

Fabrication of two-dimensionally ordered macroporous silica materials with controllable dimensions

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The formation of 2-D arrays of cavities of varying size and depth on an electrode surface via colloidal templating is described.

Porous materials have many uses in chemistry and material science. They can be used as catalytic surfaces and supports, chromatographic stationary phases, adsorbents, chemical sensors, and nanosized reactors.^{1–6} One promising approach to the formation of “spatially ordered” porous materials involves the use of templates.⁷ For example, the M41S series of materials with channel diameters that range from *ca.* 20 to 100 Å and packed in a hexagonal or cubic array are prepared using surfactant liquid crystals as the template directing agents.^{8–9} For larger diameter cavities, colloidal crystals can be prepared using latex spheres ranging in size from *ca.* 50–1000 nm as the templating agent.^{10–12} Upon removal of the template, voids of a predefined size remain in the host material.

Of utmost importance to many applications, particularly those in the areas of chemical sensing and catalysis, is the need to form thin films with an ordered array of cavities of controllable size that provides direct access to the underlying surface. Mesoporous silica films containing ordered channels can be prepared by spin casting or dip coating the surfactant doped sol on a suitable surface.^{13–15} In most cases, however, the channels run parallel to the substrate thereby restricting its use in chemical sensor applications.^{13–15} The use of colloidal particles that can be packed into a 2- or 3-D array *via* dip coating, spin coating, or Langmuir–Blodgett techniques appears to have the most promise in this regard.^{16–22} In these investigations, multilayers have been created with the goal of developing “photonic band gap” materials.^{1,18–22} A 2-D monolayer array of spheres has also been used in “nanoscale lithography” whereby metal is deposited between the spheres to create a regular array of triangular-shaped metallic structures.^{1,16–17} In the present work, we describe how these colloidal crystal arrays can be used to create a closely spaced array of nanometer sized “channels” or “cavities” in a dense silica film cast on a conducting surface. Furthermore we show the size and depth of the cavities can easily be tuned by judiciously choosing the sol–gel processing conditions. The advantage of using a conducting surface to deposit these materials on is that these channels can be used as nanosized reaction vessels for electrochemical deposition, in electrochemical sensing, or catalysis applications since a small fraction of the underlying electrode is exposed.

Polystyrene latex spheres (PS, 0.5 µm, 8%, sulfated, IDC) were added in a 1:1 volume ratio to a silica sol prepared by the sol–gel process. The sol was prepared by mixing tetramethoxysilane (TMOS), methanol, water, and HCl. Prior to the addition of the latex spheres, 5 mM sodium dodecylsulfate (SDS) was added to improve the wettability of the sol so that it can better coat the glassy carbon substrate used in this work. The PS-doped silica sol was then spin coated on a polished glassy carbon electrode surface at *ca.* 3000 rpm. After the film was dried, the latex spheres were removed from the silica film by soaking in chloroform for two-three hours. AFM images, unless otherwise noted, were acquired with a Digital Instruments Nanoscope IIIa in the contact mode at scan rate between 1 and 6 Hz.

Fig. 1A shows an AFM image of PS doped silicate film on a glassy carbon substrate. The sol in this case was prepared using a mole ratio of 1:6:9:0.003 TMOS:MeOH:Water:HCl. As can be

seen a two dimensional array of 500 nm diameter PS latex spheres is formed. The formation of a closely packed array of particles in the dense silica matrix is clearly much better than the randomly dispersing spheres across a surface as reported on in our lab^{23–24} because it maximizes the porosity that can be obtained once the particles are removed.²⁵ Since glassy carbon is not atomically smooth, there are areas where there is an abrupt change in the continuity of the spheres as well as small gaps in the array. The number of defects in the arrays depends on the glassy carbon substrate due to the presence of pits and scratches on the surface. Defect-free domain sizes typically range from 25–100 µm² depending on smoothness of the substrate.

The latex spheres can be removed from the film by soaking it in chloroform. Fig. 2A,B shows 2-D AFM images of the resultant cavities in the film. A line scan image of two cavities acquired in the tapping mode with a high aspect ratio tip is also shown in Fig. 2. The center-to-center distance between the cavities is *ca.* 500 nm, the top diameter is *ca.* 200–220 nm, and the depth of cavities are *ca.* 350–400 nm. It is apparent in this case that under these conditions, the latex spheres were embedded in the film so that only the top $\frac{1}{4}$ of the surface was exposed. A large deep cavity results after template removal. The cavities are open at the top as well as the bottom as evident from the AFM images, which show a plateau, and from the fact that copper can be electrochemically deposited in the cavities *via* electrodeposition from a copper solution.²⁴

