Microstructured Porous Silica Obtained via Colloidal Crystal Templates

O. D. Velev,* T. A. Jede,[†] R. F. Lobo,*[,‡] and A. M. Lenhoff

Center for Molecular and Engineering Thermodynamics and Center for Catalytic Science and Technology, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Received June 23, 1998. Revised Manuscript Received August 31, 1998

A novel scheme for using modified colloidal crystals as templates for silica polymerization is reported. 3D close-packed crystals of submicrometer latex spheres are assembled on a membrane surface by filtration. To induce silica polymerization, the particles are modified by adsorption of the surfactant hexadecyltrimethylammonium bromide. The colloidal crystals are then infused with a silica solution, which polymerizes in the cavities. In the final stage, the latex particles are removed by calcination, leaving behind porous silica of very low density. Scanning electron microscopy images demonstrate that the product has highly uniform and structured pores, representing a negative replica of the original colloidal crystal. The size of the pores can be controlled by changing the size of the latex used, and we were able to obtain samples with pores ranging from 150 to 1000 nm. Thus the method allows one to obtain structured silica materials of which the pore size, shape, and ordering can be controlled in a wide region that has previously been unattainable.

Introduction

The development of methods for the production of porous inorganic materials based on silica or other oxides is thriving due to their potential for wide practical application. A recent milestone in this field is the report on the formation of ordered mesoporous silica M41S phases based on the use of cationic surfactant liquid crystals as templates for silica polymerization.[1−3] Such silicas can find application in catalysis, separations, and environmental engineering. While this method, which is based on surfactant self-assembly, is simple and straightforward, the cross-section of the pores is limited by the size of the supramolecular surfactant aggregates to about 10 nm or less.[4] The formation of inorganic materials with uniform pores of arbitrary size, shape, and orientation remains a challenge[5] and therefore there is significant interest in the development of methods using other templates that can yield silica with different pore sizes and morphologies.

Recently Davis et al.[6] infiltrated bacterial threads with silica sols or MCM phases, leading to mineralization of the cell walls and the intercellular space. The removal of the biotemplates by subsequent heat treatment (calcination) resulted in a material with oriented elongated pores of micrometer size. Another important development is the use of emulsion droplets as templates for the formation of porous inorganic materials.[7] An interesting possibility, which we demonstrated in a short earlier publication,[8] is the use of colloidal crystals as templates that can lead to the formation of silica with ordered uniform submicrometer-sized pores, and this possibility is explored in detail in the present paper.

Crystalline structures assembled from colloid-sized particles ("colloidal crystals") have been studied extensively, as they reveal some of the basic principles of interactions in the colloidal domain.[9,10] The colloidal crystals exhibit remarkable optical properties due to diffraction and interference of light in the ordered arrays and may be expected to find use in diffraction gratings, light microswitches and storage devices.[11−13] Recent progress in particle assembly includes the development of new methods for controlling the formation[14−16] and

---

* Corresponding authors. E-mail addresses: velev@che.udel.edu, lobo@che.udel.edu.

[†] Presently with Procter and Gamble Pharmaceuticals, Norwich, NY 13815.

[‡] Center for Catalytic Science and Technology.

(1) Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710.

(2) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T.-W.; Olson, K. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834.

(3) Monnier, A.; Schuth, F.; Huo, Q.; Kumar, D.; Margolese, D. I.; Maxwell, R. S.; Stucky, G. D.; Krishnamurty, M.; Petroff, P.; Firouzi, A.; Janicke, M.; Chmelka, B. F. *Science* **1993**, *261*, 1299.

(4) Raman, K. N.; Anderson, M. T.; Brinker, C. J. *Chem. Mater.* **1996**, *8*, 1682.

(5) Mann, S.; Ozin, G. A. *Nature* **1996**, *382*, 313.

(6) Davis, S. A.; Burkett, S. L.; Mendelson, N. H.; Mann, S. *Nature* **1997**, *385*, 420.

(7) Imhof, A.; Pine, D. J. *Nature* **1997**, *389*, 948.

(8) Velev, O. D.; Jede, T. A.; Lobo, R. F.; Lenhoff, A. M. *Nature* **1997**, *389*, 447.

(9) Arora, A. K.; Rajagopalan, R. In *Ordering and Phase Transitions in Charged Colloids*; Arora, A. K., Tata, B. V. R., Eds.; VCH Publ.: New York, 1996; pp 1−13.

(10) Larsen, A. E.; Grier, D. G. *Nature* **1997**, *385*, 230.

(11) Kamenetzky, E. A.; Mangliocco, L. G.; Panzer, H. P. *Science* **1994**, *263*, 207.

