

Preparation of Uniform Hexapod Cu_2O and Hollow Hexapod CuO

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The atomic arrangement of the outer surface of inorganic oxides is strongly dependent on the morphology of inorganic oxides. The morphology-dependent properties of inorganic materials, such as magnetic, photocatalytic, and antibacterial activities, is one of the most important experimental issues in inorganic technology.¹⁻⁵ Many researchers have prepared uniform and specific shaped inorganic oxides to understand the morphology-dependent properties of inorganic oxides.

Most morphology-controlled synthesis has focused on the one-dimensional inorganic oxides, such as wires, rods, and ribbons with the assistance of hard-templates and soft-templates.⁶⁻⁹ Three-dimensional inorganic oxides with closed shapes such as cubes, octahedrons, cuboctahedrons, and rhombic dodecahedrons are usually prepared by hydrothermal and solvothermal reactions.¹⁰⁻¹⁴ However, few investigations have been carried out on three-dimensional inorganic oxides with open shapes such as tetrapods, hexapods, octapods, and star-like shapes.¹⁵⁻¹⁹

In general, the hollow metal oxides have superior catalytic efficiencies to non-hollow metal oxides, due to its low density, high surface-to-volume ratio, and large void spaces.^{20,21} The hollow CuO were widely used as catalysts, anodes for lithium batteries, and gas sensors.²²⁻²⁴ The hollow CuO spheres were fabricated using a droplet-to particle aerosol spray pyrolysis method.²⁵ The hollow CuO spheres were synthesized using a hydrothermal reaction of carboxylated copper precursors.²⁶ Hollow CuO microspheres were synthesized *via* a complex assisted method with hexamethylene-tetramine as a complex agent.²⁷ Hierarchically porous CuO hollow spheres were also synthesized *via* a simple one-pot template-free method.²⁴ CuO nanotubes were prepared by simple thermal oxidation of copper nanowires.²⁸ However, most of the hollow CuO had microsphere structures. It is very difficult to synthesize a uniform morphology of the three-dimensional hollowed structures of CuO . To the best of our knowledge, this hollowed hexapod CuO is the first CuO synthesized until now.

Cu_2O is one of the most important inorganic oxides that have been extensively investigated for morphology-controlled synthesis.²⁹⁻³² Cu_2O is considered to be the best candidate for the preparation of unique morphology. We also investigated the morphology evolution of Cu_2O from the thin-hexapod to the aggregated sphere *via* a thick-hexapod, truncated hexapod, truncated octahedron, and cuboctahedron.³³ However, the shape of the hexapod was not perfect and the

end of each pod was not straight. Therefore, we reinvestigated the synthetic process for the preparation of uniform hexapod-like Cu_2O . We also present a simple thermal oxidation method for the hollow hexapod of CuO from the direct oxidation of hexapod Cu_2O in air at a high temperature.

For the preparation of uniform hexapod Cu_2O , we revisited our earlier work of the morphology evolution for Cu_2O .³³ Especially, we reexamined the synthetic conditions for the hexapod Cu_2O . Even though the same chemical composition was used for the preparation of Cu_2O , we used a different type of microwave oven from that used in the earlier work. The morphology of Cu_2O is strongly dependent on the irradiation time of the microwave. The irradiation time of the microwave was adjusted for the preparation of uniform hexapod Cu_2O . Figure 1 shows the SEM images of the four Cu_2O products using the simple microwave-assisted reaction with different irradiation times with other conditions kept the same. As the irradiation time increases, the morphologies of Cu_2O evolve from the truncated octahedron to the octahedron concaved at the center of the surfaces, *via* an almost hexapod shape and a hexapod with thin pyramid arms at the end of each pod. Therefore, the microwave irradiation time of 120 s was adequate for the synthesis of the uniform hexapod morphology of Cu_2O .

