
International Journal of Bio-Inorganic Hybrid Nanomaterials

An Efficient Green Synthesis of Copper Oxide NanoCrystalline

Mahboubeh Kargar*, Majid Ghashang, Mohammad Reza Mohammad Shafiee

Faculty of Sciences, Najafabad Branch, Islamic Azad University, Najafabad, Esfahan, Iran

Received: 25 February 2015; Accepted: 28 April 2015

ABSTRACT

In this study, a feasible green method for the synthesis of copper oxide nanocrystalline is described by using sour cherry juice which has a significant effect on crystalline size, and morphology. The benefits of the green method, not only nanometer scale are formed but also low-cost method are obtained in a normal atmosphere which it has been used $(\text{CH}_3\text{COO})_2\text{Cu}\cdot\text{H}_2\text{O}$ individually as Cu sources. All samples have calcination in 600°C . The effect of sour cherry juice concentration to control crystal growth is investigated by changing the amount of it to 20, 40, and 80 mL, respectively. The synthesized particles are characterized by using X-ray Diffraction (XRD) and Field Emission Scanning Electron Microscopy (FE-SEM). Powder X-ray Diffraction analysis confirms that pure Copper Oxide nanocrystallines are in a single phase monoclinic structure which the average crystalline size has estimated via Williamson-Hall plot from the highest peak of the XRD was among 15-55 nm for all samples.

Keywords: CuO nanocrystalline; Green synthesis; Sour Cherry juice; Williamson-Hall plot; Copper oxide.

1. INTRODUCTION

In the recent years, nanomaterials have a significant role in various practical applications with their unique morphology such as spherical nanoparticles, nanorods, nanoribbons, nanobelts and nanoplatelets [1-3]. On the one hand, nanostructured transition metal oxides (MO), of a special class nanomaterials, are prerequisite for the improvement of different novel functional and smart materials. These transition metal oxides nanocrystals have been attracting much concentration for fundamental scientific research thanks to their exceptional

physical and chemical properties. These properties are strongly associated with the size of crystalline, shapes, composition, and structures of nanocrystals [4]. CuO nanoparticles are of considerable technological interest in various applications, such as solar cell, batteries, catalytic, and superconductors because of its unique properties [5]. On the other hand, Various methods are available to prepare CuO nanoparticles, including microwave irradiation [6], sol-gel [7], solid-state reaction [8], precipitation-pyrolysis [9], and thermal decompo-

(*) Corresponding Author - e-mail: mahboubeh_kargar@yahoo.com

sition [10] methods.

First of all, Some of these methods are costly and require extensive instruments. Furthermore, the addition of chemical agents causes to a large quantities of wastes inserted into water sources and environments [1-10]. Obviously, some noxious effect has been seen in the medical application because chemical synthesis methods lead to the presence of any toxic chemical absorbed on the surface. The most challenging subjects to chemist is obtaining high-quality nanomaterials, which achieve appropriate substance regard to chemical purity, phase selectivity, crystallinity and homogeneity in particle size with controlled state of agglomeration infeasible and low-cost process [11].

To solve these problems a simple and green chemical method that is biosynthesis has attracted attention using fungi, actinomycetes, fruit, and plant extracts. These methods usually are green, low cost, solvent-free, non-toxic and environmentally benign precursors for the synthesis of nanostructures.

Recently, the biosynthesis of copper oxide nanoparticles have been excessive interesting and some green methods have been advanced, including the use of *Phyllanthus Amarus* Leaf extract [11], *Gloriosa superb-L* extract [5], D-glucose [12], *Centella asiatica* plants [13], and Urea [14], gum karaya [15] which will have been investigated.

Sour Cherry juice is renowned for its bioactivities such as inhibition of tumor development, protection against a broad range of human diseases and prevention of some cardiovascular risk factors [16-18]. The anthocyanins existed in Sour cherry reduced the severity of inflammatory symptoms such as edema, gout and arthritis. Sour Cherry is rich in bioactive compounds, including hydroxycinnamates, flavonoids, and procyanidins. The existence of phenolic compounds in Sour Cherry juice make it a good candidate for the synthesis of nanomaterials due to the ability of phenolic compounds to act as chelating agents [16-18].

In the current essay, an attempt is to find the efficiency of Sour Cherry juice as a stabilizer and capping agent in the synthesis of CuO nanocrystalline, juice with varying concentration have been used for the study. The effect of sour cherry juice concentration to control crystal growth was investigated.

