

## Morphology-modulated Synthesis of Cu<sub>2</sub>O Hexapods

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The development of morphology-controlled synthesis methods is an important issue in inorganic materials science.<sup>1,2</sup> Because copper(I) oxide (Cu<sub>2</sub>O) has a cubic crystal system, it exhibits various morphologies.<sup>3,4</sup> Cu<sub>2</sub>O is a non-stoichiometric defect *p*-type semiconductor with a direct bandgap of 2.2 eV and has been used as a photocatalyst for the degradation of dye molecules and for water splitting.<sup>5-7</sup>

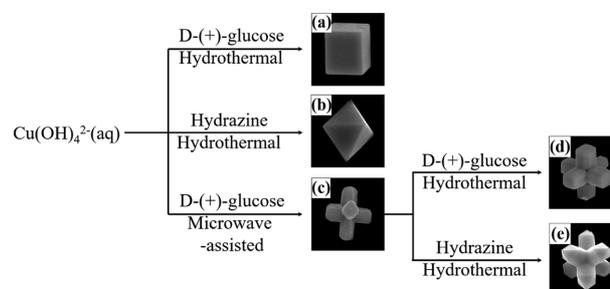
Simple closed morphologies, such as cubic, octahedral, and rhombic dodecahedral morphologies, are formed in the crystal habit to minimize the total surface free energy under thermodynamic equilibrium.<sup>8-10</sup> Cubic, octahedral, and rhombic dodecahedral Cu<sub>2</sub>O microcrystals have six {100} facets, eight {111} facets, and twelve {110} facets, respectively.<sup>11-15</sup> Because, the {100} facets of Cu<sub>2</sub>O microcrystals have different atomic arrangements from those of the {111} and {110} facets, the photocatalytic activities of Cu<sub>2</sub>O microcrystals are strongly dependent on the morphology of the Cu<sub>2</sub>O microcrystals.<sup>5,6</sup>

However, branched morphologies, such as hexapods, octapods, dodecapods, and dendrites, are formed through kinetic branching growth as a consequence of the non-equilibrium reaction conditions; these morphologies do not achieve the minimum total surface free energy.<sup>16-21</sup> Thus, the final morphologies of inorganic oxides are affected both by crystal habit formation and by branching growth. Most of the hexapodal Cu<sub>2</sub>O microcrystals have unsmoothed surfaces on their branched arms.<sup>13,22-26</sup> However, relatively little is known about the hexapodal Cu<sub>2</sub>O crystals, in which their arms covered with clean and smoothed cubic or octahedral surfaces.

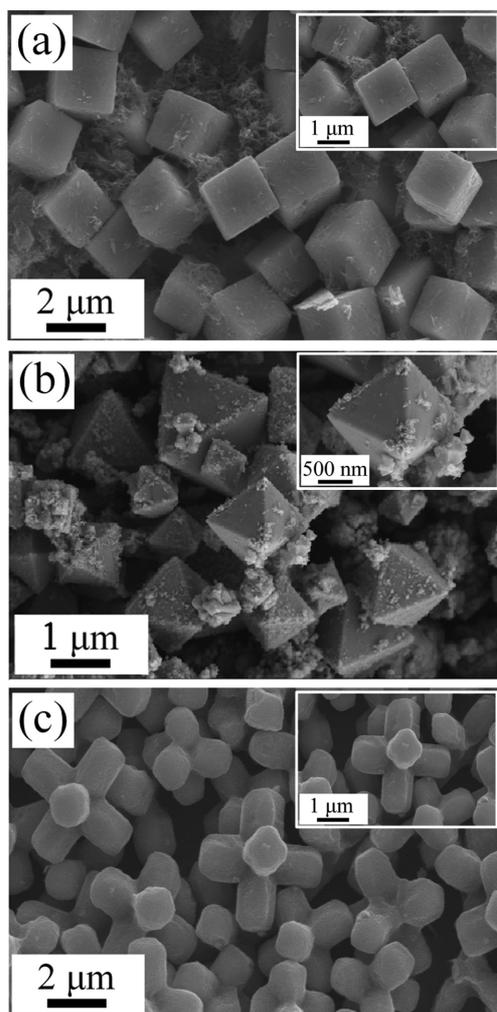
In the present paper, we present preparation methods for cubic, octahedral, and hexapodal Cu<sub>2</sub>O microcrystals. Cu<sub>2</sub>O microcrystals with six cubic arms and six square-pyramidal arms were also prepared by an additional hydrothermal reaction in which the Cu<sub>2</sub>O hexapods were used as templates. The crystal growth mechanism of the various morphologies of Cu<sub>2</sub>O products is discussed.

