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Facile Precipitation Method for Morphological Tuning of Cu_2O Crystals

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We have developed a simple method for tuning the morphologies of Cu_2O microcrystals. Cu_2O microcrystals were prepared by precipitation at room temperature from a mixture of $Cu(CH_3COO)_2 \cdot H_2O$, *N,N,N′,N′*-tetramethyl ethylenediamine (TMEDA), ascorbic acid, and polyethylene glycol (PEG). TMEDA was used to promote the formation of copper-TMEDA complexes. A variety of Cu_2O microcrystal morphologies were obtained simply by varying the concentrations of TMEDA and ascorbic acid. Aggregated Cu_2O microspheres are formed at higher concentrations of ascorbic acid in the absence of TMEDA. Aggregated Cu_2O microcubes are formed at lower concentrations of ascorbic acid and higher concentrations of TMEDA. The crystal growth mechanism of these Cu_2O morphologies is explained.

Key Words : Morphology, Cu_2O, Precipitation method, Crystal growth

Introduction

The physical and chemical properties of inorganic oxides are strongly dependent on their facets and morphologies. The various morphologies of inorganic oxides have unique surface atomic arrangements and exhibit different photocatalytic activities.[1-4] In recent years, the investigation of the dependences of the antibacterial activities and photocatalytic properties of inorganic oxides on morphology has become an active research field.[5-10] Cube, octahedron, and rhombic dodecahedron of inorganic oxides are entirely enclosed by six {100}, eight {111}, and twelve {110} facets, respectively. Therefore, the catalytic activity of cubic inorganic oxides with {100} facets is different those of octahedral inorganic oxides with {111} facets and rhombic dodecahedral inorganic oxides with {110} facets. One of the most important challenges for morphology-controlled syntheses is to selectively prepare an inorganic oxide with a specific morphology.

Generally, various morphologies of inorganic oxides can be obtained by using surfactants as morphology modifiers. The surfactants, such as oleylamine, oleic acid, sodium dodecyl sulfate (SDS), and cetyltrimethyl ammonium bromide (CTAB), are widely used for the morphology controlled synthesis of inorganic oxides.[11-13] In surfactant-assisted reaction, the product yield of inorganic oxides is very low due to a little solubility of surfactant. Therefore, it is difficult to use the surfactant-assisted reaction for the large-scale production. Hydrothermal methods with an autoclave have been also used in the morphology-controlled syntheses of inorganic oxides. 100 mL and 200 mL of the autoclave volumes are widely used for the synthesis. The reaction capacity of the autoclave is limited for the large-scale production. Therefore, the simplest way for the large-scale production with high yields is the wet chemical precipitation method at room temperature without using any surfactants or autoclaves. The simple and facile morphology-controlled precipitation method at room temperature with large-scale production of inorganic oxides must to be developed.

Cuprous oxide (Cu_2O) is considered the best material for morphology-controlled syntheses because of its cubic crystal system.[14,15] Simple closed morphologies, such as cubes, truncated cubes, cuboctahedra, octahedra, and rhombic dodecahedra have been extensively prepared. Uniform Cu_2O cubes were synthesized by reducing a copper-citrate complex solution with glucose.[16] Cu_2O crystals were synthesized in the form of truncated cubes, cuboctahedra, octahedra, and rhombic dodecahedra in an aqueous solution of $CuCl_2$, SDS, hydroxylamine, and NaOH.[17] Cu_2O crystals were obtained as rhombic dodecahedra by the reduction of $CuSO_4$ with D-(+)-glucose in an alkaline H_2O/ethanol/oleic acid system.[18] Highly symmetric 26-facet polyhedral microcrystals of Cu_2O were also prepared by reacting $CuCl_2$, sodium citrate, glucose, SDS, NaOH, and ethylene glycol.[19] Various Cu_2O crystals with open shapes, such as hexapods, flower-like crystals, and dendrites, have been obtained. Hexapod-shaped Cu_2O crystals were prepared *via* a γ-irradiation reduction route.[20] Hexapod-like Cu_2O whiskers were synthesized from a $Cu(CH_3COO)_2$ precursor under hydrothermal conditions.[21] A range of morphologies of Cu_2O microcrystals, including hexapods, truncated octahedra, cuboctahedra, and aggregated spheres, were prepared by reacting $CuCl_2$, NaOH, glucose, and poly(ethylene) glycol under microwave irradiation.[22] A variety of morphologies of Cu_2O crystals have been prepared with assistance of surfactants, such as SDS and oleic acid, or by using the autoclave reaction vessel. However, wet large-scale precipitation method at room temperature for the morphology-controlled synthesis of Cu_2O crystals has not often been investigated.

