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Porous Materials

Photochemical Preparation of Two-Dimensional Gold Spherical Pore and Hollow Sphere Arrays on a Solution Surface**

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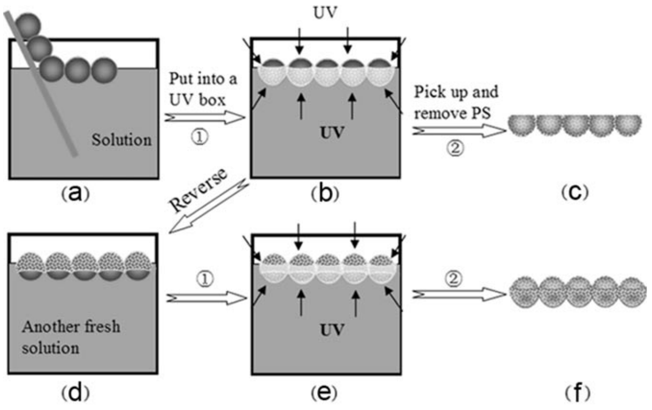
Ultraviolet (UV) light can be utilized to deposit films onto specific regions of a substrate submerged in a solution.[1] Despite its apparent advantages, the application of photochemical preparation has been limited to synthesizing some unstructured semiconductor films on solid supports.[2–7] The fabrication of nano/microstructures in free-standing films is still a challenge. The incorporation of ordered pores or hollow spheres in a film can bring about desirable properties for applications in gas sensors,[8] catalysis,[9] optics,[10,11] batteries,[12] and drug-delivery systems.[13] Such pore arrays are usually synthesized by using two-dimensional (2D) colloidal crystals as templates followed by solution dipping,[14] sol–gel processes,[15] electrodeposition,[16] or physical vapor deposition.[17] Hollow spheres can also be synthesized by using modified colloidal spheres as templates.[18–20] The problem is that the spheres are often randomly distributed and must be modified with organic compounds. Another limitation is that structured films can only grow on solid supports. It is extremely difficult to obtain freestanding films directly. Moreover, some recent works have shown that adding fine structures such as mesopores[21–23] is preferred to enhance the function of macroporous or hollow-sphere materials. Until now, suitable techniques have not been available to fabricate size-controllable hierarchical pores. A film composed of particles will naturally have small hierarchical pores on the walls of macropores or hollow spheres.[21,24] The diameter of the hierarchical pores is obviously related to the size of the particles. When a 2D colloidal crystal (template) is floated on the surface of a suitable solution before film deposition, the as-prepared film can float on the solution too and will therefore be freestanding. In this case, it is in solution that the materials are preferably deposited on the floating template. The proposed photochemical technique is ideal for this process. Gold was chosen as a model material because it has excellent optical,[25] catalytic,[26] and electronic properties.[27] The new, enhanced morphology will be attractive for applications in catalysis, sensors, and drug delivery.

Scheme 1 shows the synthesis process. A large-area (> 1 cm^2) polystyrene-sphere (PS) colloidal crystal on an ordinary glass slide is immersed slowly into a suitable precursor solution (Scheme 1a). It can be stripped off the substrate and then floats on the surface of the solution.[8,28] The colloidal crystal is divided into two parts by the liquid surface. One protrudes out of the solution, and the other is immersed in the solution. The mixture (PS/solution) is irradiated by a UV lamp (Scheme 1b), and photochemical reactions lead to the formation and growth of the corresponding crystal nuclei on the surfaces of polystyrene spheres below the liquid surface. After a period of time, shells composed of small particles are formed on the surfaces of the spheres. The shell/sphere hybrid structure can be picked up by a substrate, and the spheres removed by dissolution in dichloromethane to obtain a spherical-pore array (Scheme 1c). Alternatively, we can transfer the hybrid



Scheme 1. Strategy for photochemical preparation of spherical-pore and hollow-sphere arrays with hierarchical porosity. a) A colloidal monolayer is transferred onto the surface of a precursor solution. b) Photochemical deposition of spherical-pore array. c) Free-standing spherical-pore array. d) The pore/colloid hybrid monolayer is transferred and placed upside-down on another fresh solution. e) Photochemical deposition of hollow-sphere array. f) Free-standing hollow-sphere array.

