Ultrasonic Fabrication of Monodispersed Nano-Copper Oxide

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Abstract

A green environmental friendly process for preparing monodispersed cuprous oxide nanoparticles is reported. In this process, cuprous oxide is prepared using Cu(OH)$_4^{2-}$ as precursor and glucose as reducing agency in the presence of dispersant under ultrasonic radiation. Spherical, welldispersed Cu$_2$O nanoparticles were obtained with the average size of 200 nm or 1.5 μm, respectively, with or without cetyltrimethylammonium bromide as surfactants. In the process, the sonochemical method comparing to the other methods which have been used, is very fast and it does not need high temperature during the reaction. It is noticeable that the reducing agency is natural product and the reaction is nearly completed with less than 0.5 mg/L Cu$^{2+}$ left in the waste water under ultrasonic radiation, up to the discharge standard of wastewater.

Keyword: Green process, Cuprous oxide, Ultrasonic radiation, Nanomaterials, Semiconductors.

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1. Introduction

Cu$_2$O is an important $p$-type semiconductor with a band gap of 2.0-2.2 eV and it has received considerable attentions recently due to its potential applications in fields such as solar cells, pigments and catalysts [1-8]. Micro- and nanoscale Cu$_2$O is expected to possess improved properties compared to its bulk one. To obtain microor nanometer sized crystals of Cu$_2$O, various methods have been employed including electrochemistry [9,10], polyol process11, surfactant-assisted [12], reduction routes [13], solutionphase synthesis [14,15], hydrothermal and solvothermal methods [16], etc. In all the methods, a simple strategy for low-cost green synthesis of Cu$_2$O at mild conditions is highly desired. The sonochemical reaction technique is a new strategy to synthesize nanomaterials [17]. It has already been successfully used to prepare nanoscale molybdenum sulfide, molybdenum oxide and zinc oxide [18], while there are few papers reported to synthesize Cu$_2$O. In this paper, a simple low-cost and environmental friendly approach for the preparation of micro- and nanometer Cu$_2$O at room temperature under ultrasonic radiation is reported.

2. Materials and Methods

Copper sulfate, D-glucose, cetyltrimethylammonium bromide and sodium hydroxide were purchased from China Medicine (Group) Shanghai Chemical Reagent Corporation. All of the chemicals were analytical grade and used as purchased without further purification. Sample 1 was prepared by the following process: 150 mL of 0.1 M NaOH aqueous solution was added in 150 mL of 0.1 M CuSO$_4$ aqueous solution.

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under mechanical stirring and 40 KHz 150 W ultrasonic radiation and then 100 mL of 1 M aqueous D-glucose was added in the mixture at room temperature. The ultrasonic time is 1 h. The brick red product was separated by centrifugation and washed with deionized water three times and then dried at 40 ºC in vacuum. The synthesis of sample 2 and sample 3 was the same as sample 1 and the different is that before addition of aqueous glucose, 0.58 or 1.17 g (2 critical micelle concentration (CMC) or 4 CMC) cetyltrimethylammonium bromide (CTAB) was added, respectively. Power X-ray diffraction data was collected on a X-ray diffractometer (Bruker D8-Advance, Germany) equipped with a back monochromator operating at 40 kV and a copper cathode as the X-ray source (λ = 0.154 nm). XRD patterns were collected from 30 to 80 (2q) with a scanning step of 0.01. The size and morphology of the Cu nanoparticles were examined by using field-emission scanning electron microscope (Hitachi S4800). The left concentration of Cu²⁺ in the waste water was measured by inductive coupled plasma emission spectrometer (Thermo ICAP6300).

3. Results and Discussion
The overall sonochemical reactions of the system are believed to occur [19,20]:

\[
\text{Cu}^{2+} + 4\text{OH}^- \rightarrow \text{Cu(OH)}_4^{2-} \overset{\text{ultrasonic radiation}}{\longrightarrow} \text{Cu}_2\text{O} + \text{C}_2\text{H}_5\text{O}_2\text{COOH}
\]

In the process, Cu(OH)₄²⁻ ions are reduced first to Cu⁺, followed by three possible reactions in competition for the Cu⁺ ions:

\[
\begin{align*}
\text{Cu}^+ & \longrightarrow \text{Cu}^0 \\
2\text{Cu}^+ & \longrightarrow \text{Cu}^0 + \text{Cu}^{2+} \\
2\text{Cu}^+ + 2\text{OH}^- & \longrightarrow 2\text{CuOH} \rightarrow \text{Cu}_2\text{O}
\end{align*}
\]

