

Microwave Assisted Synthesis of Cu₂O Crystals with Morphological Evolution from Octapod to Octahedron

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The morphology-controlled synthesis of inorganic oxides is one of the most important goals of material sciences. In recent years, many researchers have investigated development of a synthetic method for preparing inorganic oxides with different morphologies, such as cube, cuboctahedron, octahedron, hexapod (6-pod), octapod (8-pod), and dodecapod (12-pod). The optical, catalytic, and antibacterial properties of {100} surfaces are quite different from those of {111} surfaces, due to the different unique atomic arrangements on the {100} and {111} surfaces of inorganic oxides.¹⁻⁵ Among the various morphological changes, the morphological evolution from cube to octahedron *via* truncated cube, cuboctahedron, and truncated octahedron was focused on understanding the crystal growth rate ratio of the <100> direction to the <111> direction. Therefore, it is very important to investigate the morphological evolution from cube to octahedron, by preparing the various morphologies with fine adjustments of chemical synthetic conditions.

Cuprous oxide (Cu₂O) has cubic crystal symmetry, and it has been extensively investigated for morphology-controlled synthesis. Many efforts have been devoted to prepare specific type morphologies, such as star-like, 6-pod, cube, octahedron, and other polyhedron.⁶⁻⁸ The multi-pod, star-like, and cubic Cu₂O crystals were synthesized by reducing the copper-citrated complex with glucose.⁹ The hexapod Cu₂O crystals were prepared by γ -irradiation reduction route at room temperature.¹⁰ The highly symmetric 26-facet crystals were synthesized by a hydrothermal reaction using sodium citrate as a complexing agent.¹¹ The cubic, octahedral, rhombic dodecahedral Cu₂O crystals were also prepared in a weak acid solution.¹² For the morphological evolution of Cu₂O products, most researches have focused on the closed shape of Cu₂O crystals, from cube to octahedron.¹³⁻¹⁶ However, there are few reports on the morphological evolution of the Cu₂O products with branched structures, such as 8-pod, 12-pod, (6 \times 4)-pod, and 6-pod. Ho *et al.* reported the systematic morphological evolution of Cu₂O from cube, through cuboctahedron, and octahedron, finally to 6-pod, by varying the concentration of hydroxylamine used as a reducing agent.¹⁷ The morphological evolution of Cu₂O from octahedron to 6-pod was observed by controlling the reaction temperature and time.¹⁸ We also reported the morphological evolution of Cu₂O from 6-pod to aggregated sphere *via* truncated 6-pod, truncated octahedron, and cuboctahedron.¹⁹ In this work, we

present systematic morphological evolution of the Cu₂O products from 8-pod to octahedron *via* 12-pod, (6 \times 4)-pod, 6-pod, star-like, and concave octahedron, by using the microwave assisted reaction.

The Cu₂O products were prepared by reacting CuCl₂·2H₂O, *N,N,N',N'*-tetramethyl ethylenediamine (TMEDA), glucose, and polyethylene glycol (PEG), using a microwave assisted method. TMEDA acts as both ligand for copper-TMEDA complex, and hydroxide ion (OH⁻) generator in alkaline solution. Glucose reduces the copper ion (Cu²⁺) of copper-TMEDA complex, and reacts with hydroxide ion (OH⁻) from the Cu₂O, with release of H₂O and TMEDA. PEG was also used for the soft templates for preparing the Cu₂O products. The microwave assisted reaction has advantage for realizing reactions in a very short time, due to the higher reaction rates.^{20,21} Even though microwave assisted reaction is an efficient method for the preparation of the specific morphology of inorganic oxides, the branched shapes of inorganic oxides are obtained only in a short period of microwave irradiation time. Under the longer irradiation time of microwave, the aggregated and closed shapes of inorganic oxides were obtained.¹⁹ In this work, Cu₂O products were prepared under the microwave irradiation for only 2 min, by using a commercial microwave. After finishing the reaction, the reaction was rapidly quenched by immersion of the reaction solution beaker into cold water. We used a very short reaction time and quenching method, and the variation of reaction temperature and time are largely reduced. Therefore, only one shape of the Cu₂O product, without several multiple shapes, was prepared at the fixed reaction condition in the microwave assisted reaction.

