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Nanostructured Materials

Serial Ionic Exchange for the Synthesis of Multishelled Copper Sulfide Hollow Spheres**

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In recent years, ion exchange has been widely used as a general means for chemical transformation of inorganic nanostructured materials.[1–6] In particular, both cation and anion exchange have been investigated rather thoroughly and a considerable number of inorganic nanoparticles and nanostructures have been synthesized by this approach.[1–18] Compared to cationic species, anionic diffusion rates in general are slower owing to their larger sizes. By selecting different diffusion pairs, variation in diffusivity has been utilized in creating a central void space for nanoparticles during the chemical transformation.[7–18] The nanoscale Kirkendall effect has been widely employed to generate interior voids for nanoparticles,[7] and it has for example been recently exploited in the anion-exchange reactions between O^{2-} and S^{2-} anions.[15,17,18] Apart from single-shelled hollow particles, the solution synthesis of multishelled functional materials is a fundamental challenge for synthetic chemistry owing to a significant increase in structural complexity. Indeed, this field of research has advanced rapidly in recent years.[19–21] Nevertheless, there have been no reports to date on forming multishelled hollow spheres by employing an ion-exchange method, despite its great popularity in general transformation of nanomaterials. Herein, we exploited the capacity of the ionic exchange reaction for forming multishelled structures and found that with proper manipulation of a precursor system and thus reaction kinetics, a series of anionic exchanges with a solid precursor can actually be conducted in a consecutive manner, which leads to formation of single-, double-, triple-, or even quadruple shells. More specifically, as shown in Figure 1, we will use a hybrid of cuprous oxide (cuprites, a p-type metal oxide[22–24]) and poly(vinylpyrrolidone) (PVP) as a precursor solid to establish some general principles in controlling ionic exchange and the hollowing process for fabrication of complex multishelled Cu_2S (chalcocite[25–27]) hollow spheres.

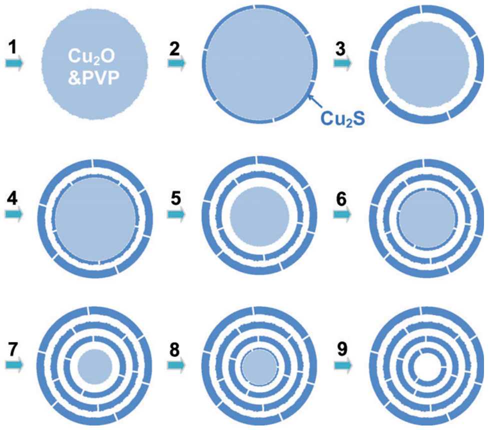

Figure 1. Formation process of multishelled Cu_2S hollow spheres. 1) Preparation of Cu_2O and PVP hybrid, 2) surface Cu_2S formed by ion exchange, 3) continuous growth of Cu_2S and formation of the first shell, 4) diffusion of S^{2-} and formation of Cu_2S on the inner Cu_2O core, 5) continuous growth of Cu_2S and formation of the second shell, 6) diffusion of S^{2-} and formation of Cu_2S on the inner Cu_2O core, 7) continuous growth of Cu_2S and formation of the third shell, 8) diffusion of S^{2-} and formation of Cu_2S on the inner Cu_2O core, and 9) continuous growth of Cu_2S and formation of the fourth shell.

The colloidal Cu_2O spheres (Figure 1, step 1) were synthesized with a PVP-assisted polyol method (Supporting Information, Section S1), and the product arising from this process was mesocrystalline in nature, in which the Cu_2O crystallites are actually incorporated with PVP, giving rise to a form of inorganic–organic hybrids. During the ion exchange, the PVP phase slows down the movement of sulfur dianions (S^{2-}) to the Cu_2O surface. In other words, incoming S^{2-} ions have to overcome this physical barrier to interact with Cu_2O and form Cu_2S surface clusters (step 2). With a continuous supply of S^{2-} for the exchange reaction, steady growth of the Cu_2S shell is anticipated. Because the mobility of oxygen anions is faster than that of the sulfur,[15] a continuous mass relocation of Cu_2O crystallites from the inside out is expected during the formation of Cu_2S. Furthermore, recrystallization (Ostwald ripening) of Cu_2S is observed, as the resulting Cu_2S shell is much more compact, compared to its porous precursor Cu_2O. Therefore, there are two major processes responsible for the creation of vacant space between the growing Cu_2S shell and depleting Cu_2O core (step 3): out-diffusion of Cu_2O crystallites and conversion of mesocrystalline Cu_2O to a denser crystalline Cu_2S shell (Supporting Information, Sections S1–S3). Note that these two factors are closely coupled upon the anionic exchange. Repeated with this reaction process route, steps (4) and (5), (6) and (7), and (8) and (9) can produce the second, third, and fourth shells of Cu_2S, sequentially, where shell imperfection must allow the penetration of S^{2-} anions to reach inner Cu_2O. Figure 2 shows some representative transmission electron microscopy