2. EXPERIMENTAL

2.1. Physical measurements

Phase identification was carried out for the as-precipitated and heat treated samples by an X-ray Diffraction (XRD) method with a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu K α radiation. Field Emission Scanning Electron Microscope (FE-SEM) images were obtained on HITACHI S-4160.

2.2. Synthesis of CuO particles

Cu(OAc)₂ was purchased from Merck Company (Aldrich) and used without further purification. CuO nanostructures were prepared by the following experimental sequence:

A solution of Sour Cherry juice combined with 20 mL aqueous ammonia was added drop wise into a solution containing (CH₃COO)₂Cu (30 mmol) and 40 mL of Sour cherry juice in 200 mL of water under magnetic stirring. The obtained mixture was stirred at room temperature for 30 min. The resultant dark blue precipitates were filtered, washed with distilled water and absolute ethanol and dried at room temperature. Moreover, the experiment was carried out by using 20, 40 and 80 mL of Sour Cherry at the same conditions, respectively. The precipitates were then heated slowly up to 600°C in an electric furnace using alumina crucibles and maintained at the stable mentioned temperature for 3h. After calcination, the obtained products of black CuO were stored in airtight container for further analysis.

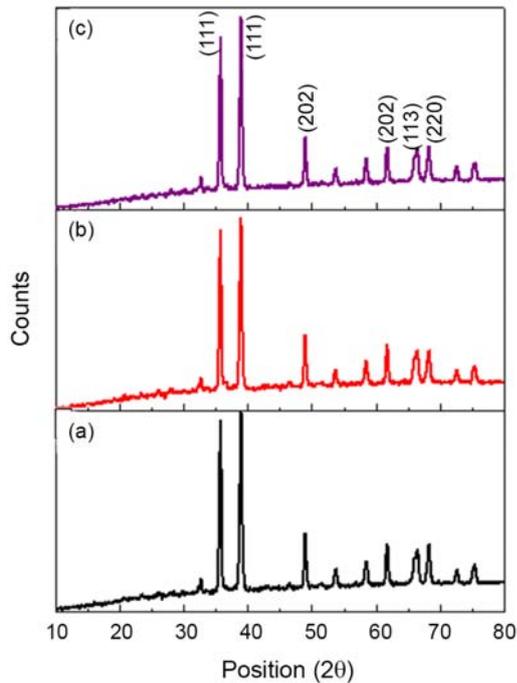
3. RESULTS AND DISCUSSIONS

The correct crystallinity corresponding to those of single phase monoclinic structure (space group C2/c), with lattice parameters $a = 4.6833\text{\AA}$, $b = 3.4208\text{\AA}$ and $c = 5.1294\text{\AA}$, $\beta = 99.5670^\circ$ (JCPDS 080-1268), was observed in the XRD pattern of powders that is represented in Figure 1. Based on the powder diffraction peak broadening, the strain value (ϵ) of CuO nanoparticles was evaluated by using the slope of the Williamson-Hall plot on Table. 1 [19].

Clearly, the crystals have grown completely and have decreased their size and crystalline by increasing the

Table 1: Determine the size of the crystal, strain value of CuO nanoparticles.

