



Shape-controlled synthesis of Cu₂O microcrystals by electrochemical method

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ABSTRACT

Cuprous oxide (Cu₂O) microcrystals have been successfully synthesized via a facile electrochemical method in alkaline NaCl solution with copper plate and graphite slice as electrodes and Na₂Cr₂O₇ as additive. The as-synthesized products have been systematically studied by X-ray powder diffraction (XRD), field emission scanning electron microscope (FESEM), transmission electron microscope (TEM), selected area electron diffraction (SAED) and ultraviolet–visible spectrum (UV–vis). The results indicate that the pH value, temperature and potential play important roles in the morphology control besides the crystal habits of Cu₂O. The possible mechanism has been explored in the article.

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1. Introduction

As a p-type semiconductor with direct band gap ~ 2.17 eV [1,2], cuprous oxide (Cu₂O) is of unique optical and magnetic properties [3–6], which has potential applications in solar energy conversion [7,8], electrode materials [5,9,10], gas sensors [11–13], photo-activated splitting of water [14,15] and catalysts [16–19]. Upon photon excitation, the excitons of Cu₂O are long-lived (10 μ s), and there is evidence that their motion through the solid can be coherent, in a manner analogous to photon coherence in lasers [20]. Recently, Cu₂O has attracted attention for the conversion of solar energy into electrical or chemical energy [21,22], showing a theoretical solar efficiency of about 9–11% [23]. In addition, it has potential applications in photon catalytic degradation of organic pollutants under visible light, and moreover, it can be used to form a solar cell with circuit voltage by combination with a suitable n-type semiconductor [24]. Currently, Cu₂O has been prepared by different methods, such as electrodeposition [25–28], thermal relaxation [29], sonochemical methods [30], vacuum evaporation [31], vapor–liquid–solid (VLS) growth [32,33], oxidation route [34] and liquid-phase reduction of metal salt [35].

The electronic structure, bonding, surface energy, and chemical activities of the materials are directly related to their morphology,

and the shapes are directly related to their properties and stabilities. The development of micro- or nano-materials with special size and well-defined shape may open new opportunities for exploring material's physical and chemical properties. Therefore, the ability to tune the shape of inorganic crystals is of extraordinary importance [36]. In the past decades, there have been an increasing number of experiments on the synthesis of Cu₂O particles with regular shapes, such as cubes [20], needles [37], octahedrons [3], flowerlike [38] and tetrakaidecahedrons [39]. At the same time, the preparation of Cu₂O powders by the anodic dissolution of copper plate in an alkaline NaCl solution has been widely used as the best suitable process on an industrial scale [40]. However, so far, very few reports have been focused on the morphology control of Cu₂O by this method.

In this paper, we demonstrate a facile electrochemical method to synthesize high-quality Cu₂O microcrystals with special morphology. The results show that the variations of potential, growth time, temperature and the compositions of electrolyte can control the morphology of Cu₂O microcrystals accurately. Furthermore, we discuss the possible formation mechanism for the novel morphology.

2. Experimental

The experiments were performed in an electrolytic cell designed by us. All of the chemical reagents used in this experiment were analytical grade and without further purification.

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A typical procedure for preparation of Cu_2O particles was carried out as follows:

Firstly, the electrolyte, made up of 280 g L^{-1} NaCl and 0.1 g L^{-1} $\text{Na}_2\text{Cr}_2\text{O}_7$, was adjusted to pH value 12.0 by 1.0 M NaOH aqueous solution. Then, a piece of polished copper plate ($30 \text{ mm} \times 40 \text{ mm} \times 0.4 \text{ mm}$) and a graphite slice were used as the anode and cathode, respectively, and immersed into the electrolyte. Followed, the as-prepared electrolyte was heated to 80°C . Electrolysis reaction was performed at 2.0 V for 30 min. The color of the solution changed to orange and then brick red. When the reaction ended, the red sediments were taken out and centrifuged. Then, the products were washed with a large quantity of deionized water. Subsequently, the obtained products were dried in vacuum loft drier at 70°C for 6 h.

