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High pressure hydrothermal synthesis of cuprous oxide microstructures of novel morphologies

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ABSTRACT

In this paper, "fiber-like" Cu_2O bundles and "tower-like" Cu_2O were successfully synthesized from a $Cu(CH_3COO)_2$ precursor under hydrothermal conditions related with pressure, examined by means of scanning electron microscopy, and X-ray diffraction. The effects of precursor concentration, pressure on the evolution of Cu_2O synthesis and morphology were investigated. The pressure were found to play a key role in the formation of "fiber-like" bundles, and "tower-like" Cu_2O.

A possible mechanism was used to explain the formation of the resultant Cu_2O. As claimed by the results, pressure could offering a very powerful way for the synthesis of novel morphologies. The present study attempts to shed some light on the roles that pressure play in influencing the microstructures of the cuprous oxide particles.

1. Introduction

In recent years, there has been increasing interest in the synthesis of inorganic micro- or nanocrystals for their widely ranged properties and potential applications [1,2]. The synthesis of inorganic micro- or nanocrystals with controlled size and shape is of special interest.

As a p-type semiconductor (direct band gap ~2.17 eV) with unique optical and magnetic properties, Cu_2O is a promising material with potential applications in solar energy conversion, magnetic storage device, catalysis micro-/nanoelectronics, and biosensing [3,4]. Moreover, Cu_2O crystals have been at the center of research on Bose–Einstein condensation of excitons [5]. Many recent efforts have been devoted to the shape-controlled synthesis of Cu_2O micro- and nanocrystals. Systematic manipulation of the morphology and architecture of Cu_2O microcrystals has been achieved using solution routes and electro deposition methods [6,7]. Meanwhile, various approaches have been reported for fabricating Cu_2O nanocrystals with varied morphologies, such as cubes, pyramids, wires, boxes, cages, and octahedral [8–14]. Crystals are often in combination, usually consisting of the simple forms such as cube, octahedron and rhombic dodecahedron [15]. Sometimes fibers, known as chalcotrichite, greatly elongated along the {0 0 1} directions, have also been observed [16].

On the other hand, mixtures of various surfactants, including alkyl amines, alkyl acids, alkylphosphonic acid and trioctyl phosphine oxide are frequently used as capping agents to tailor the crystal shape in high-temperature solution phase synthesis. Here, we report a novel route for the synthesis of "fiber-like" Cu_2O bundle and "tower-like" Cu_2O microcrystals in aqueous solution using $Cu(CH_3COO)_2{\cdot}H_2O$ as the precursor only and assisted with certain pressure. In the present paper, a newly discovered Cu_2O morphology "fiber-like" Cu_2O bundles and "tower-like" Cu_2O microcrystals were reported. The effects of precursor concentration reaction pressure on the evolution of Cu_2O synthesis and the morphology are discussed.

At the same time, the optimal synthesis parameters were given, which was found to play a key role in determining the morphologies and crystallinity of Cu_2O.

2. Experimental procedure

2.1. Preparation

$Cu(CH_3COO)_2{\cdot}H_2O$ was used as precursor for the preparation of Cu_2O with varied morphologies. In a typical synthesis, $Cu(CH_3COO)_2{\cdot}H_2O$ powder was dissolved in distilled water to prepare the precursor solution with a concentration range of 0.1–0.2 M under magnetic stirring. Next 20 mL precursor solution was tightly sealed in an autoclave, which was heated to and maintained at 200 °C for 12 h with a certain constant pressure.

After cooling down to room temperature, the precipitates on the bottom of autoclaves were collected and washed several times with deionized water and absolute ethanol. Then dried in a vacuum oven at 60 °C for 8 h. Fig. 1. is the schematic drawing of our purpose-designed equipment in the experiment.

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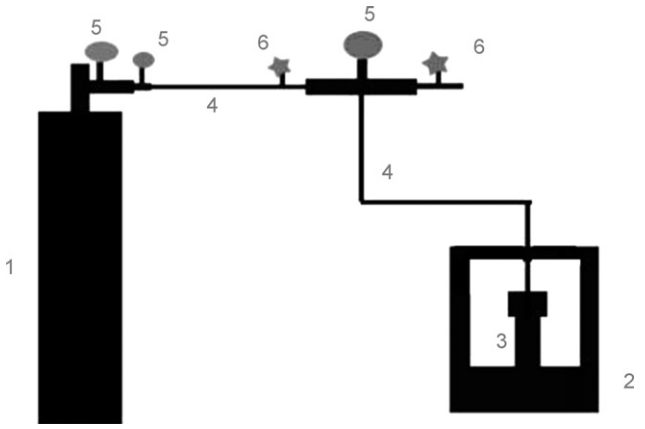

Fig. 1. Schematic drawing of the purpose-designed equipment in our experiment: (1) Argon tank. (2) Furnace. (3) Stainless steel autoclave. (4) Copper tube. (5) Pressure gauge. (6) Valve. (Part 1: It is the pressure source, which provides pressure to the stainless steel autoclave. Part 2: The furnace can provide and keep a certain temperature to the autoclave. Part 3: The stainless steel autoclave is the reaction container, which make sure the precursor solution tightly sealed. Part 4: This part is used as a tube, which can transport the argon to the autoclave. Part 5: The significance of this part is to indicate the magnitude of the pressure. Part 6: It is the leak valve that can make the argon leak out from the system after the reaction).

2.2. Characterization

The as-prepared Cu_2O nanostructures were characterized by powder X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM).