Since most microwave-assisted reactions can be completed within a few minutes, the microwave-assisted method is an attractive, simple and convenient synthetic technique. The final temperature of the reaction solution was increased

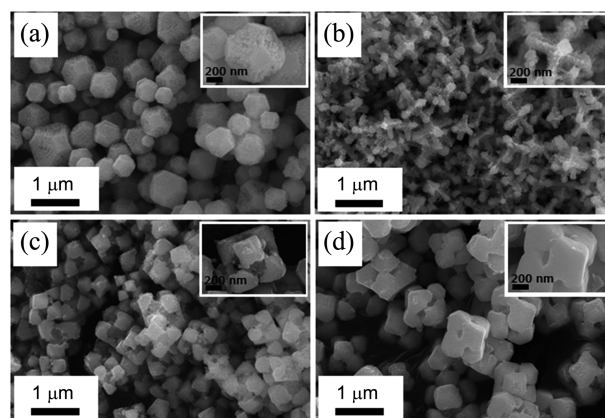


Figure 1. SEM images of the Cu_2O products prepared using the microwave-assisted method with various irradiation times; (a) 100 s, (b) 120 s, (c) 140 s, and (d) 160 s.

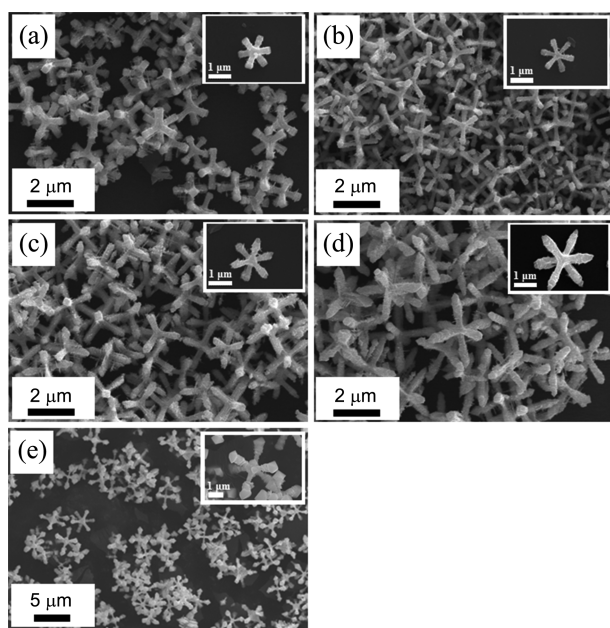


Figure 2. SEM images of the Cu_2O products prepared under the irradiation of microwave for 120 s. The cooling rates were adjusted by adding different amounts of cold water to the 150 mL of Cu_2O product solutions; (a) 200 mL, (b) 100 mL, (c) 50 mL, and (d) no cold water. (e) SEM images of thin-hexapod Cu_2O prepared in our earlier work.³³

to 90 °C within 120 s under microwave irradiation, the Cu_2O crystal grew in a short period. However, the thermal diffusion of the reaction medium may affect the fine morphology of the Cu_2O crystals. We attempted to control the thermal quenching rates of thermal diffusion by quickly pouring various amounts of cold water into the final solutions after microwave irradiation. Figure 2 shows the SEM images of the four Cu_2O products using different amounts of cold water with other conditions kept the same. All four products show similar morphologies of hexapod Cu_2O . Therefore, the hexapod structures of Cu_2O crystals were formed within a few minutes by thermal heating of the microwave irradiation. However, the shapes of the four products were slightly changed and the length of each pod was gradually elongated on a small scale as the amount of cold water decreased. The end of the each pod was formed by aggregating the small particles, as shown in Figure 2(d). This indicates that minor changes of the morphologies were formed by the thermal diffusion of the reaction medium after microwave irradiation. With a decrease in the amounts of cold water added to the final products, the thermal diffusion rate increased. The reaction process at the end of the pods occurred to increase the length of each pod, while keeping the shape of the hexapod unchanged, as shown in Figure 2. For comparison, the thin-hexapod Cu_2O prepared in our earlier work is shown in Figure 2(e).³³ We concluded that the experimental conditions of Figure 2(a) were the optimal conditions for the preparation of the uniform and perfect hexapod of Cu_2O . The average length and diameter of each pod is 800 nm and 300 nm, respectively.