Ascorbic acid is more reactive than glucose to form the Cu_2O crystals. Cu_2O microcrystals are prepared at room temperature and high temperature by using ascorbic acid and glucose, respectively. In this paper, we report the first morphology-controlled precipitation method for the produc-

Table 1. A brief summary of the experimental conditions used in the preparation of Cu_2O in this study

No	$Cu(CH_3COO)_2$ (mmol)	TMEDA (mmol)	Ascorbic acid (mmol)	PEG (g)	SEM images
1	1.00	0.00	0.10	1.20	Fig. 2(a), Fig. 4(a)
2	1.00	0.00	0.20	1.20	Fig. 2(b)
3	1.00	0.00	0.40	1.20	Fig. 2(c)
4	1.00	0.00	0.80	1.20	Fig. 2(d), Fig. 3(a)
5	1.00	0.50	0.80	1.20	Fig. 3(b)
6	1.00	1.50	0.80	1.20	Fig. 3(c)
7	1.00	2.50	0.80	1.20	Fig. 3(d), Fig. 5(d)
8	1.00	0.50	0.10	1.20	Fig. 4(b)
9	1.00	1.50	0.10	1.20	Fig. 4(c)
10	1.00	2.50	0.10	1.20	Fig. 4(d), Fig. 5(a)
11	1.00	2.50	0.20	1.20	Fig. 5(b)
12	1.00	2.50	0.40	1.20	Fig. 5(c)

tion of Cu_2O at room temperature. A variety of Cu_2O morphologies having various facets were obtained by simply adjusting the reactant concentration of *N,N,N′,N′*-tetramethyl ethylenediamine (TMEDA), which is the ligand for the Cu^{2+} ions, and that of ascorbic acid, which is the reductant.

Experimental

The Cu_2O crystals were synthesized with a simple precipitation method at room temperature. $Cu(CH_3COO)_2{\cdot}H_2O$ (98%, Alfa Aesar), *N,N,N′,N′*-tetramethyl ethylenediamine (TMEDA, 98%, TCI), L-ascorbic acid (99%, Aldrich), and polyethylene glycol (PEG, Mw 20,000, Aldrich) were used as received without any further purification. The experimental conditions for the preparation of the Cu_2O crystals are summarized in Table 1. The variations in the morphologies of the Cu_2O products with the TMEDA and ascorbic acid concentrations were examined. In a typical process, that of sample 10, 1.20 g of PEG and 2.50 mmol of TMEDA were added to a 0.10 M $Cu(CH_3COO)_2{\cdot}H_2O$ aqueous solution (50.0 mL) and distilled water was added to a volume of 99 mL. Finally, a 0.1 M ascorbic acid aqueous solution (1.0 mL) was quickly added to the mixed solution, and then distilled water was added to a volume of 150 mL with stirring for 1 min at room temperature. The 150 mL final solution was incubated for 4 h at room temperature. The products were collected by centrifugation at 4000 rpm for 5 min, then washed with water several times, and finally dried for 24 h at room temperature.

The structures of the Cu_2O products were analyzed by performing powder X-ray diffraction (XRD, PANalytical X'Pert-PRO MPD) with Cu K_α radiation. The morphologies were characterized with scanning electron microscopy (SEM, Hitachi S-4300) and transmission electron microscopy (TEM, JEOL JEM-3010).

Results and Discussion

The Cu_2O products were synthesized by simply reacting $Cu(CH_3COO)_2{\cdot}H_2O$ with ascorbic acid in the presence of TMEDA and PEG. Since TMEDA is a bidentate ligand, it binds with a Cu^{2+} ion to form a $[Cu(TMEDA)_2]^{2+}$ coordination complex. This complex then reacts with OH^- in alkaline solution to form $Cu(OH)_2$. Cu_2O is formed after the conjunction of the dehydration and reduction of $Cu(OH)_2$ in the presence of ascorbic acid. Figure 1 shows a typical X-ray diffraction (XRD) pattern of the Cu_2O product. All peaks in Figure 1 match those reported for the cubic crystal system of Cu_2O (JCPDS 05-0667, a = 0.4269 nm). No impurity peaks are evident in this XRD pattern, which indicates that Cu_2O has been successfully synthesized.

