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One-step green synthesis of cuprous oxide crystals with truncated octahedra shapes *via* a high pressure flux approach

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ABSTRACT

Cuprous oxide (Cu_2O) was synthesized *via* reactions between cupric oxide (CuO) and copper metal (Cu) at a low temperature of 300 °C. This progress is green, environmentally friendly and energy efficient. Cu_2O crystals with truncated octahedra morphology were grown under high pressure using sodium hydroxide (NaOH) and potassium hydroxide (KOH) with a molar ratio of 1:1 as a flux. The growth mechanism of Cu_2O polyhedral microcrystals are proposed and discussed.

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1. Introduction

There is a growing interest in more environmental processes in the chemical industry and new ‘Green Chemistry’ technologies are highly desired [1]. Cu_2O is a very important industrial material that is commonly used as a red pigment, a well-known antifouling agent for marine paints, and an effective photocatalyst for degradation of organic pollutants such as in dye wastewater, etc. [2]. As an important *p*-type semiconductor with a direct gap of 2.17 eV, Cu_2O can be used for solar energy conversion, electrode materials and gas sensors [3–5]. Moreover, it is an ideal compound for researching on the Bose–Einstein condensation of three-dimensional excitons owing to the large excitonic binding energy of 140 meV [6]. To date, Cu_2O crystals with a wide variety of morphologies have been prepared using solution routes, electrodeposition methods, etc. [7–12]. Most studies in this area have obtained Cu_2O particles using surfactants as capping agents to control the morphologies and structures of the particles, which are generally organic surfactants or templates such as polyethylene glycol (PEG) or cetyl trimethyl ammonium

bromide (CTAB), leading to environmental contaminations [13,14]. Among the current manufacture methods of Cu_2O , electrochemical deposition is the most prevalent and the best on a large scale in view of its short process and high quality product, in which some additives such as potassium dichromate and hydrazine are indispensable and results in an adverse impact to the environment [8,15,16]. Another industrial method is the reduction of copper sulfate (CuSO_4) by glucose (Glc), in which the residual of sulfate radical pollutes the water [17]. In both of the above two methods, there are hazardous organic materials or sulfur-substance in the aqueous solution, and the basic raw materials and the additives are complex, consumptive and non-reproducible. In addition, high-temperature sintering method also is commonly used in the industrial production of Cu_2O . However the products obtained by this way are easy to harden after sintering, difficult to spread and the purity is not high enough. The costs of this method are high energy consumption and heavy pollution. Due to the desire for environmentally friendly processes, new “green” synthesis is developed for Cu_2O crystal growth. Compared to the above methods, our flux approach is the most suitable method for this desire.

As the material science proceeds forward, different methods of tailoring the structures and specific morphologies are being developed [10,18–21]. The ability to tune the shape of inorganic crystals is of extraordinary importance because electronic structures, bonding, surface energies and chemical activity are directly

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related to the surface morphology of these crystals. Thus, great efforts have been devoted to the synthesis of materials with well-controlled shapes and sizes that are crucial to their applications [22].

Herein, we present a facile, elementary while very 'green' approach to synthesize Cu₂O at low temperature yet without any assistance of hazardous organic compounds or surfactants. The reverse dismutation reaction of Cu₂O was employed to obtain crystals with the assistance of a flux mixture of NaOH and KOH. The well-defined Cu₂O truncated octahedra exposing the active basal facets (110) are obtained in one step for the first time.

The structure of Cu₂O can be envisioned as a body-centered lattice type with close packing of O²⁻, or consisting of two independent and interpenetrating O–Cu–O zigzag frameworks, each one equivalent to the cristobalite structure [23]. As a primitive cubic crystal, the Cu₂O crystals usually possess (111) lattice planes as the basal surfaces and the (110) lattice planes with high surface energies are locked up during the growth of the crystals. However, Cu₂O microcrystals as well as Fe₃O₄ crystals that have active basal surfaces (110) is significant for their further applications [24]. Although Cu₂O crystals with various morphologies have been successfully synthesized, it is still necessary to develop effective and facile methods to synthesize the octahedral Cu₂O with (110) active surfaces [25].

In this paper, the well-defined Cu₂O truncated octahedra exposing the active basal facets (110) were obtained. To the best of our knowledge, it is the first time to grow these Cu₂O crystals with truncated octahedra in one step. The corresponding crystal growth mechanism is investigated. After a certain improvement in the near future, this new route will be an effective, novel and green way for the production of Cu₂O in large-scale in the chemical industry.

