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Synthesis and Characterization of Multipod Frameworks of Cu_2O Microcrystals and Cu_7S_4 Hollow Microcages

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A variety of multipod frameworks of Cu_2O microcrystals have been prepared through careful control of the ratios of n-butyl alcohol to water. And novel 14-pods Cu_2O frameworks are first reported. Moreover, a template-assisted synthesis of multipod frameworks of Cu_7S_4 microcages using the obtained Cu_2O microcrystals as sacrificial templates is reported.

Architectural control of inorganic materials with well-defined shapes have attracted increasing interest due to their unique shape-dependent physical and chemical properties.[1] In recent years, considerable attention has been focused on the various polyhedron-based dendrites or branched structures.[2-12] For example, PbS star-shaped nanocrystals, multipods and dendrites,[2-4] MnO multipods,[5-7] flower-shaped Ag_2O particles,[8] and branched Cu_2O crystals[9-12] from nanometer to micrometer sizes have been prepared.

Cuprous oxide (Cu_2O), as a representative p-type semiconductor with a band gap of 2.17 eV, has been widely investigated for its potential applications in solar energy conversion,[13] electrodes of lithium ion batteries,[14] gas sensing[15] and photocatalytic degradation of organic pollutants.[16-20] It is meaningful to investigate the morphological evolution of Cu_2O, especially the multipod-shaped microcrystals, which can provide important information to the fields of crystal growth, design, and morphology-controlled synthesis of Cu_2O, and further other inorganic building blocks. Many methods have been developed to prepare multipod-shaped of Cu_2O microcrystal.[21-29] Choi et al. prepared multipod-shaped Cu_2O crystals by tuning the deployed synthetic parameters (pH, temperature and concentration) in their electrodeposition processes.[21, 22] Liu et al. synthesized hexapod-shaped Cu_2O microcrystals via a γ-irradiation reduction route.[23] However, the development of facile, rapid, and green methods for fabricating Cu_2O with multipod-shaped remains a key scientific challenge.

Herein, we present a rational synthetic scheme that yields novel multipod frameworks of Cu_2O microcrystals in a model study of the shape-guiding strategy. A series of Cu_2O multipod frameworks have been synthesized by adding weak reductive agent $EDTANa_2{\cdot}2H_2O$ into $CuAc_2{\cdot}2H_2O$ solution and varying the volume ratios of n-butyl alcohol to water in the reaction solvent. Most rewardingly, novel 14-pods Cu_2O frameworks were first formed. Through understanding the effect of solvent on the branching growth of Cu_2O microcrystals, the habit growth can be independently controlled and the ability to control the morphology of Cu_2O microcrystals can be achieved. In recent years, the studies using Cu_2O crystals as sacrificial templates for the formation of Cu_xS hollow architectures have attracted increasing interests.[30-35] Compared with other templates, Cu_2O crystals have many special advantages, such as easily controlled structures, cost saving, multiple morphology, and convenient large-scale production.[36,37] Herein, a template-assisted synthesis of multipod frameworks of Cu_7S_4 microcages using the obtained Cu_2O microcrystals as sacrificial templates is reported. Hollow Cu_7S_4 microcages were obtained in three steps involving the synthesis of Cu_2O crystals with different morphologies, the formation of Cu_2O/Cu_7S_4 core/shell structures in Na_2S ethanol and aqueous mixed solution, and the dissolution of the inner Cu_2O cores in ammonia solution. Details of the experiments are provided in Supporting Information.