Cu_2O products with various morphologies were obtained by varying the concentrations of TMEDA and ascorbic acid. The morphologies of the Cu_2O products were examined with SEM. Figure 2 shows SEM images of Cu_2O products prepared with various concentrations of ascorbic acid in the absence of TMEDA. At an ascorbic acid concentration of 0.10 mmol (sample 1), aggregated Cu_2O particles in open structures with six horns denoted stellar octahedra are formed, as shown in Figure 2(a). The mean length of each horn in a stellar octahedron is approximately 1.0 μm, as shown in Figure 2(a). At an ascorbic acid concentration of 0.20 mmol (sample 2), aggregated Cu_2O particles with a

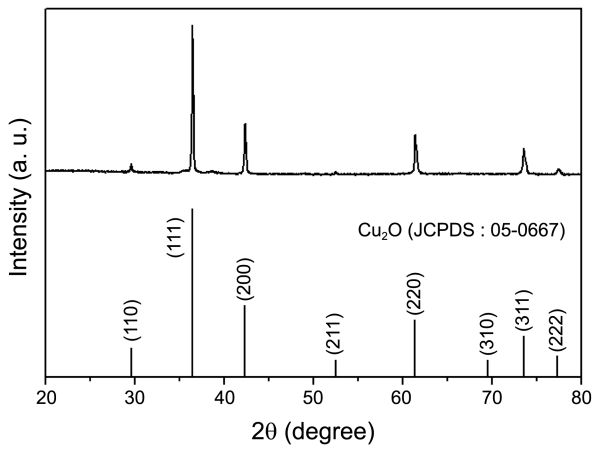

Figure 1. Typical XRD pattern of an as-prepared Cu_2O product.

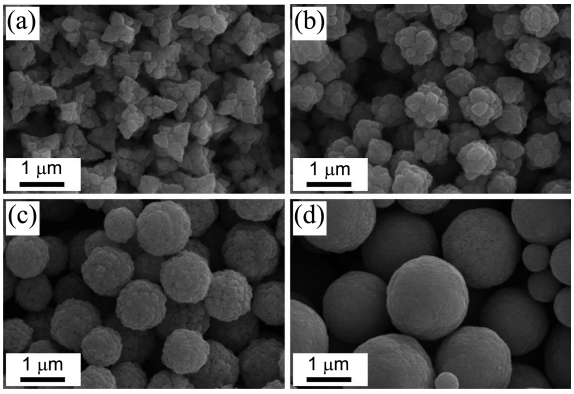

Figure 2. SEM images of Cu_2O products prepared in the absence of TMEDA with various concentrations of ascorbic acid: (a) 0.10 mmol (sample 1), (b) 0.20 mmol (sample 2), (c) 0.40 mmol (sample 3), and (d) 0.80 mmol (sample 4).

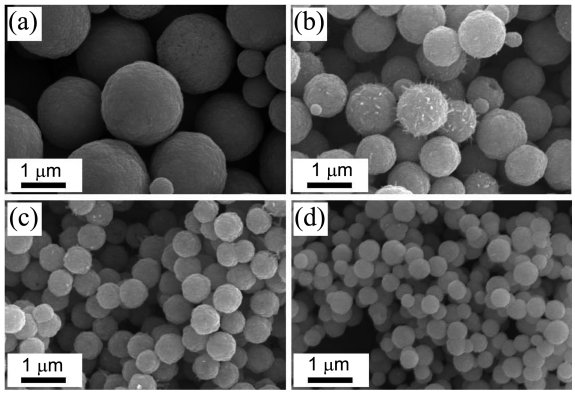

Figure 3. SEM images of Cu_2O products prepared at a fixed ascorbic acid concentration of 0.80 mmol and various TMEDA concentrations: (a) no TMEDA (sample 4), (b) 0.50 mmol (sample 5), (c) 1.50 mmol (sample 6), and (d) 2.50 mmol (sample 7).

