

Polyol Process to Large-scale Synthesis of Cu_2O with Disk-like Structure

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Abstract: A new form of Cu_2O , disk-like structure with 60 nm in thickness and 2 μm in diameter, has been successfully synthesized in bulk quantities by polyol process in the presence of PVP K-30.

Keyword: Polyol process, Cu_2O , disk-like structure.

As one of the most important p-type semiconductors, Cu_2O is the subject of much current interest^{1,2}. Cu_2O has a direct band gap of 2.2 eV, which makes it a promising material for the conversion of solar energy into electrical or chemical energy³. It was reported that excitons could propagate coherently through single crystalline Cu_2O . Thus, it might be possible to convert photons into excitons, which could travel through small apertures or small dimension waveguides with little loss to scattering and diffraction, at the end of the path the excitons could be converted back into photons⁴. Cu_2O could also be used as a stable catalyst for water splitting under visible light irradiation although its exact role is unclear⁵. Recently, it has been found that Cu_2O microspheres can be used as the negative electrode material for lithium ion batteries⁶. Moreover, Cu_2O as well as CuO is ideal compounds to study the influence of electron-correlation effects on the electronic structure of transition metal compounds in general and the high T_c superconductors in particular.

Currently, shape control has raised significant concern in the fabrication of semiconductor nanocrystals^{7,8}, metal nanocrystals⁹, and other inorganic materials such as BaCrO_4 and BaSO_4 ^{10,11}, which may add alternative variables in tailoring the properties of nanomaterials. Although several examples have been demonstrated, shape control has been more difficult to achieve and turns out to be a great challenge field for the future. Many differently shaped Cu_2O nanostructures have been synthesized using various approaches such as electrodeposition^{12,13}, thermal relaxation¹⁴, sonochemical method¹⁵, vacuum evaporation¹⁶, solvothermal method¹⁷, and liquid phase reduction of metal salts^{18,19}. In contrast to nanorods or nanowires, nanodisks are less well-known. Although a few strategies do exist for synthesizing Ag disks^{20,21} and Co disks²², there is great interest in developing new methods for making nanoparticles with control over shape.

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Herein, we report a new synthesis of disk-shaped Cu₂O nano- particles using polyol process, developed by Fievet *et al.* for generating colloidal particles of metals²³.

In this process, the polyol (ethylene glycol) could serve as both solvent and reducing reagent.

A typical procedure is as follows. 20 mL of anhydrous ethylene glycol was added to a round-bottom flask equipped with a condenser. The ethylene glycol was heated to reflux (~197 °C) for 1 h. In a separate beaker, 0.200 g of polyvinyl pyrrolidone (PVP K-30), 0.134 g of anhydrous copper chloride, and 0.160 g of sodium hydroxide were dissolved in 5 mL of ethylene glycol by sonication, then this transparent dark-blue solution was rapidly transferred (using a pipette) into the refluxing ethylene glycol under continuous stirring. After 5 minutes, the solution was quenched with 200 mL of ice-cold ethylene glycol. Finally, the resultant sample was centrifuged, and washed with distilled water and absolute alcohol, dried in air before further characterization.

The crystal structure and composition of the obtained sample were analyzed by X-ray diffraction (XRD). **Figure 1** shows an XRD pattern of the Cu₂O nanodisk. All reflectance peaks are indexed to a cubic Cu₂O phase (JCPDS 5-667). The peaks at 2θ values of 29.5°, 36.4°, 42.3°, 61.6°, 73.8° and 77.6°, to within experimental error, correspond to 110, 111, 200, 220, 311, 222 lattice planes of standard crystalline Cu₂O, respectively.

The purity was further analyzed by X-ray photoelectron spectroscopy (XPS). The XPS for the as-prepared sample were typical for Cu₂O reported by other researchers¹⁹. The morphology and size were characterized by a scanning electron microscopy. **Figure 2A** and **B** shows that the Cu₂O nanoparticles are disk-like shapes with *ca.* 60 nm in thickness and *ca.* 2 μm in diameter.

