Journal of Materials Science and Chemical Engineering, 2020, 8, 46-52
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

pH Controlled Synthesis of Tetragonal Cu_2O Particles

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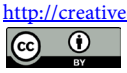
How to cite this paper: Su, Q.L., Zhang, L., Liang, Y., Liu, Y., Liu, P. and Zhang, J.D. (2020) pH Controlled Synthesis of Tetragonal Cu_2O Particles. *Journal of Materials Science and Chemical Engineering*, **8**, 46-52.
https://doi.org/10.4236/msce.2020.88005

Received: July 28, 2020
Accepted: August 24, 2020
Published: August 27, 2020



Abstract

Cuprous oxide (Cu_2O) in high yield with controlled shape and size was synthesized via a solution-phase route by reducing cupric sulphate with D-glucose. The solution pH shows strong effects on the size and morphology of the products. The products were characterized by X-ray power diffraction (XRD) and Scanning electron microscope (SEM). The infrared emissivity of Cu_2O was tested by Far infrared emissivity measurer S302. The possible crystal growth processes have been proposed.

Keywords

Chemical Synthesis, PH Value, Cuprous Oxide, Morphology

1. Introduction

Semiconductor transition-metal oxides have been of much interest because of their unique properties and widely application. In particular, as a p-type semiconductor with a band gap of 2.17 ev, cuprous oxide (Cu_2O) is a promising material with potential applications in solar energy conversion, catalysis, and sensing [1] [2] [3], biosensor and magnetic storage devices [4] [5] [6] [7], and photocatalyst for degradation of organic pollutants and decomposition of water into O_2 and H_2 under visible light [8] [9].

Many efforts have been devoted to the synthesis of Cu_2O micro- and nanocrystals with various shapes [10]-[15] by different methods. Yongming Sui and his co-workers report a facile solution-phase route for the mass synthesis of Cu_2O crystals with different morphologies in the presence of poly (vinyl pyrrolidone) (PVP) [16]. Zhao *et al.* have prepared Cu_2O of various shapes by the reduction of copper nitrate with formic acid in hydrothermal condition [17]. Xu *et al.* have prepared a wide range of novel cuprous oxide microcrystals through an

ethylene-diaminetetraacetic acid tetrasodium salt dihydrate (EDTA) reduction route by employing the EDTA molecule as both chelating reagent and reductant [18]. Wang *et al.* prepared Cu_2O cubes by reduction of copper sulphate with D-glucose in assist of sodium citrate and anhydrous sodium carbonate [19].

The methods mentioned in the literature require high temperature, special conditions, or tedious procedures. In this paper, we report a facile solution-phase method to synthesize uniform Tetragonal Cu_2O microcrystals with controlled monodispersity by PH value at low temperature. In particular, the synthesis does not require the assistance of a surfactant.

2. Experimental Sections

1) Materials

Cupric sulphate (90%) was obtained from Bodi chemical plant corporation, Tianjin. Sodium hydroxide was bought from Damao Chemical Reagent, Tianjin. D-glucose was received from Tianda Chemical Reagent, Tianjin. The above all reagents were analytically grade commercial materials. The powder was taken for characterization.

2) Preparations of Cu_2

In a typical procedure, an aqueous solution prepared by mixing 100 mL deionized water with 5 g copper sulfate, and stirred the mixture with a magnetic blender for about 20 min under room temperature. In the same way, 50 ml sodium hydroxide aqueous solution in certain concentration can be got. A dark blue precipitate was produced when the all above solutions were mixed in a four neck round-bottomed glass flask. The mixed solution was kept in a water bath at 80˚C. Then 50 mL of (3.6 g) glucose solution was slowly dropped into it with constant stirring for 30 min. Next, the dark blue precipitate gradually turned dark red, and then was allowed to cool to room temperature naturally. Afterward, the obtained particles were cleaned by deionized water, and dried at 60˚C for 20 h in a vacuum oven. Finally, the powder was taken for characterization.

3) Characterization:

The crystal phase of as-prepared products was characterized by an X-ray diffractometer (XRD) using Cu Kαradiation (λ = 1.54060 Å) in the range (20˚ - 80˚).

The morphology of the powders was investigated by field-emission scanning eletron microscopy (SEM) using S1500.

The infrared emissivity of the powders was tested by the Far infrared emissivity measurer S302, the test temperature is 34˚C.

3. Results and Discussions

The composition and purity of the products were first examined by XRD, and the results reveal that pure Cu_2O is obtained in all samples. **Figure 1(a)** displays representative XRD patterns of the Tetragonal (as show in **Figure 1(b)** SEM) as well as the standard card (JCPDS No. 65-3288), indicating that all the diffraction

peaks are readily indexed to Tetragonal Cu_2O with no impurity, when the PH value of the solution is 12 or more. **Figure 1(a)** also indicates that the peak value of crystal plane (111) is relatively sharp and high. The strong and sharp peaks indicate that the (111) crystal surface grows optimally and the obtained Cu_2O crystals are highly crystalline. **Figure 1(b)** shows the particles size of products is uniform and have perfect monodispersity.