mean diameter of 1.0 μm are formed, as shown in Figure 2(b). The surfaces of the aggregated Cu_2O particles are not smooth, which indicates that the full aggregation required for the formation of spheres has not been reached. When the ascorbic acid concentration is 0.40 mmol (sample 3), the resulting Cu_2O particles are more aggregated than those prepared at a concentration of 0.20 mmol, as shown in Figure 2(c). The mean diameter of the aggregated Cu_2O particles is higher, 1.2 μm. At an ascorbic acid concentration of 0.80 mmol (sample 4), aggregated Cu_2O microspheres with clean surfaces are obtained, as shown in Figure 2(d). The mean diameter of the Cu_2O microspheres is higher again, 1.9 μm. Thus, as the ascorbic acid concentration is increased in the absence of TMEDA, the open stellar octahedron structures are converted to small aggregated spheres, and then to larger perfect microspheres. As the ascorbic acid concentration increases, the reaction rate of the formation of the Cu_2O products is increased. The quickly prepared Cu_2O particles aggregate easily to form thermodynamically stable spheres that have the minimal total surface energy.

Figure 3 shows SEM images of the Cu_2O products prepared at various TMEDA concentrations at a fixed ascorbic acid concentration of 0.80 mmol. In the absence of TMEDA (sample 4), aggregated Cu_2O microspheres with a mean diameter of 1.9 μm are obtained, as shown in Figure 3(a). At a TMEDA concentration of 0.50 mmol (sample 5), aggregated Cu_2O microspheres with a mean diameter of 1.1 μm are formed, as shown in Figure 3(b). When the TMEDA concentration is increased to 1.50 mmol (sample 6) and 2.50 mmol (sample 7), the mean diameters of the Cu_2O microspheres are decreased to 700 nm and 400 nm as shown in Figures 3(c) and (d) respectively. The copper-TMEDA complex forms readily upon the addition of the bidentate ligand TMEDA to the aqueous solution. The number of non-complexed Cu^{2+} ions decreases with the concentration of TMEDA. At higher TMEDA concentrations, smaller numbers of non-complexed Cu^{2+} ions are involved in the reaction. Fewer Cu_2O particles form smaller aggregates of Cu_2O microspheres with increases in the TMEDA concentration, as shown in Figure 3.

Figure 4 shows SEM images of Cu_2O products prepared at various TMEDA concentrations at a fixed ascorbic acid concentration of 0.10 mmol. As can be seen in Figure 4(a) (sample 1), stellar octahedra formed by the aggregation of Cu_2O particles are obtained in the absence of TMEDA. At a TMEDA concentration of 0.50 mmol (sample 8), thicker stellar octahedra formed by the aggregation of Cu_2O particles are obtained, as shown in Figure 4(b). The open spaces of the stellar octahedra are more completely filled than those of the stellar octahedra formed in the absence of TMEDA. When the TMEDA concentration is increased to 1.50 mmol (sample 9), concave cubes are formed. The mean length of the concave cubes is 600 nm, as shown in Figure 4(c). When the TMEDA concentration is further increased to 2.50 mmol (sample 10), perfect Cu_2O microcubes with a mean length of 900 nm are obtained, as shown in Figure 4(d). The most stable form of Cu_2O is a cubic crystal structure with $a = b = c$ and $\alpha = \beta = \gamma = 90°$. Cu_2O products with cubic morphologies are a result of crystal habit formation. Under these low ascorbic acid concentration conditions, aggregated microspheres are not obtained. Therefore, Cu_2O crystal habit

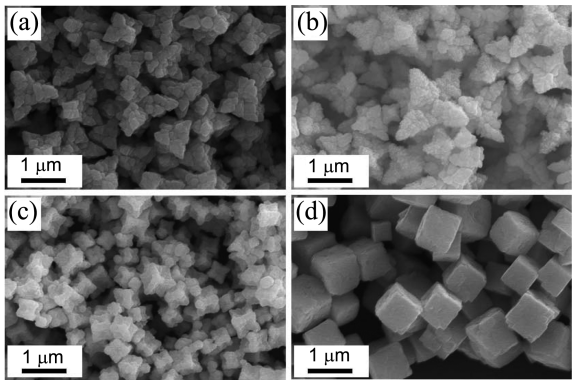

Figure 4. SEM images of Cu_2O products prepared at a fixed ascorbic acid concentration of 0.10 mmol with various TMEDA concentrations: (a) no TMEDA (sample 1), (b) 0.50 mmol (sample 8), (c) 1.50 mmol (sample 9), and (d) 2.50 mmol (sample 10).

