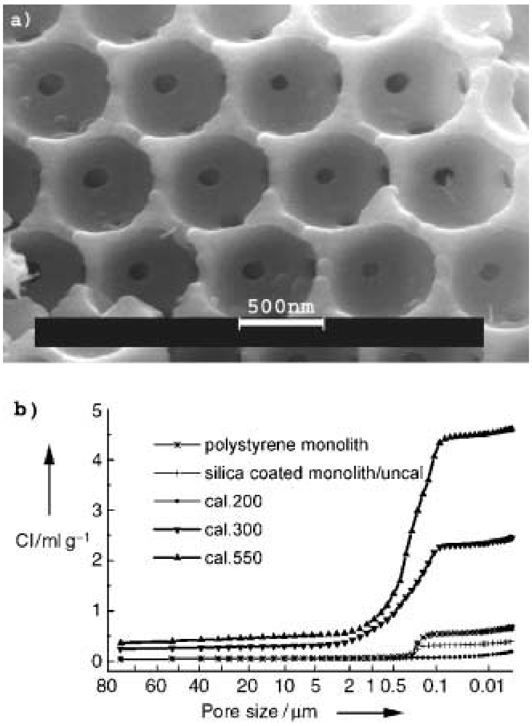

Figure 2. a) SEM of silica material synthesized by using triblock copolymer F127 and cosurfactant butanol. The latex was removed with toluene; b) Hg cumulative intrusion curves of macoporous monoliths at various stages of preparation. CI = cumulative intrusion.

extraction followed by calcination. This is the optimum route and yields exceptionally well-ordered macroporous silicas as can be seen in Figure 2a. The macropores are uniform (200–800 nm depending upon initial sphere size) with interconnected windows (70–130 nm). Removal of the latex by calcination alone retains the macroporosity, however, the macro-spheres are somewhat deformed (not shown). The progressive formation of the ordered macroporous structure can be followed conveniently with Hg porosimetry (Figure 2b). The starting monolith (without silica, sphere size = 805 nm) has Hg intrusion of 0.5 $\mathrm{ml\,g^{-1}}$ due to the O_h and T_d interstitial voids. After silica condensation this value decreases to 0.2 $\mathrm{ml\,g^{-1}}$, thus indicating that the silica coats the latex spheres and does not completely fill the voids. If the polystyrene latex is removed by calcination alone first the Hg intrusion drops to zero at 200 °C owing to latex melting but then increases finally to 3.3 $\mathrm{ml\,g^{-1}}$ after calcination at 550 °C. The high Hg intrusion is due to the void volume created by the removal of polystyrene latexes and confirms the presence of interconnecting windows.

The details of the wall structure are determined through a combination of X-ray diffraction (XRD), transmission electron microscopy (TEM) and nitrogen adsorption. The single XRD peak (d = 8 nm to 10.2 nm), not shown, in the low-angle region indicates the presence of mesoscopic ordering. The TEM images of a sample synthesised with F127 block copolymer and butanol as cosurfactant exhibits well defined mesostructure with an apparent square arrangement of pores with repeat distance $\approx$9.9 nm and pore sizes of 8.2 nm (see Figure 3a). In the presence of P123 block copolymer the TEM suggests a layered structure although it is impossible to determine the detailed structure from this information alone (see Figure 3c). A careful examination of the TEM images provides three important points: 1) the presence of macro-scale interconnecting windows $\approx$100 nm; 2) ordered mesopores $\approx$8.2 nm with 10 nm repeat distance; 3) an amorphous region around the macropore windows. The 10 nm repeat distance for the mesostructure from TEM correlates well with the d spacing from low angle XRD.

The surface area and mesopore volume of the materials were low (46 $\mathrm{m^2\,g^{-1}}$, 0.053 $\mathrm{ml\,g^{-1}}$) when the polystyrene latex was removed by direct calcination at 550°C (Figure 4a). However, removal of the latex by toluene extraction followed by calcination at 450°C resulted in a very high total surface area 531 $\mathrm{m^2\,g^{-1}}$ (Figure 4b). The total pore volume of pores less than 72 nm diameter is 0.29 $\mathrm{mL\,g^{-1}}$. The BJH desorption cumulative pore volume due to the mesopores is 0.19 $\mathrm{mL\,g^{-1}}$. The high uptake of N_2 (Figure 4b) at low relative p/p_0 clearly indicates the presence of micropores (< 2 nm) and this is further supported by a positive slope in the t-plot analysis (volume added versus thickness determined by Harkins–Jura methods; not shown, micropore surface area = 293 $\mathrm{m^2\,g^{-1}}$, micropore volume = 0.1 $\mathrm{mL\,g^{-1}}$). The narrow mesopore size distribution is due to the high ordering on the mesoporous length scale. In summary: mesopore volume $\approx$0.19 $\mathrm{mL\,g^{-1}}$, surface area $\approx$240 $\mathrm{m^2\,g^{-1}}$; micropore volume $\approx$0.1 $\mathrm{mL\,g^{-1}}$, surface area $\approx$291 $\mathrm{m^2\,g^{-1}}$.