(12) Joannopoulos, J. D.; Meade, R. D.; Winn, J. N *Photonic crystals: molding the flow of light*; Princeton University Press: Princeton, NJ, 1995.

(13) van Blaaderen, A.; Ruel, R.; Wiltzius, P. *Nature* **1997,** *385*, 321.

(14) Trau, M.; Saville, D. A.; Aksay, I. A. *Science* **1996,** *272*, 706.

(15) Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Nature* **1993**, *361*, 26.

10.1021/cm980444i CCC: $15.00

the orientation[13] of the particle lattices. However, both the 2D and 3D crystals obtained have found little practical application so far. This is largely because the colloidal crystals are formed in liquid environments and their extraction through drying can destroy or change the material. Even in systems where drying is possible, the mechanical stability of the materials obtained is poor. Our approach for turning colloidal crystals into solid-state materials is to replicate their highly ordered structure into a stable and durable silica matrix.[8] Thus, the uniform arrays of particles can create ordered pores of tunable size embedded in the silica. In this paper we describe the method for the formation of porous silica by using colloidal crystal templates and we report observations of the structure of the materials obtained.

Materials and Methods

The monodisperse latex suspensions of amidine (positively charged) and sulfate (negatively charged) latexes were obtained from IDC. The surfactant hexadecyltrimethylammonium bromide (HTAB) was obtained from Aldrich. A 1 M $Si(OH)_4$ aqueous solution was prepared by mixing of 38 g of tetramethyl orthosilicate (Aldrich, 98+%) with 250 mL of 0.02 M NaOH. This solution was stirred, filtered, and diluted with water in a 1:1 ratio before addition to the colloidal crystal films.

The latexes were filtered through 25 mm diameter polycarbonate membranes with pore size of 0.1 μm (Poretics Inc.), which were mounted on a filter stand with a stainless steel membrane support and precise back pressure control. The particle assembly procedures are described and discussed in detail in the Results section. The extracted latex/silica deposits were dried in a vacuum oven for 30 min at 50 °C and heated to 450 °C in an air atmosphere in a programmable furnace (Centurion VPM). A Cahn TG-121 thermogravimetric balance flushed with N_2 was used to characterize the calcination process. The typical amount of sample obtained and studied in a single TGA run was 10−12 mg.

Optical characterization was carried out on an Olympus BH2 microscope in transmitted illumination mode. The samples for scanning electron microscopy (SEM) were covered with a thin Au film by vacuum sputtering and observed using a JEOL JXA-840 scanning electron microscope. The original latex crystals were observed at acceleration voltages <10 kV because of sample degradation in the beam, but the silica samples were stable even at accelerating voltages higher than 40 kV.

Results and Discussion

A schematic presentation of the method for obtaining the materials described here is given in Figure 1. The first step of the process is the assembly of the latex particles into a 3D colloidal crystal matrix that will serve as a template for the subsequent silica polymerization. Formation of colloidal crystals from monodisperse microparticles is easily achieved by increasing their volume fraction in the vicinity of a flat wall,[17] by, e.g., sedimentation or filtration. We prepared the crystals by filtration, as this allows control of the speed of deposition and the thickness of the 3D crystalline layer. Another major advantage of filtration is that once the crystalline layer is deposited, it can easily be washed with different liquid media and finally infused with the silica solution to be polymerized.

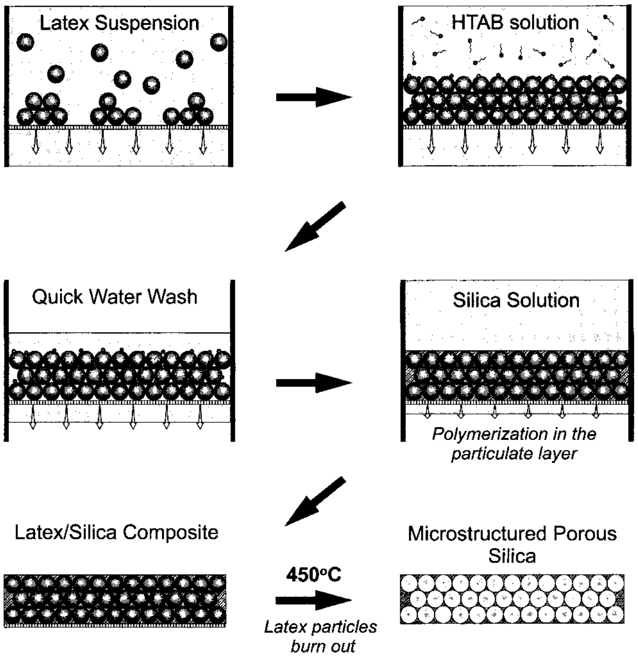

Figure 1. Schematic illustration of the stages of the synthesis method.