Figure 1 shows the SEM images of the Cu₂O crystals prepared by the microwave assisted reaction with different reactant concentrations. At 2.20 mM CuCl₂, Cu₂O 8-pod crystals were formed, as shown in Figure 1(a). The mean length of each pod of the 8-pod was approximately 900 nm. As the CuCl₂ amount was increased to 6.67 mM and 8.87 mM, shorter 12-pod and longer 12-pod crystals were obtained, as shown in Figures 1(b) and 1(c), respectively. The length of each pod of the 12-pod at 8.87 mM was larger, compared to that at 6.67 mM. At a CuCl₂ amount of 11.1 mM, complicated structures of Cu₂O products with multiple pods and arms were formed, as shown in Figure 1(d). This structure was denoted as (6 \times 4)-pod. The inset of Figure 1(d)

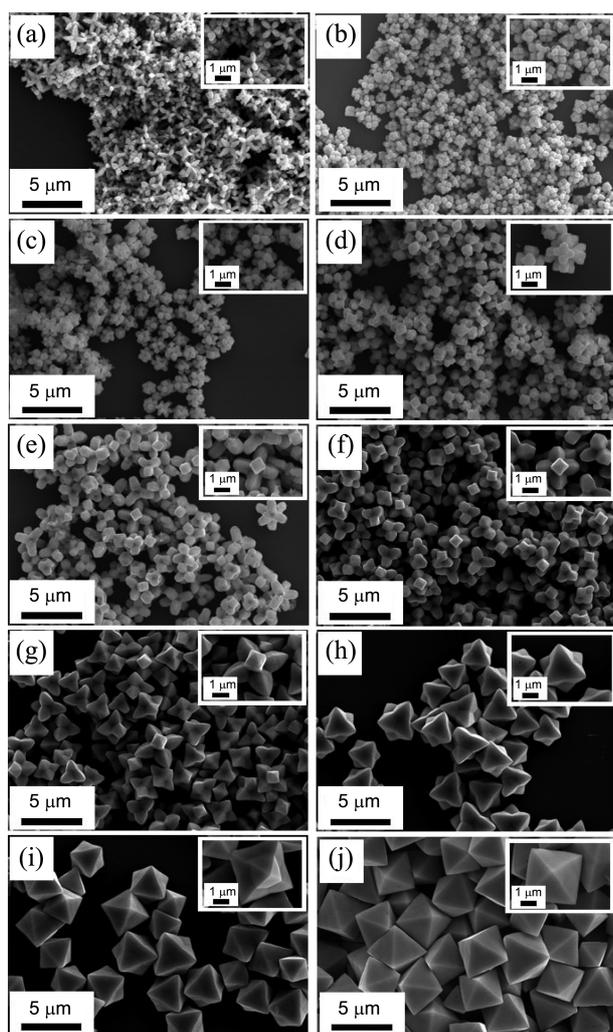


Figure 1. SEM images of the Cu_2O products obtained from the microwave assisted method with various amounts of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: (a) 2.20 mM, (b) 6.67 mM, (c) 8.87 mM, (d) 11.1 mM, (e) 13.3 mM, (f) 16.7 mM, (g) 20.0 mM, (h) 26.7 mM, (i) 33.3 mM, and (j) 40.0 mM.

shows SEM images of the (6 \times 4)-pod revealed branched structures, in which four arms were attached perpendicular to the main axis of each pod. When the amount of CuCl_2 was increased to 13.3 mM, the 6-pod Cu_2O crystals with a mean length of 1.4 μm were formed. The end of each pod has a square morphology. This happened by (6 \times 4)-pod changing to 6-pod with square end by decreasing the area of the end of each pod, and then void spaces within the 6-pod increased. This indicates that the crystal growth rate along the $\langle 100 \rangle$ direction was increased with the amount of CuCl_2 . As the amount of CuCl_2 increased further to 16.7 mM and 20.0 mM, star-like shapes with dull end and sharp end of Cu_2O were obtained, as shown in Figures 1(f) and 1(g), respectively. Figures 1(h) and 1(i) show SEM images of concave octahedrons with large void spaces and small void spaces in the middle of octahedral planes, prepared at 26.7 mM and 33.3 mM of CuCl_2 , respectively. When the amount of CuCl_2 finally increased further to 40.0 mM, perfect octahedron of Cu_2O crystals without void spaces at