The general mechanism of the Cu₂O nanodisks formation can be represented by the following reactions:

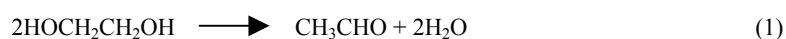
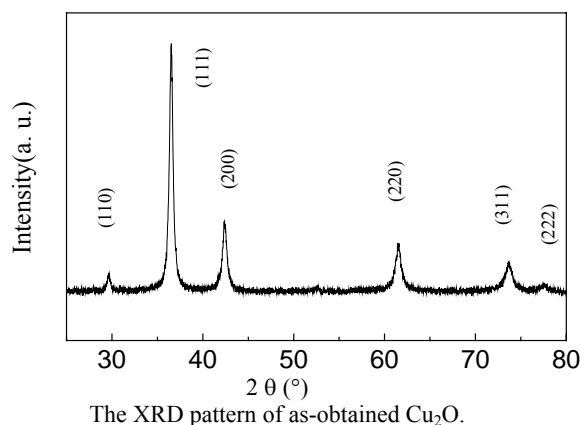
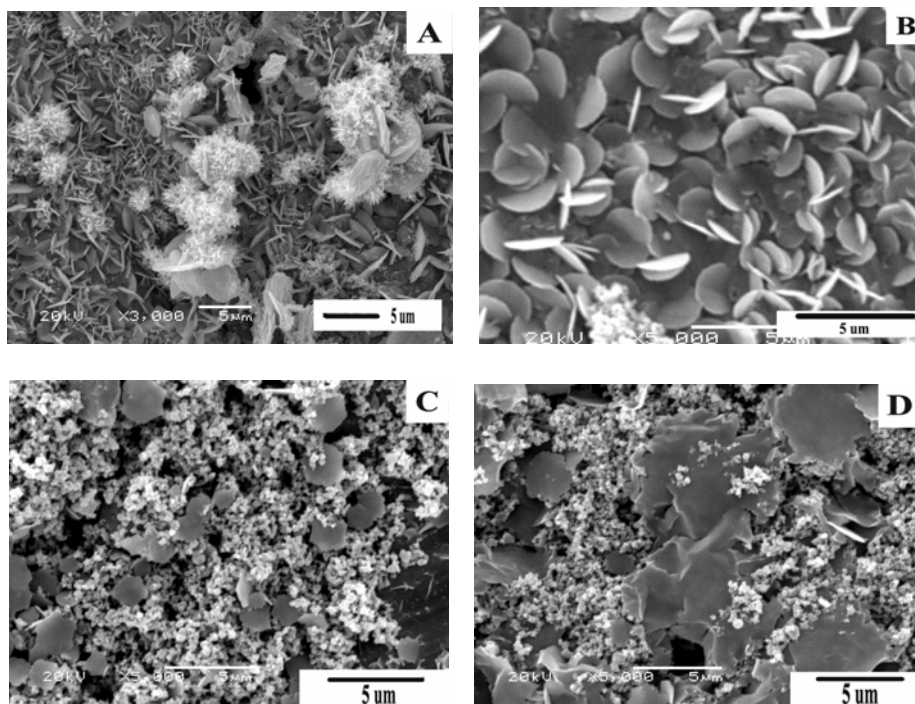


Figure 1



The XRD pattern of as-obtained Cu₂O.

Figure 2



SEM images of (A) low and (B) high magnification of disk-like Cu₂O; (C) molar ratio of CuCl₂ to NaOH is 3; (D) without adding PVP.

It was found that the molar ratio of copper chloride to sodium hydroxide played a critical role in the formation of Cu₂O nanodisks. When molar ratio is less than 2, only spherical nanocrystals were formed; when molar ratio is more than 2 and less than 4, the sample has spherical as well as disk-like shape (shown in **Figure 2C**). The Cu₂O prepared without adding PVP K-30 displaying large disk-like shape (shown in **Figure 2D**), indicated that PVP K-30 acted as not only controlling the growth process but also preventing Cu₂O nanodisks from increase in size. As claimed by Stupp and Braun²⁴, organic molecules could alter inorganic microstructures, offering a very powerful tool for the design of novel materials.

