Synthesis and Characterization of Mesoscopic Hollow Spheres of Ceramic Materials with Functionalized Interior Surfaces

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This paper describes a method based on template-directed synthesis for generating ceramic hollow spheres whose *interior* surfaces could be functionalized with the prespecified, nanoscopic objects. The templates involved in this process were crystalline lattices of monodispersed polymer beads whose surfaces had been derivatized with functional objects such as nanoparticles, quantum dots, or other nanoscale objects. These nanoscopic objects were left behind on the interior surfaces of the hollow spheres when the templates were selectively removed through etching or calcination.

Mesoscopic hollow spheres are useful in a variety of areas.[1] For example, they can serve as extremely small containers for encapsulation—a process that is actively explored for applications in catalysis, delivery of drugs, development of artificial cells, or protection of biologically active agents (such as proteins, enzymes, or DNAs). When used as fillers, pigments, or coatings, hollow spheres may also provide some immediate advantages over their solid counterparts because of their relatively low densities.[2] Ceramic hollow spheres are often prepared by templating against colloidal particles.[2] In a typical procedure, the template is coated with a thin layer of the ceramic material (or a precursor to this material) to form a core−shell structure, and subsequent removal of the template (via selective etching with a solvent or calcination in air) will lead to the formation of ceramic hollow spheres whose inner diameter is solely determined by the dimensions of the template. Although a variety of colloids (such as nanoscopic colloids of gold, silver, or CdS and mesoscopic beads of silica or polymers) have been successfully demonstrated as the templates,[3−5] very little attention has been directed toward the functionalization of the interior surfaces of the hollow spheres. Once formed, it will be very difficult to selectively modify the properties of the interior surfaces of these hollow spheres. Here, we wish to report a practical method that allows for the generation of ceramic hollow spheres with a well-defined void size, a homogeneous, tightly controlled wall thickness, and most importantly, an interior surface derivatized with the prespecified functionality. Although polymer beads have been successfully used as the template to generate hollow spheres of titania with a uniform wall thickness,[6] it was not clear whether polymer beads coated with nanoparticles were still able to serve as effective templates (because these immobilized nanoparticles inevitably increase the roughness of the polymer beads and may also greatly alter the repulsive interactions among them).

Figure 1 outlines the schematic procedure, where four polystyrene (PS) beads have been used to illustrate the templating process.[6,7] After the outer surfaces of these PS beads had been coated with submonolayers of nanoparticles (<50 nm in size),[8] they were assembled into a three-dimensional crystalline lattice between two glass substrates using our previously published procedure.[9] The packing cell was then infiltrated with a sol−

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(1) See, for example, (a) *Hollow and Solid Spheres and Microspheres: Science and Technology Associated with their Fabrication and Application*; Wilcox, Sr., D. L., Berg, M., Bernat, T., Kelleman, D., Cochran, J. K., Jr., Eds.; MRS Proceedings Vol. 372; Materials Research Society: Pittsburgh, PA, 1994. (b) Mathlowitz, E.; Jacob, J. S.; Jong, Y. S.; Carino G. P.; Chickering D. E.; Chaturvedl, P.; Santos, C. A.; Vijayaraghavan, K.; Montgomery, S.; Bassett, M.; Morrell, C. *Nature* **1997**, *386*, 410−414. (c) Huang, H.; Remsen, E. E. *J. Am. Chem. Soc.* **1999**, *121*, 3805−3806. (d) Mandal, T. K.; Fleming, M. S.; Walt, D. R. *Chem. Mater.* **2000**, *12*, 3481.