Both the depth of the cavity as well as its diameter can be easily tailored by judiciously choosing the sol–gel processing conditions. A “diluted” sol will give rise to a thinner film thus exposing a larger fraction of the embedded sphere. Fig. 3A,B shows AFM images of a 2-D arrangement of cavities embedded in a film prepared from a silica sol that has a Si:H₂O ratio of *ca.* 1:100. At first glance, it may appear the cavities are further apart compared to those shown in Fig. 2. The center-to-center distance is still 500 nm, but now the

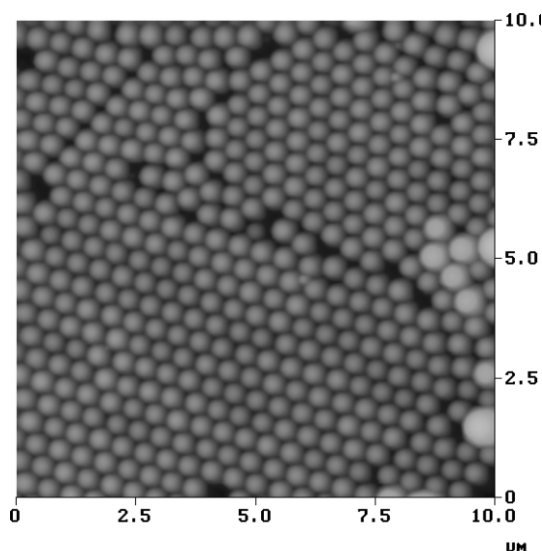


Fig. 1 AFM image of 500 nm diameter latex spheres embedded in a silica film prepared by the sol–gel process (Si:H₂O ratio of 1:9). The full gray scale image is 750 nm.

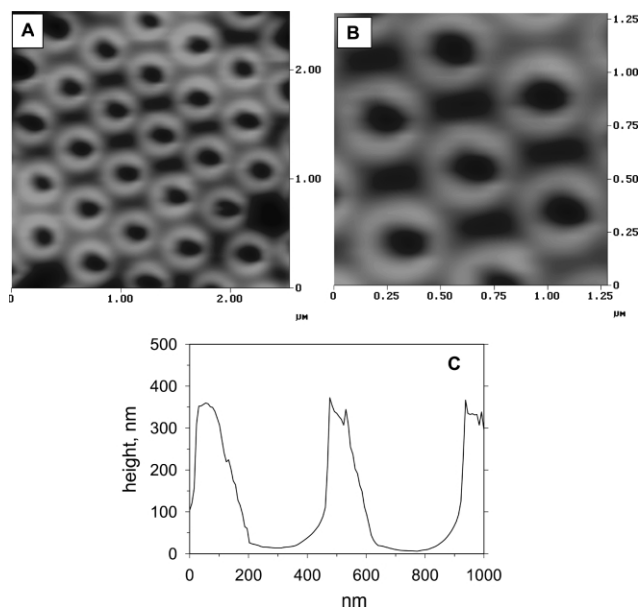


Fig. 2 AFM images of cavities formed in a silica film after template removal. Panel A: $2.5 \times 2.5 \mu\text{m}$ image. Panel B: $1.25 \times 1.25 \mu\text{m}$ expanded view. The full gray scale images are 400 nm . Panel C: Line scan of two cavities. The silica sol had a Si:H₂O mole ratio of 1:9.

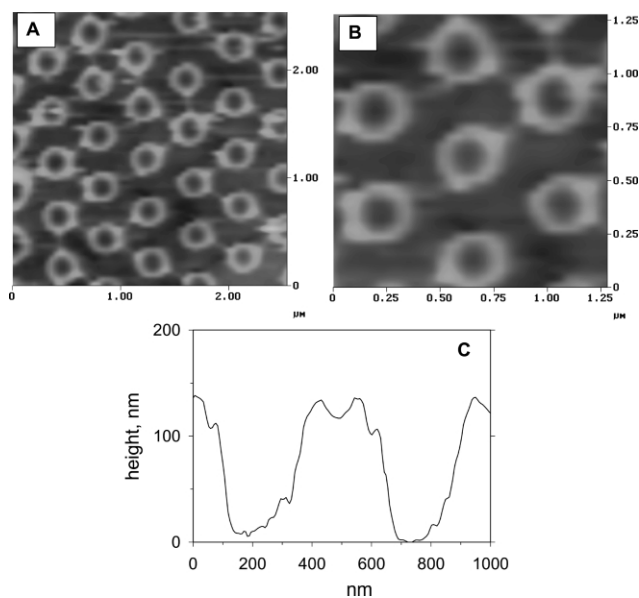


Fig. 3 AFM images of cavities formed in a silica film after template removal. Panel A: $2.5 \times 2.5 \mu\text{m}$ image. Panel B: $1.25 \times 1.25 \mu\text{m}$ expanded view. The full gray scale images are 200 nm . Panel C: Line scan of two cavities. The silica sol had a Si:H₂O mole ratio of 1:100.

diameter is *ca.* 240–260 nm and the depth is *ca.* 120–140 nm. As evident from the line scan image (Fig. 3C), the latex spheres were embedded in the film so that the top $\frac{2}{3}$ of the sphere is exposed (in contrast to only $\frac{1}{3}$ noted above). The sol composition can be tweaked even further to create larger diameter cavities in the dense silica film. A sol prepared with a Si:H₂O ratio of 1:33 gives rise to cavities with a diameter of 370–400 nm and which are 320–340 nm deep. In this case, about $\frac{2}{3}$ of the sphere is embedded in the silica film.