*Scheme 1* shows the method used to prepare the cubic,

octahedral, hexapodal, six-cubic-arm, and six-square-pyramidal-arm Cu<sub>2</sub>O microcrystals. The cubic (or octahedral) Cu<sub>2</sub>O microcrystals were prepared through reduction with D-(+)-glucose (or hydrazine) of copper in an alkaline aqueous solution, respectively, as shown in *Figs. 1(a)* and *(b)*. In our earlier work, we found that the Cu<sub>2</sub>O crystal habit changed from cubic to beveled cubic, rhombicuboctahedral, and 50-facets polyhedral with increases in the NaOH concentration. When neutral D-(+)-glucose was used as a reductant, cubic Cu<sub>2</sub>O crystals were formed at the lowest concentration of NaOH under thermodynamic equilibrium condition.<sup>10</sup> In this work, we also found that octahedral Cu<sub>2</sub>O crystals were obtained at the lowest concentration of NaOH by using a hydrazine as a reductant. Because hydrazine is a stronger and more ionic reductant compared to the D-(+)-glucose, the octahedral Cu<sub>2</sub>O crystals as another thermodynamically stable morphology are formed instead of cubic Cu<sub>2</sub>O crystals. The choice of reductant plays an important role in the formation of cubic and octahedral Cu<sub>2</sub>O microcrystals. The results show that the hydroxide ions (OH<sup>-</sup>) selectively added to the {100} or {111} facets of the Cu<sub>2</sub>O crystal seed during crystal when D-(+)-glucose or hydrazine, respectively, was used as the reductant. Because the hydrothermal reaction was used to achieve thermodynamic equilibrium, Cu<sub>2</sub>O



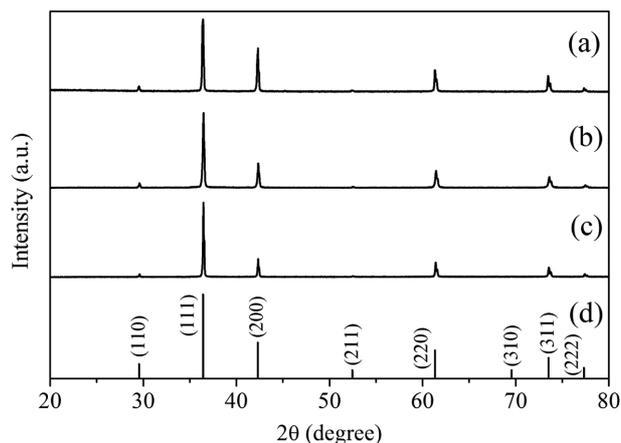
**Scheme 1.** Illustration of the method used to prepare (a) cubic (sample 1), (b) octahedral (sample 2), (c) hexapodal (sample 3), (d) six-cubic-arm (sample 4), and (e) six-square-pyramidal-arm (sample 5) Cu<sub>2</sub>O microcrystals.



**Figure 1.** SEM images of the (a) cubic (sample 1) and (b) octahedral (sample 2) Cu<sub>2</sub>O products prepared using D-(+)-glucose and hydrazine under hydrothermal reaction conditions, respectively. (c) SEM image of the hexapodal (sample 3) Cu<sub>2</sub>O products prepared using D-(+)-glucose in a microwave-assisted reaction.

microcrystals with a closed morphology, such as cubes or octahedra, were formed as part of the crystal habit.

