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One-pot growth of Cu_2O concave octahedron microcrystal in alkaline solution

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ABSTRACT

Cu_2O concave octahedron microcrystals with edge lengths of 5–10 μm were synthesized by reducing Cu^{2+} with D-glucose in alkaline solution at 50 °C. The growth process of Cu_2O was studied by field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM). The results indicated that Cu_2O concave octahedrons were formed by shape evolution of smaller regular octahedron as the edge lengths and concavity increased with time. It is also found that the reaction temperature has significant effect on the formation of Cu_2O concave octahedrons. The formation of the concave octahedrons were explained to be due to selectively dissolution of {1 1 1} facets and preferential growth of {1 0 0} facets of the octahedron crystal.

1. Introduction

The chemical synthesis of inorganic materials with unusual and novel morphologies [1] has gained considerable interest since their size and morphology have strong effects on their properties [2,3]. To date, many efforts have been devoted to the synthesis of inorganic crystals with different morphologies. However, the preparation of crystals with complex geometries is still a great challenge.

Cuprous oxide (Cu_2O), a p-type semiconductor with a direct band gap of about 2.17 eV, has potential applications in solar energy conversion [4], electronics [5], magnetic storage [6], catalysis [7], lithium ion batteries [8], and gas sensors [9].

In the past decade, several researchers have reported on shape-controlled synthesis of Cu_2O micro-nanocrystals such as wires [5,10] cubes [10–12], spheres [13,14], flowers [15]. Few reports were focused on Cu_2O crystal with complex geometrical structures [16], which are mostly synthesized by electrochemical deposition [17,18] or hydrothermal reaction [19]. Electrochemical reaction requires specific equipment and complicated procedure which is inconvenient. And hydrothermal reaction was not ideal in regards to repeatability and volume of production. Recently Liu et al. [20] has synthesized different complex shapes of Cu_2O via γ-irradiation. However it remains a challenge to synthesize Cu_2O crystal with complex shapes in a facile way.

In this paper, we synthesized Cu_2O concave octahedron in solution phase at low temperatures. The synthesis is facile and can be well repeated in high yield. The Cu_2O concave octahedron may have potential application as a gas sensor since the certain facets appeared on the surface of the crystal may have different reaction behaviors with certain gases. In addition it can be used as a catalyst to produce novel morphologies of catalysate such as carbon fibers since the morphology of the catalysate strongly depends on the morphology of the catalyst [21].

2. Experiments

All chemicals were analytical pure and were used without further purification. The synthesis procedures of Cu_2O concave octahedron were as follows: 0.057 g $CuCl_2{\cdot}2H_2O$ were dissolved in 50 mL of 3 M NaOH solution at ultrasonic bath to give a transparent blue $Cu(OH)_4^{2-}$ solution. Then 1.093 g of cetyltrimethyl ammonium bromide (CTAB) was added to the solution and magnetically stirred for 30 min to obtain a homogeneous solution. Afterwards 0.079 g D-glucose was added and the solution were magnetically stirred for another 10 min. And no color change was observed, indicating the reduction reaction had not occurred. After that the solution was transferred into 50 °C water bath and kept for a series of time intervals (10, 30 and 60 min). The color of the solution underwent a series changes form blue to light blue, colorless, yellow and finally orange indicating the Cu^{2+} were gradually reduced into Cu^+. The precipitations obtained after reaction in the above intervals at 50 °C were all brick red. The precipitations were separated by centrifugation and washed with distilled water and absolute ethanol several times and dried at vacuum at 40 °C for 5 h. Afterwards the products were collected and kept for further characterization.

The phase structure of the as-prepared products was characterized by X-ray powder diffraction (XRD) using a D/max-2500 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). The morphology and microstructure of the products were characterized using a JEOL

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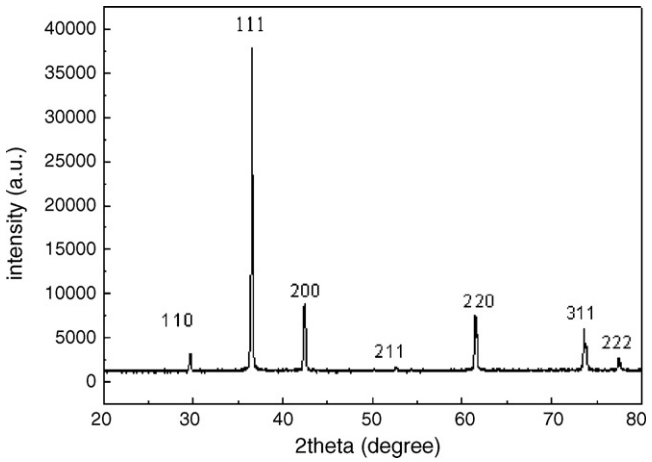

Fig. 1. XRD patterns of the Cu_2O concave octahedron microcrystal synthesized by 50 °C heating for 60 min.

JSM-6700F field-emission scanning electron microscopy (FESEM) operated at 5.0 kV and a JEM-2000EX transmission electron microscope (TEM) operated with an acceleration voltage of 160 kV.

