

Facile Synthesis and Shape Evolution of Single-Crystal Cuprous Oxide

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Tailoring the architecture of nano/microcrystals has been of great research interest due to their unique shape and size-dependent properties.^[1] Extensive studies have been devoted to the controlled synthesis and self-organization of polyhedral structures such as cubes and^[2] octahedral,^[3] whether in the dimensions of nanoscale or micrometer scale.^[4] Among them, selective adsorption of surfactant molecules or biomimetic mineralization are typical processes for this kind of morpho-synthesis.^[5,6] To date, a precise understanding of the formation mechanism of these morphologically different materials is still challenging, even though a lot of beautiful architectures have been prepared by some state-of-the-art synthetic methods. As a *p*-type semiconductor with direct band-gap of 2.17 eV, Cu₂O has excellent optical and magnetic properties, which can be applied in gas sensors,^[7] catalysis,^[8] solar-energy conversion,^[9] lithium-ion batteries,^[10] and for research on Bose–Einstein condensation.^[11] Considerable efforts have been devoted to fine-tune the properties of Cu₂O architectures by tailoring its shape. However, the present study reports on one of the so far rarely observed combinations of a nonclassical and subsequent classical crystallization process with face selective additive adsorption upon particle growth.^[12] Furthermore, this process is observed for a functional material and the mechanism is revealed.

Herein, a facile solution-phase route has been successfully developed for the preparation of a series of morphologically different Cu₂O single crystals. This method is based on the reduction of CuSO₄ with D-(+)-glucose in an alkaline H₂O/ethanol/oleic acid system. D-(+)-Glucose (Fig. S1 in the Supporting Information), a monosaccharide, is a source of energy and a metabolic intermediate of the living cell. Here, it plays the role of reducer. Interestingly, oleic acid, as a face selective adsorption additive, can subtly determine the morphology of the final products. Various concentrations of oleic acid can result in a series of morphologies of Cu₂O, such as cube, octahedron, {110} truncated octahedron, and microhombic dodecahedron with {110} surfaces. In particular, investigations on the early stages of the microcrystal formation process demonstrate its formation mechanism in the present reaction system.

With 1 mL of oleic acid in the reaction system, the product is composed of 100% relatively uniform microcubic Cu₂O bound by {100} faces with the edge length of about 500 nm (Fig. 1a). The cubic morphology can also be evidenced by the XRD patterns recorded from the microcrystals on the single-crystal Si wafer (Fig. S2, Supporting Information),^[12] where the exceptionally