2. Experimental section

The high temperature reactions of CuO and Cu were carried out in a tube furnace at 1000 and 1050 °C for 12 h in air, and at 300, 350, 400, 450, 500 and 600 °C for 6 h with argon flow, respectively. A starting material mixture of Cu (Tianjin Fuchen Chemical Reagent Corp., ≥99.5%) and CuO (Guangdong Xilong Chemical Corp., 99.99%) was put into an alumina crucible, then loaded into the tube furnace and gradually heated up to the specific temperature. A mixture of NaOH (Beijing Chemical Factory, 99.99%) and KOH (Beijing Chemical Factory, 99.99%) with the molar ratio of 1:1 was used as flux to grow the Cu₂O crystals. In the crystal growth, the starting material and the flux were mixed in the molar ratio of 1:5. High pressure was employed using a LECO hydrothermal apparatus (HR-1B-2-847, LECO Corp., US). In the experiment for crystal growth, charge of about 0.90 g of the starting materials and flux was sealed into a Cu capsule with 6 cm in length and 0.5 cm in diameter, and then loaded into the high-pressure autoclave. The autoclave was heated up to 300, 350, 400 and 450 °C at 0.2 GPa, and maintained for 6, 12, 24, 96 and 240 h, respectively. After the pressure was released, the experiment was cooled down to room temperature naturally. The final crystals were washed several times in an ultrasonic bath with distilled water in order to remove hydroxides and dried at 120 °C in air.

The obtained products and the starting materials were characterized by X-ray powder diffraction (XRD, D/max 2550VB+18 kW rotating anode X-ray Diffractometer, Rigaku Corp., Japan) using CuK α radiation ($\lambda=0.15418$ nm) with a step of 0.02° and a counting time of 2 s for phase determination. The morphologies of the samples were examined by scanning electron microscopy (SEM, JSM-6700 F, JEOL Corp., Japan). The X-ray photoelectron spectrum

Table 1

Crystal structure data of single crystal Cu₂O.

Empirical formula	Cu ₂ O
Formula weight	143.08
<i>T</i> (K)	298(2)
λ (nm)	0.071073
Crystal system, space group	Cubic, <i>Pn-3m</i>
Unit cell dimensions (nm)	<i>a</i> =0.42712
<i>V</i> (nm ³)	0.077920(6)
<i>Z</i> , calculated density (mg m ⁻³)	2, 6.098
μ (mm ⁻¹)	26.675
<i>F</i> (000)	132
Crystal size (mm)	0.05 × 0.05 × 0.05
θ range for data collection	6.76–42.53°
Limiting indices	–8 ≤ <i>h</i> ≤ 7, –6 ≤ <i>k</i> ≤ 8, –7 ≤ <i>l</i> ≤ 7
Reflections collected/unique	1027/69 [R(int)=0.0106]
Completeness to $\theta=42.53$	100%
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	69/0/5
Goodness-of-fit on <i>F</i> ²	0.750
Final <i>R</i> -indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ ^a =0.0106, <i>wR</i> ₂ ^b =0.0164
<i>R</i> -indices (all data)	<i>R</i> ₁ ^a =0.0145, <i>wR</i> ₂ ^b =0.0176
Largest diff. peak and hole (e Å ⁻³)	0.285 and –0.216

$$^a R_1 = \frac{\sum(\Delta F / \sum(F_o))}{\sum(F_o)}$$

$$^b wR_2 = \frac{(\sum[w(F_o^2 - F_c^2)])}{\sum[w(F_o^2)]^{1/2}}, w = 1/\sigma^2(F_o^2)$$

(XPS) was collected on an ESCALAB M K α X-ray photoelectron spectrometer using MgK α X-ray as the excitation sources. Single crystal reflection data were collected using a Bruker Apex II CCD diffractometer equipped with a CCD bidimensional detector using graphite-monochromatic MoK α radiation ($\lambda=0.071073$ nm). Data processing was accomplished with the SAINT processing program. The structure was solved by direct methods and refined by full-matrix least-squares on *F*² using SHELXTL 97. Final parameters and other relevant experimental details are given in Table 1.