3. Result and discussion

3.1. The phase structure of the products

The phase structure of the as-synthesized products was determined from the XRD patterns shown in Fig. 1. All the recorded peaks can be indexed into the cubic symmetry of Cu_2O (JCPDS05-0667) with lattice constant $a = 4.269$ Å. No impurity peaks are observed indicating that the products are phase-pure Cu_2O.

3.2. Morphology study of the Cu_2O concave octahedron growth process

The morphology of the products at various growth intervals (10, 30, 60 min) were studied by FESEM and TEM to get a better understand of the formation process of the Cu_2O concave octahedron. Fig. 2 shows the morphology of the products synthesized at 50 °C for 10 min. Octahedrons with edge lengths of 1–5 μm were obtained. It is notable to observe the shallow indentions in the center of the surfaces while the edges of these octahedrons with indentions were still straight at this time.

As is shown in Fig. 3a, a large quantity of concave octahedron with edge lengths of 5–7 μm were obtained at 50 °C reaction for 30 min. It is also found that the concavity of these concave octahedrons increases with the increase of edge length. Meanwhile among the concave octahedrons exists smaller concave crystals with the shape of regular octahedron with edge lengths of 1–5 μm. Fig. 3b shows a higher magnification of the concave octahedron which has eight sunken faces. It is observed that every surface has an obvious dropwell in the center (seen the circled parts in Fig. 3b) and the concave octahedrons are both centrosymmetric and axisymmetric. TEM image of a concave octahedron with (1 1 0) facet perpendicular to the electron beam is a rhombus with an internal angle equals to 60° (Fig. 3c); A dodecagon evolved from edge incurvature of a hexagon is observed in Fig. 3d (the TEM image of a concave octahedron with (1 1 1) facet perpendicular to the electron beam). Six sharp angles are observed in the dodecagon corresponding to the six apexes of the concave octahedron. TEM image of a concave octahedron with (1 0 0) facet perpendicular to the electron beam exhibits a square with four slightly incurvated edges (Fig. 3e). The corresponding diffraction patterns of the Cu_2O concave octahedron with the incident electron beam along [1 1 1] direction (Fig. 3f) indicated that the Cu_2O concave octahedron was single crystal structure.

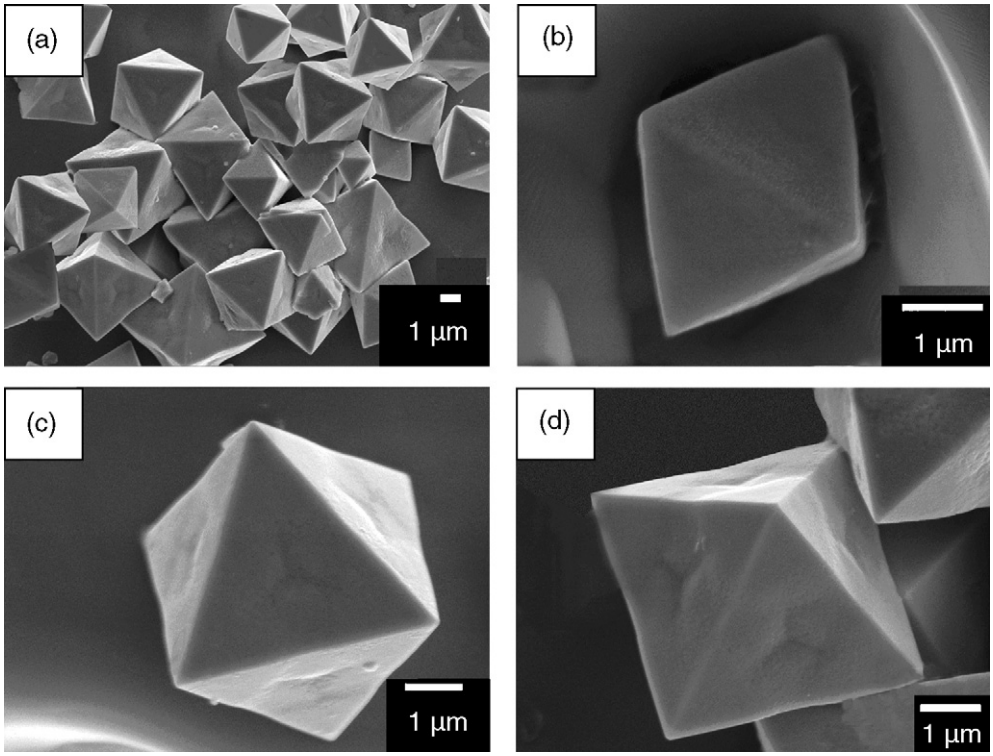

Fig. 2. Low magnification (a) FESEM images of the products synthesized at 50 °C for 10 min; high magnification FESEM images of Cu_2O octahedron synthesized at 50 °C for 10 min with (1 1 0) facet (b), (1 1 1) facet (c), (1 0 0) facet (d) parallel to the substrate.