Aerosol-assisted Fabrication of Porous Silica Spheres with a Hierarchical Pore System through Multicomponent Assembly

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Hierarchical porous silica spheres with a trimodal pore system are prepared through multicomponent assembly, which is a facile one-pot fabrication and can best be employed for industrial mass-scale production.

The field of nanoarchitectured porous materials has expanded tremendously.[1] Both uniform-sized pores and high-surface areas are of great interest over a wide range of applications such as catalysts, catalyst supports, absorbents, and chromatography. Recently, hierarchical porous structures containing interconnected macropores as well as meso- and micropores have attracted great interest owing to the further enhancement of their material properties compared with porous materials containing single-sized pores.[2–8] The hierarchical pore systems should contribute to increased mass transport through the macropores. The presence of tuned meso- and micropores in the macropore walls can provide higher specific surface areas, yielding higher performance and better control of selectivities. Most previous procedures have consisted of two steps: the formation of closely packed colloidal crystals followed by the penetration of surfactant-based sol–gel solutions. In some cases, the use of specialized surfactants (such as KLE and amphiphilic ionic liquid) is needed.[6,7] Though one-step procedures have also been reported, the fine control of the surface environments of the colloidal spheres is needed.[8] In addition, the above strategies do not necessarily result in the desired multimodal pore-size distribution because of a formation of amorphous silica region[4,5] and/or a lack of interconnectivity among the poorly packed macropores.[8]

Here we report the facile and efficient preparation of hierarchical porous silica spheres with a trimodal pore system through aerosol-assisted multicomponent assembly. A trimodal pore system can be realized by the simultaneous templating of both polymer latex spheres and surfactants in a one-step preparation. In our strategy, the latex spheres produce controlled, three-dimensionally (3D) interconnected macroporosity, block copolymers produce uniform mesoporosity, and the hydrophilic tails of the individual polymers result in microporosity. In the present aerosol-assisted process, droplets containing surfactant, latex spheres, Si species, and solvents are generated from a nozzle. In the heating zones, the droplet volume gradually shrinks along the center point as the solvents are evaporated. Therefore, the close packing of several latex spheres can forcibly occur within each droplet. In addition, the surfactant can be completely filled into the voids among the spheres. In the spray drying process, the compositions of the final products are of course determined by the starting compositions of the precursor solutions.[9–11] Therefore, if the composition ratio of the surfactants to the latex spheres is suitable, the desired hierarchical porous system can be achieved without poorly packed macropores.

In this experiment, the precursor solutions were prepared by mixing 28 mL of tetraethylorthosilicate (TEOS), ethanol, and 12.5 mL of HCl solution (pH 2). These mixtures were mixed with 7.9 g of Pluronic F127 and ethanol. Then, various amounts of poly(methyl methacrylate) (PMMA) spheres (Soken Kagaku Co., Ltd., Japan) were added to the above mixtures (0 g (Sample **1**), 2.2 g (Sample **2**), 10.4 g (Sample **3**), 20.8 g (Sample **4**), and 32 g (Sample **5**)). For the spray drying of the precursor solutions, a laboratory-made apparatus[12,13] based on Spray Dryer GB22 (Yamato Scientific Co.) was used in this study. The obtained white powders were calcined at 500 °C for 8 h. The calcined samples were characterized by using SEM, TEM, and N_2 adsorption isotherms as well as conventional XRD. The detailed experimental procedures are described in Electronic Supplementary Information (ESI).[14]

The SEM image of the calcined Sample **5** showed excellent spherical morphology (Figure S2, See the ESI). Furthermore, the SEM image and mathematical calculations proved that the particles were close to being spherical (See the ESI.). The sphericity was calculated to be 0.0128, which further testified to the closeness to the spherical morphology. TEM observation was employed to examine the presence of macropores and the effects of the number of doped PMMA spheres (Figure S4). In each of the four samples except the Sample **1**, the macropores were observable within the particles. The measured macropore size was about 200 nm, which was in accordance with the original size of the PMMA spheres. The macropore concentration inside the particles was examined by taking TEM images at the same magnification and accounting for the number of macropores in that area. The macropore concentration gradually increased as the number of the added PMMA spheres in the precursor solutions was increased (from 0 to 32 g). In the Sample **1**, prepared from precursor solution without PMMA spheres, no macropores were observed. Samples **2**–**3** were observed to have loosely packed macropores inside the particles.

In Sample **4**, the macropores were assembled in the center of the particles. Before spray drying, the PMMA spheres were well dispersed in the precursor solution. During the drying process, the droplets which were generated from the nozzle shrank toward the center. Therefore, the spheres were gathered in the center, packing macropores in the center of the particles (Sample **4**). However, in the case of the Samples **2** and **3**, the number of doped PMMA spheres was insufficient to fill the particles. Therefore, during the drying of the droplets, the PMMA spheres moved more easily throughout the droplets, resulting in the random existence of the observed macropores inside the particles.

