Crystal Engineering

Morphosynthesis of Rhombododecahedral Silver Cages by Self-Assembly Coupled with Precursor Crystal Templating**

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The self-assembly and higher-order organization of micro- and nanostructured building blocks into complex architectures with hierarchy across extended length scales is a key challenge in current materials synthesis and device fabrication.[1–8] In particular, many recent efforts have been devoted to the controlled organization of primary building blocks into hollow spheres or cages,[9–14] as these hollow structures with nanometer-to-micrometer dimensions have widespread potential applications, including in catalysis, in drug delivery,

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as artificial cells, as light fillers, and as photonic crystals.[15] In most cases, however, only spherical hollow structures have been obtained either by using colloidal particles[9] or emulsion droplets[10] as templates, or by direct self-assembly of the primary particles without using external templates.[11–13] It is expected that tailoring the external morphology of hollow structures would endow them with unique properties as a consequence of the importance of shape and texture in determining the properties of the materials.[16] It is noteworthy that hexagon-based drums formed by textured self-assembly of ZnO nanocrystals were recently produced in a solid–vapor deposition process involving epitaxial surface oxidation;[14] however, the geometrical shapes of the polyhedral cages are, in general, not well-defined, and such a process could be largely limited to specific oxide systems. Thus, it is desirable to explore feasible methods to organize primary building blocks into hollow cages with well-defined, novel geometrical morphologies.

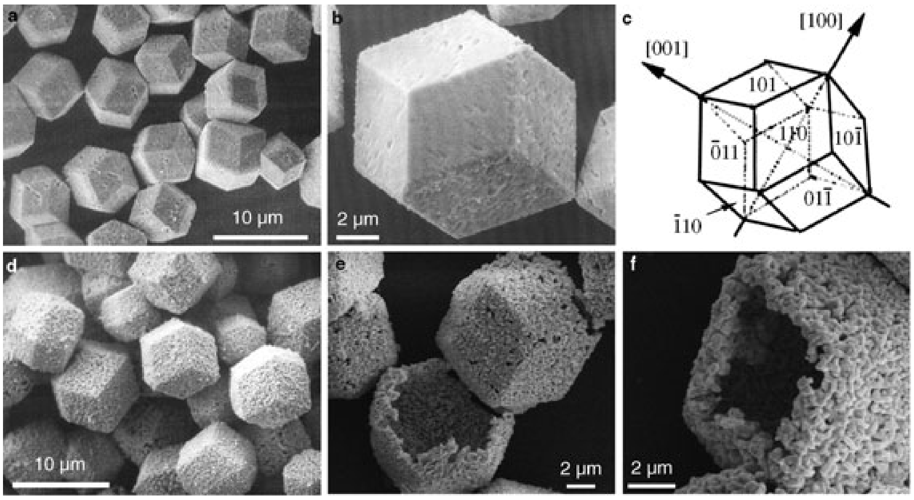

Figure 1. a, b) SEM images of Ag_3PO_4 rhombododecahedral crystals formed in a mixed water/formamide solvent, and c) index of a rhombododecahedral crystal model. SEM images of single-walled Ag rhombododecahedral cages: d) before and e, f) after sonication. The Ag cages were produced by reducing the Ag_3PO_4 precursor crystals shown in (a) with ascorbic acid at 20 °C.

The controlled synthesis of metal particles has attracted much attention because of their important roles in many areas of modern science and technology.[17–23] Considerable progress has been made in recent years in the shape-controlled synthesis of metal nanoparticles; examples include silver nanorods,[17] nanoprisms,[18] and nanocubes.[19] Hollow spheres of a variety of metals, such as Pd,[20] Pt,[21] and Ag,[22] have also been successfully produced by employing hard or soft sacrificial templates. Interestingly, unique polyhedral Au–Ag alloy nanoboxes have been synthesized by the replacement reaction between silver nanocubes and chloroauric acid in a refluxing aqueous medium.[19,23] However, to the best of our knowledge, there have been no reports on the hierarchical assembly of hollow structures from nonspherical metal particles. Inspired by a promising recent study on the formation of hollow nanocrystals of cobalt oxide and chalcogenides by cobalt nanocrystal templating through a nanoscale Kirkendall effect,[24] we extend this strategy here to the facile synthesis of well-defined, rhombododecahedral silver cages by the reduction of micrometer-sized silver phosphate crystals with a perfect rhombododecahedral shape through a microscale Kirkendall effect. We demonstrate that the controlled self-assembly of silver particles produced in situ around the precursor crystal surfaces leads to the formation of morphology-preserved, single- or double-walled silver cages constructed from different building units, such as particles, nanoplates, and quasispherical assemblies of nanoplates. This method of self-assembly coupled with templating of the precursor crystals has been further used for the synthesis of unique hollow silver cones consisting of silver nanoplate assemblies.