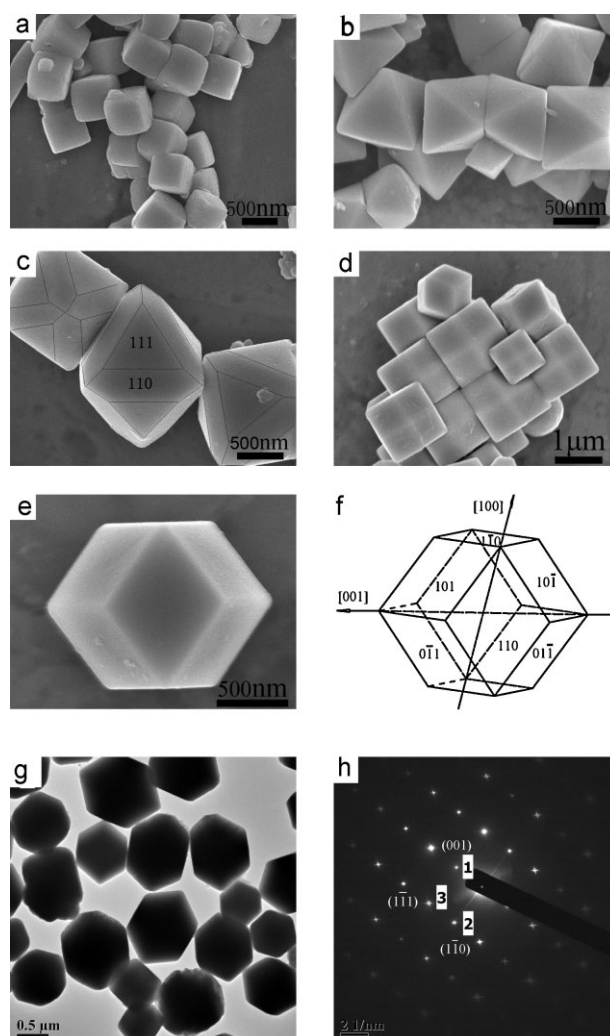


Figure 1. SEM images of Cu₂O microcrystals formed using various amounts of oleic acid: a) microcubes, 1 mL, b) micro-octahedra, 2.5 mL, c) {110} truncated octahedra, 3 mL, d) microrhombic dodecahedra, 4 mL, e) high-magnification SEM image of the microrhombic dodecahedral Cu₂O, f) model of the microrhombic dodecahedral Cu₂O with {110} planes, g) TEM image of the microrhombic dodecahedral Cu₂O, and h) corresponding SAED pattern.

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strong (200) diffraction peak for the cubic microcrystals indicates that the {100} surfaces of microcube are preferentially parallel to the substrate. When the amount of oleic acid increases to 2.5 mL, the shape of the product becomes a regular micro-octahedron enclosed by a {111} plane (Fig. 1b). With the further enhancement of the amount of oleic acid to 3 mL, the typical shape of the samples transforms into {110} truncated octahedra with the complete growth in the $\langle 100 \rangle$ directions (Fig. 1c). It actually has 20 facets, including 8 {111} planes and 12 {110} planes with both surfaces and edges developed quite well. As the amount of oleic acid reaches 4 mL, the products become rhombic dodecahedral Cu_2O enclosed by {110} planes with smooth surfaces and sharp edges (Fig. 1d–f). It is the first time for the achievement of Cu_2O structures fully enclosed by {110} planes. For the transmission electron microscopy (TEM) image (Fig. 1g), most of the microrhombic dodecahedra look hexagonal in shape with slight differences in symmetry due to slight changes in projection direction, and the corresponding SAED pattern reveals that they are single crystals (Fig. 1h). It should be noted that the particle in Figure 1e is selected from well-developed particles, and so it appears a little larger than the particles in Figure 1g. The synthesized microcrystals have a tendency to self-assemble into a regular pattern (Fig. 1d). Moreover, these microcrystals exhibit shape-dependent color changes (Fig. S3, Supporting Information). In addition, if we continue to increase the amount of oleic acid up to 8 mL, the shapes of the products are still all perfect rhombic dodecahedra enclosed by {110} planes.

To disclose the formation mechanism of Cu_2O microcrystals, we studied the morphological evolution process of microrhombic dodecahedra with reaction time (Fig. 2). The samples are quasi-spherical aggregates, and the coalescence of the small particles on the surface can be clearly seen with a shortened reaction time of 15 min, which indicates that the quasi-spherical aggregates should be composed of a lot of small particles. Increasing the reaction time to 20 min, they basically change into quasi-rhombic dodecahedra, although their surface is rather rough. It is thought that this morphology transformation process of Cu_2O crystals is due to the classical ion-mediated growth process (ripening). After reaction for 25 min, the degree of

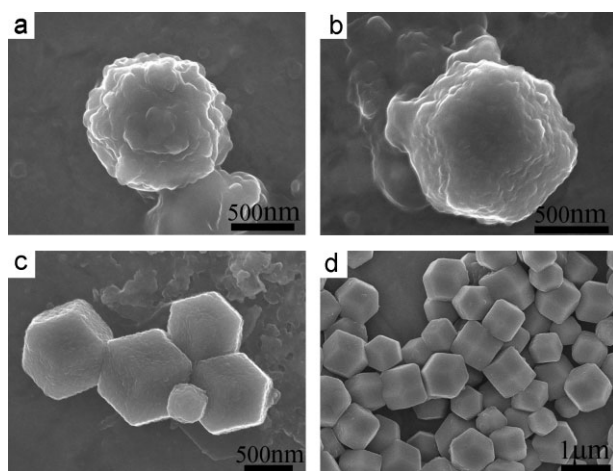


Figure 2. SEM images of Cu_2O microcrystals obtained with 4 mL oleic acid at reaction times of a) 15, b) 20, c) 25, and d) 60 min.

surface roughness decreases. When increasing the reaction time to 60 min, perfect rhombic dodecahedra with smooth surfaces and sharp edges are obtained. Although the final product is single crystalline, the analysis of high-resolution (HR)-TEM images shows that there defects exist in it (Fig. S4, Supporting Information), which should be the trace of this kind of nonclassical particle-based crystallization process.