As showing in **Figure 2** monodisperse of particles for various quality fractions of sodium hydroxide in the precursor solution. SEM observations indicate that, When the PH value is 9 and other experimental conditions are kept the same, **Figure 2(a)** shows obvious agglomeration in particles. When the PH value is 10 and 11, loose Cu_2O particles were obtained, as shown in **Figure 2(b)**, **Figure 2(c)**. Fully developed Cu_2O Tetragonal is observed when the sodium hydroxide concentration is increased to 0.6 M. The as-obtained Cu_2O crystals possess perfect monodispersity and Tetragonal morphology, as shown in **Figure 2(d)**. So, increasing the reactant sodium hydroxide concentration enhances the reaction and increases the diffusion rate, or nucleation and growth rates. Hence, stable and dispersible particles are more easily formed. These results show that the initial solution PH value plays a key role in the formation of Cu_2O crystals.

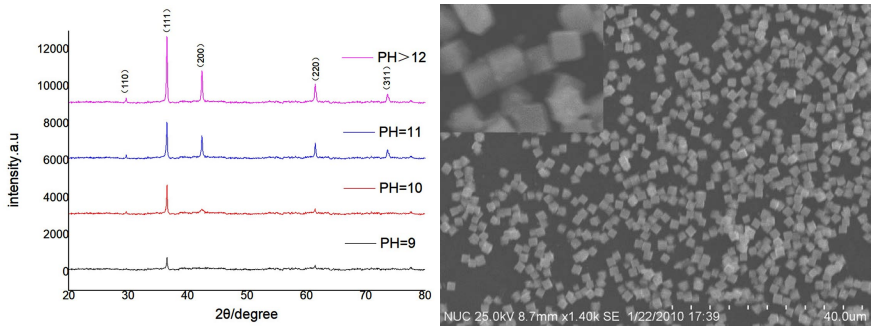
The stabilities and monodispersities of Cu_2O are controlled by dispersants as a rule. the following growth mechanism of controlling dispersity with reactant sodium hydroxide can be proposed based upon our experimental results. When the appropriate contents of D-glucose, NaOH, and $CuSO_4$ are used at relatively high reaction temperatures, Cu_2O crystals can be synthesized from the following reactions.

$$Cu^{2+} + 2OH^- \rightarrow Cu\left(OH\right)_2 \downarrow$$

$$Cu\left(OH\right)_2 + 2OH^- \rightarrow \left[Cu\left(OH\right)_4\right]^{2-}$$

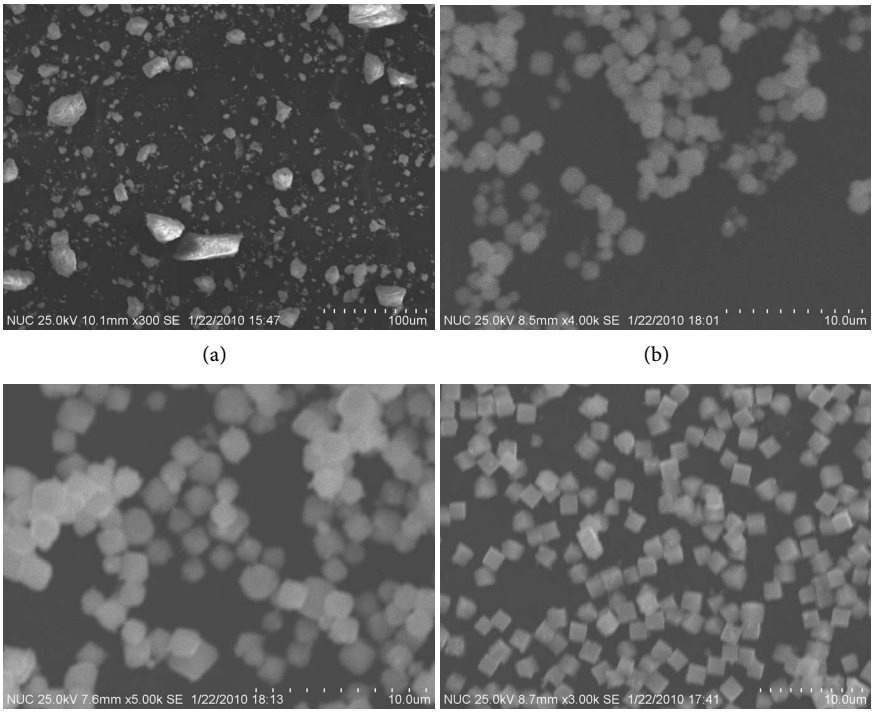
$$2\left[Cu\left(OH\right)_4\right]^{2-} + C_5H_{11}O_5 - CHO \rightarrow Cu_2O \downarrow + C_5H_{11}O_5 - COOH + 4OH^- + 2H_2O$$