Because the microwave-assisted reaction was only carried out for 2 min, the kinetic branching growth mechanism was involved in the formation of Cu<sub>2</sub>O hexapods, as shown in Fig. 1(c). The mean length of each Cu<sub>2</sub>O pod was 1.5 μm. It exhibited rough surfaces with irregular end spheres. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was used as a chelating agent for the formation of copper-TMEDA complex. Without TMEDA chelating agent, the Cu<sub>2</sub>O hexapods with thin and sharp arms were formed.<sup>22</sup> TMEDA may affect the release rate of copper ion from the copper-TMEDA complex. Thus, TMEDA plays an important role in the formation of regular Cu<sub>2</sub>O hexapods with thick



**Figure 2.** XRD patterns of the (a) cubic (sample 1), (b) octahedral (sample 2), and (c) hexapodal (sample 3) Cu<sub>2</sub>O products. (d) The XRD pattern and Miller indices of Cu<sub>2</sub>O (JCPDS 05-0667) are shown for comparison.

arms. The regular Cu<sub>2</sub>O hexapods with thick arms are adequate for the preparation of the six-cubic-arm and six-square-pyramidal-arm Cu<sub>2</sub>O microcrystals from Cu<sub>2</sub>O hexapods as templates. The XRD patterns of the cubic, octahedral, and hexapodal Cu<sub>2</sub>O products matched the cubic crystal structure of Cu<sub>2</sub>O (JCPDS 05-0667, *a* = 0.4269 nm), as shown in Fig. 2. The XRD intensity ratios of (200) to (111) are 0.62 and 0.35 for cubic and octahedral for Cu<sub>2</sub>O products, respectively. The characteristics of (100) planes resembles those of (200) planes. It indicates that cubic and octahedral Cu<sub>2</sub>O products are covered by the {100} and {111} surfaces, respectively.

The Cu<sup>2+</sup> ions react with TMEDA in solution to form a copper-TMEDA complex, [Cu(TMEDA)<sub>2</sub>]<sup>2+</sup>. The following reaction mechanism is proposed for the formation of Cu<sub>2</sub>O products via dehydration and subsequent reduction of the Cu(OH)<sub>4</sub><sup>2-</sup> by D-(+)-glucose from the copper-TMEDA complex:

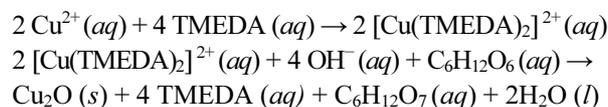
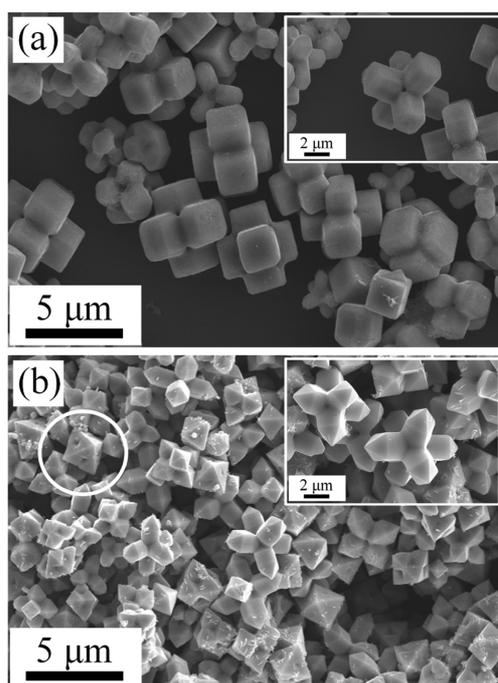


Fig. 3 shows the preparation of the six-cubic-arm and six-square-pyramidal-arm Cu<sub>2</sub>O microcrystals from Cu<sub>2</sub>O hexapods as templates. These Cu<sub>2</sub>O products were prepared by an additional hydrothermal reaction involving the reduction of a copper solution with D-(+)-glucose or hydrazine using the Cu<sub>2</sub>O hexapods as a template. Because the hydroxide ions (OH<sup>-</sup>) selectively added to the {100} facets of the Cu<sub>2</sub>O crystal under reduction by D-(+)-glucose, as shown in Fig. 3(a). The surfaces of the arms became