The presence of micropores in a mesoporous sample prepared by using triblock copolymers (F127 or P123) was

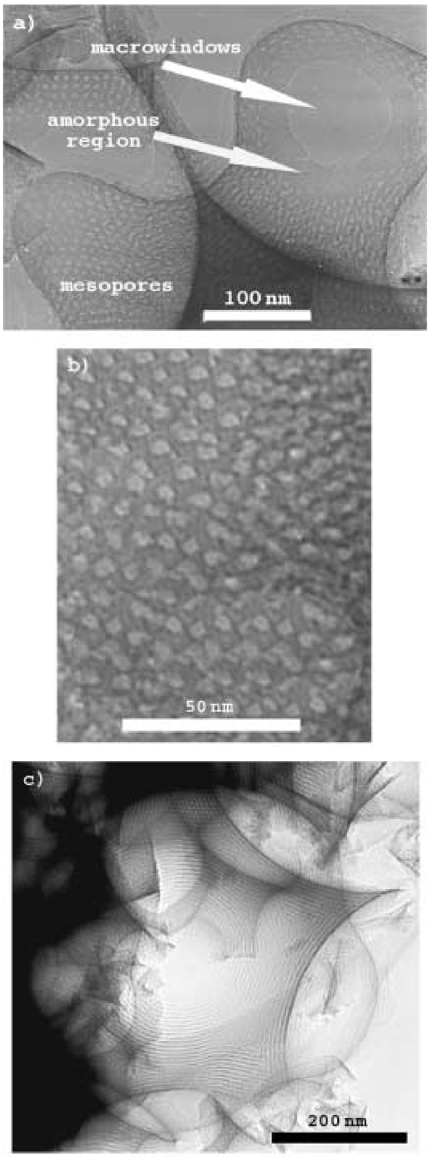

Figure 3. TEM images of silica materials synthesized by using triblock copolymer: a) F127 b) enlarged form of selected region of (a), c) P123.

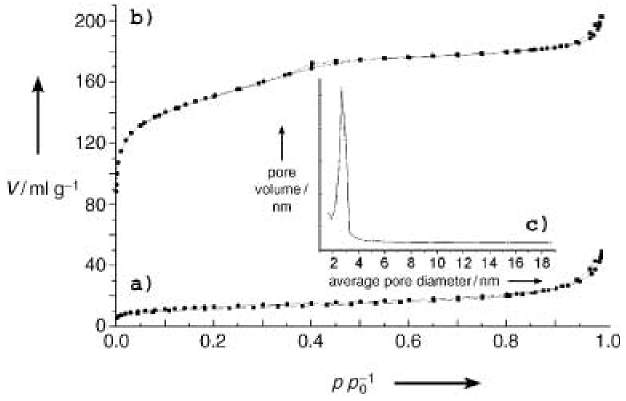

Figure 4. N_2 adsorption isotherms of a) silica material prepared by calcination alone, and b) silica material prepared by toluene extraction followed by calcination with c) associated desorption pore size distribution. circle adsorption and square desorption.

reported earlier.[16,17] As a comparison with the bulk materials synthesised with P123 mentioned in these references typical micropore volumes are 0.1 mL g^{-1} and mesopore volumes are 0.5–0.6 mL g^{-1}. The micropore volume is similar to our material but the mesopore volume is substantially larger. Consequently, the formation of a thin silica membrane around the latex spheres has resulted in a lower mesoporosity. This will in part be due to the thinness of the silica membrane (≈100 nm from TEM) which results in a different organization of the block copolymer over the latex in comparison to a bulk synthesis.