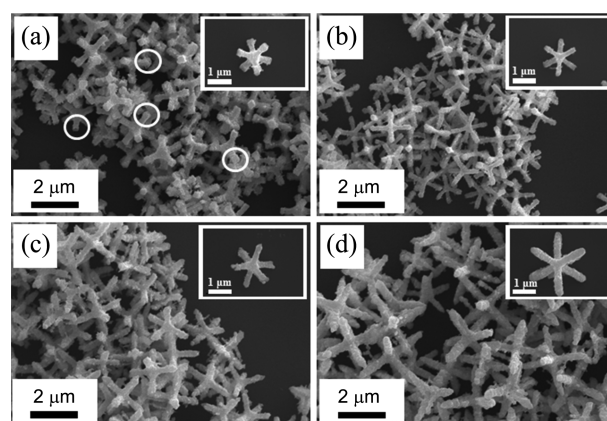


Figure 3. SEM images of the CuO products prepared from the direct thermal oxidation in the air at 400 °C for 5 h with the Cu_2O precursors, the cooling rates of which were adjusted by adding different amounts of cold water to the 150 mL of Cu_2O product solutions; (a) 200 mL, (b) 100 mL, (c) 50 mL, and (d) no cold water.

Figure 3 shows the SEM images of the four CuO products prepared by the direct thermal oxidation of the four Cu_2O precursors in air at 400 °C for 5 h. The outer shapes of the CuO products resemble those of Cu_2O precursors. However, the surfaces of the hexapod were rather roughened. Moreover, the ends of each pod showed opened structures as shown in the circle area in Figure 3(a). This indicates that CuO products have the hollowed structures. The hollow hexapod of CuO products obtained by the thermal oxidation of hexapod Cu_2O precursors was confirmed by the XRD measurement. Figure 4 shows the XRD patterns of the hexapod Cu_2O precursors and the hollow hexapod of the CuO products. The observed hexapod Cu_2O and hollow hexapod of CuO matched with the reported data of the cubic Cu_2O

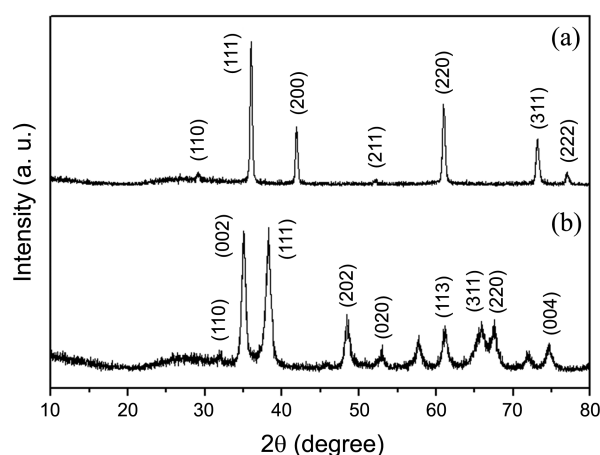


Figure 4. XRD patterns and Miller indices of SEM images of (a) hexapod Cu_2O prepared under the irradiation of microwave for 120 s and 200 mL cold water added to the 150 mL of product solution and (b) hollow hexapod CuO prepared from the direct thermal oxidation in the air at 400 °C for 5 h with the Cu_2O precursors prepared under the irradiation of microwave for 120 s and 200 mL cold water added to the 150 mL of the product solution.

(JCPDS 05-0667, $a = 0.4269$ nm) and monoclinic CuO (JCPDS 45-0937, $a = 0.4685$ nm, $b = 0.3425$ nm, $c = 0.5130$ nm, and $\beta = 99.549^\circ$), respectively. No impurities in the hexapod Cu₂O and the hollow hexapod of CuO in the XRD patterns indicated that pure Cu₂O and CuO were formed, respectively. The formation process of the Cu₂O product is followed by the consecutive reactions of the first step for the formation of Cu(OH)₂ by reaction with Cu²⁺ ion and OH⁻ ions and then the second step for the dehydration and reduction to form Cu₂O by using the glucose as an reducing agent. The hollow hexapod of CuO was formed by the direct thermal oxidation of hexapod Cu₂O precursors reacted with oxygen in the air.

Checking TEM images for the verification of hollowed materials is more effective than checking SEM images. Figure 5 shows the TEM images of hexapod Cu₂O precursors and the hollow hexapod of CuO products. Most of the arms of the hexapod Cu₂O show a dark region in the TEM images, indicating that the inside of the arms of the hexapod Cu₂O is filled, as shown in Figures 5(a) and (b). The lattice spacing of 0.30 nm corresponding to the (110) plane of Cu₂O was confirmed from the fringe pattern of the hexapod Cu₂O, as shown in Figure 5(c). The inset in Figure 5(c) showed the fast Fourier transform (FFT) pattern of the hexapod Cu₂O. However, the inside of the arms of the hexapod CuO show a relatively light region compared to the outside of the arms of the hexapod CuO, as shown in Figures 5(d) and (e). Similarly, the FFT pattern and lattice spacing of 0.27 nm corresponding to the (110) plane of CuO was also observed, as shown in Figure 5(f). Therefore, the hollow hexapod structures of CuO were formed by the thermal oxidation of the filled hexapod structures of Cu₂O. These hollowed structures may be formed by the diffusion of the inner parts of the Cu₂O particles in the hexapod to the outer parts of the hexa-