The experiments were carried out with commercially available latexes in the size range of 200−1000 nm. To demonstrate the versatility of the procedures, both positively and negatively charged particles have been used. In a typical experimental run, the latex suspensions were diluted to 0.1 vol % and were slowly filtered through a smooth narrow-pore membrane. The filtration was sustained by a small pressure drop across the membrane of typically about 5 kPa. The latex particles accumulated on the membrane surface in 2−3 h, building closely packed 3D ordered layers of thickness $\approx$20 μm. Due to diffraction of light from the ordered lattices, these layers typically showed a few brightly colored reflections (red and green for 300 nm latexes), when viewed at different angles after drying. The colors were entirely an optical effect arising from the diffraction of light in the ordered colloidal arrays, as the polystyrene latex microspheres are colorless.

The deposited crystalline layer could be broken and detached from the membrane surface for analysis by optical microscopy and SEM. An example of the appearance of the broken crystalline flakes in optical microscopy is shown in Figure 2a. While the resolution of the optical microscope does not allow observation of the discrete structure of the material, it can be seen that the layer is built up of small domains of different color with sharp boundaries. When the flakes were observed by SEM, they were found to be built up of completely crystalline domains with different orientations, each domain including between a few hundred and many thousand particles. Most of these domains exhibit hexagonal packing on their surface (Figure 3a), but square arrays of particles are occasionally seen (Figure 3b). Previous experimental and theoretical research on

---

(16) Denkov, N. D.; Velev, O. D.; Kralchevsky, P. A.; Ivanov, I. B.; Yoshimura, H.; Nagayama, K. *Langmuir* **1992,** *8*, 3183.

(17) Davis, K. E.; Russel, W. B.; Glantschnig, W. J. *Science* **1989**, *245*, 507.

(18) Pusey, P. N.; van Megen, W.; Bartlett, P.; Ackerson, B. J.; Rarity, J. G.; Underwood, S. M. *Phys. Rev. Lett.* **1989**, *63*, 2753.

(19) Zhu, J.; Li, M.; Rogers, R.; Meyer, W.; Ottewill, R. H.; STS-73 Space Shuttle Crew; Russel, W. B.; Chaikin, P. M. *Nature* **1997**, *387*, 883.

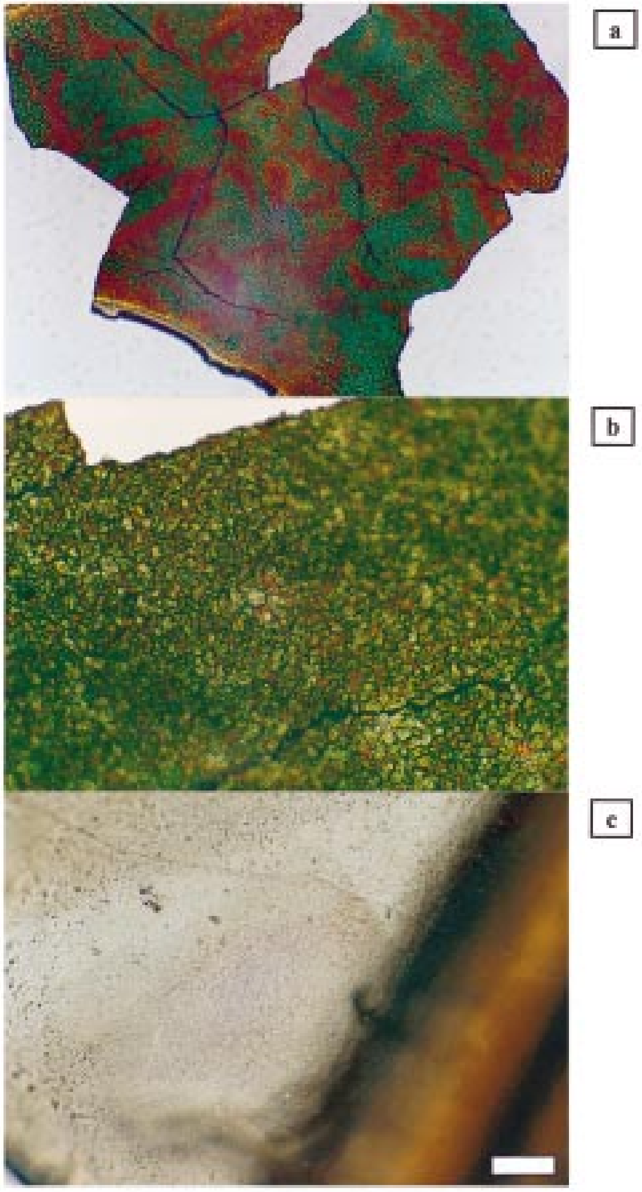

Figure 2. Optical microscopy photographs in transmitted light of the material at the different stages of the process. (a) Flakes comprising ordered latex crystals. Different colors correspond to crystal domains of different orientation. (b) Flakes from latex infused with polymerized silica; note the shift in colors and domain appearance. (c) An analogous sample after calcination at 450 °C. The porosity of the resulting silica-only material is seen, although the discrete structure cannot be resolved by regular optical microscopy. Scale bar = 50 μm.