The crystal structure of as-prepared products was identified by X-ray powder diffraction (XRD) with an X-ray diffractometer (Rigaku D/max-2500) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The morphology, particle size and microstructure of the products were examined by field emission scanning electron microscope (FESEM, JEOL JSM-6700F), transmission electron microscope (TEM, JEOL JEM-EX2000) equipped with selected area electron diffraction (SAED). Room temperature ultraviolet–visible (UV–vis) absorption spectrum was recorded on a UV-2550 spectrophotometer in the wavelength range of 200–800 nm.

3. Results and discussion

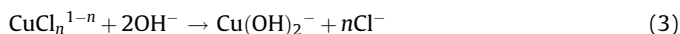
The reactions on each electrode are described as follows: Anodic reaction (anodic dissolution of copper plate) [41]:



Cathodic reaction (hydrogen evolution):



Chemical reactions (hydrolysis precipitation):



Thus, the cell reaction is the summation of Eqs. (1)–(4), that is:



Fig. 1 shows XRD patterns of the corresponding samples synthesized at different pH values (7.0, 8.0, 9.0, 10.0, 11.0, 12.0 and 13.0, respectively). It should be pointed out that the mixed solution of the NaCl (280 g L^{-1}) and $\text{Na}_2\text{Cr}_2\text{O}_7$ (0.10 g L^{-1}) is slightly acidic, having a pH value of 5.2. The electrolytes can be adjusted to demanded pH values by 1.0 M NaOH aqueous solution. It is clearly shown that each curve of Fig. 1a–f contains seven peaks and all peaks are in well agreement with those for Cu_2O powder obtained from the International Center of Diffraction Data card (ICDD, formerly JCPDS No. 05-0667). No other peaks from any other impurities are detected. However, according to Fig. 1g, the peaks of Cu are detected at the pH value 7.0. The appearance of Cu in the product is due to the subsidiary reaction of cathode [41]:



Based on the reaction mechanism of Cu_2O produced by electrochemical oxidation, it indicates that the element of Cu goes through a complex course: $\text{Cu} \rightarrow \text{CuCl}_{\text{aq}} \rightarrow \text{CuCl}_n^{1-n} \rightarrow \text{Cu}(\text{OH})_2^- \rightarrow \text{Cu}_2\text{O}$ ($n = 2, 3$). The standard electrode potential is shown in Table 1 [42]. The potentials of reactions (2) and (6) are calculated based on Nernst equation:

$$E = E^0 - \frac{0.0592}{n} \text{pH} \quad (7)$$

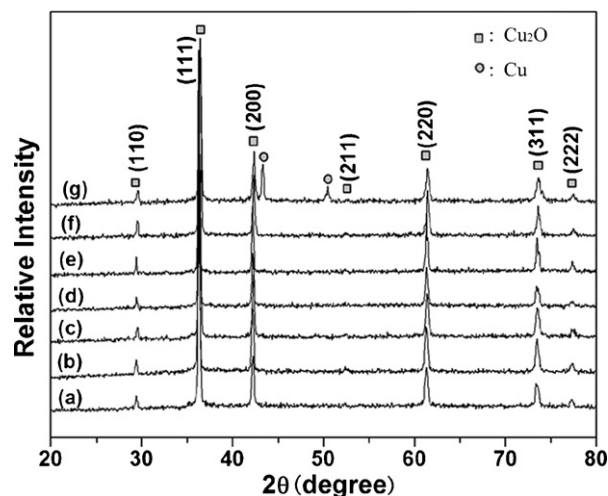
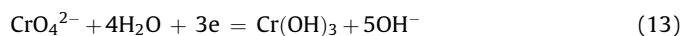
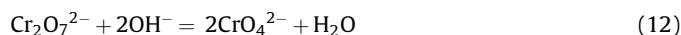


Fig. 1. XRD patterns of the products obtained at different pH values: (a) 13, (b) 12, (c) 11, (d) 10, (e) 9, (f) 8, and (g) 7, respectively.

It is found that the potential of the reaction (6) calculated by the above formula is always higher than that of the reaction (2). This indicates that the Cu_2O is prior to deoxidize in case touching with the cathode, which causes the presence of metal copper in the products.