3. Results and discussion

The chemical reaction for the synthesis of Cu₂O mentioned above can be expressed as follows:



It is generally considered as a reverse dismutation reaction of Cu₂O, which makes ultimate use of the Cu and O elements to obtain Cu₂O and is normally carried out under extremely high temperature. From the perspective of green chemistry, lower reaction temperatures are much more desirable. In order to lower the synthesis temperature of Cu₂O and further understand the reaction, a series of experiments were carried out. First, the reaction was carried out in air at different temperatures. The starting material mixture of CuO and Cu was heated up to 1000 °C and then to 1050 °C. The corresponding XRD patterns of the products and the starting materials are shown in Fig. 1. The results show that there is only CuO in black color when the reaction temperature is 1000 °C. Although there is no reaction between CuO and Cu below 1000 °C, Cu is already oxidized into CuO by the oxygen in air. When the temperature is increased to 1050 °C, an analysis of XRD pattern shown in Fig. 1b reveals that the final products are mixtures of Cu₂O and CuO, which is shown in a dark red color. The above results suggest that Cu is fully oxidized into CuO that stably exists below 1000 °C in air, and CuO begins to decompose into Cu₂O when the temperature further rises to 1050 °C. Thus, Cu₂O in the final products is not obtained from the direct reaction between Cu and CuO but rather from the decomposition of CuO in air. We can conclude that this synthesis approach of Cu₂O must be at higher temperature than 1050 °C or for more reaction time in air, and it is actually a two-step reaction: the oxidation of Cu and the

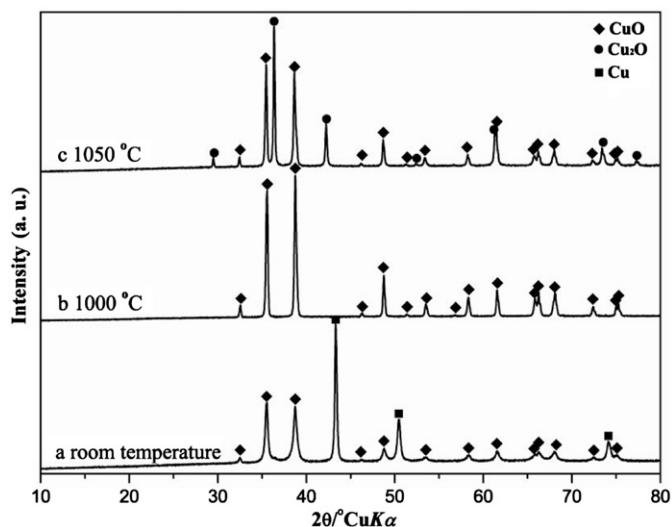


Fig. 1. XRD patterns for the mixture of CuO and Cu after heating at (a) 1000 °C and (b) 1050 °C for 12 h in air. The diffraction peaks of CuO, Cu₂O and Cu phase were denoted with rhombus, circle and square, respectively.

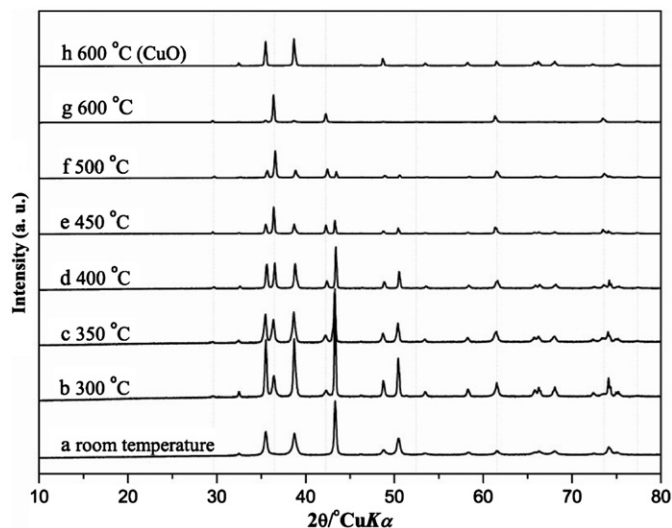


Fig. 2. XRD patterns of the mixture of CuO and Cu at (a) room temperature and after heating at (b) 300 °C, (c) 350 °C, (d) 400 °C, (e) 450 °C, (f) 500 °C and (g) 600 °C for 6 h in argon atmosphere. (h) XRD pattern of the CuO powder after heating at 600 °C for 6 h in argon atmosphere.