If there are enough OH⁻ ions, the reaction tendency expressed in eqn. 3 becomes dominant. So in present experiments, excessive NaOH was added to provide sufficient OH⁻ ions. In the process, glucose plays two roles. It acts not only as reducing agency, but also as protective agency. When aqueous glucose solution was added, the light blue colloidal Cu(OH)₄²⁻ turned into cyan, indicating the formation of coordination complex. The hydroxyl ligands of glucose coordinate with Cu²⁺, forming a cage. The spatial steric hindrance contributes to form smaller particle. The XRD patterns of samples prepared by different procedures are shown in figure 2. All diffraction peaks can be indexed to the cubic phase of Cu₂O (JCPDS 05- 0667) and no peaks of impurity are observed in the XRD patterns. In the absence of CTAB, the diffraction peaks of sample 1 are acute, showing that ultrasonic radiation contributes to the crystallization of Cu₂O. With the presence of 2 CMC and 4 CMC CTAB, the diffraction peaks broaden, which indicates the smaller size of the products. Several reports are available in literature on the effect of ultrasound on chemical reactions and have suggested some proposed explanations [21], such as the "hot spot explanation", the "electrical explanation" and a proposed model based on plasma discharge.

![Figure 1. Schematic figure of the role of glucose](image-url)
Figure 2. XRD patterns of the Cu$_2$O prepared under ultrasonic radiation: (a) in the absence of CTAB; (b) in the presence of 2 CMC CTAB; (b) in the presence of 4 CMC CTAB.

Figure 3. SEM images of the Cu$_2$O prepared under ultrasonic radiation: (a) in the absence of CTAB; (b) in the presence of 2 CMC CTAB; (c) in the presence of 4 CMC CTAB.
Most theories imply that the harsh conditions generated upon bubble collapse lead to the formation of free radical, mechanical shocks, high shear gradients and very rapid and efficient mixing in multiphase systems. When an ultrasonic wave passes through a liquid medium, a large number of microbubbles form, grow and collapse in the very short time of a few microseconds, which is called ultrasonic cavitation. Sonochemical theory calculations and the corresponding experiments suggest that ultrasonic cavitation can generate local temperature as high as 5000 K and local pressures as high as 100 MPa, with heating and cooling rates greater than 10^9 K/s, which is an extreme environment [22]. This considerably changes the physicochemical parameters of the processed medium [23-25].

In the process for preparing the Cu_2O nanoparticles, the sonochemical method comparing to the other methods which have been used, is very fast and it does not need high temperature during the reaction. At room temperature the colloidal complex Cu^{2+}-glucose reaction system turn into khaki in 20 min under ultrasonic radiation. With further ultrasonic radiation, the system will become brick red in 10 min and the reaction can complete in 1 h. It is believed that acoustic cavitation provides higher energy for the reduction reaction and it contributes to the rapid nucleation and crystallization of Cu_2O particles. Figure 3 shows SEM images of Cu_2O prepared under ultrasonic radiation. In the absence of CTAB, monodisperse Cu_2O particles with diameter 1.0-1.5 μm were obtained. The surfactant CTAB has a drastic effect on the size in this work. When the concentration of CTAB is 2 CMC, the sizes of nanoparticles are 100-400 nm, but distribute broad. It is found that higher concentration of CTAB contributes to get smaller size distribution of Cu_2O. When the concentration is 4 CMC, the sizes of Cu_2O nanoparticles distributes narrowly with the diameters of about 200 nm. The present preparation process has several advantages. Firstly, the reducing agency is natural product and surfactant CTAB is widely used innoxious scour, so the process is environmental friendly. Secondly, the reaction is nearly completely with less than 0.5 mg/L Cu^{2+} left in the wastewater under ultrasonic vibration, enhancing the raw materials. Furthermore, if hydrochloric acid is adopted to neutralize the wastewater, the wastewater is up to the discharge standard without complicated disposal.

4. Conclusion
In summary, the present synthesis technique of Cu_2O under ultrasonic radiation was simple and environmental friendly compared to the previous methods, using natural product glucose as reducing agent at room temperature. In the process, ultrasonic acoustic cavitation provides higher energy for the reduction reaction and it contributes to the rapid nucleation and crystallization of Cu_2O particles. Glucose acts not only as reducing agent, but also as protective agent. The reaction is nearly completely with less than 0.5 mg/L Cu^{2+} left in the waste water under ultrasonic vibration, up to the discharge standard of wastewater.

References