Synthesis of Uniformly Sized Cu_2O Crystals With Star-Like and Flower-Like Morphologies

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Abstract: Uniformly sized single-crystalline Cu_2O crystals with star-like and flower-like morphologies have been successfully prepared via the reaction of d-glucose, copper (II) chloride and sodium hydroxide in aqueous solution, this synthesis was intended to found new morphology for solar cell, semiconductor materials and other application in chemical synthesis and electronic sensor. The products were characterized by X-ray powder diffraction (XRD) to measure the purity of the synthesis results, this purity was confirmed using electron diffraction (ED) pattern along the 111 axis as comparator test, to find the deepness and detail characteristic of both results, transmission electron microscopy (TEM) was employed.
Keywords: Cu_2O; Crystal growth; Morphology

1. Introduction

Cuprous oxide (Cu_2O) and related materials have attracted much current interest. It is a p-type semiconductor with a direct band gap of about 2 eV, which make it a promising material for the conversion of solar energy into electric energy[1,2)]. The capability and characteristics of cuprous oxide, therefore, have potential application in energy cultivation and storage in aerospace application, especially for operational satellite power source. Cu/Cu_2O layered nanostructured materials prepared by electrodeposition have interesting optoelectronic properties[3,4,5)]. Another exciting development is that Cu_2O was reported to act as a stable photo catalyst for the photochemical decomposition of water into O_2 and H_2 under visible light irradiation[6,7)]. Cu_2O submicrospheres can be used as the negative electrode material for lithium ion batteries[8)]. Snoke[9)] reported that excitons can propagate coherently through single crystalline Cu_2O. It is possible to convert photons into excitons, which can be used to produce light for microscopes and are used by plants to collect sunlight for photosynthesis.

2. Methodology

Many efforts have been devoted to the synthesis of Cu_2O thin films and Cu_2O-polymer composite films[1,2,10)]. Recently, preparation of Cu_2O nanowires[11-14)], nanoparticles[15)] and cubes have been reported1[6,17)]. Chen et al.[18)] reported the growth of hex-podlike Cu_2O whisker under hydrothermal conditions. Chang and Zeng[19)] reported the synthesis of multi-pod frameworks of Cu_2O microcrystals in $C_2H_5OH–H_2O$ solvents at 150–220 ^oC. Wu et al.[20)] reported stellar Cu_2O crystals synthesized under microwave irradiation in the presence of surfactant p-octyl polyethylene glycol phenylether. In this paper, we report on the preparation of single-crystalline Cu_2O crystals with star-like and flower-like morphologies via a simple solution method by reaction of d-glucose and $CuCl_2$ under alkaline conditions without any template or surfactant.

3. Experiments

All of the chemicals were analytical grade and used as purchased without further purification. Copper chloride, d-glucose and sodium hydroxide were purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation. Sample 1 was prepared by following process: 0.05 g d-glucose was dissolved in 50 mL 0.01 M $CuCl_2$ aqueous solution, and 5 mL 0.1 M NaOH aqueous solution was added under magnetic stirring. The solution was heated to 95 ^oC by oil bath. Then, 10 mL 0.1 M NaOH aqueous solution was added dropwise and kept at 95 ^oC for 5 min. After the mixture was cooled to room temperature, the product was separated by centrifugation and washed with deionized water three times and dried at 60 ^oC in vacuum. Sample 2 was synthesized as follows: 0.05 g d-glucose was

dissolved in 50 mL 0.01 M CuCl2 aqueous solution under magnetic stirring. The solution was heated to 70 °C by oil bath. Then, 15 mL 0.1 M NaOH aqueous solution was rapidly added. The solution was heated until it turned to yellow completely. The products were separated by centrifugation, washed with deionized water three times and dried at 60 °C in vacuum. XRD patterns were carried out on a Rigaku D/max 2550 V X-ray diffractometer with Cu K_α radiation. TEM images were obtained on a Hitachi H-800 transmission electron microscope.

4. Results and Discussion

Fig. 4.1 shows XRD patterns of samples 1 and 2. Each XRD pattern can be indexed to a single phase of crystalline Cu_2O with the cubic structure (JCPDS No.78-2076). No other phase was observed in XRD patterns. The synthesis of Cu_2O can be simplified as following reaction:

$$Cu^{2+} + \quad C_5H_{11}O_5\text{-}CHO \rightarrow Cu_2O + C_5H_{11}O_5COOH$$

The morphology and microstructure of the products were investigated by TEM and ED. Fig. 4.2 shows TEM micrographs of sample 1, from which one can see uniformly sized Cu_2O crystals with star-like morphology. The longest diagonal diameter of Cu_2O crystals was ≈0.8 μm. The inset of Fig. 4.2.b shows the ED pattern of a single star-like Cu_2O crystal. The ED pattern was obtained by focusing the incident electron beam along the [111] zone axis. It can be indexed to the cubic Cu_2O, consistent with the XRD result. ED patterns on different individual crystals were essentially the same, indicating that the star-like Cu_2O crystals are single-crystalline in structure.
Fig. 4.3 shows TEM micrographs of sample 2, from which one can see flower-like Cu_2O crystals with longest diagonal diameter of ≈1.8 μm. Fig. 3b shows a single flower-like Cu_2O crystal and the corresponding ED pattern obtained by focusing the incident electron beam along the [111] zone axis. It can be indexed to the cubic Cu_2O, consistent with the XRD result. ED patterns on different individual crystals were essentially the same, indicating that flower-like Cu_2O crystals were single-crystalline in structure.