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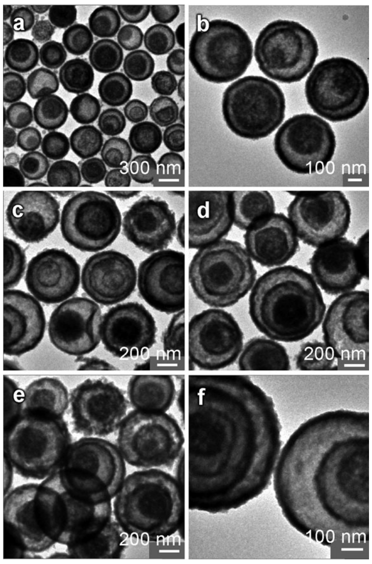

Figure 2. Multishelled Cu_2S hollow spheres: a),b) largely in double-shelled Cu_2S (210/220 °C); c)–f) mainly in triple-shelled Cu_2S (220/220 °C). $Cu(NO_3)_2/CH_4N_2S = 2:1$ (Supporting Information, Section S1).

(TEM) images of multishelled Cu_2S hollow spheres prepared with this approach, and further materials characterization with X-ray diffraction (XRD), high-resolution TEM (HRTEM), and energy dispersive X-ray spectroscopy (EDX) line profiles and mappings can be found in the Supporting Information, Section S2.

In the above formation of hollow spheres, sulfide ions diffuse onto the Cu_2O surface, while Cu^+ cations migrate from bulk Cu_2O to the forming Cu_2S/Cu_2O interface, and this exchange reaction is thermodynamically favorable, as K_{sp} of Cu_2S is extremely small (2.5×10^{-48}, 18 °C) compared to that of Cu_2O (2.0×10^{-15}, 25 °C). One of the important factors attributed to the success of this serial hollowing pathway is a lasting supply of sulfur dianions from the solution phase. First, the required S^{2-} anions for the exchange reaction actually come from the source compound thiourea (CH_4N_2S) at a temperature range of 190–220 °C. Because the reaction itself takes time, a longer presence of this anion for the multiple shell formation is anticipated. Second, slow addition of thiourea into the colloidal Cu_2O solution can also prolong the supply of this anion and thus increase the number of Cu_2S shells. And third, with an appropriate amount of thiourea added, more shells for the Cu_2S hollow spheres can also be expected. As a general observation, rapid injection of thiourea stock solution to the colloidal Cu_2O solution most likely leads to the formation of $Cu_2O@Cu_2S$ yolk–shell products (Supporting Information, Section S2), whereas a dropwise introduction of this sulfur precursor to the same Cu_2O suspension significantly increases the number of the shells, given a set of identical synthetic parameters (Figure 2). This is understandable, because an instant supply of excessive sulfide ions can result in an immediate formation of thicker deposit on the Cu_2O spheres, which makes further diffusion inwards of S^{2-} anions more difficult. In fact, our Cu_2S spheres prepared in this way have a compact thick single shell (Supporting Information, Section S3), which relies primarily on diffusion outwards of oxygen anions, and their exchange reaction with sulfur anions would mainly take place on the external surface of the shell.