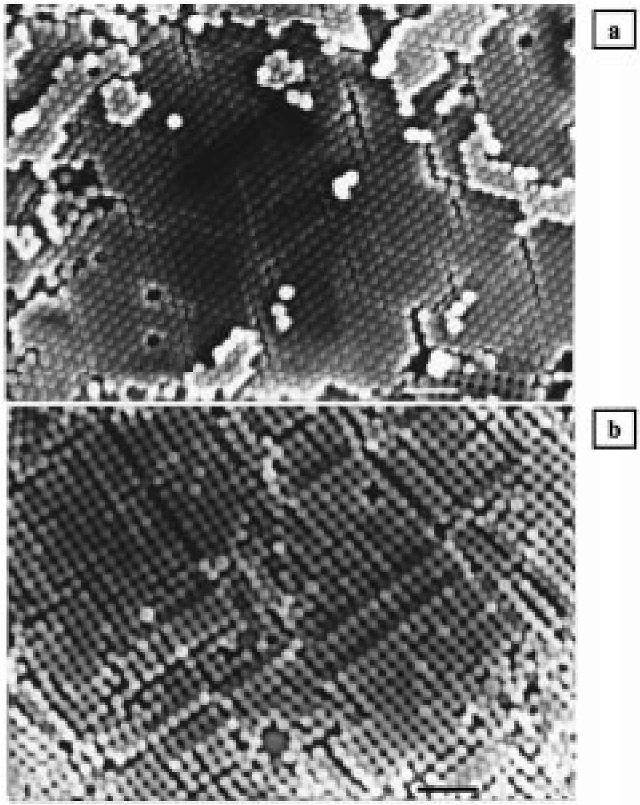

Figure 3. SEM micrographs of two typical areas on the surface of the 3D crystals from 300 nm latex particles: (a) hexagonal lattice and (b) square lattice. Scale bar = 1 μm.

the 3D crystallization of colloidal particles has shown that in typical laboratory conditions the microspheres crystallize in mixtures of both random stacking of hexagonally close-packed planes (rhcp) and face-centered cubic (fcc) lattices.[18,19] While both of these types of packing may be present in our crystallites, the difference observed between the hexagonal and the square arrays may be attributed to the orientation of the stacked crystalline planes (parallel or perpendicular to the membrane surface) rather than to the lattice type. Our data thus suggest that the crystalline domains are more likely to be oriented with the hexagonal planes of particles parallel to the membrane surface, as is to be expected in view of the mechanism of colloidal crystal growth.

The latex arrays obtained in this way are unsuitable for direct use as templates for the formation of porous silica due to the lack of initiators of the polymerization process. Most of the original surface of the latex microspheres is pure hydrocarbon and does not display any specific reactivity with the silica solution. When materials of the M41S type are produced, the positively charged surfactant groups on the surface of the micelles induce the polymerization. One possibility in our case was to infuse the latex crystals with freshly prepared M41S phases, which could fill up the space between the latexes and solidify there. This simple solution, similar to that reported in ref 6, would result in an interesting "mesoporous–macroporous" material that has large ordered cavities (from the latex beads) connected to small channels (from the surfactant micelles). We decided, however, to implement a more comprehensive scheme, resulting in a material templated solely by the latex microspheres. It is based on the fact that the same cationic surfactant (HTAB) used as a micellar template in the M41S scheme adsorbs very well on the latex surfaces, rendering them highly positively charged and effectively functionalized to serve as a basis for silica polymerization. With positively charged (amidine) latexes, the HTAB was added to the original latex suspension at a concentration of 0.02 M. The negatively charged (sulfate) particles can coagulate in the presence of positively charged surfactant, so in this case the latex layer was deposited first and then washed with HTAB solution for 20 min. In both cases, the excess unad-