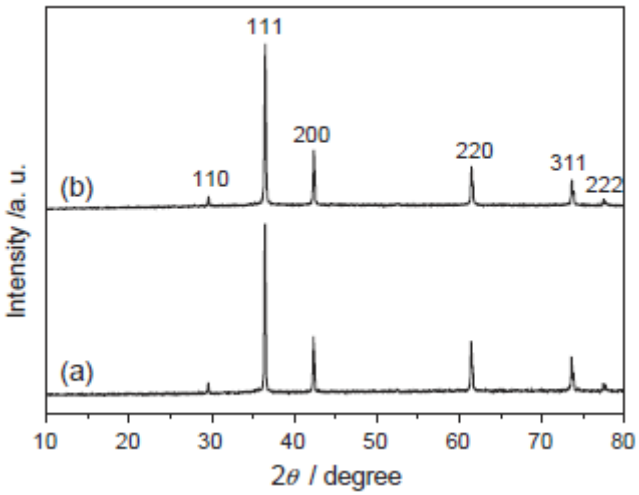

Fig. 4.1. XRD patterns of two samples: (a) sample 1, (b) sample 2.

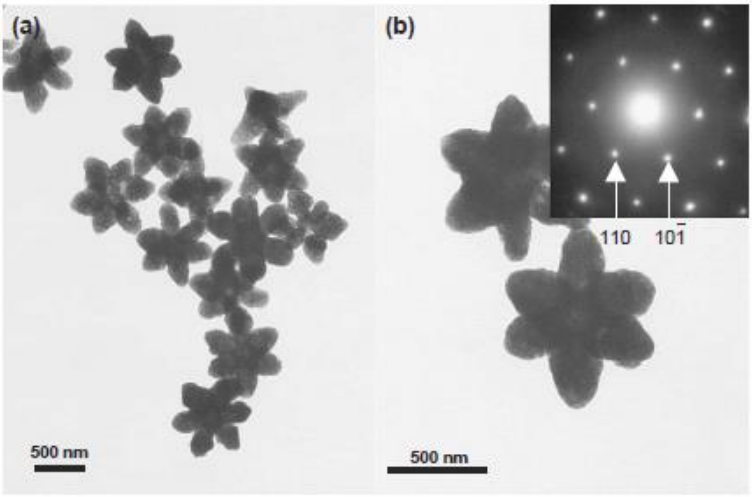

Fig. 4.2. TEM micrographs of sample 1. The inset of panel (b) shows ED pattern of a single star-like crystal obtained by focusing the incident electron beam along the [111] zone axis.

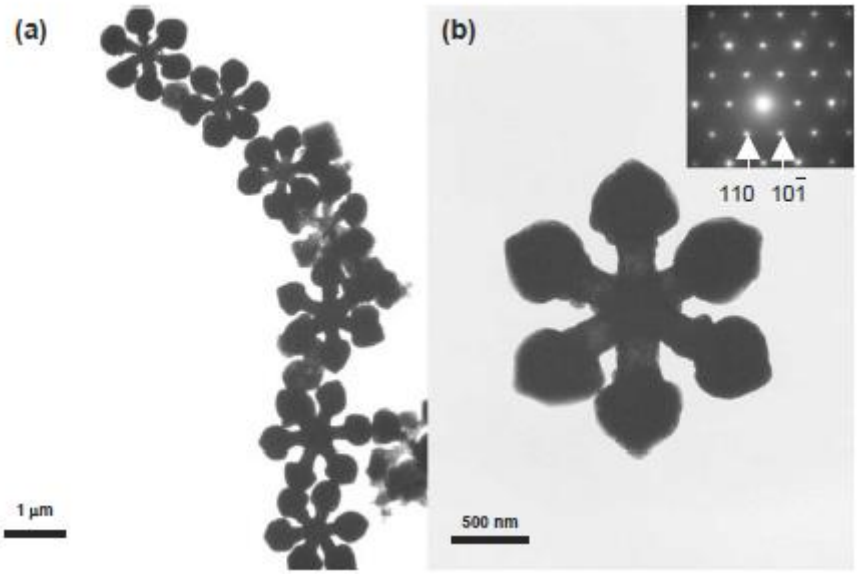

Fig. 4.3. TEM micrographs and ED pattern of sample 2. ED pattern of an individual Cu_2O crystal (inset of panel (b)) was obtained by focusing the incident electron beam along the [111] zone axis.

5. Conclusion

In summary, powders of single-crystalline Cu_2O crystals with star-like and flower-like morphologies have been successfully synthesized by a simple solution method via the reaction of d-glucose, copper (II) chloride and sodium hydroxide in aqueous solution. Cu_2O crystals with a specific morphology prepared have uniform size. This method is simple, low-cost and suitable for large-scale production of powders of Cu_2O crystals with a specific morphology.

6. Suggestion

It is still unclear that the different morphology results was produced by the same reaction in the different temperature condition, the elucidation of crystal growth mechanisms is suggested to uncover this phenomena.

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