Our synthesis of hierarchical silver hollow structures involves the sulfated dextran-directed crystallization of Ag_3PO_4 with specific morphologies in mixed solvents, followed by reduction of the Ag_3PO_4 precursor crystals with different reducing agents in aqueous solution. It is well known that soluble macromolecules can considerably influence the form and appearance (crystal habit) by specific interactions with inorganic crystal surfaces in solution, and the effect of macromolecular additives can be further modified by varying the solvent composition.[2] Here we chose the anionic derivative of dextran (dextran sulfate) as an effective crystal-growth modifier for the crystallization of Ag_3PO_4 in a water/formamide mixture, as our preliminary experiments suggested that usually only irregular Ag_3PO_4 polyhedrons are obtained in pure water. Figure 1 a presents a typical scanning electron microscopy (SEM) image of the Ag_3PO_4 crystals obtained in the presence of $10\,g\,L^{-1}$ dextran sulfate, and shows that all of the obtained Ag_3PO_4 crystals exhibit a uniform rhombododecahedral morphology. The size of the rhombododecahedra, as estimated from the distance between the two parallel surfaces, typically ranges from 4 to 8 µm, with an average size of about 6 µm. The related X-ray diffraction (XRD) pattern (see the Supporting Information) shows sharp reflections characteristic of simple cubic Ag_3PO_4 (JCPDS No. 6-0505), thus suggesting that the rhombododecahedra are pure Ag_3PO_4 crystals. An enlarged SEM image (Figure 1 b) clearly shows that the ideal rhombododecahedron consists of 12 well-defined crystal faces and exhibits cubic symmetry, thus confirming that each rhombododecahedron is a single crystal of cubic Ag_3PO_4. The 12 faces can be indexed to the {110} planes (Figure 1 c).

As Ag_3PO_4 can be readily reduced by a variety of reductants to metallic Ag, Ag_3PO_4 crystals with well-defined morphologies may be used as precursors for the morphology-preserved synthesis of silver particles. Ascorbic acid, hydrazine, and $NaBH_4$ are three widely used reducing agents with an increasing reducing ability; moreover, they are expected to show increasing diffusion ability in water, as their molecular volume decreases from ascorbic acid through hydrazine hydrate to the BH_4^- ion. It was therefore interesting to explore the synthesis of silver particles by reduction of the rhombododecahedral Ag_3PO_4 precursor crystals with these three reductants. Figure 1 d shows a typical SEM image of the silver product obtained by the reduction of the precursor crystals in 0.02 M ascorbic acid solution at 20 °C; it suggests the formation of silver particles with a well-preserved rhombododecahedral morphology. The rhombododecahedra have an average size of about 7 μm, which is slightly larger than the precursor rhombododecahedra (ca. 6 μm), and exhibit rather rough surfaces, in contrast to the smooth surfaces of the precursor rhombododecahedra. The corresponding XRD pattern (see the Supporting Information) exhibits sharp reflections attributed to fcc silver (JCPDS No. 04-0783), thus confirming a complete transformation of the Ag_3PO_4 precursor crystals to silver crystals. After 10 min of ultrasonic treatment in water, the rhombododecahedral particles can be broken and the hollow structure of the rhombododecahedra is clearly revealed by the SEM images (Figure 1 e, f). It can be seen that the rhombododecahedral cages have a shell consisting of interconnected, irregularly shaped, primary particles about 200–400 nm in size, which results in an average shell thickness of about 300–400 nm. Although there is a clear difference in the length scale, this formation of micrometer-sized, rhombododecahedral cages around rhombododecahedral precursor crystals is analogous to the reported formation of hollow nanospheres around spherical precursor nanoparticles,[24] which was attributed to a fundamental solid-state phenomenon, known as the Kirkendall effect[25] that deals with the movement of the interface between a diffusion couple. In the present case, ascorbic acid and Ag_3PO_4 can react with each other and form a diffusion pair. The coupled reaction/diffusion at the crystal/solution interface could lead to the quick formation of an interconnected silver shell around the external surfaces of the Ag_3PO_4 crystals. This process is followed by a continuous outward flow of Ag_3PO_4 from the solution to and through the porous silver shell to form a hollow interior and a relatively compact shell, as well as some small, individual silver particles precipitated outside the shell. This result demonstrates that, similar to the nanoscale Kirkendall effect used for the fabrication of hollow nanoparticles, a microscale Kirkendall effect can be used for the fabrication of micrometer-sized hollow cages with well-preserved morphologies if a suitable reaction-diffusion process exists at the solid/liquid interface. It may be argued that the polymer could play a role in the self-assembly process, for example, by gluing together the primary particles; however, this role is likely to be negligible, as a preliminary thermogravimetric analysis (TGA) suggested that the Ag_3PO_4 crystals do not contain significant amounts of polymer after being washed thoroughly with water.