In order to improve the purity of the products, $\text{Na}_2\text{Cr}_2\text{O}_7$ is used, and significant improvement is resulted. In alkaline solutions, $\text{Cr}_2\text{O}_7^{2-}$ convert into CrO_4^{2-} and then CrO_4^{2-} convert into $\text{Cr}(\text{OH})_3$ as following chemical reactions:



The higher the pH value is, the more completely the $\text{Cr}_2\text{O}_7^{2-}$ convert into CrO_4^{2-} , and the more easily the $\text{Cr}(\text{OH})_3$ form. Then the $\text{Cr}(\text{OH})_3$ will form a conductive film on the surface of cathode, which contributes to reaction (2) but prevent the occurrence of reaction (6). So, pure Cu_2O particles are obtained in alkaline condition (Fig. 1a–f). While pH 7, OH^- concentration is very low, reaction (12) is restrained and the conductive film cannot be formed. As a result, the Cu element is detected in the products of pH 7. But, if the concentration of $\text{Na}_2\text{Cr}_2\text{O}_7$ is too high, Cu_2O is easy to oxidize. In this study, we think that the best concentration of $\text{Na}_2\text{Cr}_2\text{O}_7$ is 0.10 g L^{-1} .

In order to elucidate the origin of the branching growth of Cu_2O produced in alkaline NaCl solution by electrochemical method, we have investigated the dependence of branching growth on various synthetic parameters independently (e.g., pH value, temperature, potential and reaction time). We first study the effect of pH value on branching growth. The FESEM images of Cu_2O samples prepared

Table 1
Possible chemical reactions at the cathode.

Reaction number	Reduction	E^0 (V)
(2)	$2\text{H}_2\text{O} + 2e = \text{H}_2 + 2\text{OH}^-$	−0.828
(6)	$\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2e = 2\text{Cu} + 2\text{OH}^-$	−0.361
(8)	$\text{Cu}^+ + e = \text{Cu}$	0.522
(9)	$\text{CuCl}_{\text{aq}} + e = \text{Cu} + (nq\text{Cl})^-$	0.124
(10)	$\text{CuCl}_2 + 2e = \text{Cu} + 2\text{Cl}^-$	0.190
(11)	$\text{CuCl}_3^{2-} + e = \text{Cu} + 3\text{Cl}^-$	0.178

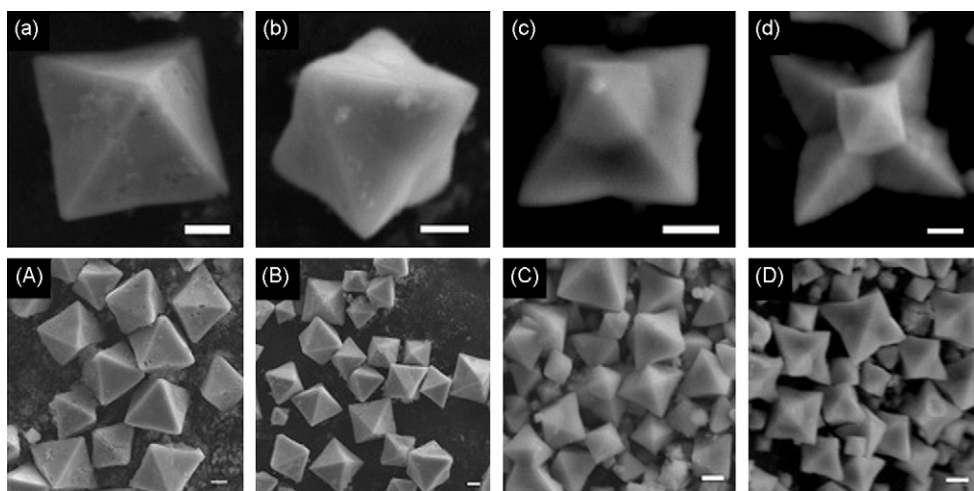


Fig. 2. FESEM images of Cu_2O microcrystals obtained at different pH values: (a) 8.0, (b) 10.0, (c) 12.0, and (d) 13.0, respectively. The scale bar represents 1 μm .