The formation of macrospheres, interconnecting windows, mesoporous wall structure, amorphous region around windows, and microporosity is explained diagrammatically in the Figure 5. The macrospheres and interconnecting windows are formed due to the removal of polystyrene spheres. The formation of windows is due to the close-packed arrangement of polystyrene spheres (touching points). The meso- and microporosity is generated by the micelle formation of the EO–PO–EO (EO: ethylene oxide, PO: propylene oxide) block copolymer in the presence of cosurfactant butanol or pentanol. Owing to the hydrophobic nature of PO and hydrophilic nature of EO, the PO forms a solid impenetrable core and the EO tails project more loosely around this core. The PO core consequently templates the mesoporous structure and the EO tails individually template the microporous structure. The diameter (8 nm) of the micellar core correlates well with the mesopore sizes (8.2 nm) from the TEM results. The formation of micelles is excluded in regions near where polystyrene spheres touch resulting in the amorphous region around the windows.

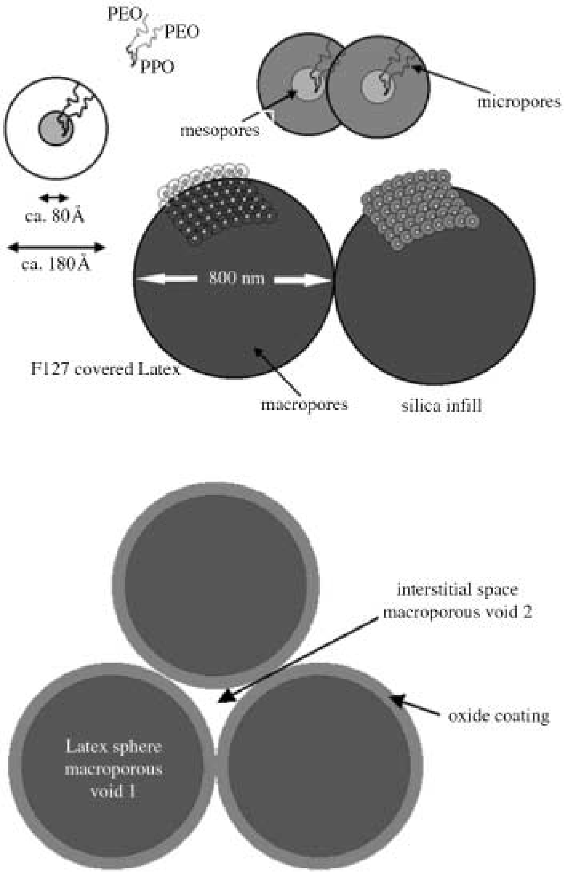

Figure 5. Diagrammatic presentation of macro-, meso-, and micropores formation.

In conclusion, hierarchically ordered porous silica materials are prepared with ordering on three different scales, that is, macropores (200–800 nm), interconnecting windows (70–130 nm), ordered mesoporous walls (80 nm) with narrow micropores < 2 nm in the presence of multiple templates, that is, polystyrene latex spheres, surfactants (triblock copolymers) and cosurfactants (butanol or pentanol). This method of synthesis will extend the preparation of inorganic composites with tunable pores over various length scales with ordering in three dimensions.

Experimental Section

Noncross-linked, monodisperse polystyrene spheres were synthesized by using emulsifier-free polymerization techniques according to literature procedures.[12] Styrene (105 mL, Fluka, > 99 % purity) was washed in a separating funnel five times with 100 mL of 0.1 M NaOH (BDH, 99 % purity) then five times with 100 mL deionised water. After this step the colorless styrene became pale yellow and the NaOH solution became pink. A five necked, 2000 mL round bottom flask was filled with the required amount of deionised water and heated to 70 °C with an isopad heating isomantle before washed styrene (100 mL) was added. One neck of the flask was attached with stirrer glands (quickfit) connected with a PTFE stirring rod. The stirring rod was fitted with an electric motor with a display of the rotation speed (Heidolph RZR2051). The other four necks had a water condenser, thermometer, septum, and a pasteur pipette connected to a N_2 cylinder by a rubber tube. In a separate 100 mL polypropylene beaker, the required amount of potassium persulfate (initiator, Sigma, 99 % purity) was dissolved in water (50 mL) and heated to 70 °C. The persulfate solution was added to the reaction flask containing the mixture of deionised water and washed styrene at 70 °C. The whole mixture was stirred at a specific stirring speed for 28 h. The temperature was kept at 70 °C during the reaction. The product was collected with a syringe for particle size distribution measurement. The final reaction mixture was milky white and transferred into a polypropylene bottle. The colloidal solution of polystyrene spheres was cooled down to room temperature before storage in a refrigerator at 4 °C. A close-packed latex sphere monolith was produced by centrifugation at 4000 rpm, which was dried at 60 °C.