Figures 1a, b present typical scanning electron microscopy (SEM) images of the 14-pods Cu_2O prepared in a medium of n-butyl alcohol/water at a volume ratio of 3.2: 6.8. The detailed structures of Cu_2O microcrystal particles are shown in high-magnified SEM images. The sizes of the 14-pods Cu_2O typically range from 10 to 15 μm, with an average branching length of ~5 μm. This type of multipod framework has fourteen uniform branching: along 6 <100> directions and along 8 <111> directions. They are marked as type II 14-pods Cu_2O in this work. Through the reaction of these 14-pods Cu_2O with a mixed ethanol and aqueous Na_2S solution at 0 °C in air, followed by dissolution of the Cu_2O cores in ammonia solutions, 14-pods Cu_7S_4 cages with uniform morphologies similar to those of the Cu_2O templates were obtained (Figure 1c). Inset of (c) is the high magnification image of a broken14-pods Cu_7S_4 cage, which clearly shows a hollow interior. The branching of a broken 14-pods Cu_7S_4 cage is shown in high-magnified SEM images (Figure 1e), which indicates microcages with a wall thickness of about 50 nm. The detailed structure of individual 14-pods Cu_7S_4 cage is shown in high-magnified SEM images (Figure 1c), which clearly indicates the

14-pods Cu_7S_4 cages have a smooth surface. The morphology and interior structure of the 14-pods Cu_7S_4 cages are further investigated by transmission electron microscopy (TEM).

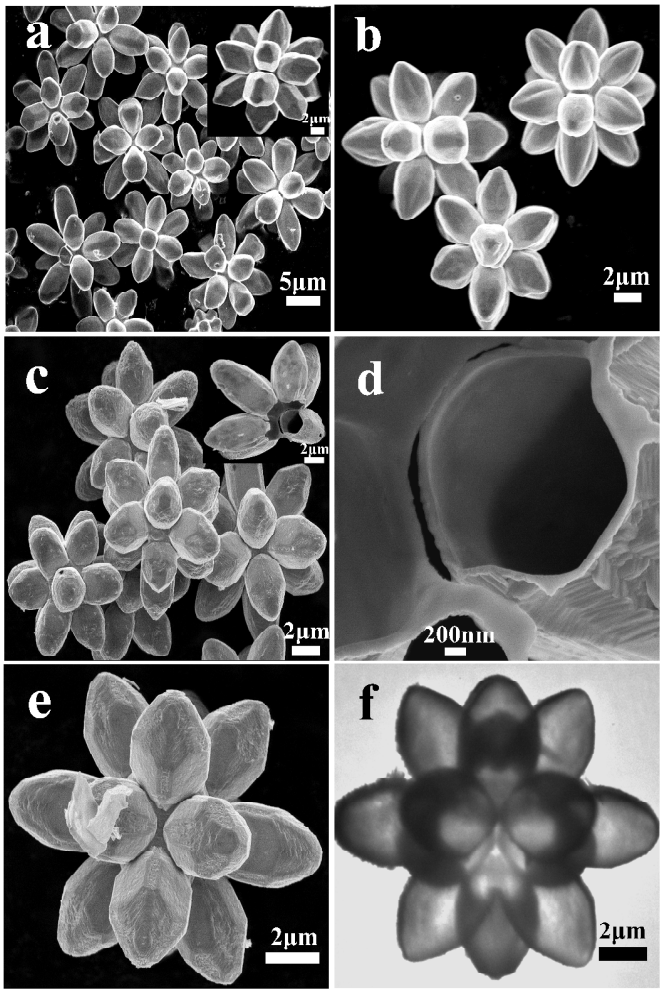

Figure 1. SEM images of a, b) 14-pods Cu_2O, and c, e) 14-pods Cu_7S_4 cages. Inset of (a) is the high magnification image of 14-pods Cu_2O. Inset of (c) is the high magnification image of a broken14-pods Cu_7S_4 cage. d) SEM images of a branch of the broken14-pods Cu_7S_4 cage. f) TEM images of 14-pods Cu_7S_4 cages. The14-pods Cu_7S_4 cages were prepared by reaction of the 14-pods Cu_2O precursor crystals shown in (a) with Na_2S solution at 0 °C in air followed by dissolution in ammonia solution.

