



Facile synthesis of copper (I) oxide and copper nanoparticles using different solvents under microwave irradiation

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Abstract

The present paper reports the effect of solvents, on the synthesis of both copper (I) oxide and copper nanoparticles in large scale using oxalic acid as reducing agent under microwave irradiation. A weighed ratio of copper acetate and oxalic acid were subjected to microwave irradiation in the presence of diethylene glycol and ethanol, followed by calcinations at 500°C. The solvents seem to play an important role during the synthesis. It was interesting to observe that in case of diethylene glycol, spherical aggregates of copper oxide (I) nanoparticles were formed as cotton ball shaped whereas, in case of ethanol, spherical shaped copper nanoparticles were formed as confirmed by scanning electron microscopy (SEM). The nanoparticles so formed were also characterised and confirmed more precisely by X-ray diffraction measurements (XRD) and Fluorescence microscopy.

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Introduction

Compared with conventional materials, copper nanoparticles have some unusual properties, such as small dimensions, large specific surface area and low electric resistance. They also display quantum size effect and macroscopic quantum tunnel effect. Therefore, copper nanoparticles have been the subject of much attention in recent years, due to their potential applications in several fields¹⁻⁴. Copper nanoparticles are particularly attractive for their lower cost than others like gold and silver⁵⁻⁶. These possess various applications in printed circuit boards (PCBs) and flexible electronics^{3, 7-9}, catalysts¹⁰⁻¹¹, light emitting diodes (LED)¹² and biocompatibility¹³⁻¹⁴. However, the disadvantage is the difficulty of copper reduction in mild reaction conditions as well as the easy oxidation of copper nanoparticles in air under ambient atmosphere conditions in comparison to noble metals like gold and silver. To date, thermal reduction¹⁵, thermal decomposition^{5,16}, direct electrochemical reduction from CuO nanoparticles¹⁷, mechanochemical process¹⁸, polyol process^{7,9,17}, chemical reduction¹⁹⁻²⁰, in-situ synthesis in polymers²¹, electro-exploding wire (EEW), metal salt reduction²², microwave heating²³, radiation methods²⁴, micro emulsion techniques²⁵, laser ablation²⁶, solvothermal method²⁷, sonochemical reduction²⁸ and ion beam radiation²⁹ have all been developed to prepare copper nanoparticles.

Chemical thermal reduction is one of the most convenient method for the synthesis of metals and metal oxide nanoparticles because the synthesis process is simple and the size and shape of nanostructured copper can easily be controlled. Among various techniques developed for the synthesis of copper and copper oxide nanoparticles, microwave heating was found to be the simpler method. In order to improve the thermal reduction process to prepare copper nanoparticles with controllable size and shape, we have first carried out the synthesis of copper nanoparticles under microwave irradiation at lower energy, followed by calcination at higher temperature. The synthesis was carried out in both di-

ethylene glycol and ethanol instead of water to study the effect of solvents on the size and stability of the copper nanoparticles. It was interesting to observe that in case of diethylene glycol, spherical aggregates of copper oxide (I) nanoparticles (Cu₂O) were formed whereas in case of ethanol, spherical shaped copper nanoparticles (Cu) were formed as confirmed by X-ray diffraction measurements (XRD). In both the cases, the size of the nanoparticles were below 50 nm. The nanoparticles so formed were characterised by scanning electron microscopy (SEM) and Fluorescence microscopy.

Experimental

Materials

The chemicals used in the present work are Copper acetate, oxalic acid, di-ethylene glycol, ethanol and doubled distilled water.

Method

Copper acetate and oxalic acid were taken in diethylene glycol in 1: 1 ratio. The mixture was then vigorously stirred and sonicated for 20-30 minutes. After sonication, the solution was kept in microwave oven at 180 W. Light grey coloured precipitate was obtained within a minute. The precipitate was then centrifuged, filtered, washed and dried. The dried product was calcined at 500°C for 30 min. A brown-black coloured precipitate was observed, which was filtered, washed several times with solvent and finally dried for 3-4 hours. Similarly, when copper acetate and oxalic acid in 1: 1 ratio were taken in ethanol as solvent and then following the same procedure, light brown coloured precipitate was obtained within a minute at 180 W. The precipitate was then centrifuged, filtered, washed and dried. The dried product was calcined at 500°C for 30 min. Brownish-black coloured precipitate was observed, which was filtered, washed several times with ethanol and finally dried for 3-4 hours.

Results and Discussion

Formations of Cu_2O and Cu nanoparticles from copper acetate and oxalic acid have been reported in this work. The role of solvents on the synthesis of both types of nanoparticles has been reported under microwave irradiation at low power, followed by calcinations at higher temperatures. In case of diethylene glycol as solvent, individual spherical aggregates of Cu_2O nanoparticles were observed which varied from 2-4 micrometers (Fig. 1a, 1b). This demonstrates that the copper oxide nanostructures are composed of many interconnected sheet-like crystallites. The SEM micrographs of copper nanoparticles in ethanol have been shown in Figs 2a and 2b. Agglomerates of spherical copper nanoparticles were observed with nearly uniform size (below 50 nm).

