

Preparation of Monodispersed Cuprous Oxide Nanoparticles Under Ultrasonic Radiation

WEI YU, HUAQING XIE, LIFEI CHEN and YANG LI*

*School of Urban Development and Environmental Engineering,
Shanghai Second Polytechnic University, Shanghai, P.R. China*

Fax: (86)(21)50216301; Tel: (86)(21)50216301

E-mail: yuwei@eed.sspu.cn

A green environmental friendly process for preparing monodispersed cuprous oxide nanoparticles is reported. In this process, cuprous oxide is prepared using $\text{Cu}(\text{OH})_2$ as precursor and glucose as reducing agency in the presence of dispersant under ultrasonic radiation. Spherical, well-dispersed Cu_2O 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.

Key Words: Green process, Cuprous oxide, Ultrasonic radiation, Nanomaterials, Semiconductors.

INTRODUCTION

Cu_2O 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 catalysts¹⁻⁸. Micro- and nanoscale Cu_2O is expected to possess improved properties compared to its bulk one. To obtain micro- or nanometer sized crystals of Cu_2O , various methods have been employed including electrochemistry^{9,10}, polyol process¹¹, surfactant-assisted¹², reduction routes¹³, solution-phase synthesis^{14,15}, hydrothermal and solvothermal methods¹⁶, *etc.* In all the methods, a simple strategy for low-cost green synthesis of Cu_2O at mild conditions is highly desired.

The sonochemical reaction technique is a new strategy to synthesize nanomaterials¹⁷. It has already been successfully used to prepare nanoscale molybdenum sulfide, molybdenum oxide and zinc oxide¹⁸, while there are few papers reported to synthesize Cu_2O . In this paper, a simple low-cost and environmental friendly approach for the preparation of micro- and nanometer Cu_2O at room temperature under ultrasonic radiation is reported.

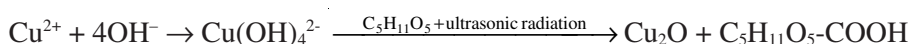
EXPERIMENTAL

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 CuSO₄ aqueous solution 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 °C 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.

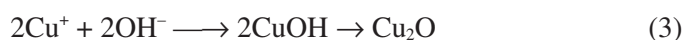
Power X-ray diffraction data was collected on a X-ray diffractometer (Bruker D8-Advance, Germany) equipped with a back monochromator operating at 40 kV and a copper cathode as the X-ray source ($\lambda = 0.154$ nm). XRD patterns were recorded from 30 to 80 (2θ) with a scanning step of 0.01. The size 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).

RESULTS AND DISCUSSION

The overall sonochemical reactions of the system are believed to occur^{19,20}:



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



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 Fig. 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