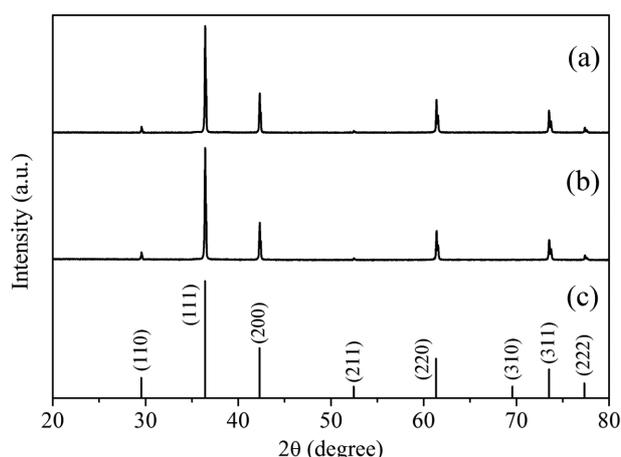
**Figure 3.** SEM images of the (a) six-cubic-arm  $\text{Cu}_2\text{O}$  products (sample 4) prepared using D-(+)-glucose and (b) six-square-pyramidal-arm  $\text{Cu}_2\text{O}$  products (sample 5) prepared using hydrazine.

smooth as additional  $\text{Cu}_2\text{O}$  crystals filled along the  $\{100\}$  facets of the  $\text{Cu}_2\text{O}$  hexapods.

Similarly, the  $\text{Cu}_2\text{O}$  microcrystals with six square-pyramidal arms were obtained after additional reduction with hydrazine solution, as shown in Fig. 3(b). As expected, the square-pyramidal arms were formed by filling of the  $\text{Cu}_2\text{O}$  crystal along the  $\{111\}$  facets of each arm. With increasing filling along the  $\{111\}$  facets of hexapodal  $\text{Cu}_2\text{O}$  crystals, octahedral crystals with some voids at the center of the  $\{111\}$  facets were also formed, as shown in the white circled region in Fig. 3(b). The XRD patterns of samples 4 and 5 confirmed that the  $\text{Cu}_2\text{O}$  products were prepared without any impurities, as shown in Fig. 4.

Thus,  $\text{Cu}_2\text{O}$  products with six cubic arms and six square-pyramidal arms were prepared by the consecutive reaction method, which first involved the branching growth mechanism, followed by the crystal habit formation mechanism. This consecutive reaction method can provide new insights into the synthesis of extended and unique morphologies in which both branched shapes and closed shapes are combined.

In conclusion, the choice of reductant plays an important role in the formation of cubic and octahedral  $\text{Cu}_2\text{O}$  microcrystals through crystal habit formation.  $\text{Cu}_2\text{O}$  hexapods were obtained through branching growth during microwave-



**Figure 4.** XRD patterns of the (a) six-cubic-arm (sample 4) and (b) six-square-pyramidal-arm (sample 5)  $\text{Cu}_2\text{O}$  products. (c) The XRD pattern and Miller indices of  $\text{Cu}_2\text{O}$  (JCPDS 05-0667) are shown for comparison.

assisted reaction. Six-cubic-arm and six-square-pyramidal-arm  $\text{Cu}_2\text{O}$  products were obtained from the  $\text{Cu}_2\text{O}$  hexapods through additional crystal habit formation. The consecutive synthesis method that is branching growth followed by crystal habit formation provides unique branched morphologies such as six-cubic-arm and six-square-pyramidal-arm  $\text{Cu}_2\text{O}$  products.