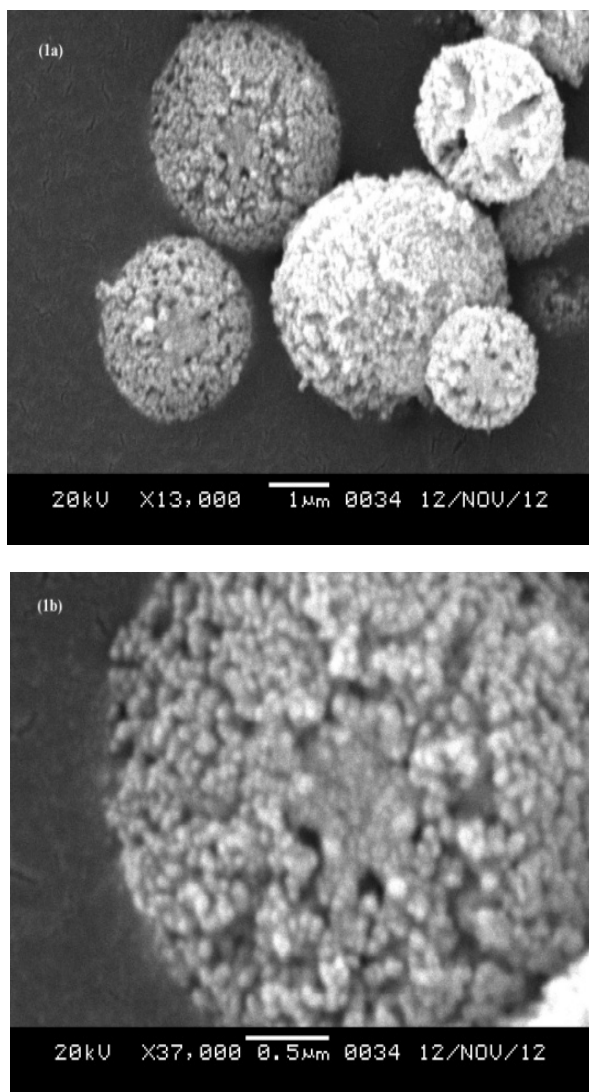


Figure 1: SEM of copper (I) oxide nanoparticles in di-ethylene glycol.

The XRD pattern of as prepared Cu_2O nanoparticles is shown in Fig. 3a. Sharp peaks of Cu_2O nanoparticles were observed at 2θ value of 36.6° and 59.8° representing (111) and (220) planes respectively. Bragg's reflections for Cu nanoparticles (Fig. 3b) were observed in XRD pattern at 2θ value of 44.2° and 51.1° representing (111) and (200) planes respectively. The XRD peaks in both figures confirm the formation of two forms of copper nanoparticles in presence of two different solvents.

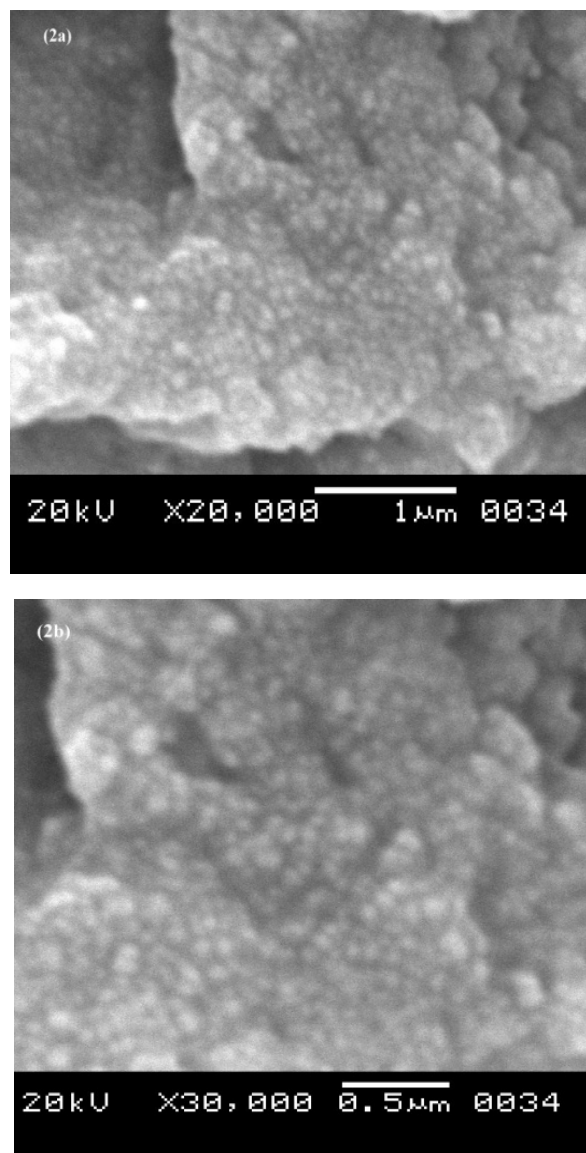
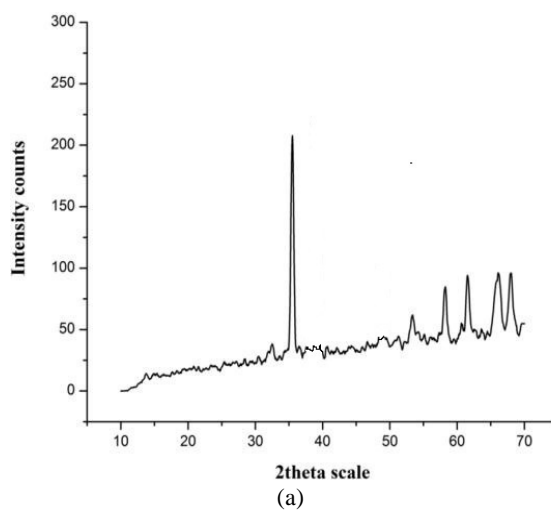