Based on the above time-dependent transformation process, first a large amount of Cu_2O nanocrystallites nucleate and grow into small seed particles. To minimize the overall energy of the system, a great number of small seed particles tend to aggregate together.^[13] Meanwhile, due to the ripening mechanism, the quasi-spherical aggregates change into perfect rhombic dodecahedra. Therefore, Cu_2O microrhombic dodecahedra are obtained through the synergic effect of oriented attachment and ripening mechanism. A nonclassical particle-based crystallization process yields the initial microparticles, followed by classical ion-mediated growth involving face-selective oleic acid adsorption. In order to demonstrate this kind of crystal growth, a control experiment was conducted in which the seed crystals produced without oleic acid were used for the subsequent growth in a solution containing a certain amount of oleic acid. Figure 3a and b shows the TEM and HRTEM images of the seed crystals grown without oleic acid for 1.5 min with the other experimental conditions kept the same. It can be seen that when the reaction lasts for 1.5 min, the small seed crystals with the sizes of about 4–5 nm are formed and have already had the tendency to aggregate into a new nanoparticle. This also indicates that the oriented-attachment growth process is dynamically very fast. Figure 3b shows that the lattice fringes of the seed nanoparticles have been oriented and partly attached, although the crystallization domains ascribed to different seed crystals can be still distinguished at this stage. When these initial crystals are used as the seeds for the subsequent growth in a solution involving 4 mL of oleic acid, the same morphology of microrhombic dodecahedra can be gained (Fig. 3c).

Therefore, the growth process of the Cu_2O microcrystals undergoes two different stages. At the initial stage, an oriented-attachment process dominates, and at the subsequent stage a ripening process dominates. The initial oriented attachment process is of critical importance for this kind of growth process. However, it is based on the slow reduction process. When glucose was replaced by a stronger reducer, NaBH_4 , only irregular nanoparticles were formed (Fig. S5, Supporting Information). So, fast reduction yields only undefined nanoparticles, and slow reduction is necessary for the formation of microcrystals. For the fast reduction process, considerable nuclei form instantaneously and quickly, and the precursor (Cu^+) needed for the subsequent growth process is supplied. However, for the slow reduction process, after the formation of nuclei, the precursor (Cu^+) needed is suppressed, inducing the initial nanoparticles to aggregate to reduce the energy of the whole reaction system. Therefore, D-(+)-glucose, a weak reducer, plays its role in the process of aggregation, resulting in this kind of nonclassical particle-based crystallization process.

Oleic acid, as a face selective adsorption additive in the present process, can subtly affect the final morphologies of Cu_2O microcrystals. First, oleic acid can slow down the formation rate of Cu_2O crystallites, which is dynamically beneficial to the