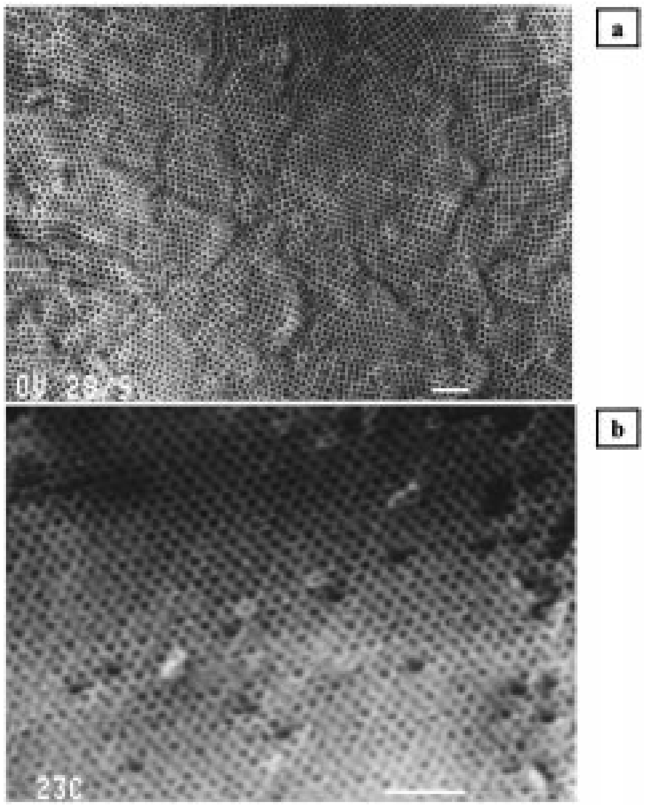

Figure 4. Micrographs of silica structures formed by using templates of 300 nm latex particles: (a) typical low-magnification picture of the silica surface and (b) expanded view of a domain with highly ordered pores. Figure 2c shows optical microscopy photographs of analogous samples, of which TGA calcination curves are presented in Figure 7. Scale bars = 1 μm.

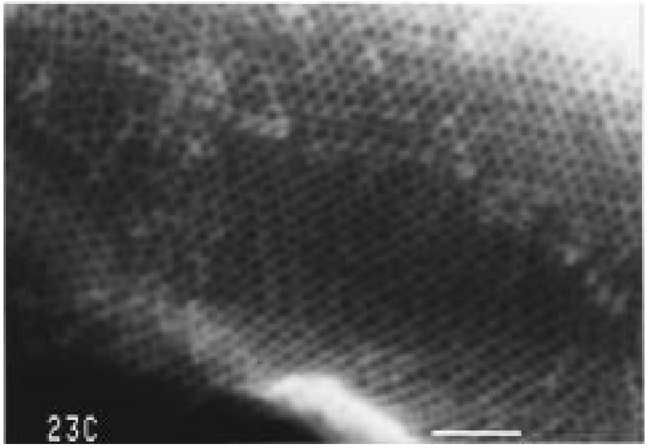

Figure 5. SEM micrograph of a silica flake obtained from 300 nm amidine latex. An edge runs from the upper left to the lower right corner of the picture and two cutoff planes are exposed: top, to the right of the edge, and front, to the left of the edge. Thus the ordered porous structure is exposed in a 3D view.

sorbed surfactant within the latex layers was removed by a brief (≈30 s) wash with deionized water.

Following the HTAB treatment, the cavities in the arrays were mineralized by infusing the latex-covered filter with a 0.5 M silica solution. It is likely that the silica polymerized from the latex surfaces toward the void spaces in the deposit. The rapid polymerization could be followed by the decreasing permeability of the layers. In most cases the flow through the filter stopped in less than 1 min. Once the silica solution gelled in the voids between the colloidal particles, the excess solution on top was removed and the latex/silica composite was dried under vacuum at 50 °C for 30 min. When flakes from the material obtained at this stage of the process were observed by optical microscopy, the original domains in the colloidal crystal template were still distinguishable, but there was a general shift and smearing of their colors due to the presence of the silica between the particles (Figure 2b). To assess the importance of the HTAB modification of the particles for the success of the procedure, a control experiment with particles that had not been treated with HTAB was performed (to avoid ambiguity, only negatively charged particles were used). In this case, the silica solution flow through the filter did not stop and the material obtained collapsed upon subsequent calcination, which provides a clear indication that the HTAB functionalization step is critical for obtaining the product.

The composite materials obtained were dried under vacuum and the latex templates inside the polymerized silica were removed by calcination at 450 °C for 4 h with an initial temperature increase of 1−1.5 °C/min. The final products from the calcination were off-white silica flakes of very low density. Investigation of the flakes by optical microscopy showed them to be highly porous, though the discrete structure of the material was below the resolution of the microscope (Figure 2c). The discrete morphology of the material could, however, be observed by SEM along cracks and abrasions on the surfaces of the flakes. Large 3D ordered arrays of spherical cavities that obviously represented a negative replica of the original colloidal crystal embedded in the silica were observed (Figure 4).