Figure 1f shows that the particle has a regular 14-pods shape and a strong contrast between their edges (dark) and centers (bright), which also indicates microcages with a hollow interior. It has been reported that the crystal shape is determined by two growth processes: habit formation and branching growth.[38-43] Crystal habit is determined by the relative order of surface energies of different crystallographic planes of a crystal.[38,39] Branching growth is created by the diffusion effect.[40,41] When a crystal grows, ions or molecules near the surface are taking up by the growing crystal and a concentric diffusion field forms around the crystal.[42,43] This process forms the apexes of a polyhedral crystal, which protrude further into the region of higher concentration and grow faster than the central parts of facets, thus forming branches. The branching growth, however, generates rough and unstable surfaces that have many surface dangling bonds. The surface dangling bonds can rapidly increase the growth kinetic coefficient in these regions and compensate for the diffusion effect, resulting in faceting growth to form flat and smooth faces.[40, 41] Therefore, preference for branching and faceting growth can be altered by growth conditions that amplify or minimize the diffusion effect.

X-ray diffraction (XRD) analysis was used to determine the phases of the pure Cu_2O microcrystals and the hollow Cu_7S_4 microcages (Figure S1-S3). Figure S1c shows the XRD pattern of the as-prepared type II 14-pods Cu_2O. All the diffraction peaks are labeled and can be indexed according to the cubic phase of Cu_2O with PDF file No. 05-0667 (Figure S1a). No peaks from impurities such as CuO and Cu were observed. Figure S1d shows the XRD pattern of type II the14-pods hollow Cu_7S_4 formed by reaction of the14-pods Cu_2O with Na_2S solution in air. The pattern of the obtained type II 14-pods cages is consistent with the standard spectrum of monoclinic Cu_7S_4 with PDF file No. 23-0598 as shown in Figure S1b.

Our crystal growth experiments clearly showed that the branching was extremely sensitive to the chemical environment which in turn determined the final crystal morphology. In Figure 2, major branching patterns and the whole shape evolution of Cu_2O microcrystals from 6-pod frameworks to 14-pod frameworks of Cu_2O are presented as a function of solvent composition. The volume ratio of n-butyl alcohol to water in the reaction solvent played a crucial role in directing the overall morphologies of these intermediate structures. Under the n-butyl alcohol/water volume ratio of 6.5:3.5, Cu_2O crystal branching took place along all orientations of <100>, which resulted in the formation of 6-pod frameworks (type (a), Figure **2**).

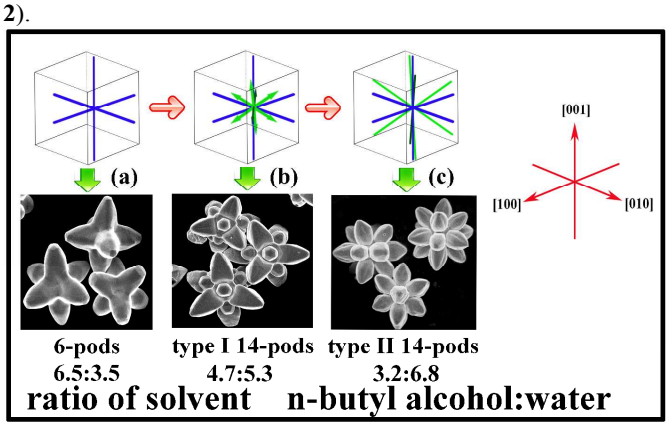

Figure 2. A flowchart summary of various types of branching fashions (inset indicates the coordinate system) and corresponding SEM images of Cu_2O microcrystals under the current synthetic conditions: (a) six branching along <100> directions; (b) six branching along <100> directions and eight shorter branching along <111> directions; and (c) six branching along <100> directions and eight shorter branching along <111> directions. Colored lines within a cubic box are equivalent; they are used to enhance the visibility.