at various pH values are shown in Fig. 2. The high magnification FESEM images are shown in Fig. 2a–d, which are corresponding to Fig. 2A–D. It is obvious that the pH value has a distinctive effect on branching, and the degree of branching increases systematically as pH value increases. In Fig. 2A and a, octahedral-shaped aggregates with 3 μm crystal size are the dominant products at pH 8.0. While most of the particles are octahedral-shaped at pH 10.0 as shown in Fig. 2B, a few of them have a tendency to become six-horn-shaped (Fig. 2b). When the pH value increases to 12.0, the octahedral-shaped are replaced by six-horn-shaped icositetrahedron (Fig. 2C). Each crystal has six apexes and each apex connects with four sides to form an icositetrahedron. The crystal size is varying from 3 to 5 μm . The more detailed information about the icositetrahedron microcrystals can be obtained in TEM image (Fig. 6a). When the pH value increases to 13.0, the edges and corners of icositetrahedron-shaped Cu_2O become more extrusive (Fig. 2d and D).

A basic crystal shape is determined by two growth processes: habit formation and branching growth. Crystal habit is determined by the relative order of surface energies in different crystallographic planes [39,43]. While, branching growth is created by diffusion effect. Diffusion-limited branching occurs when the initial growth rate of a crystal is faster than the diffusion rate of nutrient ions, which results in a depletion zone around the crystal. The apexes of a polyhedral crystal protrude further into the region of higher concentration as they can grow faster than the central parts of the facets and form branches [44]. In this case, under the effect of electric field, copper plate dissolves and changes to Cu^+ ions entering into the solution, which are surrounded by amount of Cl^- ions immediately. Then, the OH^- ions pass through Cl^- area to contact with Cu^+ forming $\text{Cu}(\text{OH})_2^-$. Thus, Cu_2O crystal nucleus are formed in the electrolyte by decomposition reaction of $\text{Cu}(\text{OH})_2^-$ (Eq. (4)). With the crystal growing, the OH^- and other ions or

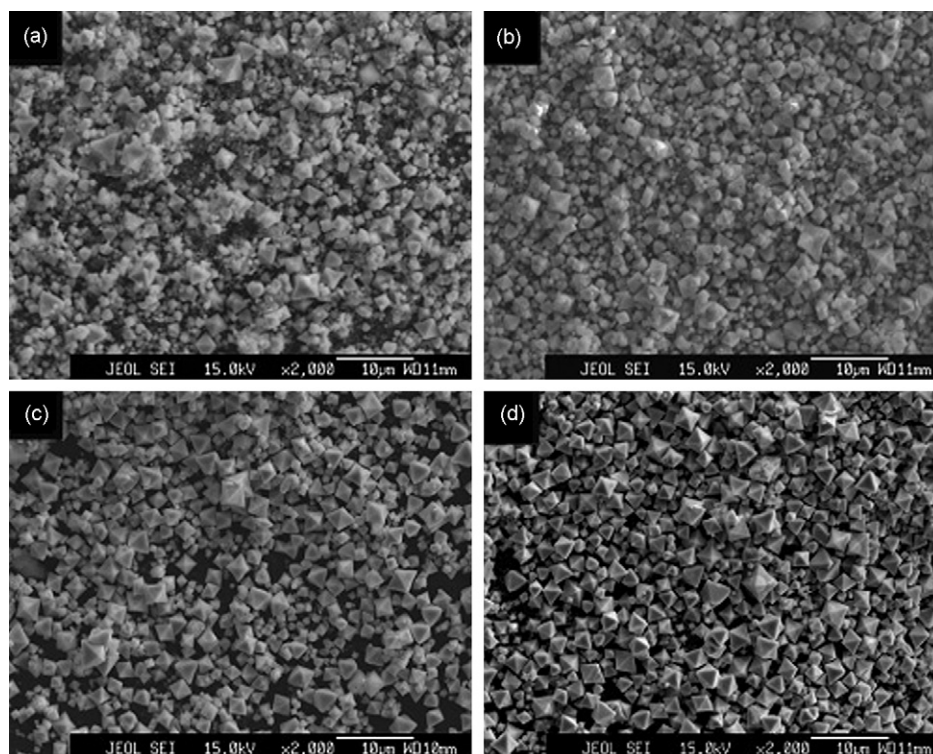


Fig. 3. FESEM images of Cu_2O microcrystals synthesized at different temperatures: (a) 30, (b) 50, (c) 70, and (d) 90 $^{\circ}\text{C}$, respectively.

molecules near the Cu_2O crystal nucleus are consumed, and a concentric concentration diffusion field around the crystal is formed. The crystal growth and crystal shape are limited by diffusion when such a depletion layer is formed. In the area of high concentration, the crystal growth rate is faster and generates salient branches. As the OH^- concentration increases, the degree of branching becomes more pronounced and the morphology of Cu_2O evolves from octahedrons to six-horn-shaped icositetrahedron (Fig. 2). Therefore, Cu_2O with different morphologies could be obtained by adjusting the pH value.