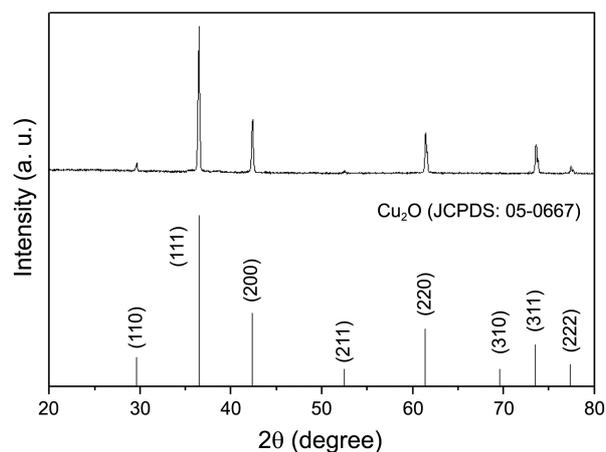


Figure 2. Typical XRD patterns of the Cu_2O products obtained from the microwave assisted method.

the surfaces of octahedral planes were obtained, as shown in Figure 1(j). Therefore, the morphology evolution of the Cu_2O products from 8-pod, through shorter 12-pod, longer 12-pod, (6 \times 4)-pod, 6-pod with square end, star-like with dull end, star-like with sharp end, concave octahedron with large void spaced plane, concave octahedron with small void spaced plane, finally to perfect octahedron were prepared with increasing the reactant amount, by microwave assisted reaction. Figure 2 shows the typical X-ray diffraction (XRD) patterns of the Cu_2O product by microwave assisted reaction. All of the diffraction peaks match with cubic crystal type of Cu_2O (JCPDS 05-0667, $a = 0.4269$ nm). This indicates that Cu_2O products have been successfully prepared.

In general, the crystal growth processes are controlled by both crystal habit formation, and branching growth.²² The crystal habit formation is processed by thermodynamically controlled reaction associated with the surface energy of the crystal planes. The branching growth is processed by kinetically controlled reaction associated with the diffusion effects. Therefore, the closed shapes and open shapes of crystals were formed by the thermodynamically controlled reaction and kinetically controlled reaction, respectively. The open shapes of crystals, such as 8-pod, (8 \times 3)-pod, 12-pod, (6 \times 4)-pod, and 6-pod, corresponding to the closed shapes of crystals, such as cube, truncated cube, cuboctahedron, truncated octahedron, and octahedron, respectively. When the closed shapes of reaction products were prepared by the hydrothermal reaction, the reaction time is long enough to have the thermodynamically controlled reaction. However, we used the microwave assisted reaction, and the Cu_2O products were obtained for only 2 min. The branching growth of Cu_2O products was controlled in low and moderate reaction concentrations. The 8-pod, 12-pod, (6 \times 4)-pod, 6-pod, and star-like Cu_2O crystals were formed. On increasing the reaction concentration, the reaction rates are increased. Since the progress of the reaction is almost finished at the higher reaction concentration, the Cu_2O products are gradually controlled by the thermodynamic effects. The Cu_2O products with closed shapes, such as concave octahedron

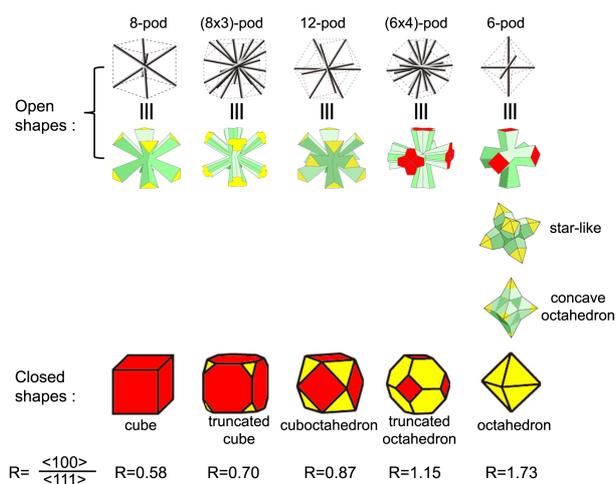


Figure 3. Top row: ideal morphological evolution from 8-pod through (8×3)-pod, 12-pod, and (6×4)-pod to 6-pod with open shapes of crystals. Middle rows: realistic morphological evolution from 8-pod through (8×3)-pod, 12-pod, and (6×4)-pod to 6-pod with open shapes of crystals formed by the chemical reaction. Bottom row: morphological evolution from cube through truncated cube, cuboctahedron, and truncated octahedron to octahedron with closed shapes of crystals. The R values, ratios of crystal growth rate along the $\langle 100 \rangle$ direction to that of $\langle 111 \rangle$ direction, are presented for cube, truncated cube, cuboctahedron, truncated octahedron, and octahedron of the closed shaped crystals. The red, yellow, and green colors represent the $\{100\}$, $\{111\}$, and unidentified planes, respectively.

and octahedron, were formed at higher reactant concentrations.