Apart from the concentration of reactants, the reaction temperature also turns out to be crucial to multiple shell formation. The use of high temperatures apparently favors the thermal decomposition of thiourea and ensures a sufficient supply of sulfide ions. More importantly, it increases diffusion rates of all the ionic species (S^{2-}, O^{2-}, and Cu^+) involved in this exchange reaction. When the Cu_2O cores were converted to Cu_2S, expulsed PVP molecules would be accumulated, serving as a capping agent to the smooth Cu_2S shell. We observed that the number of Cu_2S shells increases simply in accordance to the rise in process temperature combination (210/220 °C and 220/220 °C; Figure 2) under similar experimental conditions. From Figure 1 and the above results, we notice that to perform multistep hollowing, the pristine Cu_2O phase must possess certain dimensions, as Cu_2O itself serves as copper stock to sustain this serial ion exchange reaction and matter relocation. We found that the Cu_2O spheres in a diameter range of 300–500 nm are practicably workable to achieve targeted multiple shells. To test this point further, we used smaller Cu_2O solid spheres (Supporting Information, Section S3), which were synthesized at a lower temperature, for the same ion exchange reaction. In Figure 3 a, quite expectedly, the Cu_2S product is exclusively thick single-shelled hollow spheres, because of the small-sized Cu_2O and rapid injection of thiourea (Supporting Information, Section S3). By lowering the reaction temperature, we can actually slow down this hollowing process. As shown in Figure 3 b–f and the Supporting Information, Section S3, we carried out another set of experiments at 25 °C by switching the thiourea to sodium sulfide solution in which the sulfide ions are readily available at room temperature. The diameter of the product Cu_2S hollow spheres is in the range of 100–125 nm, which is larger than that of the

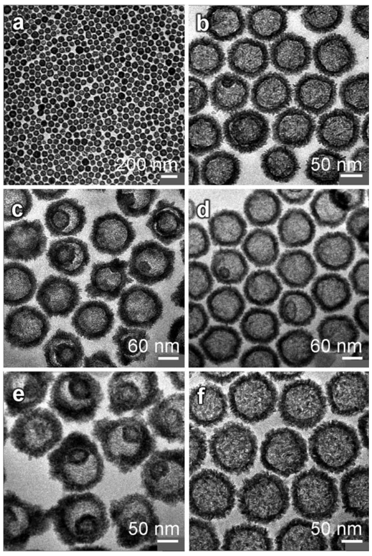

Figure 3. Single- and double-shelled Cu_2S hollow spheres: a) prepared with $Cu(NO_3)_2/CH_4N_2S = 2:1$ at 200/215 °C, and b)–f) prepared with $Cu_2O:Na_2S = 1:1.5$, 1:2, 1:3, 1:4, and 1:5, respectively, at room temperature (Supporting Information, Sections S1, S3).

original Cu_2O solid precursor (Supporting Information, Section S3). This observation indicates that at a lower reaction temperature, the ion exchange mainly takes place on the external surface of the solid spheres. By further increasing S^{2-} concentration (molar ratio $Cu_2O/Na_2S = 1{:}4$), the population of double-shelled hollow spheres increases (Figure 3e). Nonetheless, when the same molar ratio is overly changed to $Cu_2O/Na_2S = 1{:}5$, fast nucleation and rapid growth of the Cu_2S shell occur, and only few double-shelled Cu_2S hollow spheres can be kept (Figure 3f; Supporting Information, Section S3). As mentioned earlier, this was due to formation of a compact Cu_2S shell, preventing diffusion inwards of the sulfide ions. Once again, to conduct the serial ion exchange and to form multishelled spheres, an optimal steady supply of sulfide ions to the reaction system plays a pivotal role.