Figure 2: SEM of copper nanoparticles in ethanol.



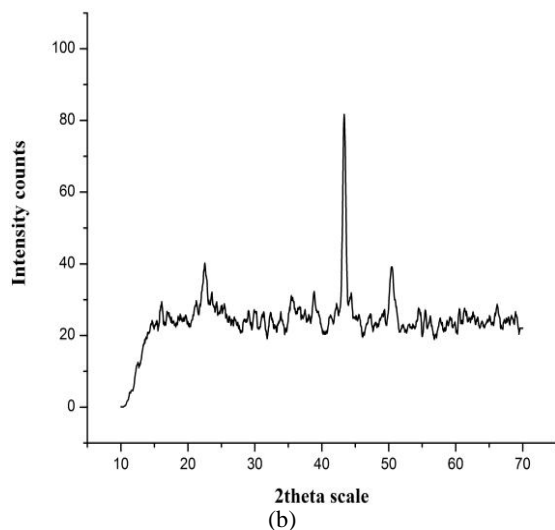
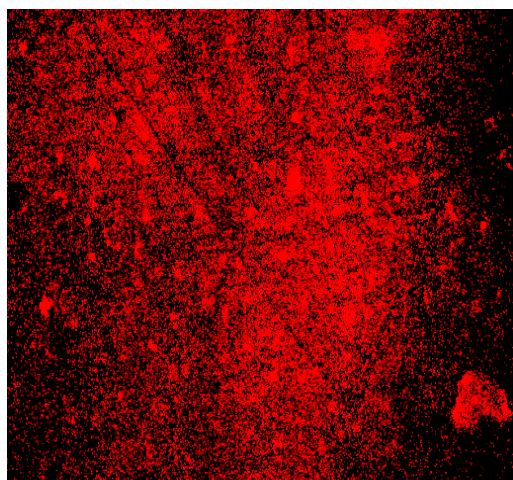
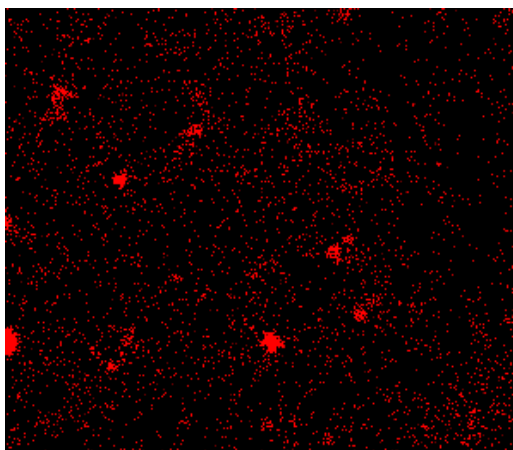


Figure 3: XRD of copper (I) oxide and copper nanoparticles in (a) di-ethylene glycol and (b) ethanol respectively

Further, both forms of copper nanoparticles were fluorescent in nature, but Cu_2O nanoparticles have been found more fluorescent properties than Cu nanoparticles as shown in Figure 4.