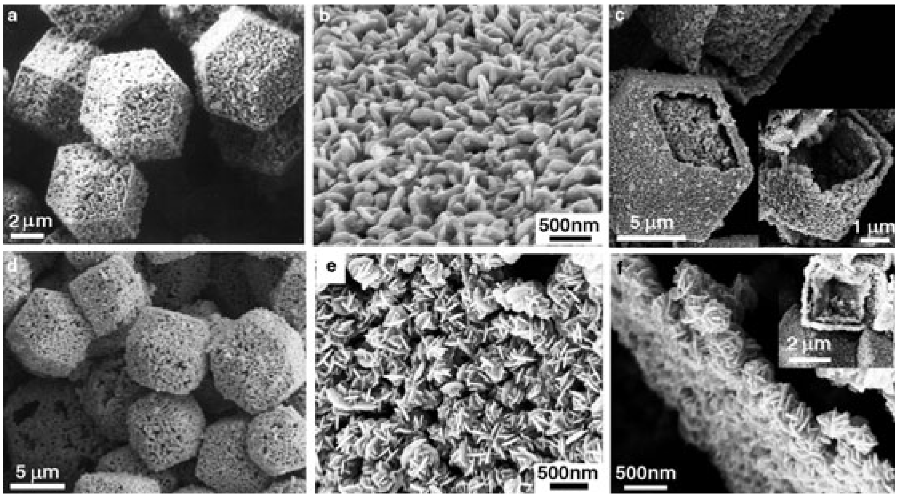

Figure 2. SEM images of double-walled Ag rhombododecahedral cages produced by reducing the Ag_3PO_4 precursor crystals shown in Figure 1 a with hydrazine at: a–c) 20 °C and d–f) 4 °C. The images shown in (c) and (f) correspond to the broken cages after sonication. The insets show the double-walled structures of the broken rhombododecahedral cages.

The formation of single-walled silver cages when using ascorbic acid as the reductant indicates that the outward diffusion of Ag_3PO_4 is most likely faster than the inward diffusion of ascorbic acid. Hydrazine is a stronger reductant than ascorbic acid, and has a higher diffusion ability. As shown in Figure 2 a, well-defined, rhombododecahedral silver particles of about 6–7 μm were again obtained when hydrazine was used to reduce the rhombododecahedral Ag_3PO_4 crystals at 20 °C instead of ascorbic acid. A high-magnification image (Figure 2 b) reveals that the shell mainly consists of nanoplates ranging from 200 to 400 nm in size and less than 100 nm in thickness. The TEM image and electron diffraction (ED) pattern of separated silver nanoplates obtained by ultrasonically breaking the rhombododecahedral particles suggest that the nanoplates normally exhibit a hexagonal shape and that they are single crystals of fcc silver with the top face bounded by the {111} planes (see the Supporting Information); this arrangement is typical for platelike silver nanocrystals.[18] The representative SEM images of the broken rhombododecahedral particles shown in Figure 2 c suggest that most of the rhombododecahedra are actually double-walled hollow cages. It should be noted that single- and triple-walled cages can be occasionally observed in the product, although the double-walled cages form the overwhelming majority. The primary platelike particles and the double-walled structure are unique for the rhombododecahedral cages synthesized under these conditions. Platelike silver nanocrystals with a (111) top face are usually obtained in the presence of an appropriate surface-capping reagent;[18] therefore, it can be reasonably assumed that the reductant (hydrazine) may also act as an effective stabilizer for the silver nanoplates here. The formation of the double-walled structure is surprising. However, it is still in accordance with the Kirkendall effect because significant inward hydrazine transport could occur after the initial formation of the shell around the rhombododecahedral precursor crystals, as hydrazine diffuses considerably faster than ascorbic acid. This leads to the formation of a second shell inside the first as a result of the coupled reaction/diffusion process. The double-walled pattern is reminiscent of the well-known Liesegang patterns[26] that typically form by a periodic precipitation through the moving reaction front when two coprecipitating reactants interdiffuse in a gel medium. The Liesegang phenomenon observed in reaction/diffusion systems has been studied for a long time because of its similarities with natural, pattern-forming systems and potential applications in materials patterning; however, the mechanisms responsible for the patterns are still under discussion because of the rich, nonequilibrium dynamics involved.[27] Nevertheless, the formation of multiwalled hollow cages in a coupled reaction/diffusion process is unprecedented, and the exact mechanism is worthy of further study.