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(7) All chemicals were used as received. The titanium(IV) isopropoxide (97%) was obtained from Aldrich. We only used monodispersed PS beads obtained from Polysciences (Warrington, PA). The surfaces of these beads contained a relatively low density of anionic charge groups (resulting from the persulfate initiator) and are claimed to be surfactant free by the vendor. Prior to use, these aqueous dispersions of PS beads were diluted to ~0.5% (wt) with deionized water. The packing cell was constructed from two glass substrates and a square frame of photoresist or Mylar film (10−70 μm in thickness) and tightened with binder clips. One side of the square frame had channels that were able to retain the PS beads while letting the solvent flow through. After the water was completely evaporated by drying the sample in air for several days, the cell was placed in a glovebox (filled with N_2) and subsequently infiltrated with the sol−gel precursor solution. When the cell was removed from the glovebox, the sol−gel precursor hydrolyzed into the oxide ceramics as a result of its exposure to the moisture in air. While the top substrate was still on, the cell was immersed in toluene to dissolve the PS beads. These hollow spheres were released from the glass substrate by sonicating the sample in a water bath.

(8) A commercial kit (HE-300, Peacock Laboratories, PA) that is commonly used for electroless deposition of silver films was employed to produce silver nanoparticles in the form of a decorative coating on the surface of polystyrene beads. Before coating, a sensitizing solution (Peacock No. 93) was used to thoroughly activate the surface of polystyrene beads. For a detailed procedure, please see: Xia, Y.; Venkateswaran, S.; Qin, D.; Tien, J.; Whitesides, G. M. *Langmuir* **1998**, *14*, 363−371.

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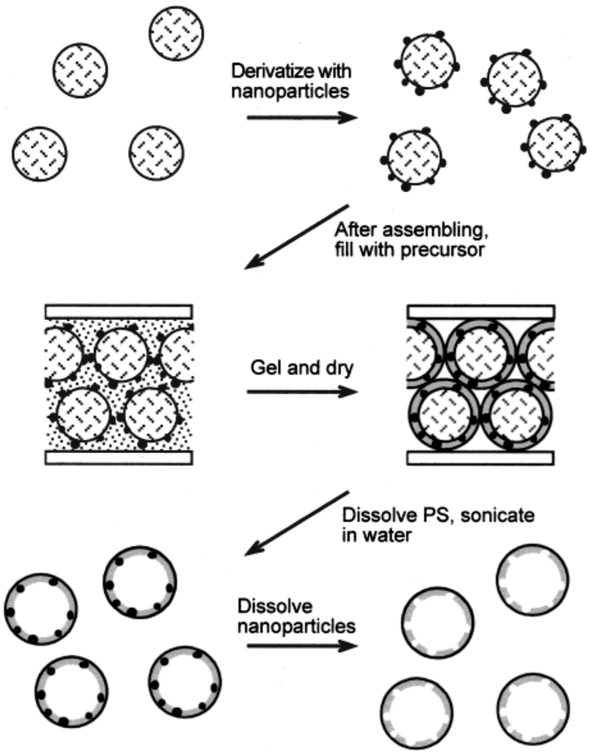

Figure 1. Schematic outline of the experimental procedure. The polymer template could be either dissolved with a solvent or burnt out through calcination at elevated temperatures.

gel precursor solution—titanium (IV) isopropoxide in 2-propanol[10]—to coat the surface of each bead with a homogeneous, thin layer of amorphous titania.[6] After the PS beads had been dissolved in toluene, uniform hollow spheres were generated, with their interior surfaces being functionalized with the nanoparticles that were originally coated on the PS beads. If desired, these nanoparticles could be selectively removed with another wet etchant to leave behind an array of nanometer-sized cavities on the interior surface of each hollow sphere. These nanoscale cavities may have a functionality similar to that of the nanoscale template, as has been demonstrated in the area of molecular imprinting.[11] In this process, the void size of the hollow spheres was mainly determined by the diameter of the polymer beads, the thickness of their ceramic walls was controlled by the concentration of the sol−gel precursor solution, and the functionality of their interior surfaces was defined by the nanoparticles precoated on the surfaces of the template beads.