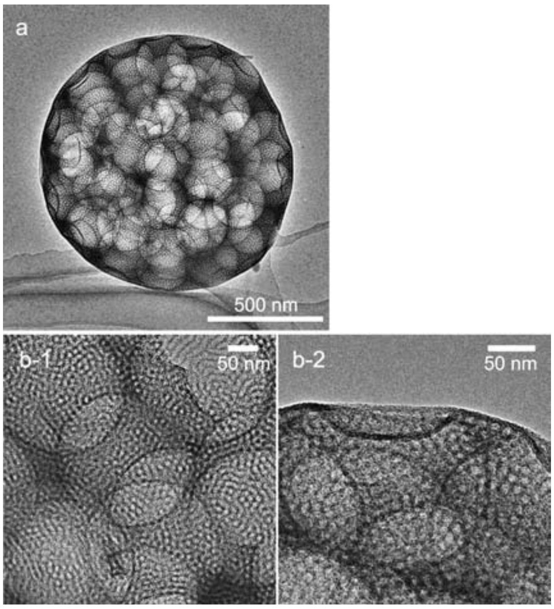

Figure 1. TEM images of the calcined Sample **5**. Figures (a) and (b) are low- and high-magnified TEM images, respectively. Figures (b-1) and (b-2) are the inner part and the surface of the particles. In the Figure (b-2), the macropores are exposed on the outer surface of the particles.

When more of the PMMA spheres were doped in the precursor solution (Sample **5**), the observed macropores were closely packed inside the particles and were exposed to the outer surface of the particles (Figure 1), as indicated by the arrows (Figure S4). The macropore walls contained mesopores of uniform size. Careful TEM observation proved a well-defined mesostructure with a periodic arrangement of mesopores, a repeat distance of ca. 12 nm (Figure 1). A single XRD peak ($d \approx 12$ nm) in the low-angle region indicated the presence of mesoscopic ordering (not shown). The d spacing from low-angle XRD well coincided with the 12-nm repeat distance for the mesostructure from TEM.

A more important point is that no amorphous regions were observed, though amorphous regions have often been found around the macropores in previous work.[4,5] If the silica condensation reaction is terminated before complete solvent evaporation, the unevaporated solvent molecules are incorporated in the core of each self-assembled micelle, making the formation of ordered mesostructures more difficult. It is generally known that in the formation of mesoporous films, dip-coating results in a higher occurrence of formation of amorphous silica region and/or disordered regions compared with a spin-coating.[15] This is because that solvent evaporation speed of the dip coating is much lower than that of the spin-coating method. In the present study using the spray dryer, solvents such as water and ethanol were evaporated immediately and sufficiently, like the spin-coating method. Therefore, no amorphous silica region was observed, even around macropores.

The porosity was investigated by using both N_2 adsorption–desorption isotherms (Figure 2). The BET total surface area was 410 m^2/g and the total pore volume was 0.63 cm^3/g. The narrow mesopore size distribution was confirmed by the BJH method because of the high ordering of the mesoscale length (Figure 2, inset image). The peak top was located at about 8 nm. Also, the high uptake at a relatively low pressure clearly indicated the presence of micropores (less than 2 nm). This fact was also supported by a positive slope in the t-plot analysis. Micropore and mesopore volumes were 0.04 and 0.34 cm^3/g, respectively. It was proven that the macropore walls were composed of two distinguishable types of pores of different sizes. The large spherical mesopores (about 8 nm) were attributable to the surfactant assemblies, and the small micropores (smaller than 2 nm) were attributable to the F127 tails incorporated within the silica walls. The smaller micropores were thought to be located between the larger mesopores.

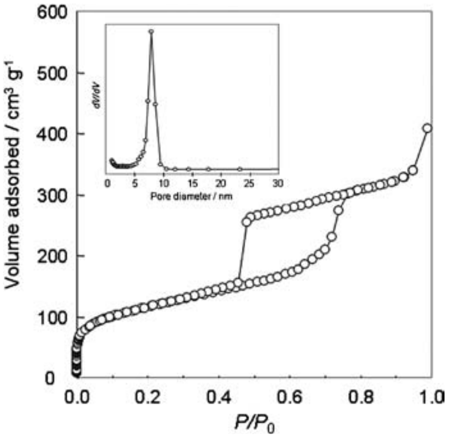

Figure 2. N_2 adsorption–desorption isotherms of the calcined Sample **5**. Inset image is mesopore size distribution obtained by the BJH method.

In this letter, we have established the one-step preparation of hierarchical porous silica spheres with a trimodal pore system through multicomponent assembly. Our strategy is based on a spray–dry technique, which is essentially one-pot preparation and can best be employed for industrial mass-scale production.

References and Notes

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