For crystallization, temperature is another main factor that affects the basic shape-guiding processes. For example, in nature snow crystals can grow into thousands of different forms with various crystal habits and degrees of branching by subtle changes in temperature and humidity [45,46]. Therefore, we investigate the effects of the temperature (30, 50, 70 and 90 °C) on branching growth of Cu_2O microcrystals at a fixed solution pH value of 12.0. FESEM images of Cu_2O crystals grown at different temperatures are shown in Fig. 3. At 30 °C, Cu_2O particles are disordered with wide particle size distribution. As the temperature increases, branches become more extrusive, and the particles become more uniform and smooth (Fig. 3b–d). When the temperature is 90 °C, many Cu_2O particles become icositetrahedron-shaped with smooth surfaces (Fig. 3d).

These tendencies indicate that temperature is the primary factor that exerts homogeneous effects on crystals surface in electrocrystallization. It can be explained by the kinetics and thermodynamics of the process of crystal growth. The diffusion becomes fast as the temperature increases, which generates rough and unstable surfaces between branches that have many surface dangling bonds. Simultaneously, the increase in temperature can rapidly increase the growth kinetic coefficient in these regions and compensate for the diffusion effect to result in faceting growth that develops flat and smooth faces. That is to say, the increase in

the temperature is beneficial to the integrity of the crystal shape and smooth surface.

In electrochemistry, the rate of the electron transfer reaction is directly proportional to the current. We next perform an experiment to study the effect of the applied potential on branching growth at a fixed solution pH value of 12.0 with 80 °C. FESEM images of Cu_2O microcrystals synthesized at different potentials are shown in Fig. 4. Comparing the FESEM images, it can be distinctly found that the surfaces of the microcrystals become rougher as the potential increases. When the potential achieves 5.0 V, the surface of Cu_2O becomes very rough, and the shapes are no longer regular icositetrahedron, but six-horn-flower like morphology (Fig. 4d).

The influence of potential on the morphology of Cu_2O microcrystals can be straightforwardly understood by considering the dependence of the relative concentration of Cu^+ ions on those of Cl^- and OH^- . From above discussion we know that the decomposition rate of $\text{Cu}(\text{OH})_2^-$ determines the morphology of Cu_2O . The higher the concentration is, the rapider the $\text{Cu}(\text{OH})_2^-$ decomposes, and the faster the crystal grows. At low potential (2.0 V), the intensity of the current is small. Thus, the copper plate dissolves slowly and the concentration of Cu^+ is low. Once Cu^+ ions appear in the solution, they can find a thermodynamically favorable place to attach, which results in the formation of flat and smooth surface with low surface energy. As the potential increases, the intensity of electric field will boost up and the current will rise, leading to further increase in concentration of Cu^+ . However, the ratios of $[\text{OH}^-]/[\text{Cu}^+]$ and $[\text{Cl}^-]/[\text{Cu}^+]$ are decreasing. Under these conditions, Cu^+ ions initially attach to a thermodynamically unfavorable place. This means that they will crystallize where they are produced even if the resulted shapes are not thermodynamically favorable. As a result, they can partially redissolve and form rough surfaces. Or they will continue crystallization to form more big crystal with more rough surfaces.