In summary, for the first time, Cu₂O nanodisks have been generated in large quantities by a polyol process approach. These particles have thicknesses of 60 nm and diameters around 2 μm. XRD, XPS and SEM investigations on these nanodisks have been carried out.

Acknowledgments

This work was supported by the National Natural Science Foundation of China and Natural Science Foundation of Qinghai Province. We would like thank Prof. ZhongXin Zhang, JianCao Wang of Qinghai Normal University for helpful discussion.

References

1. M. Y. Shen, T. Yokouchi, S. Koyama, T. Goto, *Phys. Rev. B*, **1997**, *56*, 13066.
2. W. Shi, K. Lim, X. Liu, *J. Appl. Phys.*, **1997**, *81*, 2822.
3. R. N. Briskman, *Sol. Energy Mater. Sol. Cells*, **1992**, *27*, 361.
4. D. Snoke, *Science*, **1996**, *273*, 135.
5. P. E. de Jongh, D. Vanmaekelbergh, J. J. Kelly, *Chem. Commun.*, **1999**, 1069.
6. P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J. M. Taraccon, *Nature*, **2000**, *407*, 496.
7. X. G. Peng, L. Manna, W. D. Yang, *et al.*, *Nature*, **2000**, *404*, 59.
8. Z. A. Peng, X. G. Peng, *J. Am. Chem. Soc.*, **2001**, *123*, 1389.
9. J. Tanori, T. Gulik, M.-P. Pileni, *Langmuir*, **1997**, *13*, 632.
10. D. D. Archibald, S. Mann, *Nature*, **1993**, *364*, 430.
11. L. M. Qi, H. Colfen, M. Antonietti, *Angew. Chem. Int. Ed.*, **2000**, *39*, 604.
12. J. K. Barton, A. A. Vertegel, E. W. Bohannon, J. A. Switzer, *Chem. Mater.*, **2001**, *13*, 952.
13. L. M. Huang, H. T. Wang, Z. B. Wang, *et al.*, *Chem. Mater.*, **2002**, *14*, 876.
14. S. Deki, K. Akamatsu, T. Yano, A. Kajinami, *J. Mater. Chem.*, **1998**, *8*, 1865.
15. R. V. Kumar, Y. Mastai, Y. Diamant, *et al.*, *J. Mater. Chem.*, **2001**, *11*, 1209.
16. H. Yanagimoto, K. Akamatsu, K. Gotoh, *et al.*, *J. Mater. Chem.*, **2001**, *11*, 2387.
17. S. J. Chen, X. T. Chen, L. H. Lia, *et al.*, *J. Cryst. Growth*, **2002**, *246*, 169.
18. Y. J. Dong, Y. D. Li, A. L. Cui, *et al.*, *J. Colloid Interface Sci.*, **2000**, *243*, 85.
19. W. Z. Wang, G. H. Wang, X. S. Wang, *et al.*, *Adv. Mater.*, **2002**, *14*, 67.
20. S. H. Chen, Z. Y. Fan, D. L. Carroll, *J. Phys. Chem. B*, **2002**, *106*, 10779.
21. M. Maillard, S. Giorgio, M. P. Pileni, *Adv. Mater.*, **2002**, *14*, 1084.
22. V. F. Puentes, D. Zanchet, C. K. Erdonmez, *et al.*, *J. Am. Chem. Soc.*, **2002**, *124*, 12877.
23. P. Toneguzzo, G. Viau, O. Acher, *et al.*, *Adv. Mater.*, **1998**, *10*, 1032.
24. S. I. Stupp, P. V. Braun, *Science*, **1997**, *277*, 1242.

Received 26 December, 2003