The powder X-ray diffraction (XRD) patterns were recorded with a X-ray diffractometer (Rigaku D/max-rA) using Cu Kα radiation (λ = 1.5418 Å). Data were collected in steps of 0.05° with a count time of 1 s, at an operating potential of 40 kV and a current of 100 mA. Respectively, the morphologies of Cu_2O were examined by a SEM (JEOL JXA-8200) operated at 15.0 kV and the transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were performed on a Hitachi Model H-800 transmission electron microscope. The ultraviolet and visible light (UV–vis) absorption spectra were recorded on an UV 2401 PC spectrophotometer.

3. Results and discussion

The experimental conditions, imposed pressures, product phases, and the Cu_2O morphologies are summarized in Table 1. It shows that the outside pressure used is the critical factor for the synthesis of novel morphologies. Cu_2O was easily prepared under hydrothermal conditions assisted with a certain pressure, when $Cu(CH_3COO)_2$ was used alone as the precursor.

Self-hydrolyzation-reduction reactions in the autoclave possibly take place under hydrothermal conditions with elevated pressure at 200 °C. The one possible fundamental reaction involved can be simplified as follows:

$$Cu(CH_3COO)_2 + 2H_2O = Cu(OH)_2(s) + 2CH_3COOH \quad (1)$$

$$Cu(OH)_2(s) = CuO(s) + H_2O \quad (2)$$

$$8CuO(s) + CH_3COOH = 4Cu_2O(s) + 2H_2O + 2CO_2 \quad (3)$$

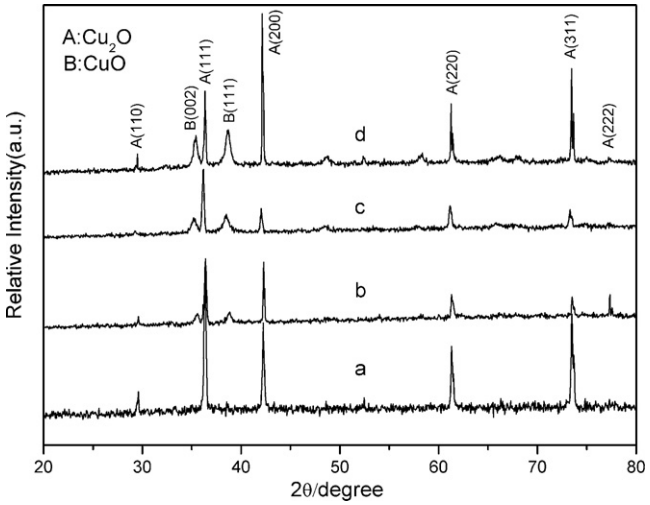

Fig. 2. Effect of reaction pressure on the synthesis of Cu_2O crystals obtained in a 0.1 M $Cu(CH_3COO)_2{\cdot}H_2O$ aqueous solution at 200 °C under the pressure of (a) 0.1 MPa, (b) 1 MPa, (c) 2 MPa, and (d) 3 MPa.

It is well-known that the $Cu(OH)_2$ powder was easily dehydrated in water when the temperature was higher than 70 °C [17]. Therefore, CuO powder in reaction (2) could be obtained during further hydrothermal treatment. The formation of solid-phase CuO in reaction (2) was confirmed during the hydrothermal treatment process. The corresponding XRD results indicated that the presence of two CuO and Cu_2O phases in the prepared powders under certain pressure (see below in Fig. 2). Moreover, the intensities of the diffraction peaks of CuO and Cu_2O changed significantly (Fig. 2). With a further increase in the reaction pressure to 3.0 MPa, XRD pattern (Fig. 2d) shows that the intensities of diffraction peaks of CuO increase.

The CH_3COOH act not only as an acid, but also a reducing agent. Because there was no special reducing agent added in our reaction solution, it could be deduced that the CH3COOH generated from the hydrolysis of $Cu(CH_3COO)_2$ had an obvious reducing action for the phase transformation of CuO to Cu_2O. Similar to previous reports [18] that formic acid (HCOOH) acted as a weak reducing agent for the phase transformation of CuO to Cu_2O, Viswanathiah et al. [19] found that the formic acid (HCOOH) was an effective reducing agent for the hydrothermal synthesis of magnetite (Fe_2O_3). Kutty et al. [20] also found a similar result when they synthesized metal powders from the corresponding metal hydroxides. Therefore, CH_3COOH or CH_3COO^- must be reducing agents in the system studied.

In this study, CH_3COOH in reaction (3) resulted in the formation of Cu_2O precipitates.

It is necessary to enhance reducing action of CH_3COOH in order to prepare Cu_2O. The following two aspects should be taken into consideration. One is the precursor concentration. From Table 1, we found that the final product was a mixture of CuO and Cu_2O When the precursor concentration was 0.1 M. In this case, the reducing

Table 1
Summary of the reaction conditions and products formed.

Samples	Given pressure (MPa)	Product formed	Morphologies
0.1 M (12 h)	0.1	Cu_2O	Hollowmicrospheres(main) + Polyhedron
0.1 M (12 h)	1.0	CuO + Cu_2O	Hollowmicrospheres(main) + Polyhedron
0.1 M (12 h)	2.0	CuO + Cu_2O	Polyhedron + Cube
0.1 M (12 h)	3.0	CuO + Cu_2O	Polyhedron + "Fiber-like "Bundl + "Tower-like"rod
0.2 M (12 h)	0.1	Cu_2O	Polyhedron + Cube
0.2 M (12 h)	1.0	Cu_2O	Polyhedron
0.2 M (12 h)	2.0	CuO + Cu_2O	"Tower-like"rod + Hollowmicrospheres + Polyhedron
0.2 M (12 h)	3.0	CuO + Cu_2O	"Tower-like"rod(main) + Hollowmicrospheres + Bundle + Polyhedron