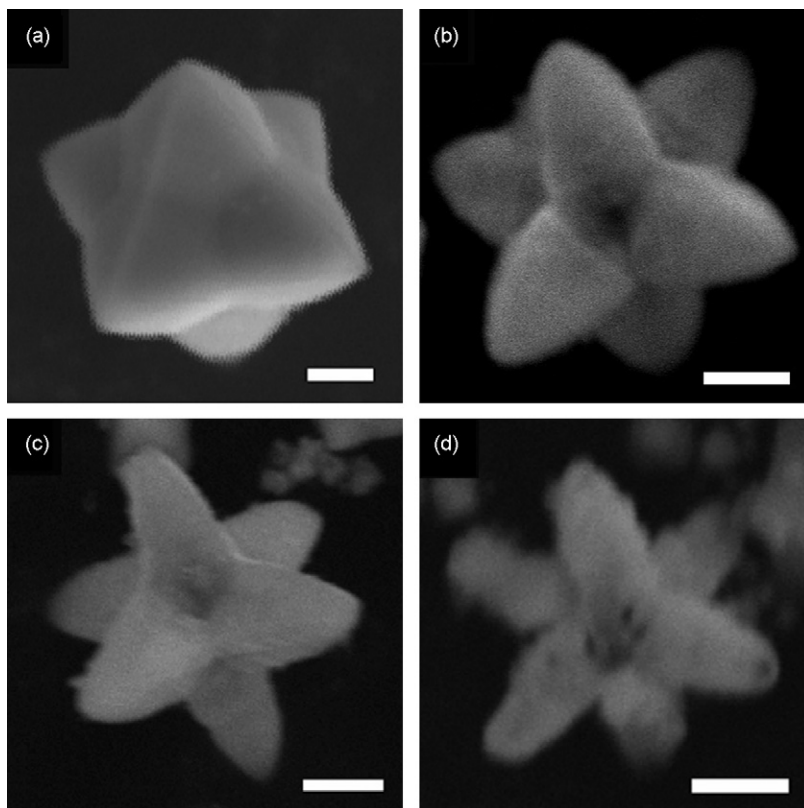


Fig. 4. FESEM images of Cu_2O microcrystals obtained at different potentials: (a) 2.0, (b) 3.0, (c) 4.0, and (d) 5.0 V, respectively. The scale bar represents 1 μm .

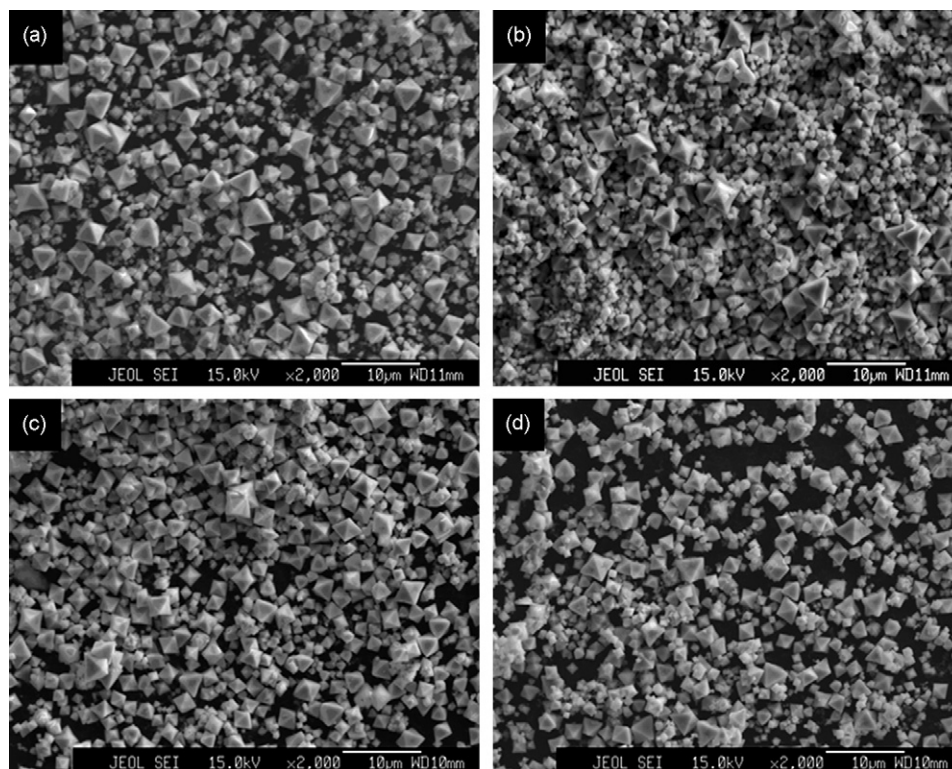


Fig. 5. FESEM images of Cu_2O microcrystals synthesized at different reaction times: (a) 10, (b) 30, (c) 60, and (d) 120 min, respectively.