Figure 2A shows the transmission electron microscopy (TEM) image of a few polymer beads whose surfaces were homogeneously coated with submonolayers of silver nanoparticles (10−20 nm) using an electroless deposition procedure.[8] The silver nanoparticles were only visible at the edge of each polymer bead because these PS beads were too large (~1 μm in diameter) to be penetrated by the electron beam. Figure 2B shows the TEM image of two hollow spheres of titania that were produced by templating the sol−gel solution (1:19 in volume) against a crystalline lattice of the silver-coated PS beads. Because the PS beads had been dissolved in toluene, the silver nanoparticles left behind on the interior surface of each hollow sphere could now be clearly observed under a TEM. The titania wall of these hollow spheres was approximately 50 nm in thickness, as measured from this TEM image. This TEM image also indicates that the adjacent hollow spheres had not been fused together at their boundary; they were simply in touch physically. Figure 2C shows a blowup TEM image of the edge of a hollow titania sphere that was obtained by templating against a 380-nm PS bead coated with 20-nm silver nanoparticles. The wall thickness was ~30 nm. This TEM image indicates that all silver nanoparticles had been confined to the interior of this hollow sphere, as schematically illustrated in Figure 1. Figure 2D shows the electron diffraction pattern obtained by focusing the beam spot on an individual hollow sphere. Because all these diffraction peaks could be attributed to the silver, the titania wall was essentially amorphous in nature. In all of these SEM and TEM studies, the hollow spheres were redeposited onto a silicon substrate or a TEM grid after they had been released from the original glass slides through sonication.[6] Obviously, the hollow spheres described here were rigid enough to maintain a spherical shape without collapsing into other irregular objects during the entire templating and post-treatment process.

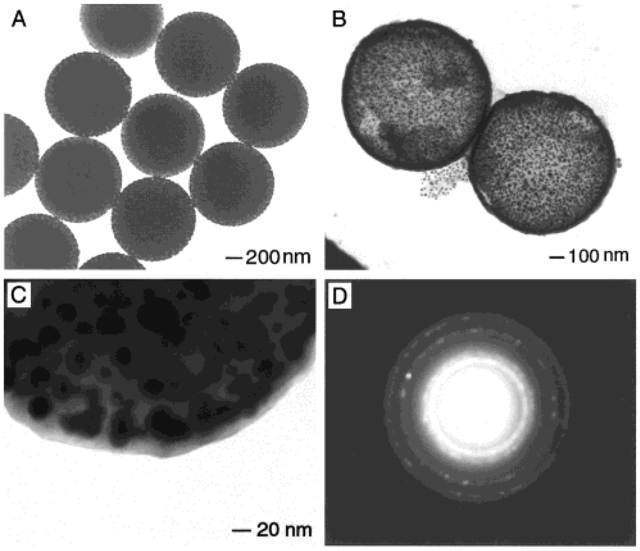

Figure 2. (A) TEM image of a number of 1-μm PS beads whose surfaces have been derivatized with nanoparticles of crystalline silver (~20 nm in size). (B) The TEM image of two hollow spheres of amorphous TiO_2 whose interior surfaces are functionalized with the silver nanoparticles. These hollow spheres were released form the original support and redeposited onto the TEM grid from an aqueous solution. The thickness of the ceramic wall was ~50 nm. (C) A blowup TEM image of the edge of one titania hollow sphere (~380 nm in diameter, the thickness of the wall was ~30 nm). This image indicates that all silver nanoparticles had been confined to the interior of this hollow sphere, as has been illustrated in Figure 1. (D) Electron diffraction pattern obtained by focusing the e-beam on an individual hollow sphere. All of these diffraction rings could be assigned to the silver, suggesting that the ceramic wall was amorphous.

