Eco Friendly Synthesis, Spectroscopic Investigation of Copper and Its Oxide Nanoparticles with Excellent Electrical Conductivity

Abstract
A facile and rapid route for the synthesis of uniform Nano copper and its oxide (CuO NPs) by a microwave assisted method is demonstrated. The copper and its oxide nanoparticles (CuO NPs) prepared exhibit excellent conductivity, which is comparable with electrosprun copper nanofibers. Among various metal nanoparticles, Copper and its oxide nanoparticles (CuO NPs) have attracted considerable attention because copper is one of the most important in modern technology and is readily available. Copper Nanoparticles have been much attractive because it is easily available, cost effective and conducting nature. Copper and its oxide Nanoparticles were synthesized using Copper (II) succinate by microwave conventional method. Copper and its oxide Nanoparticles so obtained were characterized by UV-Visible spectroscopy, Fourier Transform Infrared Spectroscopy and X-Ray diffraction analysis. X-Ray diffraction analysis proved the formation of Copper and its oxide Nanoparticles. SEM and AFM analyses showed the presence of Nanoparticles.

Keywords: Copper sulfate; UV visible; XRD; FT-IR; AFM

Introduction
Metal Nanoparticles have attracted considerable attention because of their excellent electronic and optical properties. They have been used in many fields, such as displays, solar cells, touchscreens, sensors, and electromagnetic interference shielding [1]. However, for most of these applications, metal Nanoparticles with high electrical conductance are required. Compared with various other metals, copper is more abundant and less expensive, while having favourable mechanical, electrical, and optical properties [2]. Copper Nanoparticles have thus been suggested as a low cost alternative to indium tin oxide (ITO), investigated extensively and compared against conductive polymers, carbon nanotubes, graphene and Ag nanowires [3-6]. To date, various methods have been developed for synthesizing Copper and its oxide Nanoparticles (CuO NPs), including electrochemical deposition, electrosprinning, template processes, hydrothermal reduction and reverse micellar systems [7-12]. On the other hand, the microwave-assisted synthesis [13,14], which is generally quite fast, simple and efficient in energy, has been developed and is widely used in various fields such as molecular sieve preparation, radiopharmaceuticals, the preparation of inorganic complexes and oxide, organic reactions, plasma chemistry, analytical chemistry and catalysis. Generally speaking, the power, heating frequency and on/off irradiation cycles are the main heating parameters of a microwave oven and each of them may have a great effect on the structure and properties of the products. To the best of our knowledge, although such a heating method has been a focus of research, most of previous reports were limited to fixed working conditions of the microwave oven [15-20] and there is no comprehensive report addressing the effects of these heating parameters on the synthesis of nanomaterials [21-23]. Furthermore, there are few reports on synthesizing the Copper and its oxide Nanoparticles without template at mild condition by the use of microwave method. Here, we report a simple microwave method to fabricate well aligned Copper and its oxide Nanoparticles (CuO NPs) on a Copper surface without any template and surfactant [24-26].

Experiment
Materials
All the chemicals, reagents used in our experiments were of analytical grade and were used as received without further purification. Succinic acid, Copper sulphate and NaOH were purchased from Aldrich and were used as received, hexane SDF and ethanol from distillery.

Synthesis of the Copper(II) succinate precursor
The CuSO₄·5H₂O (2 mmol) was dissolved in 10 mL of distilled water to form a homogeneous solution. A stoichiometric amount
of sodium hydroxide (NaOH) and succinic acid were dissolved in distilled water. The sodium succinate thus formed was drop wise added into the above solution under magnetic stirring. The solution was stirred for about 30 min and a green precipitate was obtained which was centrifuged and washed with ethanol several times. The product was dried. The Copper (II) succinate was characterized various spectral techniques [27].

**Synthesis of the copper and its oxide nanoparticles**

Copper and its oxide nanoparticles were synthesized by a domestic microwave method in the presence of Copper (II) succinate. The Copper (II) succinate placed in a domestic microwave. Finally, the reaction system was heat treated at 473K for 2 h. Copper and its oxide Nanoparticles were obtained black powder (Scheme 1 & 2).

