Packings of Uniform Microspheres with Ordered Macropores Fabricated by Double Templating

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Self-assembly approaches for making three-dimensional photonic crystals have been demonstrated by a number of research groups recently.1–6 Ordered macroporous structures, which have been fabricated by templating closed-packed colloidal crystals of polymer latexes, silica spheres, and emulsion droplets, are of practical significance for making optical materials with photonic band gaps. Recently, forming such macroporous materials into different shapes and sizes has attracted a great deal of interest because regularly shaped particles with controlled pore sizes are useful in a variety of applications such as size-exclusion chromatography (separations), catalysis, and absorption.7 Furthermore, controlling the size and shape of photonic crystals at micrometer length scales enables their use as building blocks for novel photonic crystals or as model systems for light scattering and efficient light diffusion. Previous work on controlling the shape of colloidal crystals and their inverse structures has succeeded in forming only relatively large millimeter-size crystal structures created from large droplets of colloidal suspensions8 or smaller micron-size structures but with very broad size distributions. A remaining challenge is to control the size of self-assembling colloidal materials at micrometer length scales.

Here, we report a fabrication method for making an array of uniform micron-sized ceramic spheres with ordered macropores having pore diameters comparable to optical wavelengths. Henceforth, each sphere of these well-defined structured materials will be referred to as “photonic balls” because of their unique photonic properties resulting from the ordered spherical voids embedded inside of the spherical shapes. Our synthetic route for making the photonic ball arrays is a two-step template-assisted fabrication process, illustrated in Scheme 1. To begin, micron-sized silica spheres are assembled into a closed-packed colloidal crystalline array and then encapsulated by polymerizing some convenient polymer in the interstices. The silica spheres are then removed by selective chemical etching leaving behind micron-sized air cavities. Next, polymer latex spheres are injected into the spherical cavities inside the polymer matrix. The polymeric spheres assemble within the voids to form an ordered closed-packed structure. Finally, an inorganic precursor is infiltrated into the interstices between the latex spheres and gelled to capture the ordered structure. Thermal decomposition of all of the organic material produces the inorganic photonic balls. Similar procedures, called “double templating”, have been applied for the synthesis of structured materials of nanoscopic feature sizes.

Colvin’s group produced solid and hollow titania colloidal crystals by a two-step replication method9 that was developed by

Mallouk et al.9 Recently, Ozin et al.10 have used this method to obtain monodisperse mesoporous spheres by filling the voids with silicatropic liquid crystals.

A key feature of our polymer template is that the macropores are interconnected with windows large enough for small polystyrene latex particles of about 500 nm in diameter to pass through. The wide windows with a uniform opening between large pores are created by using a highly viscous polymeric precursor solution to infiltrate the silica colloidal crystalline array in the first templating process. Sintering of silica colloidal crystals has been reported as an alternative way to produce large pores, but such crystals tend to crack, producing line defects in the resulting template.

Figure 1 shows scanning electron micrographs of polymeric microstructures that were fabricated by templating silica colloidal crystals. Five-micrometer silica particles of 10 wt %, which were purchased from Bangs laboratories, Inc., were crystallized by slow evaporation in a Hele-Shaw cell with 60-μm spacing by polyimide film (Kapton), which was purchased from Dupont (see Figure 1c). Subsequently, a UV-curable precursor for polyurethane (NOA60, Norland Products, New Brunswick, NJ) or poly(acrylate-methacrylate) copolymer (PAMC, Summer Optical, Fort Washington, PA) was infiltrated into the interstices between the silica colloidal spheres. Extraction of the silica spheres using 10% hydrofluoric acid for 8 h left behind windows about 1 μm in diameter, which is almost consistent with the quarter-window-size law in previous work.11 CAUTION: Hydrofluoric acid (HF) is extremely corrosive and should be handled with care. The window size can be controlled by changing the viscosity of prepolymer as reported by Colvin’s group.5 In general, the equilibrium infiltration of a liquid into a microcapillary is proportional to surface tension and the reciprocal capillary diameter. For unsteady capillary infiltration, however, the
viscosity of infiltrated liquid is known to be the dominant factor
determining the capillary rise.

Concentrated aqueous suspensions of polystyrene spheres of 500
nm in diameter were synthesized by emulsifier-free emulsion
polymerization by a method outlined in the literature12 and were
infiltrated into the macropores of the polymer skeleton under
agitation by applying pulsed sonic energy at 42 kHz for about 40
min in an ultrasonic bath (Bransonic 2510). It is noteworthy that
the high concentration of polystyrene suspension above 20 wt %
was good enough for complete and fast filling inside macropores.

Figure 2a shows several millimeter-sized polymer skeletons filled
with small latex particles. Meanwhile, standard self-assembling
methods of centrifugation or evaporation failed to fill the large pores
in the polymer matrix with small particles. Instead, most of the
particles stacked outside the macroporous polymer matrix with only
a small quantity of the particles entering the interior. In some cases,
water-soluble surfactants were added to prevent irreversible adsorp-
tion of latex particles onto the polymeric wall. After the large pores
were filled with polymer particles and the remaining water was
dried out, the metal alkoxide precursor for silica or titania was
infiltrated into the interstices formed between the latex particles
(see Figure 2b), after which the organic polymer matrix and latex
particles were burned out at 500 °C in air for 3 h, in which the
ramp rate was 2 °C/min. Figure 2c shows that photonic balls with
ordered spherical macropores were successfully produced. The
size distribution of the photonic balls is determined by the size of
the silica particles that were used in the original templating process.

The inset of Figure 2c shows that the internal structure of each
photonic ball is highly ordered.

The significance of the present report is three-fold. First, this
novel process produces highly uniform 3-D ordered macroporous
sphere arrays by an extension of a double templating process
previously reported by several groups. These structured materials
could open up significant opportunities in a variety of areas ranging
from absorbent to novel photonic crystals. Second, changing the
matrix to non-cross-linked polymer would enable us to create
isolated photonic balls, which might be useful for model colloids
in light scattering. Third, by skipping the second templating process,
3-D colloidal assemblies can be produced by this process. If the
polymer latex spheres in the second step templating were replaced
by silica particles, burning out the polymer network would produce
uniform-sized 3-D colloidal assemblies of silica spheres.

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References
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Figure 1. Ordered macroporous templates of polyurethane (a) and PAMC
(b), which were prepared by using silica colloidal crystals as templates
formed in a Hele-Shaw cell (c). (Scale bars are 1 μm.)

Figure 2. Scanning electron micrographs show (a) shaped colloidal crystals
in polyurethane skeleton, (b) composite of shaped colloidal crystals and
infiltrated titanium alkoxide precursor solution, and (c) ordered macroporous
titanium spheres by burning out the organic polymer phase of the previous
composite. (Scale bars are 1 μm.)