It is interesting to note that with the decrease of volume ratio of n-butyl alcohol/water, a new type of multipod framework emerged (type (b), Figure **2**). This type of multipod framework showed fourteen branching: six branching along <100> directions and eight shorter branching along <111> directions. With further decrease of the n-butyl alcohol/water volume ratio to 3.2:6.8, the branching along <111> directions was gradually grown, finally leading to the formation of type II 14-pods Cu_2O

with fourteen uniform branching: 6 along <100> directions and 8 along <111> directions (type (c), Figure 2). With further decrease of the n-butyl alcohol/water volume ratio to 0:10, the branching along <111> directions was gradually grown, finally leading to the formation of 8-pods Cu_2O with eight uniform branching <111> directions (Figure S4). Therefore, it seems that n-butyl alcohol selectively adsorbs onto the (111) surface of Cu_2O which hinders its further growth.

Figure 3a shows a typical SEM image of the 14-pods Cu_2O prepared in a solvent of n-butyl alcohol/water at a volume ratio of 4.7: 5.3. The detailed structure of a Cu_2O microcrystal particle is shown in high-magnified SEM image (Inset of (a)). The sizes of the 14-pods Cu_2O typically ranged from 10 to 15 μm, with an average branching length of ~5 μm. This type of multipod framework has fourteen branching: six branching along <100> directions and eight shorter branching along <111> directions. They are marked as type I 14-pods Cu_2O in this work. The corresponding hollow 14-pods Cu_7S_4 cages also exhibit uniform regular 14-pods morphology with smooth surfaces (Figure 3b,c). A typical TEM image of the 14-pods Cu_7S_4 cage (Figure 3d) shows a perfect interior with a wall thickness of about 50 nm.

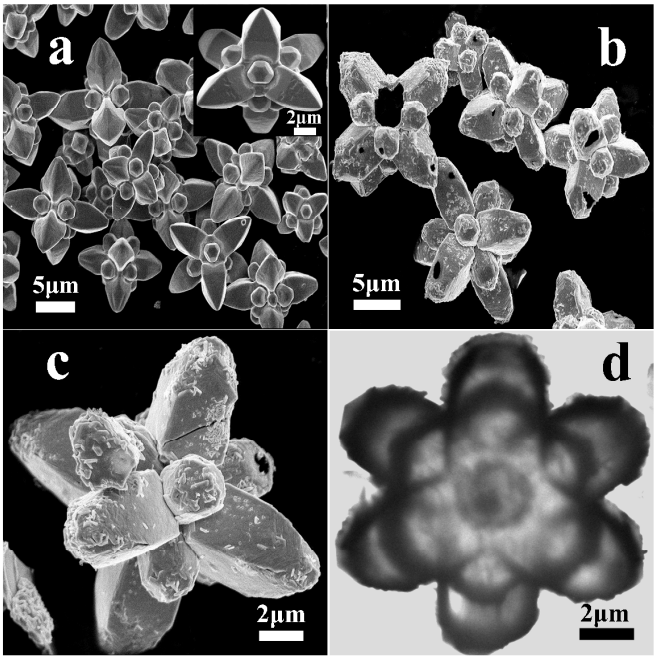

Figure 3. SEM images of a) 14-pods Cu_2O, and b,c) 14-pods Cu_7S_4 cages. Inset of (a) is the high magnification image of 14-pods Cu_2O. d) TEM images of 14-pods Cu_7S_4 cages.

Figure 4a shows a typical SEM image of the 6-pods Cu_2O prepared in a medium of n-butyl alcohol/water at a volume ratio of 3.2: 6.8. The detailed structure of a Cu_2O microcrystal particle is shown in high-magnified SEM image (Inset of (a)). This type of multipod framework showed six uniform branching along <100> directions. Figure 4b-d show typical SEM and TEM images of a hollow Cu_7S_4 that was formed against the 6-pods Cu_2O crystal, which clearly indicates a hollow 6-pods structure.