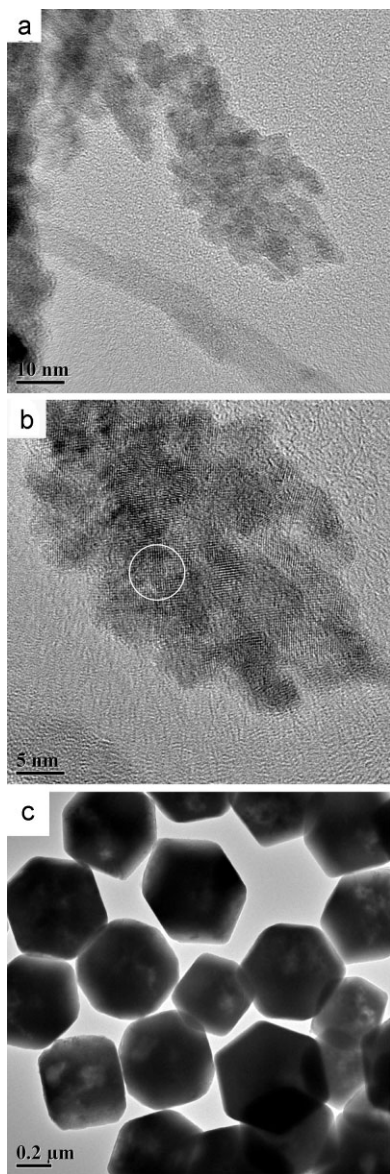


Figure 3. a) TEM image of Cu_2O seed crystals prepared without oleic acid at $100\text{ }^\circ\text{C}$ for 1.5 min. b) Corresponding HRTEM of Cu_2O seed crystals, the circle showing one of the areas where the nanoparticles have already fused and have the same lattice fringe orientation. c) TEM image of Cu_2O microhombic dodecahedron prepared using the above seed crystals for the subsequent growth in a growth solution containing 4 mL oleic acid at $100\text{ }^\circ\text{C}$ for 1 h.

effective subtle control of the morphologies of Cu_2O microcrystals. We observed that in the absence of oleic acid, the reaction can finish at a lower temperature of only $60\text{ }^\circ\text{C}$ and a shorter time of about 15 min. Second, the results of the above control experiment of the seed crystals obtained without oleic acid for subsequent growth in a growth solution containing a certain amount of oleic acid also suggest that in the present reaction system, oleic acid mainly plays its role in the ripening process by the face-selective adsorption to control the final shape of the microcrystals. Obviously, the concentration of oleic acid molecules can affect the shapes of Cu_2O crystals because of

their preferentially selective adsorption on the $\{100\}$, $\{111\}$, $\{110\}$ surfaces (Fig. 1 and Fig. S6, Supporting Information). As reported, the shapes of the cubic crystals, such as Cu_2O , are determined by the growth ratio R of the growth rate along the $\langle 100 \rangle$ directions to the $\langle 111 \rangle$ directions.^[14] When the amount of oleic acid is 1 mL, it first interacts with the $\{100\}$ planes of Cu_2O crystal. Preferential adsorption on the $\{100\}$ face confines crystal growth along $\langle 100 \rangle$ directions, therefore microcubic Cu_2O form, with a corresponding R of 0.58 (Fig. 1a). As the concentration of oleic acid increases, not only is the $\{100\}$ surface completely covered, but also the $\{111\}$ face begins to adsorb oleic acid. Continuous adsorption of oleic acid on the $\{111\}$ faces confines the growth of $\{111\}$ planes. When the amount of oleic acid reaches 1.5 mL, $\{111\}$ truncated cubes appear (Fig. S6a, Supporting Information). The amount of oleic acid continues to increase, and Cu_2O irregular micro-octahedra are obtained at 2 mL of oleic acid (Fig. S6b, Supporting Information). When the value of R increases from 0.58 to 1.73, micro-octahedral Cu_2O are obtained at the oleic acid amount of 2.5 mL (Fig. 1b). When the concentration of oleic acid continues to increase, both $\{100\}$ and $\{111\}$ crystal planes show saturated surface coverage, and oleic acid begins to be adsorbed on the $\{110\}$ crystal planes, resulting in the formation of $\{110\}$ truncated octahedra with the exposure of $\{110\}$ and $\{111\}$ surfaces (Fig. 1c). As the oleic acid concentration increases, the area of $\{110\}$ surface continuously increases, and $\{111\}$ faces gradually disappear. Finally, the rhombic dodecahedra with complete $\{110\}$ coverage are obtained (Fig. 1d). Based on the above experimental results and analysis, there should be a strong interaction between the surface of Cu_2O particles and oleic acid molecules, although the nature of selectivity of oleic acid with different crystal planes is still to be studied further.