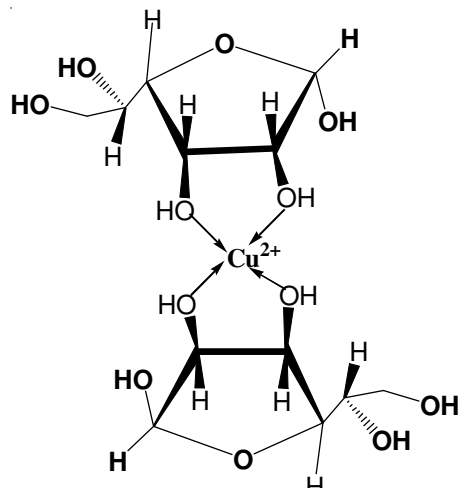


Fig. 1. Schematic figure of the role of glucose

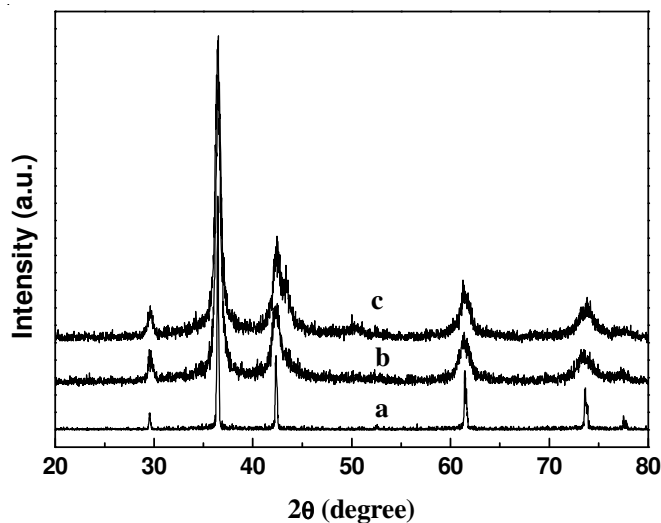


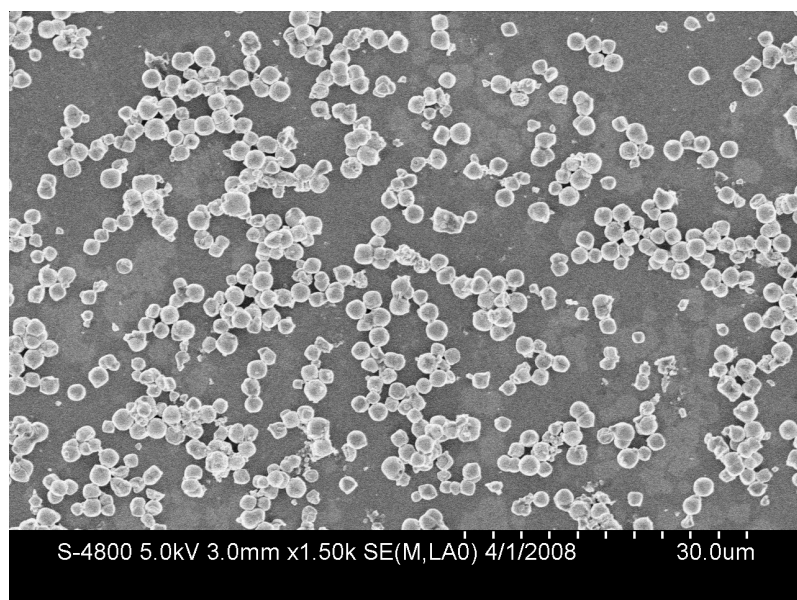
Fig. 2. XRD patterns of the Cu_2O prepared under ultrasonic radiation: (a) in the absence of CTAB; (b) in the presence of 2 CMC CTAB; (c) in the presence of 4 CMC CTAB

CTAB, the diffraction peaks of sample 1 are acute, showing that ultrasonic radiation contributes to the crystallization of Cu_2O . With the presence of 2 CMC and 4 CMC CTAB, the diffraction peaks broaden, which indicates the smaller size of the products.

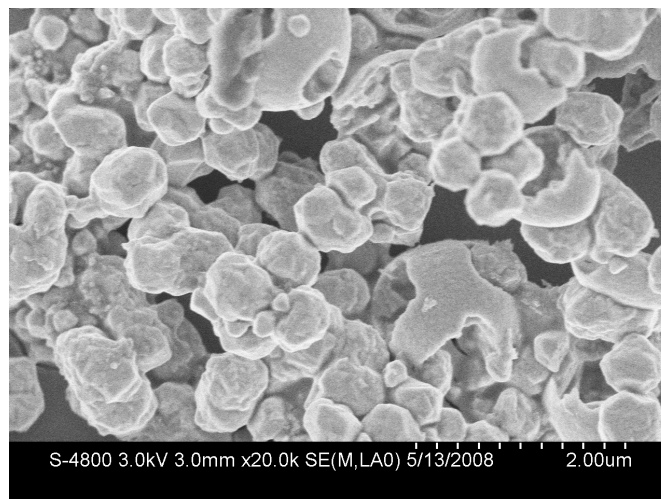
Several reports are available in literature on the effect of ultrasound on chemical reactions and have suggested some proposed explanations²¹, such as the "hot spot explanation", the "electrical explanation" and a proposed model based on plasma discharge. Most theories imply that the harsh conditions 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 109 K/s, which is an extreme environment²². This considerably changes the physico-chemical parameters of the processed medium²³⁻²⁵. In the process for preparing the Cu₂O 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 Cu²⁺-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 Cu₂O particles.

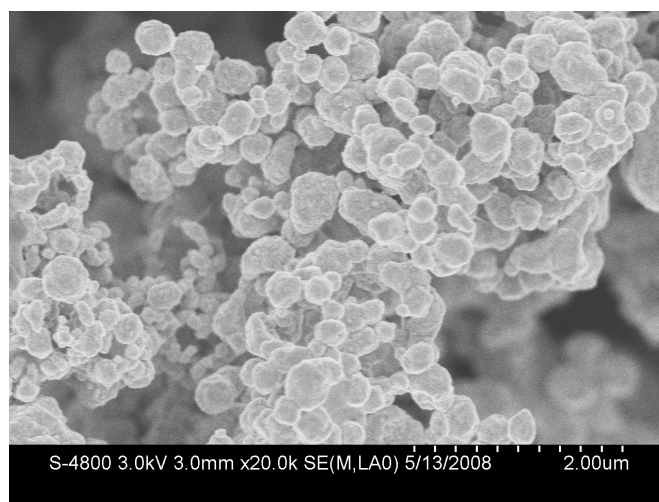
Fig. 3 shows SEM images of Cu₂O prepared under ultrasonic radiation. In the absence of CTAB, monodisperse Cu₂O particles with diameter 1.0-1.5 μm were obtained. The surfactant CTAB has a drastic effect on the size in this work. When the concentration of CTAB is 2 CMC, the sizes of nanoparticles are 100-400 nm, but distribute broad. It is found that higher concentration of CTAB contributes to get smaller size distribution of Cu₂O. When the concentration is 4 CMC, the sizes of Cu₂O nanoparticles distributes narrowly with the diameters of about 200 nm.