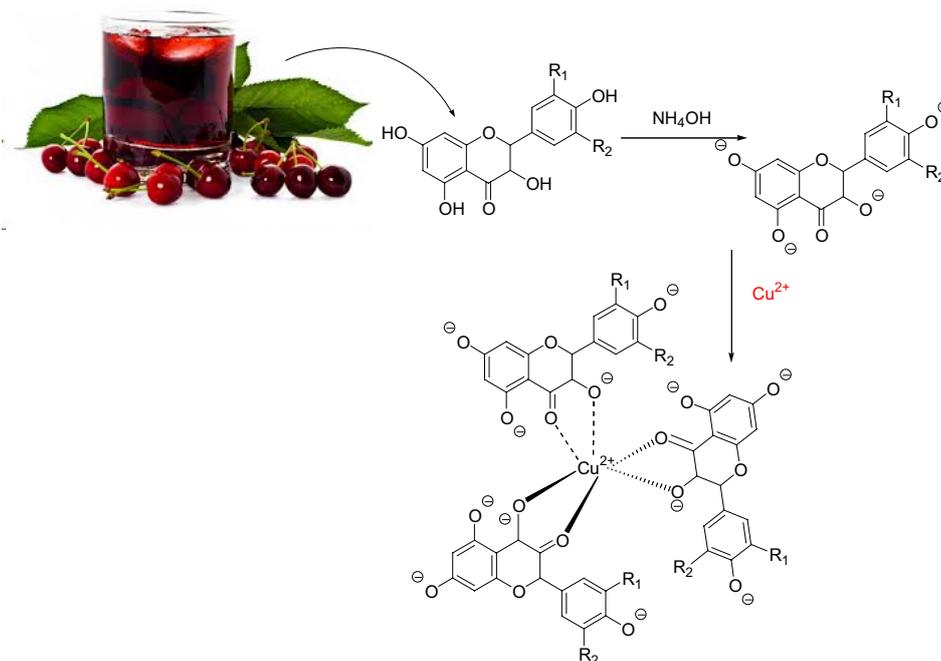
Amount of sour cherry juice	Strain value (ϵ)	Crystallinity size by Williamson-Hall (nm)
20cc	0.0038	55
40cc	0.0009	15
80cc	0.0009	15

**Figure 1:** XRD patterns of CuO particles synthesized using (a) 20 mL; (b) 40 mL (c) 80 mL of Sour Cherry juice.

amount of Sour Cherry juice.

In this essay, the Sour Cherry juice was used as an effective controlling agent of size and morphology. The presence of this surfactant produces the particulate centers for nucleation and outgrowth of discrete particles. Anthocyanins are the major component present in Sour Cherry and most likely are responsible for uniform shapes and sizes of the ensuing nanoparticles [20]. Schematic diagram illustrates the effect of antioxidants from Sour Cherry fruit on Figure 2.

In order to have further investigation, the effect of concentration of the Sour Cherry juice was studied by changing the amount of Sour Cherry juice from 20 to 40 and 80 mL and changing on the morphology of the samples was investigated by FE-SEM technique (Figure 3). From Figure 3, it was revealed that as synthesized CuO samples undergoes a high degree of agglomeration and taken a mud pottery like shape. Only a small difference is observed between nano-particles