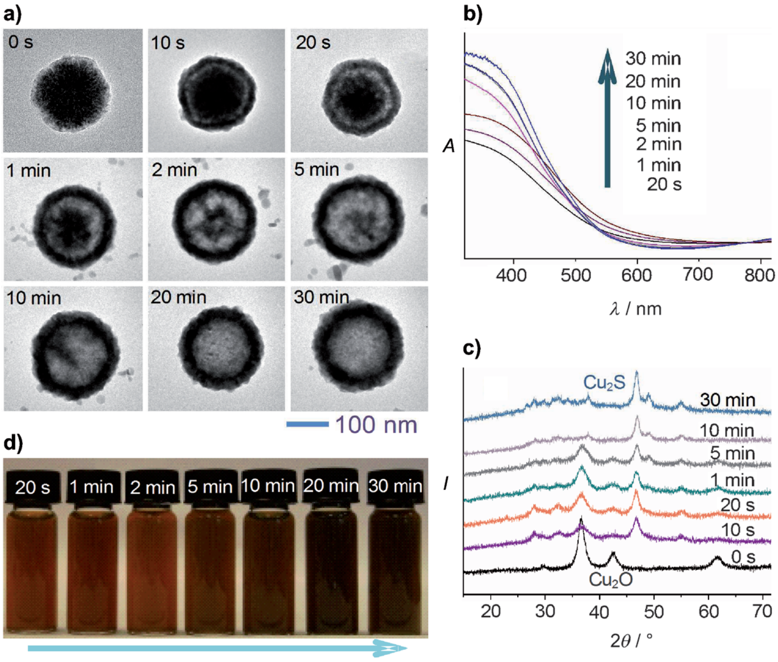

Figure 4. Evolution of Cu_2O solid spheres to Cu_2S hollow spheres (Supporting Information, Section S1): a) representative TEM images, b) UV/Vis absorbance spectra of the samples that are shown in (d), and c) XRD patterns of the corresponding solid samples.

Besides the PVP trapped in the primary Cu_2O crystallites, we found that addition of PVP to the synthesis is indispensible to form smooth internal and external surfaces for the resultant shells. In absence of PVP, Cu_2S hollow particles could still be produced, but the spherical structure was not retained at all, and irregular final Cu_2S particles were aggregated (Supporting Information, Section S3). With a smaller amount of PVP, freestanding Cu_2S hollow structures could also be prepared, but the pristine spherical structure of Cu_2O precursor was hardly preserved. Along with its templating role for the Cu_2S shell, PVP also reduced mobility of S^{2-} and thus slowed down the ion-exchange reaction. The fingerprint absorption characteristics of PVP can be detected in both the original Cu_2O spheres and Cu_2S products by FTIR spectroscopy (Supporting Information, Section S3). A comparative surface analysis with X-ray photoelectron spectroscopy (XPS) for the samples studied is also provided in the Supporting Information. During multiple shell formation, the shell imperfection (or porous channels) must be present to allow in-diffusing S^{2-} and PVP to enter a next inner space. Such viable entrances were indeed present in the multishelled spheres (Supporting Information, Section S3).

To gain more insights into the hollowing process, we carried out time-dependent experiments, and the results are shown in Figure 4 (with rapid injection). Within 10 seconds of ion exchange, we found that there are voids between the Cu_2O cores and Cu_2S shells in the structural intermediate (Figure 4a). The relationship of composition and structure of this type of core–shell spheres was also investigated in detail with TEM/EDX methods (Supporting Information, Section S4). The ion-exchange reaction did take place very fast, as indicated in the sequential color change from light brown–yellow, starting with Cu_2O colloidal precursor solution, to dark gray Cu_2S product (see Figure 4d) within a reaction timeframe of 30 min (Supporting Information, Section S1). This sequential color change is also reflected in the corresponding UV/Vis spectra (Figure 4b). After 10 minutes, absorption bands for Cu_2O disappear, and the ion-exchange reaction (that is, Cu_2S formation) is nearly complete. In Figure 4a, we can clearly see the solid bridges that connect the forming Cu_2S and disappearing Cu_2O. These bridges serve as a fast transport medium for the outward diffusion of Cu_2O core that can then reach the Cu_2S shell. Most of the void volumes already formed during the first 2 minutes, whereas it took about 20 minutes for the remaining Cu_2O to disappear. Apparently, the conversion rate of Cu_2O to Cu_2S was decreased when little of the Cu_2O phase was left, because the bridges themselves were also consumed during the reaction, providing only limited cross-sectional areas for solid-state ionic transport. Related to the TEM observation, the XRD patterns (Figure 4c) also reveal the crystallographic phase transformation from pure cubic Cu_2O (JCPDS card no. 05-0667) to almost pure hexagonal Cu_2S (JCPDS card no. 84-0208) when the reaction proceeded for only 10 minutes, indicating a small quantity of Cu_2O remained at this moment, which is in good agreement with our TEM observation (Figure 4a). With longer process times (20 or 30 minutes), the pure hexagonal phase of Cu_2S could be fully developed. As the mobility of ions in the diffusion depends strongly on temperature, we also examined the same solid evacuation process at room temperature, and affirmed that the ionic transport is indeed much slower at the low temperature. Despite much smaller sizes, only $Cu_2O@Cu_2S$ yolk–shell structures could be prepared with a process time of 5 minutes (Supporting Information, Section S4), which is quite different from that with the same process time in Figure 4a.