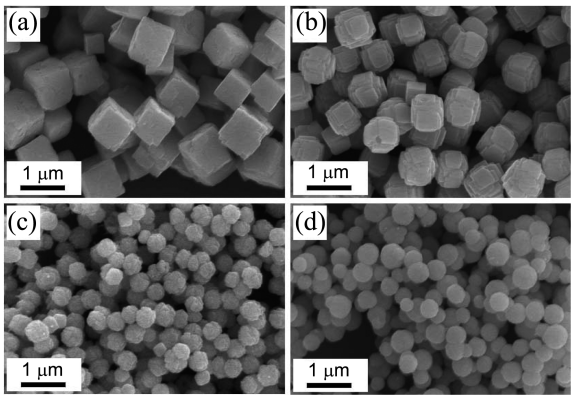

Figure 5. SEM images of Cu_2O products prepared at a fixed TMEDA concentration of 2.50 mmol with various concentrations of ascorbic acid: (a) 0.10 mmol (sample 10), (b) 0.20 mmol (sample 11), (c) 0.40 mmol (sample 12), and (d) 0.80 mmol (sample 7).

formation is preferred at low concentrations of ascorbic acid. In contrast, thermodynamically controlled reactions involving the aggregation of Cu_2O microspheres are preferred at higher concentrations of ascorbic acid.

Figure 5 shows various SEM images of Cu_2O products prepared with various concentrations of ascorbic acid at a TMEDA concentration of 2.50 mmol. At an ascorbic acid concentration of 0.10 mmol (sample 10), perfect Cu_2O microcubes are obtained, as shown in Figure 5(a). Figure 5(b) shows the imperfect Cu_2O microcubes prepared at an ascorbic acid concentration of 0.20 mmol (sample 11). The surfaces of these Cu_2O microcubes contain many terraces, which indicates that the complete habit formation of microcubes is not possible under these conditions. At an ascorbic acid concentration of 0.40 mmol (sample 12), aggregated Cu_2O microspheres with some rough surfaces are formed, as shown in Figure 5(c). When the concentration of ascorbic acid is increased to 0.80 mmol (sample 7), aggregated Cu_2O microspheres with clean surfaces are obtained, as shown in Figure 5(d). As the ascorbic acid concentration is increased while the TMEDA concentration is fixed at 2.50 mmol, the microcubes become imperfect microcubes, somewhat rough microspheres, and finally perfect clean microspheres. These results suggest that microcube crystal habit formation arises at lower ascorbic acid concentrations, and thermodynamically stable microspheres are formed at higher ascorbic acid concentrations.

We conclude that Cu_2O microcube crystal habit formation occurs at both lower concentrations of ascorbic acid and higher concentrations of TMEDA. These results indicate that crystal habit formation correlates with the lowest reaction rate for the formation of Cu_2O particles. Under these conditions, there is enough time for the Cu_2O particles to aggregate in microcubes in a cubic crystal system due to the crystal habit formation. However, Cu_2O particles prepared at higher reaction rates simply and rapidly aggregate to form microspheres as the thermodynamically stable form with the lowest surface energy. To obtain higher Cu_2O particle reaction rates, higher concentrations of ascorbic acid and the absence of TMEDA are required in our reaction system. When the aggregation to form microspheres happens over a short period due to the higher reaction rates, the microspheres are likely to have hollow structures with empty interior spaces. To confirm this expectation, we examined the TEM images of the Cu_2O products prepared with various ascorbic acid concentrations at a TMEDA concentration of 2.50 mmol, as shown in Figure 6. As can be seen in Figures 6(a) and (b), the microcubes and imperfect microcubes formed by crystal habit formation do not have empty interiors. In contrast, the aggregated microspheres prepared at higher concentrations of ascorbic acid have empty interior spaces,