Sun *et al.* [20] have been demonstrated that Cu(II) can coordinate with excess OH^- ions to generate $[Cu(OH)_4]^{2-}$ complexes. When the concentration of OH^- ions was higher enough, $[Cu(OH)_4]^{2-}$ complexes would be formed. Therefore, it is proposed that the formation of Cu_2O with different dispersities may be related to the characteristics of the complex precursors synthesized in different reaction conditions (Equations (1)-(3)). The varied $[Cu(OH)_4]^{2-}$ complexes formed in different conditions can modify the reduction process (Equation (3)), which might affect the competition between kinetics and thermodynamics during the reduction of precursors, nucleation, and growth of Cu_2O crystals. The similar rule has been reported [21], During the growth of Cu_2O crystal, the concentration of Cu^{2+} remains unchanged, the concentration of OH^- controls the PH value of the solution, and the concentration ratio of Cu^{2+} and OH^- affect the production rate of crystal orientation, that is to say, the concentration and activity of OH^- in the solution will affect the growth and crystal orientation of Cu_2O.



(a) (b)

Figure 1. XRD patterns of the Cu_2O Tetragonal.

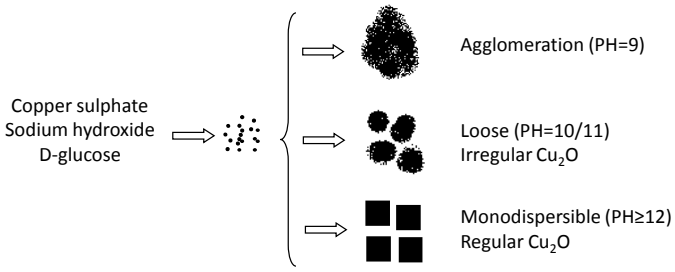


(a) (b)

(c) (d)

Figure 2. SEM images corresponding the various PH value ((a) = 9, (b) = 10, (c) = 11, (d) > 12).

Schematic Illustration of the Process of Cu_2O Crystals as a Function of the PH value



The infrared emissivity of Tetragonal Cu_2O.

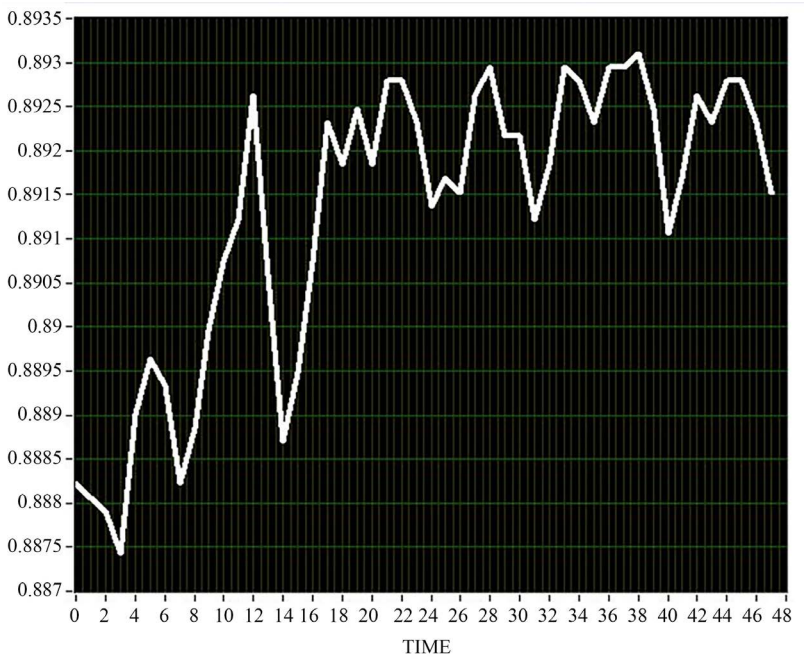


Figure 3. Infrared emissivity of tetragonal Cu_2O particles.

The infrared emissivity test results of Tetragonal Cu_2O particles indicates that the infrared emissivity value is between 0.887 to 0.893, the average value is 0.89 as show in Figure 3, as the test temperature is 34˚C.

4. Conclusion

In summary, we have prepared uniform tetragonal Cu_2O in high yield by the reduction of cupric sulphate without surfactants. The concentration of source materials shows strong effects on the phase purity and morphology development of the products. The results indicate that the stable and dispersible Cu_2O particles could be prepared by adjusting the concentration of Sodium hydroxide concentration. When the PH value is 9, the obtained Cu_2O particles hold agglomeration. When the PH value is 10 and 11 leads to loose irregular Cu_2O. Fully developed monodisperse Cu_2O uniform tetragonal is observed when the sodium hydroxide concentration is increasing, the PH value is 12 or more. This method could be extended to prepare other similar inorganic oxides.

Acknowledgements

We thank Dr. Ling Zhang for helpful discussion. This work is supported by the Major special project of Shanxi Province Science and Technology (Grant No. 20181101020).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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