With the present preparative method, anions of the copper precursor salts also determine the final hollow structures of Cu_2S. This provides an additional means to control product morphology. Along with the spherical type of products synthesized with copper nitrate ($Cu(NO_3)_2$), our investigation shows that copper acetate ($Cu(CH_3COO)_2$) as well as copper acetylacetonate ($Cu(C_5H_7O_2)_2$) can form cubical Cu_2O, which in turn give rise to formation of multishelled Cu_2S hollow boxes (Supporting Information, Section S5). It should be mentioned that these hollow spheres are extremely stable under ambient conditions. We have observed that $Cu_2O@Cu_2S$ yolk–shells and Cu_2S hollow spheres with single-, double-, triple-, quadruple-, and even quintuple shells are very stable even they were simply stored at room temperature under air atmosphere for a period of one and a half years (Supporting Information, Section S5). As these spheres were prepared by polyol methods and were decorated with PVP, their dispersity is excellent in polar solvents such as water or ethanol. Homogeneous colloidal solutions of these products are usually stable for months, especially for Cu_2O solid spheres and single-shelled Cu_2S hollow spheres. We have also determined optical band gaps for these materials; the band gaps of the products of the single-, double-, and triple-shelled Cu_2S hollow spheres show a gradual decrease from 2.10, to 1.49, and to 1.42 eV with an increasing diameter of the spheres (Supporting Information, Section S5).[25–27] The reduction in the band-gap energy may originate from an increase in crystallinity and crystallite sizes in the Cu_2S shell structures because of rise in process temperature and sphere dimensions. Compared to the value for bulk Cu_2S (1.21 eV), the optical band gaps of all of the as-synthesized Cu_2S products are larger owing to the quantum confinement effect of the thin shells. As a preliminary exploration for the application of these materials, we have further prepared single-shell Cu_2S hollow spheres into supracrystals (Supporting Information, Section S5). As Cu_2S is an important p-type semiconductor material in application such as solar cells, cold cathodes, and nanoscale switches,[25–27] this type of orderly arranged hollow spheres may add in new applications as photonic crystals when more sophisticated assembly techniques are developed.

In summary, we have used the chemical conversion of Cu_2O into Cu_2S to demonstrate that ion exchange, starting with mesocrystalline precursors, can be an effective pathway for nanoscale fabrication of multishelled hollow structures. Through this fundamental study, we have identified a number of important process parameters such as reactant concentrations, reaction temperature, and amount of capping agents. Along with the mesocrystalline precursors, in principle, this ion exchange approach should also be applicable to solid precursors that comprise randomly aggregated crystallites.

Experimental Section

Cu_2O solid spheres were prepared by high-temperature polyol-mediated methods with copper(II) nitrate trihydrate ($Cu(NO_3)_2\cdot 3H_2O$), polyvinylpyrrolidone (PVP), and diethylene glycol (DEG) as starting chemicals. The starting solution, in a three-neck glass flask and with vigorous magnetic stirring, was heated from room temperature to 190–220 °C under argon atmosphere; the Cu_2O solid precursors were thus obtained. The synthesis of single-, double-, or multishelled Cu_2S hollow spheres involved an ion-exchange reaction between the as-prepared Cu_2O solid spheres and thiourea (CH_4N_2S) in DEG in the presence of PVP at different reaction temperatures (for example, 190–230 °C; argon atmosphere). Afterward, the reaction system was cooled to room temperature, and reaction products were collected by centrifuging and then washed with acetone and ethanol. Along with the thermal decomposition of CH_4N_2S at elevated temperatures, sodium sulfide hydrate ($Na_2S\cdot H_2O$) was also used to provide sulfur dianions for the same exchange reaction at room temperature. Detailed synthetic procedures and related materials characterization can be found in the Supporting Information, Section S1.

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Keywords: copper oxides · copper sulfides · core–shell materials · hollow spheres · ion exchange

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