(a)



(b)

Figure 4: Fluorescence images of copper (I) oxide and copper nanoparticles in (a) di-ethylene glycol in (b) ethanol respectively

Conclusions

Cu_2O and Cu nanoparticles were synthesized in large scale by changing the solvents, maintaining same reaction conditions. The solvents seem to play an important role during the synthesis. The XRD patterns confirmed the formation of both type of nanoparticles. In case of diethylene glycol, spherical aggregates of Cu_2O nanoparticles were formed, whereas in case of ethanol, individual spherical shaped Cu nanoparticles were formed as confirmed by XRD. In both the cases, the sizes of the nanoparticles were below 50 nm. Thus, both forms of copper nanoparticles can be prepared by varying the solvents under green conditions.

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References

1. I. K. Shim, Y. I. Lee, K. J. Lee, J. Joung, *Mater. Chem. Phys.* 110, 2008, 316.
2. K. J. Lee, B. H. Jun, T. H. Kim, J. Joung, *Nanotechnology* 17, 2006, 2424.
3. S. K. Volkman, T. Pei, D. Redinger, S. Yin, V. Subramanian, *Mat. Res. Soc. Symp. Proc.*, 814, 2004, 17.
4. D. Kim, S. Jeong, S. Lee, B. K. Park, J. Moon, *Thin Solid Films*, 515, 2007, 7692.
5. M. S. Niasari, F. Davar, *Mater. Lett.*, 63, 2009, 441.
6. W. K. Han, J. W. Choi, G. H. Hwang, S. J. Hong, J. S. Lee, S. G. Kang, *Appl. Surface Sci.*, 252, 2006, 2832.
7. B. K. Park, D. Kim, S. Jeong, J. Moon, J. S. Kim, *Thin Solid Films* 515, 2007, 7706.
8. K. Woo, D. Kim, J. S. Kim, S. Lim, J. Moon, *Langmuir*, 25, 2009, 429.
9. S. Jang, Y. Seo, J. Choi, T. Kim, J. Cho, S. Kim, D. Kim, *Scr. Mater.* 62, 2010, 258.
10. P. Singh, A. Katyal, R. Kalra, R. Chandra, *Tetrahedron Lett.*, 49, 2008, 727.
11. M. Grouchko, A. Kamyshny, K. Ben-Ami, S. Magdassi, *J. Nanopart. Res.* 11, 2009, 713.
12. S. Chen, J. M. Sommers, *J. Phys. Chem. B*, 105, 2001, 8816.
13. A. Gu, G. Wang, X. Zhang, B. Fang, *Bull. Mater. Sci.*, 33, 2010, 17.
14. Y. Y. Liu, D. M. Liu, S. Y. Chen, T. H. Tung, T. Y. Liu, *Acta. Biomater.* 4, 2008, 2052.
15. T. H. L. Nghiem, T. H. La, X. H. Vu, V. H. Chu, T. H. Nguyen, Q. H. Le, E. Fort, Q. H. Do, H. N. Tran, *Adv. Nat. Sci.*, 2010.
16. M. S. Niasari, Z. Fereshteh, F. Davar, *Polyhedron* 28, 2009, 126.
17. Y. H. Kima, D. K. Lee, B. G. Jo, J. H. Jeong, Y. S. Kang, *Physicochem. Eng. Asp.* 364, 2006, 284.
18. S. Sheibani, A. Ataie, S. Heshmati-Manesh, *J. Alloys. Compd.*, 465, 2008, 78.
19. Park B K, Jeong S, Kima D, Moon J, Limb S and Kim J S 2007 *J. Colloid Interface Sci.* 311, 2007, 417.
20. Thi My Dung Dang¹, Thi Thu Tuyet Le¹, Eric Fribourg-Blanc and Mau Chien Dang, *Adv. Nat. Sci.: Nanosci. Nanotechnol.* 2, 2011, 7.
21. Wu C, Mosher B P and Zeng T, *Mater. Res. Soc. Symp. Proc.* 879E Z6.3.1, 2005.
22. Pulkkinen P, Shan J, Leppanen K, Kansakoshi A, Laiho A, Jarn M and Tenhu H, *Appl. Mater. Interfaces* 2, 2009, 519.
23. Cheng X, Zhang X, Yin H, Wang A and Xu Y, *Appl. Surface Sci.*, 2006, 253, 2727.
24. Siwach O P and Sen P J. *Nanopart. Res.* 10, 2008, 107.
25. Joshi SS, Patil SF, Iyer V, Mahumuni S. *Nanostruct Mater.* 10, 1998, 1135-44.
26. Pileni MP, Ninham BW, Gulik-Krzywicki T, Tanori J, Lisiecki I, Filankembo A. *Adv Mater.* 11, 1999, 1358-62.
27. Song RG, Yamaguchi M, Nishimura O, Suzuki M. *Appl Surface Science*, 2007, 253, 3093-7.
28. Xin-ling T, Ling R, Ling-na S, Wei-guo I, Min-hua C, Chang-wen H. *Chem Res Chinese U*, 22, 2006, 547-51.
29. Schwarz F, Thorwarth G and Stritzker B, *Solid State Sci.* 11, 2009, 1819.