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structure to a fresh solution and place it upside-down (Scheme 1 d). After a second UV irradiation (Scheme 1 e), a hollow-sphere array is formed on removing the spheres (Scheme 1 f). Because photochemical reactions occur as soon as the sample is irradiated with UV light, many crystal nuclei form simultaneously on the surface of the spheres. As a result, the walls of the final pores or hollow spheres are composed of many small particles and hierarchical pores (Scheme 1 c,f), the size of which is dependent on the rate of formation of the nuclei and the subsequent growth rate. The composition of the precursor and the concentration of the corresponding free ions control the size of the hierarchical pores.

Figure 1 shows SEM images of gold spherical-pore arrays with hierarchical porosity. Colloidal crystals of 1000-nm PS were chosen as template. The precursor solutions contained 3 mM $HAuCl_4$ and different concentrations of Na_2SO_3. Figure 1 a shows the ordered spherical-pore array after irradiating the precursor (containing 100 mM Na_2SO_3) for 12 h. Since the arrays are formed on the surface of the precursor solution, they are freestanding and can be manipulated according to our requirements. For example, they can be turned upside-down or curved without destroying the structures (Figure 1 b and c, respectively). All the spherical pores are hexagonally arranged and the adjacent pores contact each other at the tangent points. Among three adjacent pores, a triangular hole can be clearly seen. Figure 1 b and c shows that the pores are very unusual hollow hemispheres. The film is just slightly thicker and the pores are a bit smaller than the corresponding polystyrene hemisphere. Interestingly, some small pores (insets of Figure 1 b and c), which are constituted by the particles, can be discerned on the macropore walls. The size is closely related to that of the small particles and is dependent on the concentration of SO_3^{2-}. Figure 1 d shows the backside of the hollow hemispherical-pore array obtained from a 75 mM Na_2SO_3 precursor solution. In comparison with the array in Figure 1 b, it has larger hierarchical pores and particles. This preparation approach can also be applied to construct hollow-sphere arrays. Figure 2 shows the hollow-sphere array synthesized by a second UV irradiation of the colloidal crystal/hemispherical pore hybrid after placing it upside-down on the surface of fresh precursor solution (Scheme 1 d–f). To further explain the size dependency of the hierarchical pores on the concentrations of photoexcited ions, we repeated the experiment by using a precursor containing 50 mM SO_3^{2-}. The resulting morphology is similar to that of the backside of the spherical-pore array, except that there are no triangular holes among three adjacent hollow spheres. The hierarchical structures on the walls are related only to the concentrations of the photoexcited ions, regardless of whether they are macropores or hollow spheres. Compared with samples shown in Figure 1 b and d, the hierarchical pores of this sample are clearly larger. Further experiments confirm the concentration of SO_3^{2-} must be confined in a certain range. No array can be formed when the concentration of Na_2SO_3 is either too low or too high.

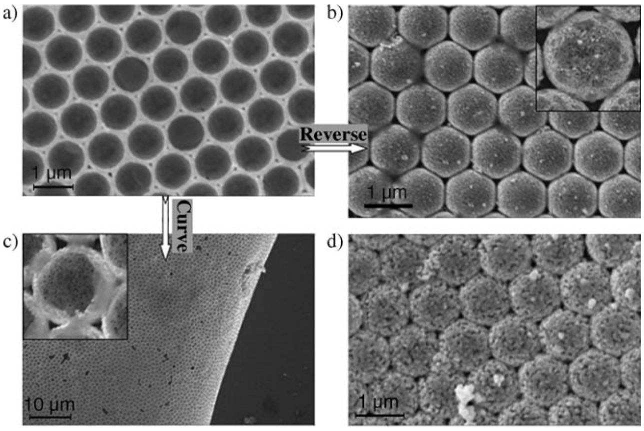

Figure 1. SEM images of gold spherical-pore arrays with different morphologies after different manipulations. a) Pore array on flat substrate. b) A pore array that was reversed. c) Curved pore array. d) Pore array with hierarchical porosity different from that in (a) on a flat substrate. PS diameter was 1000 nm. In the precursor solutions, [$HAuCl_4$] was 3 mM for all samples, and [Na_2SO_3] was 100 mM (a–c) or 75 mM (d). Insets of (b) and (c) are locally magnified images.