When the reduction reaction was conducted at a lower temperature (ca. 4 °C), the reaction rate and the reactant diffusion decreased considerably, which led to the formation of double-walled, rhombododecahedral cages with relatively loose shells (Figure 2 d–f). It is worth noting that the shell is composed of quasispherical assemblies of interconnected silver nanoplates about 50 nm thick and 200–300 nm wide. We propose that a lower reaction and diffusion rate would favor the formation of loosely packed nanoplate self-assemblies rather than densely packed nanoplate aggregates, which results in a change of the building units of the rhombododecahedral shells at different temperatures. The unique silver product shows a multilevel structure: nanoplates→quasispherical assemblies→rhombododecahedral shell→double-walled rhombododecahedral cage, which is similar to the complex, hierarchical structures adopted by biological minerals, such as the shells of single-celled organisms.[16] This one-pot, organic-free method based on self-assembly coupled with templating of the precursor crystals may form the basis of a new route to hierarchical inorganic hollow structures.

If $NaBH_4$, which has an even higher reducing ability and diffusion ability, is used as the reducing agent, novel core–shell-structured silver rhombododecahedra can be produced. As shown in Figure 3 a, the silver product consists of rhombododecahedral particles (ca. 7 μm) with some small particles attached to the exterior surfaces. The rhombododecahedra show a core–shell structure with a dense shell and a loose core after having been broken by sonication (Figure 3 b). A high-magnification image of the core (Figure 3 c) suggests that it consists of entangled nanowires ranging in diameter from 60 to 100 nm. The formation of the core–shell structure can be rationalized by considering that the very fast inward diffusion of BH_4^- ions could bring about a quick reduction of the Ag_3PO_4 inside the silver shell that is formed immediately after mixing the Ag_3PO_4 rhombododecahedra and $NaBH_4$ in solution. The formation of the clewlike core could be related to the specific reduction reaction between Ag_3PO_4 and $NaBH_4$, although the mechanism is still unclear.

All three reducing agents can therefore be used successfully for the synthesis of well-defined silver rhombododecahedra by reducing Ag_3PO_4 crystals. Our preliminary experiments have shown that a minimum reductant concentration is necessary for the morphology-preserved transformation from Ag_3PO_4 to silver. For example, only rhombododecahedral Ag_3PO_4 skeletons along with small separated silver particles were produced at a low $NaBH_4$ concentration (see the Supporting Information), which indicates that a quick formation of extended silver networks is essential to preserve the morphology. Accordingly, a tentative mechanism for the formation of the three different types of silver rhombododecahedra can be proposed (see the Supporting Information). Briefly, a layer of interconnected silver networks forms around the exterior surface of the Ag_3PO_4 rhombododecahedra as long as they are surrounded by a sufficient concentration of the reductant. Then, the network layer develops into a denser shell, which is accompanied by the formation of a depletion layer near the shell as a result of the coupled reaction/diffusion process. The final silver structure depends on the inward diffusion rate of the reductant relative to the outward diffusion rate of the Ag^+ ions, namely, single-walled rhombododecahedra form with ascorbic acid, which has a low diffusion rate, whereas double-walled rhombododecahedra form with hydrazine, which has a medium diffusion rate, and core–shell structured rhombododecahedra form with $NaBH_4$, which has a high diffusion rate. Such a morphology-preserved transformation process is not limited to the Ag_3PO_4/Ag system. For example, hollow Ag octahedra have been readily fabricated by reducing octahedral Ag_2O crystals with ascorbic acid following a similar strategy (see the Supporting Information).

This method of self-assembly coupled with templating of the precursor crystals can be extended to the morphology-preserved synthesis of hierarchical silver structures with morphologies other than polyhedra. As shown in Figure 4 a and b, hollow Ag_3PO_4 cones consisting of parallel fibers (longer than 100 μm) were formed in a solution of dextran sulfate in mixed water/acetamide solvent. It should be noted that similar hollow-cone structures have been obtained in the polymer-controlled morphogenesis of $BaSO_4$[28] and bundles of $BaCrO_4$[29] nanofibers. The hollow Ag_3PO_4 cones

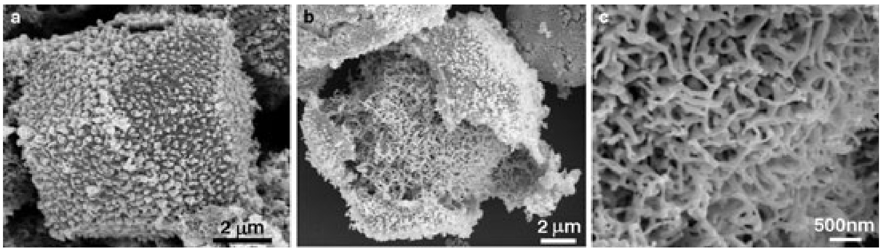

Figure 3. SEM images of: a) intact and b, c) broken Ag rhombododecahedral particles with a core–shell structure that were produced by reducing the Ag_3PO_4 precursor crystals shown in Figure 1 a with $NaBH_4$ at 20 °C.