decomposition of CuO. Second, the reaction was carried out in an argon flow. The mixture of the starting materials was heated up to 300, 350, 400, 450, 500 and 600 °C for 6 h. The corresponding XRD patterns including the starting raw materials are shown in Fig. 2. The results indicate that Cu₂O appears in the products after the temperature reaches 300 °C. When the temperature rises gradually, the intensity of Cu₂O increases, which suggests the contents of Cu₂O increase gradually. Thus, CuO starts to react with Cu at 300 °C, while CuO and Cu still remain intact when they are heated up below 600 °C, which indicates higher temperature can activate the reaction slowly but not fully. In order to ensure the reaction between CuO and Cu, the CuO powder was also heated up to 600 °C in an argon flow. The XRD pattern is shown in Fig. 2h, which shows that the CuO remains stable up to 600 °C. Therefore, it is clear that the Cu₂O is from the reverse dismutation reaction of Cu₂O in an argon flow; however, if the reaction is still not completed for 6 h, then longer reaction time is required. Finally, the reaction was carried out in a

closed system. The mixture of CuO and Cu was placed into the Cu tube and sealed with no free space, and was then heated up to 450 °C and maintained for 12 h. The XRD pattern of final product is shown in Fig. 3a. The result reveals that Cu₂O can be obtained but the starting materials do not fully react. Both the argon atmosphere and the closed system can be considered as oxygen-free, so Cu cannot be oxidized by oxygen and only the reverse dismutation reaction of Cu₂O can proceed. In general, the reaction between CuO and Cu is rather different with or without the existence of oxygen, which means it is quite sensitive to oxygen. The reverse dismutation reaction of Cu₂O can undergo at very low temperature, but longer reaction time is required for a full reaction of Cu₂O.

Only a polycrystalline sample can be obtained from the above reaction, thus a flux was employed in order to grow Cu₂O crystals, and the mixture of NaOH and KOH with a molar ratio of 1:1 was used as the flux. During the crystal growth, the starting materials and the flux were mixed in a molar ratio of 1:5. First, the starting CuO and Cu were mixed with the hydroxides flux and heated up to 300 °C, then maintained for 12 h in an argon flow. As shown in Fig. 3b, the XRD pattern of the final product reveals that there is a coexistence of Cu₂O and other copper oxides, so the reaction in the flux can potentially be the same as the direct solid reaction between CuO and Cu. In general, Cu₂O can be obtained but the reaction time cannot be shortened using the above methods, while simply raising the temperature cannot help improve the reaction. In this paper, another thermodynamic parameter, pressure, is taken in account to shorten the reaction time and improve the crystal growth. High pressure, the leading tool for atmosphere widely tuning the interatomic/intermolecular interactions in fluid and solid materials, is applied to the flux growth, because high pressure method normally provides a close system in which the oxygen is lacking, and also increases the reaction rates [26]. The crystals synthesized at 0.2 GPa and 450 °C for 24 h were crystals with sizes of 50~100 μm. The XRD patterns for the experimental product and the simulated data based on their single crystal analysis are shown in Fig. 4. The good agreement between experimental and simulated powder X-ray diffraction patterns of the high pressure products supports the phase purity of the as-synthesized product. The single crystal analysis shows that the crystals are pure Cu₂O with cubic structure (*Pn-3m*, No. 224) having a corresponding lattice constant of $a=0.42712$ nm. The copper atoms locate at the positions (0, 0, 0) and oxygen atoms at