The formation of hollow Cu_7S_4 microcages was the result of the small solubility product constant K_{sp} of copper sulfide (Ksp $\approx 10^{-48}$). Cu_2O particles suspended in the Na_2S solution were immediately converted into Cu_2O/Cu_7S_4 core/shell structures in air as shown in Reaction 1.

$$14Cu_2O + 16S^{2-} + O_2 + 16H_2O \rightarrow 4Cu_7S_4 + 32OH^- \quad (1)$$

The formation of the Cu_2O/Cu_7S_4 core/shell structures can be considered as the Kirkendall effect.[44] In this approach, the specific Cu_2O structure allows diffusion of copper (I) ions from the central region to the surface and Cu_7S_4 was produced there at first. Cu_2O/Cu_7S_4 core/shell particles with cracked shells were formed. After dissolving the Cu_2O core in ammonia solution according to Reaction 2, hollow Cu_7S_4 microcages were obtained.[26]

$$2Cu_2O + 16NH_3 \cdot H_2O + O_2 \rightarrow 4[Cu(NH_3)_4]^{2+} + 8OH^- + 12H_2O \quad (2)$$

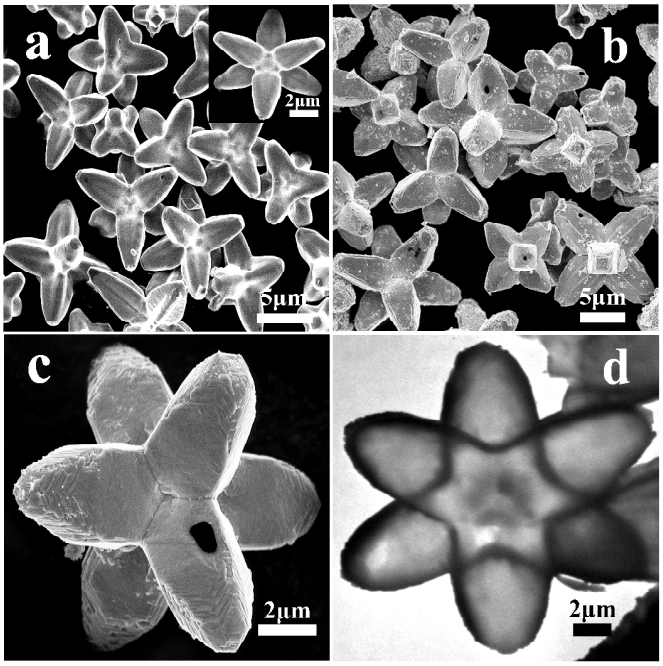

Figure 4. SEM images of a) 6-pods Cu_2O, and b,c) 6-pods Cu_7S_4 cages. Inset of (a) is the high magnification image of 6-pods Cu_2O. d) TEM images of 6-pods Cu_7S_4 cages.

Conclusions

In summary, a variety of multipod frameworks of Cu_2O microcrystals have been prepared through careful control of the volume ratios of n-butyl alcohol to water in the reaction solvent. In particular, 14-pods Cu_2O frameworks were first prepared. These results provide a facile procedure for the controlled preparation of novel multi-morphologic Cu_2O microcrystals. Moreover, a template-assisted synthesis of multipod frameworks of Cu_7S_4 microcages using the obtained Cu_2O microcrystals as sacrificial templates was established. This study revealed an important strategy in the design, controlled crystal growth, and morphology-controlled synthesis of multipod frameworks of Cu_2O microcrystals and Cu_7S_4 microcages. It will also promote the synthesis and application of other inorganic building blocks.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section and the XRD of products obtained at different reaction conditions (Figure S1-S3).

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Synthesis and Characterization of Multipod Frameworks of Cu_2O Microcrystals and Cu_7S_4 Hollow Microcages

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The 14-pods Cu_2O frameworks are first prepared through control of the ratios of n-butyl alcohol to water.