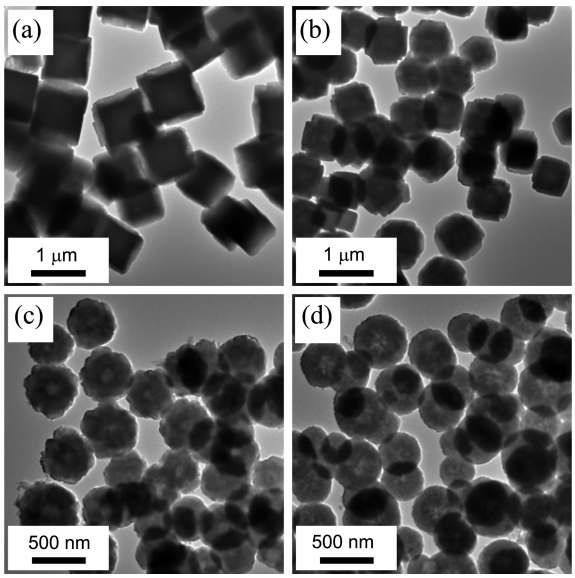

Figure 6. TEM images of Cu_2O products prepared at a fixed TMEDA concentration of 2.50 mmol with various concentrations of ascorbic acid: (a) 0.10 mmol (sample 10), (b) 0.20 mmol (sample 11), (c) 0.40 mmol (sample 12), and (d) 0.80 mmol (sample 7).

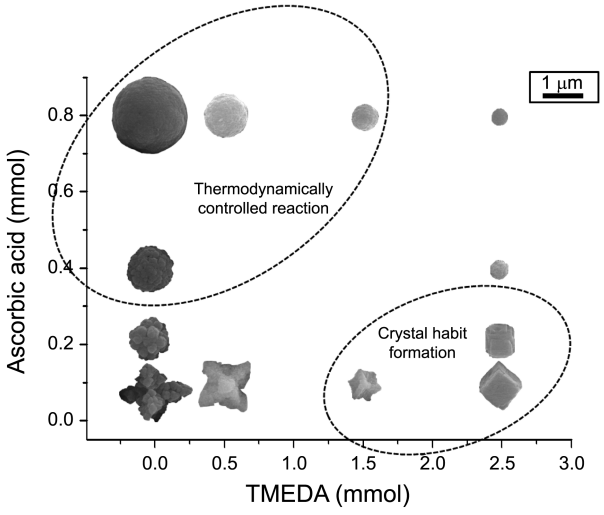

Figure 7. Schematic diagram of the variations in morphology of Cu_2O microcrystals as functions of the TMEDA and ascorbic acid concentrations.

as shown in Figures 6(c) and (d). Thus hollow structures with empty interior spaces are formed by the rapid aggregation that occurs in the formation of microspheres at higher reaction rates. Therefore, the TMEDA and ascorbic acid concentrations play important roles in both crystal habit formation and the thermodynamically controlled reaction.

In this reaction system, thermodynamically controlled reactions produce aggregated Cu_2O microspheres at the higher reaction rates that arise at higher ascorbic acid concentrations. However, Cu_2O microcube crystal habit formation occurs at the lowest reaction rate, which arises at the lowest ascorbic acid concentration in the presence of TMEDA. Figure 7 shows a schematic diagram of the variations in the morphologies of the Cu_2O crystals as functions of the TMEDA and ascorbic acid concentrations.

Conclusion

We have developed a simple precipitation method for tuning the morphologies of Cu_2O microcrystals at room temperature. A variety of Cu_2O morphologies were obtained by varying the TMEDA and ascorbic acid concentrations. Aggregated Cu_2O microspheres are obtained at higher ascorbic acid concentrations. Cu_2O microcubes are obtained at the lowest ascorbic acid concentration and highest TMEDA concentration. The thermodynamically controlled reaction that produces the aggregated Cu_2O microspheres and the Cu_2O microcube crystal habit formation occur when the reaction rates for the formation of Cu_2O particles are faster and slower, respectively. Both the thermodynamically controlled reaction and crystal habit formation can be controlled in order to tune the Cu_2O morphologies by varying both the TMEDA and ascorbic acid concentrations. Aggregated Cu_2O microspheres with empty interior spaces were also obtained.

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