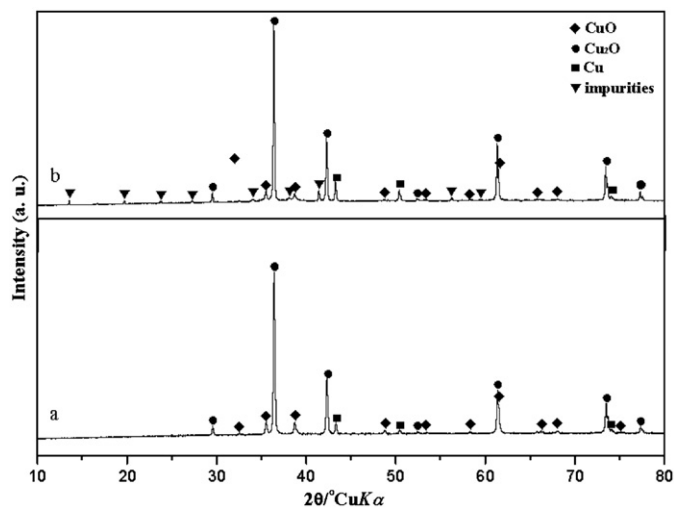


Fig. 3. XRD pattern for (a) the mixture of CuO and Cu after heating at 450 °C for 12 h in Cu tube; (b) XRD pattern of the mixture of CuO and Cu with mixed hydroxides as heated at 300 °C for 12 h in argon flow. CuO, Cu₂O and Cu phases were denoted with rhombus, circle and square, respectively. The diffraction peaks arising from impurity phases were denoted with the inverted triangle.

the positions (1/4, 1/4, 1/4) in the cubic cell. Fig. 5 presents XPS of as-synthesized samples, which is calibrated with C1s (284.6 eV) as the reference. The peaks at 932.8, 952.5 and 529.8 eV corresponds to the binding energy of Cu 2p_{3/2}, Cu 2p_{1/2} and O1s, respectively, which are in good agreement with the published XPS data of Cu₂O [27]. The very small satellite peaks in Cu spectrum and the slight asymmetric O1s peak may be caused by the contamination and the adsorption of oxygen on the surface of Cu₂O crystals. Thus, the XPS results also confirm that the sample we obtained in this paper is indeed pure Cu₂O.

In our experiments, CuO is dissolved in a solution of molten mixed KOH and NaOH eutectic ~200 °C or lower [28]. It is decomposed into Cu²⁺ and O²⁻, and Cu²⁺ is gradually reduced to Cu⁺ by Cu⁰ in the flux. Therefore, the mechanism involved in our synthesis of Cu₂O crystals is the real reverse dismutation reaction under high pressure and low temperature. Compared to the previous methods for the synthesis of Cu₂O, our flux approach is the most suitable method for the desire for environmentally friendly processes. First of all, this approach utilizes the reaction of the elements between Cu and O in the largest scale. The metal copper is used as the chemical reducing agent without the organic solvents, which results in an adverse impact to the environment. Secondly, the raw materials are stable and conveniently obtained from copper minerals, and there are no other reducing reagents to

convert Cu²⁺ to Cu⁺, which makes the reduction relatively simple. Thirdly, the alkali flux is conventional while more environmentally friendly compared with traditional solvents. The substitution of the conventional liquid containing the organic and sulfate solvents avoids the pollution to the environment because the alkali can be easily disposed. Finally, this reaction can proceed under very low temperature and within an extremely short time (even to 10 min) to give the Cu₂O powder, thus much energy can potentially be saved. In summary, this flux approach is novel and “green”, and applicable to the material industry production to improve the manipulation of the process and the efficiency of the raw materials, and lower the cost of the production and reduce the environmental pollution.

The SEM morphologies of the Cu₂O crystals synthesized at 450 °C and 0.2 GPa for 24 h are shown in Fig. 6a, which reveals that the as-grown Cu₂O crystals are shown as truncated octahedra. Such a special shape of crystal is closely related to its growth environments and conditions. The influence of temperature is investigated over the morphology of the product. The growths are firstly carried out for 6 h at the pressure of 0.2 GPa and the temperatures of 300 and 350 °C separately, whose SEM images of the final crystals are shown in Fig. 6b and c, respectively. These results reveal that the crystal surface is rough due to the lower temperature and shorter reaction time. The SEM images of Fig. 6a–c also show that the morphology of as-synthesized Cu₂O crystals is identical and the temperature affects little over the growth of Cu₂O crystal. After checking many temperatures and with the consideration of the reduction of CuO at high temperature, 450 °C is found to be the optimal temperature for the growth of Cu₂O crystal [29–31]. In order to study the effect of reaction durations to the crystal growth, the growths are also carried out for 24 and 96 h (extremely prolonging to 240 h) under 0.2 GPa and 450 °C. The SEM images of the final crystals are shown in Fig. 6d–f. The results suggest that there is little geometric change in the products and only the average size of the as-grown Cu₂O increased with the reaction time. Therefore, the reaction duration has no impact on the growth habit and morphology of Cu₂O crystals in this approach but only on the sizes.