In the open shaped crystal, the crystal growth rates along the $\langle 100 \rangle$ and $\langle 111 \rangle$ affect the morphologies of the reaction products. The 8-pod is usually obtained when the crystal growth rate of the $\langle 111 \rangle$ direction is much faster than that of the $\langle 100 \rangle$ direction. Whereas, the 6-pod is formed when the crystal growth rate of the $\langle 100 \rangle$ direction is faster than that of the $\langle 111 \rangle$. The ratio of crystal growth rate along the $\langle 100 \rangle$ direction to that of the $\langle 111 \rangle$ direction, R, is usually used as the reaction rate parameter for the closed shaped crystals. The values of R for the formation of cube, truncated cube, cuboctahedron, truncated octahedron, and octahedron are 0.58, 0.70, 0.87, 1.15, and 1.73, respectively.²³ Therefore, the crystal growth rates of $\langle 100 \rangle$ and $\langle 111 \rangle$ directions affects strongly the morphology formation of the inorganic oxides with cubic crystal system, such as Cu_2O and Ag_2O .

Figure 3 shows a schematic illustration of the crystal growth evolution from the cube to octahedron with both kinetically controlled reaction and thermodynamically controlled reaction. The morphological evolution of Cu_2O products prepared with microwave assisted reaction in this work as a function of reactant concentration is also presented in Figure 4. In this work, we observed the morphological evolution of Cu_2O products from 8-pod, through 12-pod, (6×4)-pod, 6-pod, star-like, concave octahedron to octahedron, with the concentration of the reactants. This indicates that the branching crystal growth occurred for the lower reactant concentration, and the crystal habit formation occurred for the higher reaction concentration. Simultaneously, the crystal

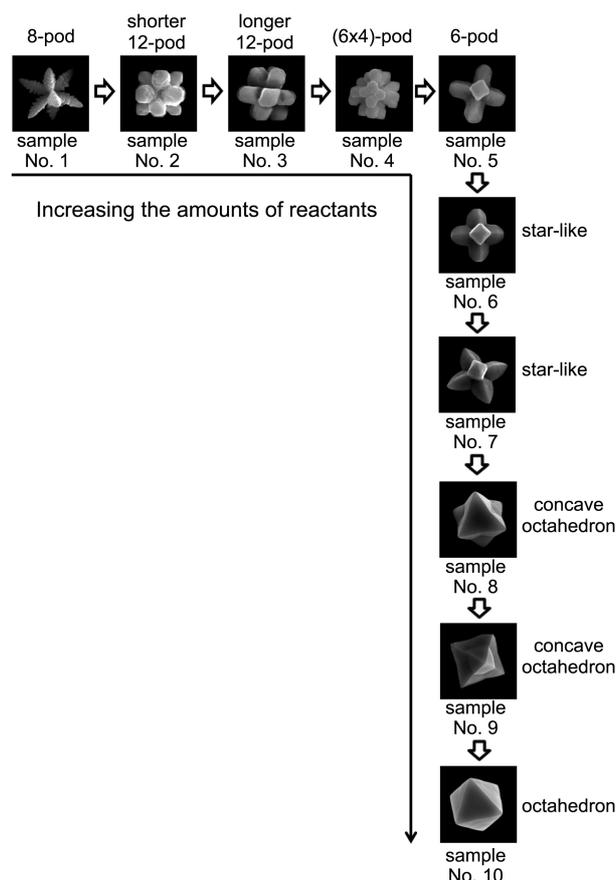


Figure 4. Schematic diagram for the morphological evolution of Cu_2O products prepared with increasing the amount of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ by microwave assisted reaction.

growth rate ratio (R) of $\langle 100 \rangle$ direction to $\langle 111 \rangle$ direction is increased with the reactant concentration. Therefore, the 8-pod as open shape with large void space was formed due to the larger crystal growth rate of the $\langle 111 \rangle$ direction, compared to that of the $\langle 100 \rangle$ direction, with kinetically controlled reaction at lowest reactant concentration. The octahedron as closed shape with no void space was formed due to the larger crystal growth rate of the $\langle 100 \rangle$ direction under the thermodynamically controlled reaction at the highest reactant concentration.