The images obtained by SEM are essentially a 2D scan on the surface of the porous flakes, and while it is intuitively clear that the whole volume of the materials should contain ordered pores, a microscopic confirmation of this hypothesis is required. This could be achieved by observation of the edges along the flake boundaries, where cuts into the flake interiors are exposed. One example of a micrograph taken along the edge of a broken flake is presented in Figure 5. The micrograph shows two faces of a hexagonal close-packed lattice of pores, one on the surface of the flake, and another across the broken edge. Such observations show that the volume of the silica flakes is built up of many domains with different crystal orientations, as of course is the case with the original latex crystals. Similarly to the latex crystals, while most of the domains on the surface display hexagonal symmetry of the ordered pores, a few square lattices could also be found (Figure 6).

A comparison between the repeat units of the silica replicas and the original latex crystals showed that the calcined materials had shrunken by 20−35%. This value is higher than, but comparable to, that in the M41S mesoporous silicas. To obtain additional information on the porosity of the material and the thermal aspects of its formation, thermogravimetric analysis (TGA) experiments on the calcination of the latex/silica composites were carried out. The results of two typical runs comparing the thermal decomposition of the latex−silica composite and of pure latex crystals are shown in Figure 7. Even after the vacuum-drying, the composite

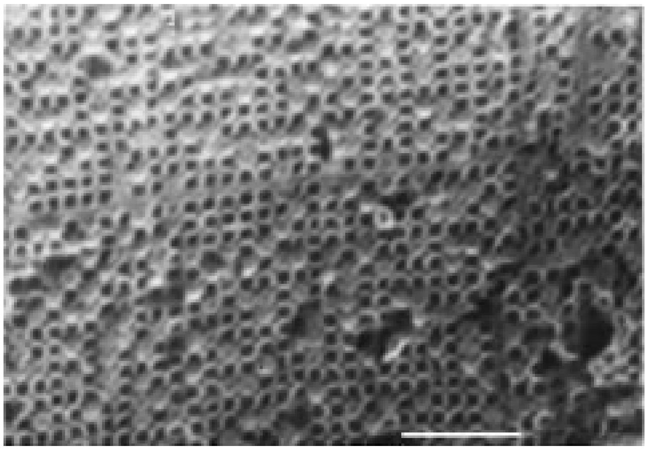

Figure 6. Large domain with cubic packing of the pores in a sample from 190 nm amidine latex.

contained some residual water, which started to evaporate above 100 °C and appears to have been completely lost at ≈160 °C. Therefore, the weight of that sample was normalized to 100% at 160 °C, where the only remaining components were the silica and the polystyrene in the microspheres. The silica-free latex crystal did not display any loss of water, which means that it had been completely dried in the vacuum oven. This is not surprising, bearing in mind its high porosity. Both samples started losing weight rapidly above 190 °C, presumably as a result of the thermal degradation and evaporation of the polystyrene in the microspheres. The latex-only sample lost weight more quickly and was totally decomposed and evaporated by 280 °C. By that temperature the latex−silica composite had lost approximately 61% of its normalized weight, and the additional loss from there on to the terminal temperature of 450 °C was less than 2%. The remaining weight of 37.5% may be attributed to the silica in the porous sample obtained, though in the nonoxidizing atmosphere of the TGA the presence of very minor amounts of residual carbon in the flakes (which appear slightly brownish) may be suspected.

An estimate of the porosity of the final material can be obtained from the simple formula

$$\epsilon = \frac{w_l/\rho_l}{w_s/\rho_s + w_l/\rho_l}$$

where ϵ is the porosity, w_l and w_s are the weights of latex and silica, respectively, in the sample, and ρ_l and ρ_s are their corresponding densities. Substituting the above TGA values and assuming a polystyrene latex density[20] of 1.06 and a density of the amorphous fused silica[21] of 2.20, one obtains an estimated porosity of 78 vol %. This value is close to that which may be expected for a material with close-packed ordered spherical pores[19] (≈74%). Bearing in mind the unpredictable effects of silica shrinkage, this agreement may be coincidental to a certain extent, but there is little doubt that the materials obtained are highly porous with the pore volume fraction close to the volume fraction of the original latex templates.