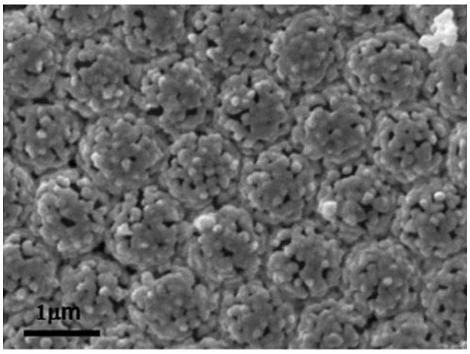

Figure 2. SEM image of gold hollow-sphere array synthesized with 1000-nm PS colloidal monolayer. The precursor solution was composed of 50 mM Na_2SO_3 and 3 mM $HAuCl_4$.

We propose a mechanism for the formation of the pore/hollow-sphere arrays and the controllability of the corresponding hierarchical structures. The composition and concentration of the precursor solution are crucial factors. $HAuCl_4$ is the source of the initial Au^{III}, some of which immediately forms Au^{I} once it is placed in the solution containing SO_3^{2-},[29] whereas Na_2SO_3 plays two important roles, that is, as complexing agent and as the supplier of the photoexcited ions. In the solution, $[Au(SO_3)_2]^{3-}$ complex ions with a stability constant of 10^{10} are formed.[30] The relatively low stability constant means the complex ion can decompose easily to form free Au^+ and SO_3^{2-}. The Au^+ is not stable and will form Au^{3+} and metallic gold by disproportionation [Eqs. (1) and (2)].

$$[Au(SO_3)_2]^{3-} \rightleftharpoons Au^+ + 2\,SO_3^{2-} \tag{1}$$

$$3\,Au^+ \rightleftharpoons Au^{3+} + 2\,Au^0 \tag{2}$$

To control the photochemical reactions, the precursor solution must be stable and have appropriate concentrations of free photoexcited ions (SO_3^{2-}) and electron acceptor (Au^+). An effective method is to control the concentrations of the free ions to drive the two reactions to the left. The concentration of $HAuCl_4$ was kept at 3 mM, so the concentration of SO_3^{2-} was decisive. Experiments showed that when the concentration of SO_3^{2-} was higher than 25 mM, no Au^0 was produced and hence the solution could be kept stable. Once the UV light irradiated the stable solution, free SO_3^{2-} would absorb photons and release solvated electrons,[5,31] and then the free Au^+ accepts the electrons to form metallic gold [Eqs. (3) and (4)].

$$SO_3^{2-} + h\nu \rightarrow SO_3^- + e^- \qquad (3)$$

$$Au^+ + e^- \rightarrow Au^0 \downarrow \qquad (4)$$

The SO_3^- is a radical species that can be transformed into the stable species $S_2O_6^{2-}$ by scavenging electrons [Eq. (5)].[31]