(a)



(b)



(c)

Fig. 3. SEM images of the Cu_2O 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.

The present preparation process has several advantages. Firstly, the reducing agent 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 waste water 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.

Conclusion

In summary, the present synthesis technique of Cu₂O 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 Cu₂O 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 Cu²⁺ left in the wastewater under ultrasonic radiation, up to the discharge standard of wastewater.

ACKNOWLEDGEMENTS

The work was supported by Shanghai Educational Development Foundation and Shanghai Municipal Education Commission (08CG64) and the Program for Professor of Special Appointment (Eastern Scholar) at Shanghai Institutions of Higher Learning.

REFERENCES

1. D. Snoke, *Science*, **298**, 1368 (2002).
2. T. Takata, S.A. Ikeda, T.S. Hara, J.N. Kondo and K. Domen, *Appl. Catal. A Gen.*, **200**, 255 (2000).
3. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont and J.M. Taracón, *Nature*, **407**, 496 (2000).
4. N. Liu, D. Wu, H.X. Wu, C. Liu and F. Luo, *Mater. Chem. Phys.*, **108**, 511 (2008).
5. H.M. Yang, J. Ouyang and A.D. Tang, *Mater. Res. Bull.*, **41**, 1310 (2006).
6. R.N. Briskman, *Sol. Energy. Mater. Sol. Cells*, **27**, 361 (1992).
7. W.X. Zhang, C.Y. Luan, Z.H. Yang, X.T. Liu, D.P. Zhang and S.H. Yang, *Appl. Surface Sci.*, **253**, 6063 (2007).
8. J.J. Zhang, J.F. Liu and Y.D. Li, *Chem. Mater.*, **18**, 867 (2006).
9. H.G. Zhang, Q.S. Zhu, Y. Wang, C.Y. Zhang and L. Tao, *Mater. Lett.*, **61**, 23 (2007).
10. R. Liu, E.A. Kulp and J.A. Switzer, *Chem. Mater.*, **17**, 725 (2005).
11. J.W. Zhu, Y.P. Wang, X. Wang, Y.J. Yang and L.D. Lu, *Powder Technol.*, **179**, 26 (2007).
12. L. Gou and C.J. Murphy, *Nano Lett.*, **3**, 231 (2002).
13. J. Pike, S.W. Chan, F. Zhang, X.Q. Wang and J. Hanson, *Appl. Catal. A Gen.*, **303**, 273 (2006).
14. Z. Wang, X. Chen, J. Liu, M. Mo, L. Yang and F.Y. Qian, *Solid State Commun.*, **130**, 585 (2004).
15. F. Luo, D. Wu, L. Gao, S. Lian, E. Wang, Z. Kang, Y. Lan and F.L. Xu, *J. Cryst. Growth*, **285**, 534 (2005).
16. M.Z. Wei, N. Lun, X.C. Ma, S.L. Wen, *Mater. Lett.*, **61**, 2147 (2007).
17. P.T. Zhao, G. Chen, Y. Hu, X.L. He, K. Wu, Y. Cheng and K.X. Huang, *J. Cryst. Growth*, **303**, 632 (2007).
18. Y.L. Wei and P.C. Chang, *J. Phys. Chem. Solids*, **69**, 688 (2008).
19. S.J. Shen, X.T. Chen, Z.L. Xue, L.H. Li and X.Z. You, *J. Cryst. Growth*, **246**, 169 (2002).
20. Y.J. Dong, Y.D. Li, C. Wang, A.L. Cui and Z.X. Deng, *J. Colloid Interface Sci.*, **243**, 85 (2001).
21. G.Q. Zhang, H.P. Wu, M.Y. Ge, Q.K. Jiang, L.Y. Chen and J.M. Yao, *Mater. Lett.*, **61**, 2204 (2007).
22. T.J. Mason, *Advances in Sonochemistry*, Vol. 1, London: JAI Press (1990).
23. W.B. McNamara, Y.T. Didenko and K.S. Suslick, *Nature*, **401**, 772 (1999).
24. V. Misik, N. Miyoshi and P. Riesz, *J. Phys. Chem.*, **99**, 3605 (1995).
25. M.A. Alavi and A. Morsali, *Ultrasonics Sonochem.*, **15**, 833 (2008).