The results show that the nucleation and growth of the microcrystals are governed by a nucleation–dissolution–recrystallization growth mechanism.

Further controlled experiments have also been carried out to investigate the effects of reaction time on the morphology and the size of these products. FESEM images of Cu_2O crystals grown at different times (10, 30, 60, and 120 min) are shown in Fig. 5. It is found that the morphologies of Cu_2O change slightly as the reaction time prolong to 120 min. This indicates that the influence of reaction time on the morphology is feeble.

Apropos of above phenomenon, it can be explained that the Cu_2O crystals are formed in the electric field. Simultaneously, the Cu_2O crystals grow fast, and once the crystals are formed, it will subside in the bottom of the solution and depart from the electric field to stop growth. As a result, the influence of the reaction time on the morphology is relatively small.

In order to study the characteristic of the products synthesized by electrochemical method, we have selected one sample to do

TEM, SAED and UV–vis analysis. The samples were synthesized in the electrolyte mentioned above with pH value 12.0. Electrolysis reaction was performed at 2.0 V and 80 °C for 30 min. The TEM image of an individual Cu_2O particle (Fig. 6a) exhibits a six-horn-shaped polyhedron with an edge length about 1 μm , which is in accordance with the FESEM image (Fig. 2c). At the same time, it indicates that the Cu_2O particles are infarctate and the edges of the octahedron are no longer straight. A typical SAED pattern of Cu_2O crystals is shown in Fig. 6b, which shows concentric rings corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) lattice planes of Cu_2O . From the SAED image, we can infer that the as-synthesized product by this method is polycrystalline Cu_2O . At the same time, we confirm that all samples synthesized at above different conditions have polycrystalline structures. This is beneficial to the application in the conversion of solar energy into electrical or chemical energy.

As the size of the Cu_2O microcrystals is too large, the UV–vis absorption spectrum consists of absorption and reflection due to

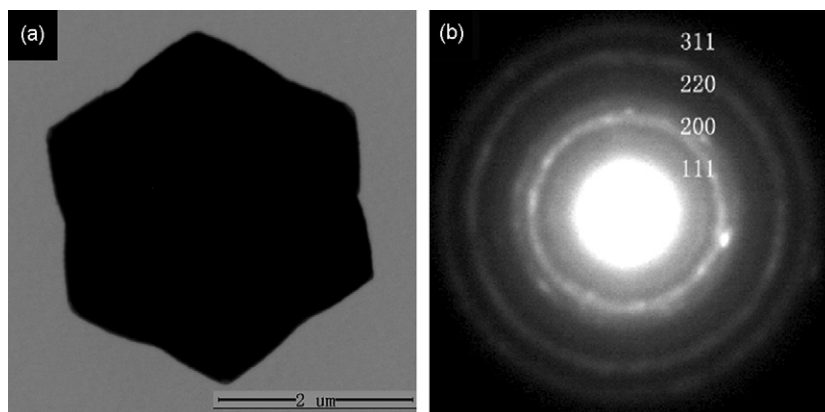


Fig. 6. (a) TEM image and (b) SAED pattern (particles crushed down) of Cu_2O microcrystals.