$$2\,SO_3^- \rightarrow S_2O_6^{2-} \qquad (5)$$

In general, the crystal nuclei preferentially form on specific interfaces in the solution where suitable concentrations of the precursors are present. The colloidal crystal floating on the surface of the solution clearly provides such interfaces, and hence Au nuclei are concentrated on the surface of polystyrene spheres. As shown in Figure 3a, when the 2D colloidal crystal floats on the surface, the solution can fill the triangular interstices among three adjacent polystyrene spheres under the action of capillary force, and the resulting meniscus lies above the tangent-point plane because of surface tension.[14] Thus PS/solution/air three-phase boundaries and PS/solution interfaces around single spheres are formed. When irradiated by UV light, crystal nuclei form on the surfaces of polystyrene spheres according to Equations (3) and (4) (Figure 3b). If the rate of formation of crystal nuclei is suitably high (as in the cases of Figures 1 and 2), nuclei can be homogenously deposited on the surfaces of polystyrene spheres. Each nucleus absorbs the corresponding ions and grows gradually. Finally, a shell composed of small particles and hierarchical pores is formed around the polystyrene spheres below the liquid surface. In the area covered by colloidal crystal, the gold is only deposited onto the spheres, so the macropores are truncated hollow spheres. The backsides of the pores exhibit a truly spherical shape, which is different from that of the spherical pores reported earlier.[11] Because the PS/solution/air boundaries lie above the tangent-point plane (Figure 3), the openings of adjacent pores are not tangential, and this leads to slightly smaller diameters of the openings and deeper pores compared to the polystyrene hemispheres. The triangular holes induced by polystyrene spheres can also be replicated, depending on the original size of the polystyrene spheres and the thickness of the pore wall. For the formation of hollow spheres, when the truncated hollow-sphere shell and PS complex array is reversed on the solution, the second photochemical reaction would occur on the naked polystyrene spheres and the portion of the shells submerged in the solution (Scheme 1d). Such hollow spheres can be thought as a combination of two single hollow hemispheres (Scheme 1e and f). Other interfaces in the system where gold particles can also be deposited include the solution/solid and solution/air interfaces. Some gold particles are found on the walls of the container and the surface of solutions in the areas not covered by PSs during the course of the photochemical reaction, but this does not affect the formation of the macropores/hollow spheres. Since the corresponding sites for forming nuclei are not available in the body of the solution, no Au nanoparticles can form there.

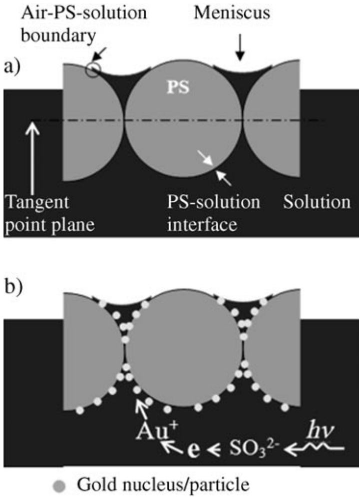

Figure 3. Schematic description of the formation of the spherical-pore array. a) State of the colloidal monolayer on the surface of the precursor solution. b) Formation of gold nuclei and particles on the surfaces of polystyrene spheres after UV irradiation.

The size of the small particles that make up the walls is affected by the rate of formation of nuclei, which is influenced by the concentration of free ions in the precursor solution. Here the free gold ions come from $[Au(SO_3)_2]^{3-}$, as shown in Equation (1). According to the reaction equilibrium, the number of free gold ions would decrease when the concentration of SO_3^{2-} is increased. Efficient deposition of gold requires appropriate amounts of free Au^+ and photoexcited ions. Therefore, an appropriate concentration of SO_3^{2-} is essential to achieve morphological control of the pores/hollow spheres. In our experiments, the critical concentration is 100 mM, at which the nuclei quickly form on the surfaces of PSs. As a result, the walls of the spherical pores/hollow spheres are composed of the smallest particles and pores (Figure 1a–c). When $[SO_3^{2-}]$ is decreased to 75–50 mM, fewer electrons are photogenerated and the rate of nucleus formation decreases. Larger particles and hierarchical pores are hence formed on the surface of polystyrene spheres (Figure 1d and Figure 2). Further decreasing the concentration to 30 mM (Figure 4) results in a very slow reaction and only scattered gold particles are formed on the surfaces of polystyrene spheres.[32] This phenomenon further supports the formation mechanism of the pores/hollow spheres. When the concentrations exceeded 100 mM, though the number of photoexcited ions was increased, the number of free Au^+ ions decreased, which could also slow down the photochem-

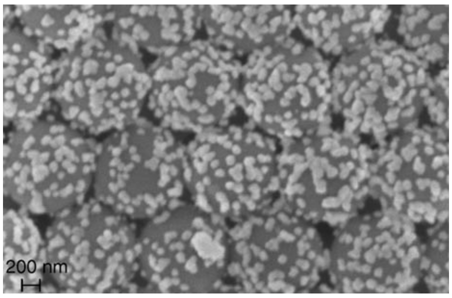

Figure 4. SEM image of gold particle/colloidal monolayer hybrid synthesized with a precursor solution containing 30 mm Na_2SO_3 and 3 mm $HAuCl_4$.

ical reactions. With increasing concentrations, such hierarchical structures as those in Figures 1d, 2, and 4 were obtained in turn. At concentrations higher than 300 mm, the $[Au(SO_3)_2]^{3-}$ ions become so stable that they cannot release any free gold ions. Hence, the photochemical reaction stops and no gold structure is obtained. For the same reason, after the photochemical reaction was finished, the residual solution was clear and became stable under UV irradiation. All the photochemical reactions reported here could be completely finished in 12 h. Further experiments showed the morphologies of the microstructures to be independent of the initial concentrations of $HAuCl_4$.