In conclusion, we present the simple and facile microwave assisted synthetic method for morphology controlled Cu_2O products. The Cu_2O products were prepared for only 2 min of microwave irradiation, by using a commercially available microwave oven. The Cu_2O products with various morphologies, such as 8-pod, 12-pod, (6×4)-pod, 6-pod, star-like, concave octahedron, and octahedron, were obtained by a simple adjustment of the reactant concentration. Under the lower reactant concentration, the open shaped crystals, such as 8-pod, 12-pod, (6×4)-pod, 6-pod, and star-like, were formed under the branching crystal growth mechanism. For the higher reaction concentration, the closed shaped crystals, such as concave octahedron and octahedron, were formed under the crystal habit formation. On increasing the reaction concentration, the crystal growth rate ratio of the $\langle 100 \rangle$

Table 1. Experimental conditions for the preparation of Cu₂O products with various morphologies

Sample Number	CuCl ₂ ·2H ₂ O (mM)	D-(+)-glucose (mM)	TMEDA (nM)	PEG (mM)	SEM images	Morphology
1	2.20	0.553	5.53	0.133	Fig. 1(a)	8-pod
2	6.67	1.67	16.7	0.400	Fig. 1(b)	shorter 12-pod
3	8.87	2.20	22.0	0.533	Fig. 1(c)	longer 12-pod
4	11.1	2.80	28.0	0.667	Fig. 1(d)	(6×4)-pod
5	13.3	3.33	33.3	0.800	Fig. 1(e)	6-pod
6	16.7	4.20	42.0	1.00	Fig. 1(f)	star-like
7	20.0	5.00	50.0	1.20	Fig. 1(g)	star-like
8	26.7	6.67	66.7	1.60	Fig. 1(h)	concave octahedron
9	33.3	8.33	83.3	2.00	Fig. 1(i)	concave octahedron
10	40.0	10.0	100	2.40	Fig. 1(j)	octahedron

direction to the <111> direction increases, and the crystal habit formation mechanism is preferred, compared to the branching formation.

Experimental Section

CuCl₂·2H₂O (99%, Aldrich), polyethylene glycol (PEG, Mw 20,000, Aldrich), D-(+)-glucose (ACS reagent, Aldrich), and *N,N,N',N'*-tetramethyl ethylenediamine (TMEDA, 98%, TCI) were used as received, without any further purification. The experimental conditions for the preparation of Cu₂O products with various morphologies are summarized in Table 1. For the typical preparation of Cu₂O product (sample number 9 in Table 1), 10 mL of a 0.125 M D-(+)-glucose aqueous solution and 6.0 g PEG were added to 138.1 mL of a 0.0362 M CuCl₂·2H₂O aqueous solution, with stirring at room temperature for 30 min. Then, 1.86 mL TMEDA was added to the mixed solution. The reactants concentrations of CuCl₂·2H₂O, D-(+)-glucose, TMEDA, and PEG are 33.3 mM, 8.33 mM, 83.3 mM, and 2.00 mM, respectively. To investigate the morphology evolution of the Cu₂O products, the different amounts of CuCl₂·2H₂O, D-(+)-glucose, TMEDA, and PEG were used, with keeping a constant relative amount of reactants. The total volume of the aqueous solution was fixed to 150 mL. A final mixed solution in an open beaker was placed into a commercial microwave oven (Magic MWO-230KD, 2.45 GHz, 800 W). We used the open reaction system for the safety free from unexpected explosion. The microwave was operated for just 2 min. The final temperature of the mixed solution was increased to approximately 80 °C. After finishing the microwave irradiation, the reacted solution was placed in ice-water to quench the reaction quickly, for reducing the thermal heating effect on the Cu₂O products. The powder forms of Cu₂O products were obtained by using a centrifuge at 4000 rpm for 10 min. The Cu₂O products were then washed several times with ethanol and water, and then dried at 60 °C for 12 h in a drying oven. The average yield for the preparation of Cu₂O products is ap-

proximately 46%. The crystal structure of the Cu₂O products was characterized by powder X-ray diffraction (XRD, PANalytical, X'pert-proMPD). The morphology of the Cu₂O products was examined by using scanning electron microscopy (SEM, Hitachi S-4300).

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