**Figure 2:** Schematic of effect of antioxidants from sour cherry juice in synthesis of CuO nanocrystalline.

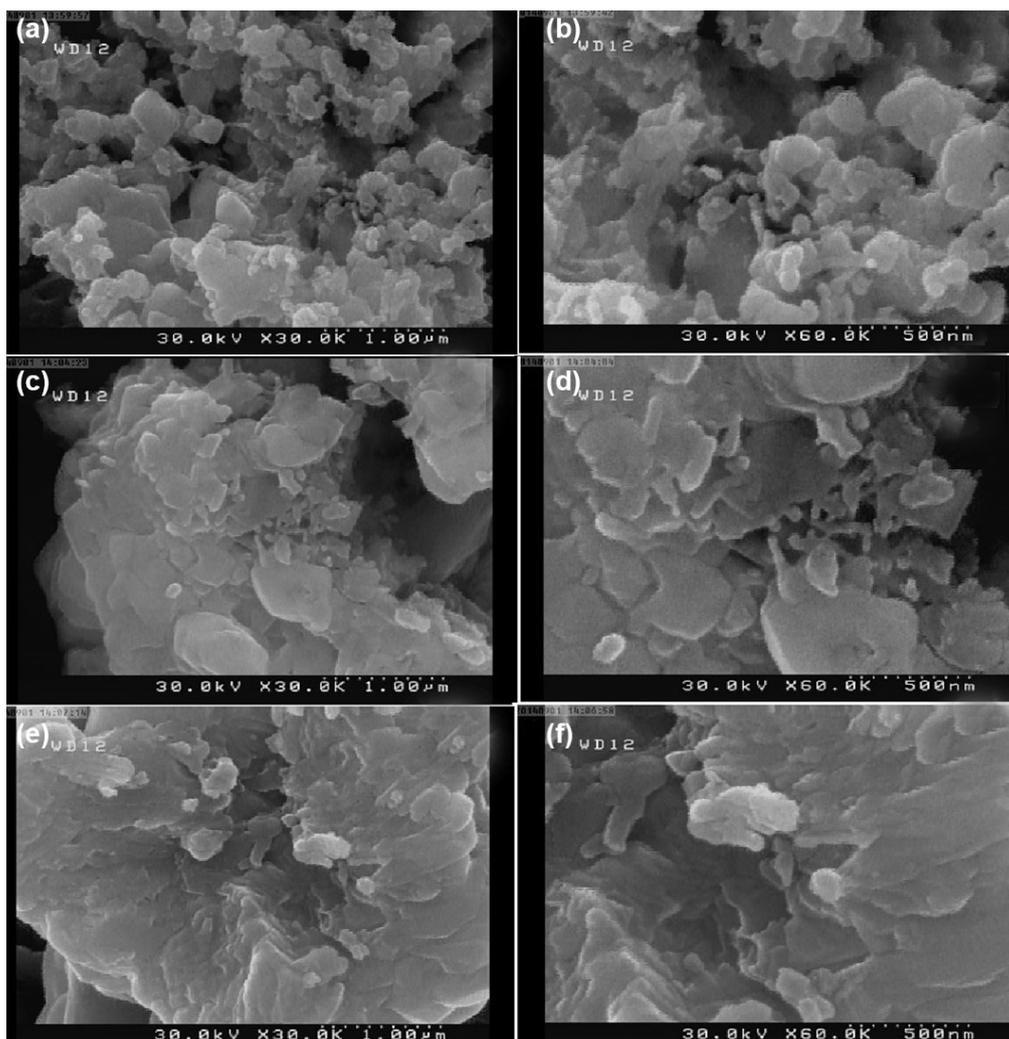


Figure 3: FE-SEM photographs of CuO nanoparticles synthesized using 20 mL (a,b), 40 mL (c,d) and 80 mL (e,f) of sour cherr juice.

shape measured by FE-SEM. The agglomeration process took place between the CuO nanoparticles capped by anthocyanin molecules in the juice due to the presence of hydrogen bonding [21].

In order to have a comparison between the size of

the as-prepared samples and to understand the effect of the sour cherry juice concentration on the particle size an statistical analysis was performed from the FE-SEM images to obtain information about the particle size distribution of the samples and the results are

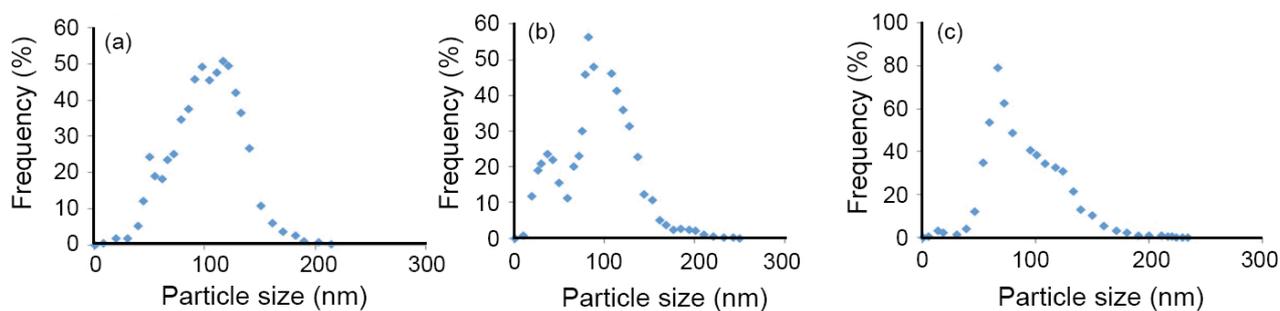


Figure 4: Diagram of CuO particles size synthesized using (a) 20 mL, (b) 40 mL, and (c) 80 mL of sour cherry juice.

shown in Figure 4. It was revealed that the diameters of the sample are in the range of 20-200 nm. Changes on the sour cherry juice concentration did not change the shape of the CuO nanoparticles, but it caused a decrease in the particle size with increasing on the juice concentration. The average particle size of the samples are 105, 90 and 70 nm for the juice concentrations of 20, 40 and 80 mL respectively. In comparison XRD results, the particle size has decreased with the enhancing of sour cherry juice which led to lower strain value. In spite of agglomerated particle, crystal size has decreased, which can be used in various applications.