The strategy presented in this communication is universal and flexible. In addition to gold, it can be used for the synthesis of many semiconductor macrospherical pores/hollow spheres, for example, CdS, CdSe, ZnSe, ZnS, SnO_2, and TiO_2. The size of polystyrene spheres can be selectively controlled in the range of 200 nm to 4.5 μm. A unique characteristic of this technique is that material growth is induced by UV light. If we control the UV irradiation by lenses[5] or masks, we can synthesize films in which the materials are deposited in specific patterns at selected locations. Moreover, codeposition is also possible by adding several source cations together to a photoexcited precursor solution. Thus pore/hollow-sphere arrays composed of functional hybrid materials such as Au/TiO_2, CdS/ZnS, and Au/Pt may be constructible.

In summary, a photochemical technique was developed to synthesize macropore/hollow sphere arrays. By using a colloidal monolayer as template, we were able to directly fabricate large-area spherical-pore (truncated hollow sphere) and hollow-sphere arrays on the surface of a precursor solution under UV irradiation. This also represents the first synthesis of freestanding inorganic ordered porous films. We could manipulate the films, for example, reversing, bending, and constructing nano/microdevices on a desired substrate, according to our requirements. The films were formed by the preferential deposition of nuclei on the surfaces of PSs and subsequent growth. The walls of the macropores/hollow spheres are composed of small pores and particles. The sizes of the hierarchical pores were easily controlled by the concentrations of free source cations and photoexcited ions. These structures (not limited to gold) would be useful in surface-area- and morphology-related fields, such as electrocatalysis,[18,33] solar cells,[34] porous electrodes,[35] gas sensors, and drug-delivery systems.

Experimental Section

Preparation of colloidal monolayers: Ordinary glass slides were washed in turn with ethanol, 98% H_2SO_4:H_2O_2 (3:1), H_2O:NH_3·H_2O:H_2O_2 (5:1:1) and distilled water. Suspensions of monodisperse polystyrene spheres (2.5 wt% in water, surfactant-free) were obtained from Alfa Aesar Corporation. A drop (ca. 10 μL) of the suspension was pipetted onto a glass slide mounted in a custom-built spin-coater. And then a large-area (> 1 cm^2) colloidal monolayer was synthesized by the spin-coating method.[36] This procedure is suitable for the synthesis of PS colloidal monolayers of any size. The as-prepared colloidal monolayer could be transferred to the surface of the precursor solution by a method reported earlier.[8]

Preparation of precursor solutions: A certain quantity of Na_2SO_3 was first solved in 10 mL of deionized water in a beaker. And then 0.15 mL of 0.2 m $HAuCl_4$ solution was dripped into the as-prepared Na_2SO_3 solution under agitation. A series of precursor solutions were thus prepared and should be used immediately. The concentration of $HAuCl_4$ was kept at 3 mm, but the concentration of Na_2SO_3 was varied between 50 mm and 300 mm. All the precursor solutions should be clear and colorless.

Photochemical deposition of spherical-pore/hollow-sphere arrays: After the colloidal monolayer was transferred to the surface of the solution, the beaker was put in a closed box and kept from vibration. Then it was irradiated with UV light (254 nm, 10 mW cm^{-2}). Gold was gradually deposited onto the surface of PSs immersed in the solution by photochemical reaction. 12 h later, the UV light was turned off. The hybrid of macropores and PSs was picked up with any desired substrate. By dissolving the PSs with dichloromethane, spherical-pore arrays were obtained on the substrate. Alternatively, the hybrid was reversed and transferred to another fresh solution, and after the second UV irradiation, hollow-sphere arrays were obtained by dissolving the PSs.

The SEM images were recorded on a LEO 1450 VP scanning electron microscope.

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