## EXPERIMENTAL

$\text{CuCl}_2 \cdot \text{H}_2\text{O}$  (Sigma-Aldrich, St. Louis, MO, USA),  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (Sigma-Aldrich),  $\text{NaOH}$  (Sigma-Aldrich), polyethylene glycol (PEG, Mw 20,000, Sigma-Aldrich),  $N,N,N',N'$ -tetramethylethylenediamine (TMEDA, 99%, Sigma-Aldrich), hydrazine (Sigma-Aldrich), and D-(+)-glucose (Sigma-Aldrich) were used as-received.

The D-(+)-glucose (or hydrazine) and TMEDA were used as a reductant and a chelating agent of  $\text{Cu}^{2+}$  ions, respectively. The experimental conditions for the preparation of various  $\text{Cu}_2\text{O}$  crystals are summarized in Table 1. For the preparation of cubic (sample 1) or octahedral (sample 2)  $\text{Cu}_2\text{O}$  products, 5 mL of a 0.044 M D-(+)-glucose (or 0.017 mL hydrazine) solution was added to 10 mL of a 0.11 M  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  solution, respectively, and 5 mL of 1.2 M  $\text{NaOH}$  solution was added to the resultant solution. The final solution was incubated for 60 min at 70 °C.

The  $\text{Cu}_2\text{O}$  hexapods (sample 3) were synthesized via a microwave-assisted reaction. Fifty milliliters of a 0.01 M D-(+)-glucose solution and 2.4 g PEG were added to 10 mL of a 0.2 M  $\text{CuCl}_2 \cdot \text{H}_2\text{O}$  solution, followed by the addition of 0.25 mL TMEDA; 89.75 mL of water was subsequently added

**Table 1.** Brief summary of the experimental conditions used in this work

Sample number	Seed	Copper source	Reductant	Chelating agent	Synthetic method	Morphology	SEM
1	No	CuCl <sub>2</sub>	D-(+)-glucose	No	Hydrothermal	Cube	Fig. 1(a)
2	No	CuCl <sub>2</sub>	Hydrazine	No	Hydrothermal	Octahedron	Fig. 1(b)
3	No	CuCl <sub>2</sub>	D-(+)-glucose	TMEDA	Microwave-assisted	Hexapods	Fig. 1(c)
4	Yes	Cu(CH <sub>3</sub> COOH) <sub>2</sub>	D-(+)-glucose	No	Hydrothermal	Six-cubic-arm	Fig. 3(a)
5	Yes	Cu(CH <sub>3</sub> COOH) <sub>2</sub>	Hydrazine	No	Hydrothermal	Six-square-pyramidal-arm	Fig. 3(b)

to the solution in a 500 mL beaker. The final solution was placed in a commercial microwave oven (Magic MWO-230 KD, 2.45 GHz, 800 W, Seoul, Korea) and irradiated for 2 min. When the microwave irradiation process was completed, the solution was quenched in ice-water.

The six-cubic-arm Cu<sub>2</sub>O microcrystals (sample 4) were prepared by adding 5.0 mL of 1.2 M NaOH solution to 5.0 mL of 0.22 M Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O solution in a 70 mL beaker, followed by the addition of 5.0 mL 0.044 M D-(+)-glucose solution and 0.015 g of the Cu<sub>2</sub>O template. The final solution was incubated for 60 min at 70 °C. For the preparation of Cu<sub>2</sub>O microcrystals with six square-pyramidal arms (sample 5), 5.0 mL of 1.2 M NaOH solution was added to 5.0 mL of 0.040 M Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O solution in a 70 mL beaker and 0.017 mL hydrazine was subsequently added, along with 0.015 g of the Cu<sub>2</sub>O template. The final solution was incubated for 60 min at 70 °C. All Cu<sub>2</sub>O products were collected by centrifugation at 4000 rpm for 10 min, washed with ethanol, and then dried for 24 h in a vacuum oven at room temperature.

The structures and morphologies of the Cu<sub>2</sub>O products were analyzed by powder X-ray diffraction (XRD, PANalytical X'Pert-PRO MPD, Almelo, The Netherlands) using Cu K $\alpha$  radiation and by scanning electron microscopy (SEM, Hitachi S-4300, Tokyo, Japan), respectively.

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