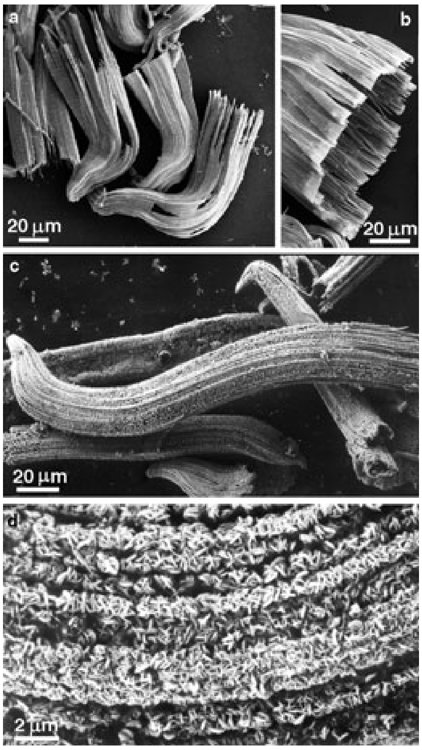

Figure 4. a, b) SEM images of Ag_3PO_4 hollow cones formed in a mixed water-acetamide solvent and c, d) hierarchical Ag hollow cones produced by reducing the Ag_3PO_4 precursor crystals shown in (a) with ascorbic acid at 20°C.

were converted into hierarchical, hollow silver cones that consist of parallel fibers constructed from nanoplate assemblies (Figure 4c, d) after reduction by ascorbic acid.

In summary, a variety of silver microstructures exhibiting a well-defined, rhombododecahedral exterior morphology and a remarkably complex hierarchy have been readily fabricated in solution by self-assembly coupled with templating of the precursor crystals. The rhombododecahedral silver cages showing faceted shells consisting of tailored, nanostructured building units could find applications in various areas, including catalysis[20] and surface-enhanced Raman scattering (SERS) detection.[30] The synthesis based on a coupled reaction/diffusion process is related to the Kirkendall effect and the Liesegang phenomenon, which suggests that it could provide a useful model for the re-examination of these well-established physical phenomena. The process provides a general route to the synthesis of silver superstructures with unique morphologies and complex hierarchies. Furthermore, the synthesis may be extended to other metal systems and could possibly be used for device fabrication with appropriate metal/precursor/reductant combinations.

Experimental Section

In a typical synthesis of Ag_3PO_4 rhombododecahedra, Na_3PO_4 (0.005 mmol) and dextran sulfate (0.05 g, Fluka, M_W 500000) were dissolved in a solvent mixture containing water (3 mL) and formamide (1.5 mL), followed by addition of 0.2 M aqueous $AgNO_3$ solution (0.5 mL), with vigorous stirring, to give a final phosphate ion concentration of 1 mM and an excess of Ag^+ ions. After stirring the mixture for 1 min the slightly yellow, cloudy solution was aged for 1 day to give a yellow precipitate, which was collected, washed with water thoroughly, and dried in air. A similar process was employed for the synthesis of Ag_3PO_4 hollow cones, except that the solvent was a mixture of water (4.5 mL) and acetamide (0.74 g) instead of the mixed water/formamide solvent, and a longer aging time (4–5 days) was adopted. The obtained Ag_3PO_4 crystals were subsequently used as templates for the precursor crystals for the fabrication of the corresponding silver hollow structures. In a typical synthesis procedure, 0.004 g of the Ag_3PO_4 precursor crystals (ca. 0.01 mmol) was dispersed in water (9 mL) and a 0.2 M aqueous solution (1 mL) of the reducing agent (ascorbic acid, hydrazine, or sodium brorohydride) was added at room temperature (ca. 20°C) to give a final reducing-agent concentration of 20 mM. After aging the mixture for 10 h in the solution, the resultant gray precipitate was collected by centrifugation at 3000 rpm and washed with water repeatedly to remove any separately precipitated small particles.

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