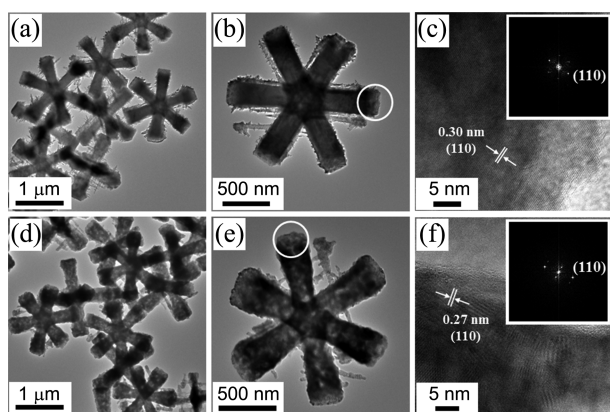


Figure 5. (a, b) HRTEM image and (c) high-magnification HRTEM image of hexapod Cu₂O prepared under the irradiation of microwave for 120 s and 200 mL cold water added to the 150 mL of the Cu₂O product solution. (d, e) HRTEM images and (f) high-magnification HRTEM image of hollow hexapod CuO prepared from the direct thermal oxidation in the air at 400 °C for 5 h with the Cu₂O precursor prepared under the irradiation of microwave for 120 s and 200 mL cold water added to the 150 mL of the product solution. The insets of (c) and (f) show the FFT patterns of an individual hexapod Cu₂O and hollow hexapod CuO, respectively.

pod. Cu₂O particles of the outer parts in the hexapod thermally reacted with oxygen in the air at a high temperature to produce CuO as the oxidation products. This diffusion behavior is known as a type of Kirkendall effect in accordance with Fick's first diffusion law.³⁴

In conclusion, the filled hexapod Cu₂O precursors were also prepared under microwave irradiation for only 120 s using a commercial microwave oven. The optimal experimental conditions for the perfect and uniform hexapod-like Cu₂O precursors were examined. The control of the cooling rate by adding cold water was also examined for the elimination of further crystal growth at the end of the arm of the hexapod Cu₂O precursors due to the thermal diffusion in reaction medium. The uniform hollow structure and hexapod CuO products were also prepared from the direct thermal oxidation of the filled hexapod Cu₂O precursors.

Experimental Section

CuCl₂·2H₂O (99%, Aldrich), polyethylene glycol (PEG, Mw 20,000, Fluka), NaOH (97%, Aldrich), and glucose (ACS reagent, Aldrich) were used as received. For the preparation of hexapod Cu₂O, 50 mL of a 0.01 M glucose aqueous solution and 2.4 g PEG were added to 10 mL of a 0.2 M CuCl₂ aqueous solution. 3 mL of 2.0 M NaOH aqueous solution was added to the mixed solution. 87 mL of deionized water was added to the mixed solution in a 500 mL beaker. A final mixed solution was placed into a commercial microwave oven (Magic MWO-230KD, 2.45 GHz, 800 W). The irradiation time of the microwave was changed from 100 s to 160 s to investigate the morphology changes with time. The final temperature of the mixed solution after microwave irradiation was 90 °C. In order to reduce the thermal diffusion effect in the reaction solution after microwave irradiation, the cold water was quickly added to the reaction solution. Various amounts (200 mL, 100 mL, and 50 mL) of cold water of 10 °C were added to the mixed solution to adjust the quenching rate for the thermal diffusion of the solution. After 30 min, the products were washed several times with ethanol and water. And the products were dried at 60 °C for 12 h in a drying oven. The structure and morphology of the Cu₂O and CuO products were characterized by powder X-ray diffraction (XRD, PANalytical, X'pert-pro MPD), scanning electron microscopy (SEM, Hitachi S-4300), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010).

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