The one-pot synthesis of hierarchically ordered porous silica materials was carried out as follows: a required quantity of HCl was diluted by the required amount of deionised water in a polypropylene beaker at room temperature. A required amount of tetramethyl ortho silicate (Aldrich) was added to the acidic solution. The tetramethyl orthosilicate (TMOS) was vigorously reacted with acidic solution and the temperature of the mixture was increased to 60 °C. The mixture was stirred for 15 minutes during which time the solution temperature decreased to 30 °C. In a separate polypropylene beaker the required amount of tri-block copolymer P123 (BSF) or F127 (Sigma) was mixed with the required amount of pentanol or butanol (Aldrich). The TMOS solution was added to the surfactant solution and stirred for 5 minutes. The molar composition of the silica gel is given in the following:

$\text{Surfactant:H}_2\text{O:Co-Surfactant:HCl:TMOS} = 0.003\text{–}0.007:6.47:0.335:0.01625:1.$

4 gm of polystyrene latex monolith was added to the silica gel and stirred gently for another 15 minutes at room temperature. Finally the monolith was separated from the gel by filtration. The uncalcined materials were dried at 60 °C before calcination at 550 °C at a rate of 1 °C/minute in air. Alternatively templates were removed by toluene extraction at room temperature followed by calcination at 450 °C in air.

Sample preparation for SEM and TEM: The SEM micrographs were recorded on a Philips XL30 with a field emission gun. The samples were prepared by sprinkling the powder materials onto double-sided sticky tape and mounted on a microscope stub. This was then coated with a thin carbon film to increase the conductivity. The TEM micrographs were recorded on a Phillips CM20 200 kV. The sample was crushed (a few mg was used) and then dispersed in acetone. The mixture was then placed onto a copper grid using a dropping pipette.

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[1] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.
[2] U. A. El-Nafaty, R. Mann, *Chem. Eng. Sci.* **1999**, *54*, 3475.
[3] M. W. Anderson, S. M. Holmes, N. Hanif, C. S. Cundy, *Angew. Chem.* **2000**, *112*, 2819; *Angew. Chem. Int. Ed.* **2000**, *39*, 2707.
[4] A. V. Blaaderen, *Science* **1998**, *282*, 887.
[5] O. D. Velev, T. A. Jede, R. F. Lobo, A. M. Lenhoff, *Nature* **1997**, *389*, 448.
[6] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chelmka, G. D. Stucky, *Science* **1998**, *279*, 548.
[7] A. Imhof, J. Pine, *Nature* **1997**, *389*, 948.
[8] P. Sepulveda, G. P. Binner, *J. Eur. Ceram. Soc.* **1999**, *19*, 2059.
[9] D. M. Antonelli, *Microporous Mesoporous Mater.* **1999**, *33*, 209.
[10] S. A. Davis, S. L. Burkett, N. H. Mendelson, S. Mann, *Nature* **1997**, *385*, 420.
[11] B. T. Holland, L. Abrams, A. Stein, *J. Am. Chem. Soc.* **1999**, *121*, 4308.
[12] B. T. Holland, C. F. Blanford, T. Do, A. Stein, *Chem. Mater.* **1999**, *11*, 795.
[13] C. Danumah, S. Vaudreuil, L. Bonneviot, M. Bousmina, S. Giasson, S. Kaliaguine, *Microporous Mesoporous Mater.* **2001**, *44*, 241.
[14] P. Yang, T. Deng, D. Zhao, P. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science* **1998**, *279*, 548.
[15] "A macroporous–mesoporous–microporous silica material with ordered mesoporosity influenced by alcohol cosurfactant": T. Sen, M. W. Anderson, J. L. Casci, C. C. Egger, G. J. T. Tiddy, UK patent GB 0201951.1, **2002**.
[16] M. Imperor-Clerc, P. Davidson, A. Davidson, *J. Am. Chem. Soc.* **2000**, *122*, 11925.
[17] R. Ryoo, C. H. Ko, M. Kruk, V. Antochshuk, M. Jaroniec, *J. Phys. Chem. B* **2000**, *104*, 11465.