We also repeat the synthesis process by replacing oleic acid with an anion surfactant of dodecyl benzene sulfonic acid sodium (SDBS) as the face-selective adsorption additive or without oleic

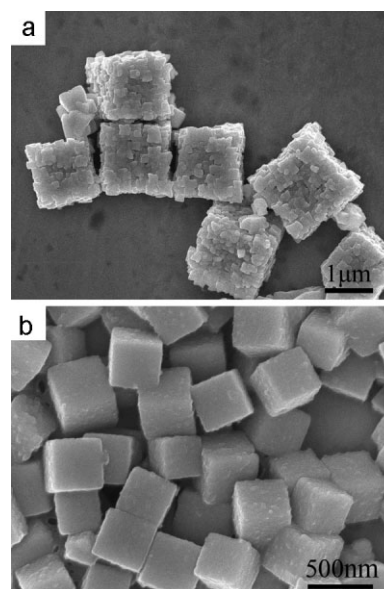
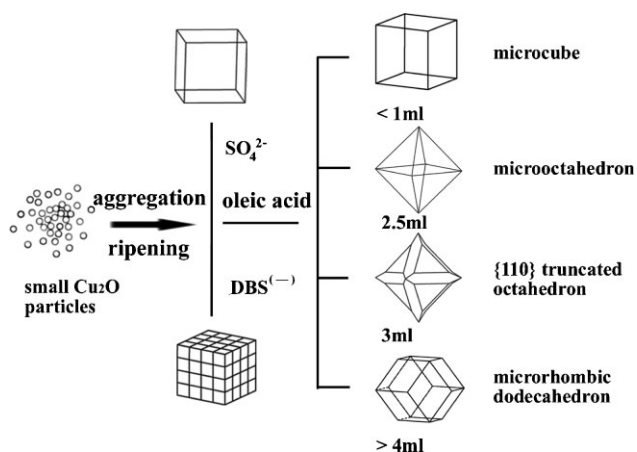


Figure 4. SEM images of the Cu_2O samples prepared through the same procedure except: a) replacing oleic acid with SDBS as the surfactant, and b) without any surfactant.



Scheme 1. Schematic illustration of the formation mechanism of Cu_2O microcrystals and the shape-evolution processes.

acid (at 60°C for about 15 min, actually SO_4^{2-} from CuSO_4 is the face selective adsorption additive), and both of them result in self-assembled microcubic Cu_2O mesocrystals.^[15] This kind of microcubes may come from the selective adsorption of $\text{DBS}(-)$ and SO_4^{2-} anion on the $\{100\}$ surfaces of the initial species, and their aggregation-based growth (Fig. 4 and Figs. S7 and S8, Supporting Information). The formation mechanism of Cu_2O microcrystals and their shape evolution can be illustrated in detail in Scheme 1.

In summary, various single-crystal Cu_2O microcrystals have been prepared through a facile solution-based one-step reduction method in an alkaline $\text{H}_2\text{O}/\text{ethanol}/\text{oleic acid}$ system in the presence of $\text{D}(+)$ -glucose. Various Cu_2O microcrystals are obtained through the synergic effect of oriented attachment and ripening mechanism with face-selective additive adsorption upon particle growth. The shape evolution of microcrystals in the present reaction system should be valuable for the precise understanding of the formation process of advanced polyhedron structures, which may be applicable to the fine fabrication of more novel morphologies of other metal oxides.

Experimental

All the chemicals were analytical grade reagents and used as received without further purification. Typically, microrhombic dodecahedral Cu_2O microcrystals were synthesized as follows: 1 mmol $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 40 mL of water to form a clear solution, then 4 mL oleic acid and 20 mL anhydrous alcohol were added successively to the above solution with vigorous stirring. When the mixture was heated to 100°C , 10 mL of NaOH solution (8 mmol) was added to it. After 5 min, 30 mL of $\text{D}(+)$ -glucose (3.42 g) aqueous solution was added into the blue suspension with constant stirring for another 60 min. A brick-red color appeared gradually. When the reaction was finished, the precipitate was separated from the solution by centrifugation, washed with cyclohexane

and alcohol several times, and dried at 60°C for 4 h in a vacuum oven. X-Ray powder diffraction (XRD) patterns were obtained using a D/max 2550V diffractometer, and the samples were prepared by dropping the microcrystal solution in cyclohexane on a single-crystalline Si wafer and evaporating the solvent. The morphologies of as-obtained samples were characterized by transmission electron microscopy (TEM, JEOL-2100F) and scanning electron microscopy (SEM, JSM-6700F).

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