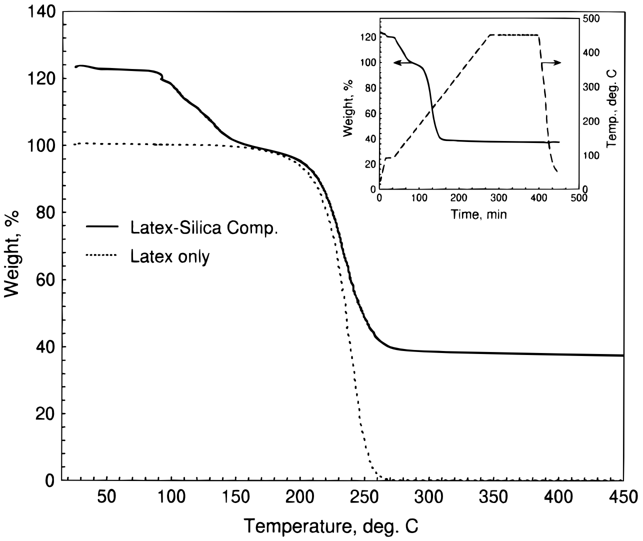

Figure 7. Thermogravimetric plot obtained during calcination of materials formed from 300 nm latex. The latex−silica composite sample is normalized to 100% after evaporation of the residual water. The inset shows the temperature cycle vs time.

One of the biggest advantages of the proposed method is the ability to control easily the dimensions of the pores obtained by varying the size of the latex beads in the templates. By using different suspensions of latex microspheres, we have been able to obtain organized materials with pore sizes ranging from ca. 150 nm to 1 μm. Examples of the materials prepared with the smallest and the biggest particles used are shown in Figure 8. The experimental limits in the case of the bigger particles were set by the long times it takes to assemble them into 3D arrays and the relatively low quality of the ordered domains. The limits in the case of the small particles were set by the size of the membrane pores, which have to be significantly lower than the particle diameter so that the pores do not interfere with the latex crystallization. It can easily be seen that these limits reflect the specific conditions in our experiment and are not physical constraints of the method. In particular, appropriate membranes of ultrafiltration type and higher pressures could conceivably allow the formation of porous silicas templated by particles as small as 10 nm in diameter. Thus, the method allows one to obtain silica with structured pores ranging from the characteristic sizes of the MCM-41 phases (ca. 10 nm) up to the micron level. The pores in these materials will typically be spherical, although this can potentially be modified by using templates from particles of different shapes.

Another feature of the method that contributes to its versatility is the in situ functionalization of the latex surfaces by cationic surfactant. Thus, almost any type of hydrophobic organic latex or similar particles could be used as templates (as we demonstrated by obtaining porous silicas from both positively and negatively charged latexes). Other studies on the templating of porous silica have relied on silica polymerization by addition of cationic surfactant (MCM-41 type) or sintering of silica gels. Both of these methods are usable in our case, and they can make the scheme simpler and

---

(20) *IDC Ultraclean Uniform Latex Microspheres (Product Guide)*; IDC: Portaland, OR, 1996.

(21) Iler, R. K. *The Chemistry of Silica*; Wiley-Interscience Publ.: New York, 1979; pp 15−29.

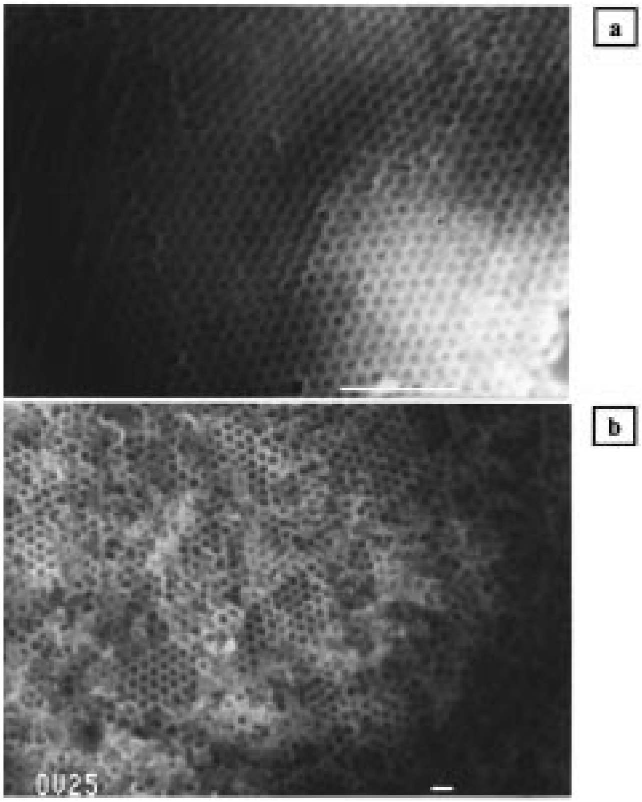

Figure 8. Examples of how the size of the pores can be tuned by changing the original latex suspension: (a) highly structured domain in sample obtained from 190 nm amidine latex and (b) porous silica obtained from 980 nm sulfate latex. Both scale bars correspond to 1 μm.