4. CONCLUSIONS

In a nutshell, CuO nanocrystalline with various morphologies have been successfully prepared via a coprecipitation method with copper acetate and sour cherry juice as surfactant is the originality of this work which the kind of surfactant has a significant effect on the crystalline size, morphology products. The advantages of the method, nanometer scale were formed by feasible and low-cost in a normal atmosphere if green synthesis. The XRD results showed that pure CuO powders were formed with the aid of this method without any impurity. It is anticipated that CuO nanoparticles have high potential applications in different fields such as bioactivity and medicinal applications along with optical/electrical devices.

REFERENCES

1. Nath S.K., Kalita P.K., *J. Nanosci. Nanotechnol.: An Int. J.*, **2** (2012), 8.
2. Sambandam A., Lee G.J., Wu J., *Ultrason. Sonochem.*, **19** (2012), 682.
3. Zhou K., Wang R., Xu B., Li Y., *Nanotechnology*, **17** (2006), 3939.
4. Zhang Q., Zhang K., Xu D., Yang G., Huang H., Nie F., Liu Ch., Yang Sh., *Mate. Sci.*, **60** (2014), 208.
5. Raja Naika H., Lingaraju K., Manjunath K., Kumar D., Nagaraju G., Suresh D., Nagabhushana H., *J. Taibah Univ. Sci.*, **9** (2015), 7.
6. Wang H., Xu J.Z., Zhu J.J., Chen H.Y., *J. Cryst. Growth*, **244** (2002), 88.
7. Zhang Q., Li Y., Xu D., Gu Z., *J. Mater. Sci. Lett.*, **20** (2001), 925.
8. Xu J.F., Ji W., Shen Z.X., Tang S.H., Ye X.R., Jia D.Z., Xin X.Q., *J. Solid State Chem.*, **147** (2000), 516.
9. Yia A.J., Li J., Jian W., Bennett J., Xu J.H., *Appl. Phys. Lett.*, **79** (2001), 1039.
10. Fan H., Yang L., Hua W., Wu X., Wu Z., Xie S., Zou B., *Nanotechnology*, **15** (2004), 37.
11. Acharyulu N.P.S., Dubey R.S., Swaminadham V., Kalyani R.L., Kollu P., Pammi S.V.N., *Int. J. Eng. Res. Technol.*, **3** (2014), 639.
12. M. Ahamed, P. Karupppiah, H. A. Alhadlaq, N. A. Al-Dhabi, M. A. Majeed Khan, *J. Nanomater.*, **2014** (2014), 4.
13. Yang R.C., Zhang Z.H., Ren Y.M., Zhang X., Chen Z.M., Xu M.D., *J. Materi. Sci. Technol.*, **31** (2014), 25.
14. Tadjarodi A., Roshani R., *J. Curr. Chem. Lett.*, **3** (2014), 215.
15. Vellora V., Padil Th., Cernik M., *Int. J. Nanomedicine*, **8** (2013), 889.
16. Bonerz D., Wurth K., Dietrich H., Will F., *Eur. Food Res. Technol.*, **224** (2007), 355.
17. Capanoglu E., Boyacioglu D., de Vos R.C.H., Hall R.D., Wilder B., *J. Berry Res.*, **1** (2011), 137.
18. M. Toht-Marcus, F. Boross, P. Molnar, 1993. *Int. Federation of Fruit Juice Producers (IFU) Symposium (Budapest)*, 329.
19. Khorsand Zak A., Abd. Majid W.H., Abrishami M.E., Yousefi R., *J. Solid State Sci.*, **13** (2011), 251.
20. Kaume L., Howard L.R., Devareddy L., *J. Agric. Food Chem.*, **60** (2012), 5716.
21. Tavakoli F., Salavati-Niasari M., Ghanbari D., Saberyan K., Mostafa Hosseinpour-Mashkani S., *J. Mater. Res. Bull.*, **49** (2014), 14.

AUTHOR (S) BIOSKETCHES

Mahboubeh Kargar, *Instructor, Faculty of Sciences, Najafabad Branch, Islamic Azad University, Najafabad, Esfahan, Iran*
Email: mahboubeh_kargar@yahoo.com

Majid Ghashang, *Assistant Professor, Faculty of Sciences, Najafabad Branch, Islamic Azad University, Najafabad, Esfahan, Iran*

Mohammad Reza Mohammad Shafiee, *Assistant Professor, Faculty of Sciences, Najafabad Branch, Islamic Azad University, Najafabad, Esfahan, Iran*