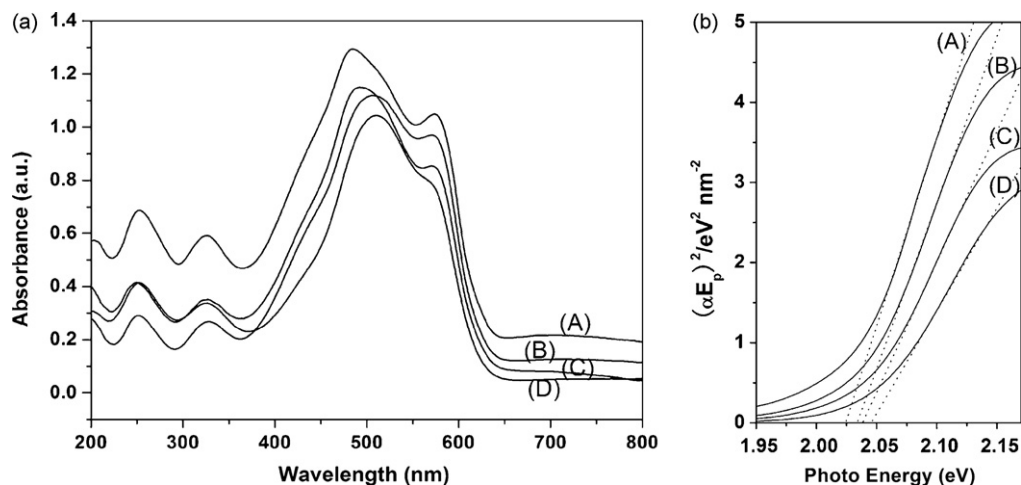


Fig. 7. (a) UV-vis absorption spectra and (b) the corresponding $(\alpha E_p)^2$ vs. E_p curves of Cu_2O particles at different pH values: (A) 8.0, (B) 10.0, (C) 11.0, and (D) 12.0, respectively.

the particle characteristics of light, and the UV-vis spectrum obtained from the suspension of the powder sample is not reasonable. Therefore, the absorption spectrum can be obtained by the measurement of the Cu_2O sample in the reflection mode. This property is analyzed on the basis of the Kubelka–Munk equation [47]: $F(R) = k/s = (1 - R)^2 / 2R$, where k and s are absorption and scattering coefficients, respectively, and R is the reflectance at the front face. $F(R)$ is an indicator of light absorption ability. The y-axis title absorbance in Fig. 7a is corresponding to the $F(R)$ in the equation. The absorption spectra of the Cu_2O prepared at different pH values (8.0, 10.0, 11.0, 12.0) are shown in Fig. 7a. As shown in this figure, there are broad absorption peaks in the range of 400–600 nm, whose centers are in the range of 480–510 nm. Comparing the four curves in different pH values, it can be found that the absorption edges shift slightly toward shortwave side with the pH value increases and the breadth of the peaks become narrow. A classical Tauc approach is employed to estimate their optical energy band gaps using the following equation for a semiconductor: $\alpha E_p = K(E_p - E_g)^{1/2}$ (where α is the absorption coefficient, K is a constant, E_p is the discrete photon energy, and E_g is the band gap energy) [48]. As shown in Fig. 7b, the best linear relationships are obtained by plotting $(\alpha E_p)^2$ vs. E_p , and the extrapolated values (the straight lines to the x-axis) of E_p at $\alpha = 0$ give absorption edge energies corresponding to $E_g = 2.024$, 2.033, 2.038, and 2.046 eV, respectively. The band gap energies are all smaller than the reported value for the bulk Cu_2O ($E_g = 2.17$ eV), and they gradually increase with the pH value increases. Here, red shift in E_g compared with bulk Cu_2O is likely to be the result of inset energy level. The barrier may be due to an energetic mismatch between the semiconductor Fermi level and the solution potential or oxygen vacancy. The increase in band gap energy of the Cu_2O microcrystals as pH value increases may ascribe to the morphology changes. This indicates that Cu_2O has better potential applications under visible light. The measurements do not give insight into the mechanism of barrier formation. More detailed work will be required to determine whether other effects, such as surface states and impurity may induce the barrier.

4. Conclusions

In summary, we investigate the effect of pH value, temperature, potential and reaction time on the branching growth of Cu_2O crystals in alkaline NaCl solution with copper plate and graphite slice as electrodes and $\text{Na}_2\text{Cr}_2\text{O}_7$ as additive via electrochemical method. This is a fairly well method to prepare Cu_2O due to its simple process and easy control. The results demonstrate a

methodical tuning of the degree of branching of Cu_2O crystals by elucidating and manipulating key conditions to control shape-guiding processes in electrocrystallization and establish a possible mechanism for the branching growth of Cu_2O . Simultaneously, the results testify that the formation and growth of Cu_2O are achieved in the electric field. Furthermore, the band gap energies of the as-synthesized products are estimated to be smaller than the reported value for the bulk Cu_2O (2.17 eV). These systems will be useful for a broad range of applications such as sensors, optoelectronics, and catalysts. The programmability and synthetic freedom demonstrated in this work will not only provide valuable information for the study of electrochemical crystal growth mechanisms, but also build a foundation for the study of directed crystal growth of various semiconducting crystals via electrochemical method.

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