Another factor that affects the growth is the kinetics that is quite related to its structure. It has been reported that the (111), (100) and possibly (110) surface of cubic structured materials are different not only in the surface atom densities, but also in the electronic structure, bonding and possibility of chemical activities [32]. Cu₂O crystallizes in a cubic structure, where each O atom is surrounded by a tetrahedral of copper ions, and each Cu cation has two oxygen neighbors. In the structure of Cu₂O crystal, the (110) surface is built from alternating Cu⁺ cation and

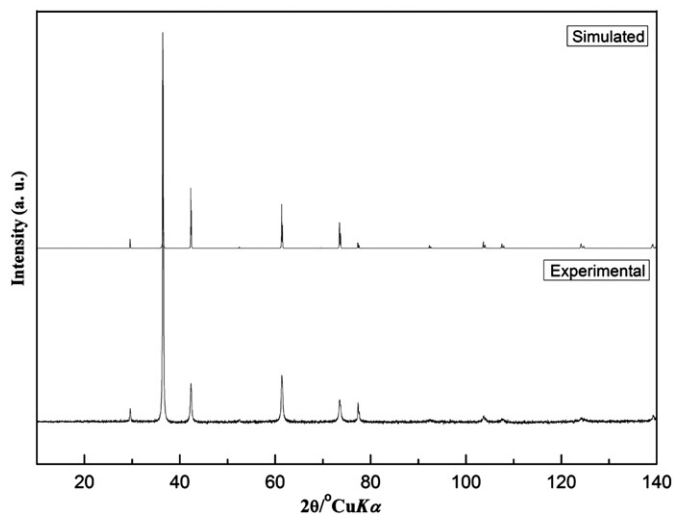


Fig. 4. Experimental and simulated XRD patterns for Cu₂O microcrystal as-synthesized at 0.2 GPa and 450 °C for 24 h.

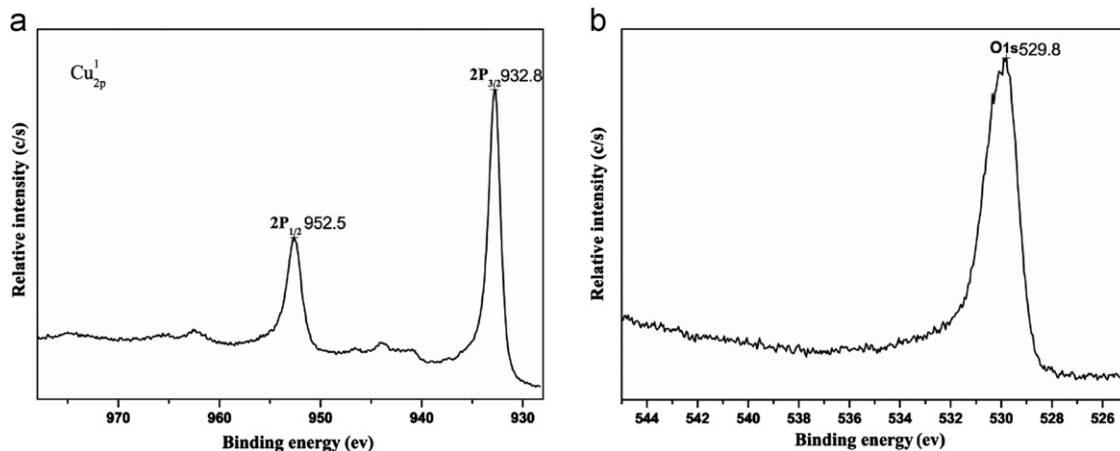


Fig. 5. (a) X-ray photoelectron spectra of Cu¹ 2p for as-synthesized Cu₂O microcrystals and (b) X-ray photoelectron spectra of O 1s for as-synthesized Cu₂O microcrystals.