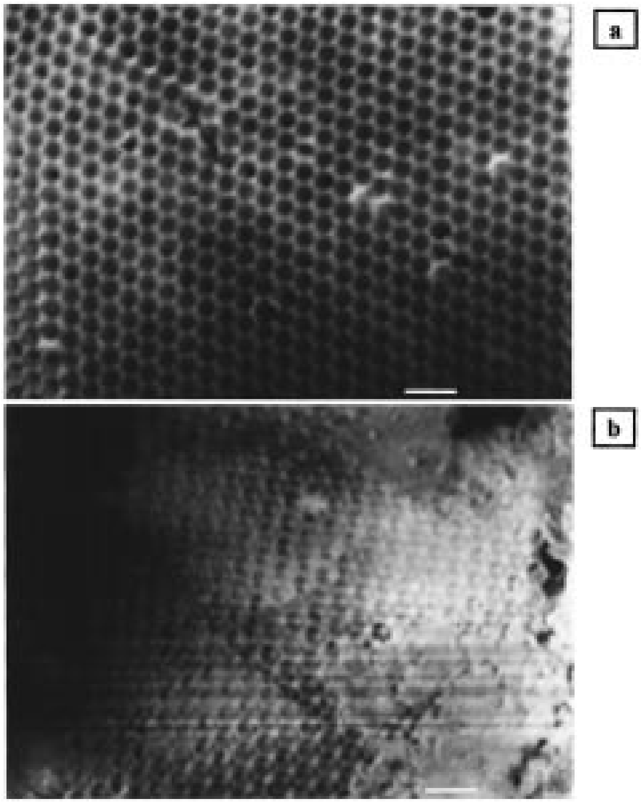

Figure 9. SEM of representative samples of microstructured silicas prepared with a 560 nm amidine latex. (a) A field in a sample with slowly assembled template reveals excellent long-range order and uniformity of the pores. (b) Sample from an aged and weakly polymerized silica solution. A delicate, lacelike 3D structure is observed due to the collapse of the walls between the cavities. Scale bars = 1 μm.

lead to materials with combinations of small and large pores. The surface functionalization scheme used has, however, proven that it is possible to obtain materials with pores templated solely by the particles in the colloidal crystals, and they thus have the simplest and most highly symmetric structure.

A unique feature of the materials obtained that can eventually make them usable in high-technology applications is the long-range ordering of the uniformly sized pores. In the cases of 200−500 nm particles, we have observed ordered domains of almost perfect hexagonal or square lattices including more than 10^3 pores of identical size in the first visible layer. An example of such a domain is presented in Figure 9a. Moreover, while control of the porosity has not been a target of our investigation at this stage, we were able to obtain a sample prepared from a silica solution that had been aged for a few weeks and polymerized more slowly and weakly than in the typical case. The material obtained shows a continuous lacelike structure, possibly as a result of the collapse of the walls between the cavities of the individual latex particles (Figure 9b). Both the materials with the spherical and those with the lacelike cavities could have interesting properties in transmitting, scattering, or absorbing light and other electromagnetic radiation, which arise from the cooperative effect of the ordered cavities.

A reasonable and pragmatic approach for the next steps should concentrate primarily on adapting the method to the formation of samples that are larger in volume and better ordered. Recent developments in template-directed colloidal crystallization demonstrate the possibility of assembling large, single-domain 3D crystals with controlled symmetry and orientation.[13] There are no obvious obstacles to using the techniques described here to replicate such crystals into highly ordered porous silicas. New materials can be created by using as templates particles of different type and morphology or using crystal mineralization by other metal oxide compositions instead of silica (e.g. TiO_2, Nb_2O_3). Interesting possibilities could be found by reverse templating or introducing catalyst metal particles inside the ordered cavities via the latex template.

Concluding Remarks

We believe this work to be the first to demonstrate the possibility of obtaining highly structured silica materials of which the pore size, shape, and ordering can be precisely controlled in a nanometer to micrometer wide region that has been previously unattainable. The scheme is based on assembling latex particles into a 3D colloidal crystal, which is functionalized with surfactants and used as a template for silica polymerization. The method appears powerful, yet inexpensive and controllable, and could be adapted for large-scale production. The future development of the method holds promise for the formation of advanced new materials with unique properties, which can find application in catalysis, separations, coatings, microelectronics, and electrooptics.

CM980444I