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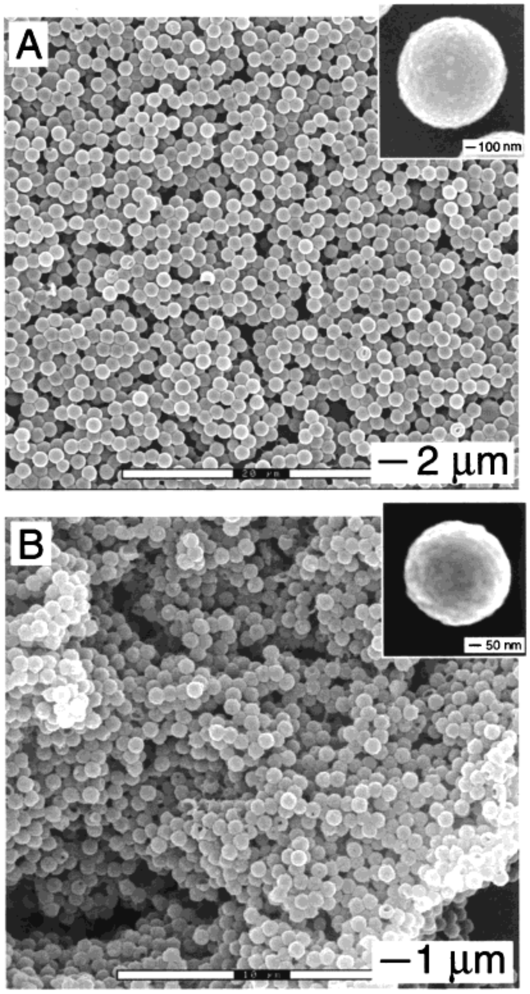

Figure 3. SEM images of some as-synthesized hollow spheres of titania that were generated by templating the sol−gel precursor solution against a crystalline array of (A) 1-μm and (B) 0.38-μm PS beads whose surfaces had been prederivatized with nanoparticles of silver. In these two samples, the percentages of broken hollow spheres were <5%. The thickness of the ceramic wall for these two samples was ∼50 and ∼30 nm.

Figure 3 shows SEM images of some titania hollow spheres (1.0 and 0.38 μm in diameter, respectively) whose interior surfaces had been derivatized with 20-nm silver nanoparticles. These images illustrate the copiousness in quantity, the uniformity in size distribution, and the smoothness of their surfaces that we could routinely achieve for these functionalized hollow spheres using the present procedure. As we have demonstrated previously,[6] the wall thickness of these hollow spheres depended on a number of parameters, such as the diameter of the polymer beads, the strength of the repulsive interactions between these PS beads in their crystalline arrays, and the concentration of the sol−gel precursor solution. When samples are prepared from the same batch of polymer beads, and in packing cells with the same thickness, the thickness of the ceramic wall should only be determined by the concentration of the sol−gel precursor solution. As a result, we have been able to control the wall thickness of these hollow spheres between 30 and 200 nm by changing the concentration of the sol−gel solution.[12] We believe we can also easily extend this procedure to many other systems having different combinations of functional nanoparticles (for example, magnetic nanoparticles and quantum dots) and wall materials (such as tin dioxide).

In summary, we have demonstrated a general route to mesoscopic hollow spheres of ceramic materials. The void size of these hollow spheres could be easily varied by changing the diameter of the polymer beads, the thickness of their walls could be tightly controlled by using sol−gel precursor solutions with different concentrations, and their interior surfaces could be functionalized with many prespecified properties. Although we have only demonstrated this procedure with 0.5- and 1-μm PS beads as examples, we believe that this method should be extendible to PS beads (or other templates) with smaller dimensions and to a range of other materials. The only requirement seems to be that a precursor solution is available that can completely wet the surface of the template and thus form a uniform coating around the template particle before the solvent evaporates. This procedure can also be extended to include nanoscale catalysts as the template that would be able to control the reactions or processes occurring inside these hollow spheres.[13] In this case, the immobilization of catalysts on the interior surfaces (rather than the exterior) of the hollow spheres should be able to facilitate these processes by eliminating the diffusion of species through the wall of each hollow sphere. This is going to be particularly significant when the material to be encapsulated in the hollow spheres is a high-molecular-weight polymer whose diffusion through the ceramic wall should be much slower than that of the low-molecular-weight monomer.

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(12) For 1.0-μm PS templates, the wall thickness was 50, 120, and 170 nm, respectively, when the volume of precursor relative to 2-propanol was 1:29, 1:19, and 1:4. For 0.38-μm PS templates, the wall thickness was 30, 60, and 100 nm when the volume of precursor relative to 2-propanol was 1:29, 1:19, and 1:9, respectively.

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