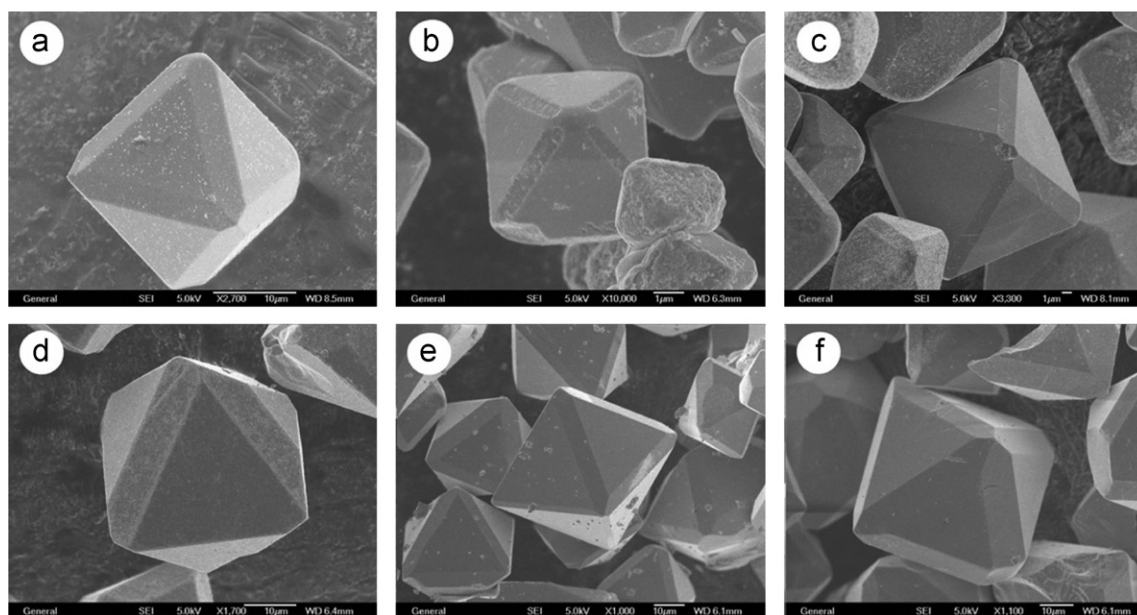


Fig. 6. SEM images of as-prepared Cu_2O crystals at different reaction conditions: (a) at 450 °C, 24 h and 0.2 GPa, (b) at 300 °C, 6 h and 0.2 GPa, (c) at 350 °C, 6 h and 0.2 GPa; SEM images of as-prepared Cu_2O crystals at different reaction duration at 450 °C and 0.2 GPa: (d) 6 h, (e) 96 h and (f) 240 h.

O^{2-} anion layers, and only Cu^+ or O^{2-} is located in the (111) and (100) surfaces. Because Cu_2O is an ionic crystal, the (110) surface is nonpolar while the (100) and (111) surfaces are both polar. The particular facet for the ionic crystal that is exposed becomes critical due to the long-range Coulomb interaction; only nonpolarized surfaces, i.e. surfaces without a dipole moment perpendicular to the surface, may be stable with only minor rearrangements of the ions [33]. Because the distance between the faces containing Cu and O along [111] direction is rather short compared to that along [100] direction, the polarity of (111) surface is very weak, so the activities of chemical reactions with these three surfaces can be expressed as a general sequence of $\gamma(100) > \gamma(111) \geq \gamma(110)$. Therefore, the (110) face is the most stable face, but has low activities. In the earlier stage of crystal growth, once the Cu_2O nuclei are formed, new reactants continuously aggregate around the nuclei. After the period for the formation of Cu_2O nuclei, the growth rate along different directions starts to control the growth of crystal. The crystal surface (100) has higher activities than surfaces (111) and (110), so Cu^{2+} preferentially adsorbs on the (100) planes or the growth rate along [100] direction is enhanced. Therefore, (111) and (110) surfaces are obtained. In this paper, the obtained Cu_2O crystals are shown as truncated octahedra. The octahedral surface may be (111) or (110) face. If it is (110) face, the truncated surfaces will be (111) and (100) surfaces. The (100) surface is Madelung unstable according to the above discussion, so the octahedral surface must be active (111) face and the truncated surface is (110) face.

4. Conclusions

In summary, Cu_2O crystals were grown in one step using the reverse dismutation reaction of Cu_2O via a high pressure flux approach for the first time, and the morphology of our as-prepared crystals was shown as truncated octahedra. The mechanism we proposed suggests high pressure was applied to increase the yield and facilitate the growth of Cu_2O crystals. The green and facile method for well-controlled synthesis of Cu_2O truncated octahedral shape with the active basal facets would

find many applications in the chemical industry. This approach also provides a chance of the green-industry production of Cu_2O .

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