Using a diluted sol, spheres with diameters smaller than 100 nm can be used as templates thus creating even smaller cavities. In previous work, we were unable to do this.²⁴

In summary, we have described a very simple procedure for the fabrication of porous thin films that contain an ordered arrangement of cavities of varying depth and diameter. Because the cavities are open at the top and bottom, a species in solution will have direct access to the underlying surface as well as to any receptor that maybe entrapped within the silica framework and exposed upon template removal. These materials have potential uses as chemical sensors, catalyst supports, “nano-sized” electrochemical reactors, and as templates to grow nanostructures within the cavities. Tuning the depth and diameter of the cavities allows for the surface area and porosity of the film to be varied for sensor and catalysis applications and it provides a means to control the dimensions and placement of nanostructures electrochemically deposited within the cavities. Future work is being directed in this manner.

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Notes and references

- 1 Y. Xia, B. Gates, Y. Yin and Y. Lu, *Adv. Mater.*, 2000, **12**, 693.
- 2 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.
- 3 T. J. Barton, L. M. Bull, W. G. Klemperer, D. A. Loy, B. McEnaney, M. Misono, P. A. Monson, G. Pez, G. W. Scherer, J. C. Vartuli and O. M. Yaghi, *Chem. Mater.*, 1999, **11**, 2633.
- 4 K. Moller and T. Bein, *Chem. Mater.*, 1998, **10**, 2950.
- 5 G. A. Ozin, A. Kuperman and A. Stein, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 359.
- 6 M. M. Collinson, in *Handbook of Advanced Electronic and Photonic Materials, and Devices*, Ed. H. S. Nalwa, **Vol 5**, Academic Press, 2001, 163.
- 7 N. K. Raman, M. T. Anderson and C. J. Brinker, *Chem. Mater.*, 1996, **8**, 1682.
- 8 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- 9 J. Y. Ying, C. P. Mehnert and M. S. Wong, *Angew. Chem. Int. Ed.*, 1999, **38**, 56.
- 10 O. D. Velev, T. A. Jede, R. F. Lobo and A. M. Lenhoff, *Nature*, 1997, **389**, 447.
- 11 B. T. Holland, C. F. Blanford and A. Stein, *Science*, 1998, **281**, 538.
- 12 O. D. Velev and E. W. Kaler, *Adv. Mater.*, 2000, **12**, 531.
- 13 M. Ogawa, *Supramol. Sci.*, 1998, **5**, 247.
- 14 D. Zhao, P. Yang, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Commun.*, 1998, 2499.
- 15 N. Nishiyama, S. Tanaka, Y. Egashira, Y. Oku and K. Ueyama, *Chem. Mater.*, 2002, **14**, 4229.
- 16 F. Burmeister, C. Schafle, B. Keilhofer, C. Bechinger, J. Boneberg and P. Leiderer, *Adv. Mater.*, 1998, **10**, 495.
- 17 J. C. Hulthen and R. P. Van Duyne, *J. Vac. Sci. Technol. A*, 1995, **13**, 1553.
- 18 Z.-Z. Gu, A. Fujishima and O. Sato, *Chem. Mater.*, 2002, **14**, 760.
- 19 P. Jiang, J. F. Bertone, K. S. Hwang and V. L. Colvin, *Chem. Mater.*, 1999, **11**, 2132–2140.
- 20 W. Wang, B. Gu, L. Liang and W. Hamilton, *J. Phys. Chem. B*, 2003, **107**, 3400.
- 21 S. Reculusa and S. Ravaine, *Chem. Mater.*, 2003, **15**, 598.
- 22 S. H. Im, M. H. Kim and O. O. Park, *Chem. Mater.*, 2003, **15**, 1797.
- 23 A. N. Khramov and M. M. Collinson, *Chem. Commun.*, 2001, 767.
- 24 A. N. Khramov, J. Munos and M. M. Collinson, *Langmuir*, 2001, **17**, 8112–8117.
- 25 The addition of SDS in a relatively high concentration in this work improved the “wettability” of the sol allowing it to better stick to the glassy carbon surface.