**Results and Discussion**

**UV Visible Spectra**

Copper Nanoparticles typically exhibit ~ 500 nm. However the Copper (II) succinate show an absorption peak at 264, 372 and 568 nm (Figure 1) and also Copper and its oxide Nanoparticles synthesized here show an absorption peak at 450 nm which can be assigned to the absorption of Nanoparticles of copper. Tauc plot for synthesized Nanoparticles is shown in Figure 1. A modest blue shift of the absorption edge relative to that of the bulk copper powder is observed. This observation alludes to the size effect of copper and its oxide Nanoparticles.

**FT - IR measurement**

FT-IR spectroscopy is a useful tool to understand the functional group of any organic molecule. Figure 2a shows IR spectrum of Copper (II) Succinate precursor. Figure 2b shows IR spectrum of copper Nanoparticles. A twin peak at 621 cm⁻¹ & 680 cm⁻¹ indicated the Cu-O Stretching vibration. The metal salt (Cu-O-C) Peak appeared at 1192 cm⁻¹. A Peak at 3541 cm⁻¹ indicates OH stretching of the water in the precursor which disappeared in the Nanoparticles. A Peak at 1637 cm⁻¹ indicates metal carbonyl (C=O) of the precursor which disappeared in the Nanoparticles B3 [28-30].
X-Ray diffraction studies

XRD pattern of Copper and its oxide nanoparticles deposited at 300°C under nitrogen environment with a collecting angle varying from 20 to 80° and the usual copper Kα1 radiation λ = 1.5406 Å is shown in Figure 2a & 2b. The hkl values (111), (200), (220), 2θ values 48.96, 53.67, and 68.24 and corresponding d values, 2.073, 1.796, and 1.274Å are used for determining lattice parameter which came to be 3.01, 4.01, and 8.00 Å, respectively using standard formula (Lattice = d√h.k.l). The relative peak intensities and the position of diffraction peaks in the XRD pattern are very similar to those reported in the JCPDS standard data 40836 and others. The Table 2 shows particle size of Copper and its oxide nanoparticles. The position and the integral width of x-ray diffraction peaks are determined to identify the crystalline phase which is found to be face centered cubic [31].

Table 1: Peak indexing from d-spacing

| 2θ  | d     | (1000/d^2) | (1000/d^2)/77.32 | hkl |
|-----|-------|------------|------------------|-----|
| 48.96 | 2.073  | 232.07     | 3.01             | 111 |
| 53.67 | 1.796  | 310.02     | 4.01             | 200 |
| 68.24 | 1.274  | 616.11     | 8                | 220 |

Figure 2a & 2b: FT-IR spectrum of P2 and copper Nanoparticles of B3.

Table 2: The particle size of B3.

| 2θ of the Intense Peak (deg) | θ of the Intense Peak (deg) | FWHM of Intense Peak (β) Radians | Size of the Particle (D) nm | d Spacing (nm) | Plane | Material | Microstrain |
|-----------------------------|-----------------------------|---------------------------------|----------------------------|----------------|-------|----------|------------|
| 32.68                       | 16.34                       | 0.1378                          | 60.4                       | 2.7401         | (202) | CuO      | 0.1175     |
| 35.75                       | 17.875                      | 0.1574                          | 53.3                       | 2.5115         | (110) | Cu, CuO  | 0.122      |
| 38.98                       | 19.49                       | 0.2362                          | 35.7                       | 2.31055        | (111) | Cu       | 0.1668     |
| 48.96                       | 24.48                       | 0.1968                          | 44.5                       | 1.8604         | (200) | Cu       | 0.108      |
| 53.67                       | 26.835                      | 0.1378                          | 65                         | 1.7077         | (20)  | CuO      | 0.0681     |
| 58.49                       | 39.245                      | 0.2166                          | 42.1                       | 1.578          | (200) | Cu       | 0.0967     |
| 61.72                       | 30.86                       | 0.1378                          | 67.5                       | 1.5029         | (200) | CuO      | 0.576      |
| 66.44                       | 33.22                       | 0.1368                          | 48.4                       | 1.4072         | (200) | Cu       | 0.0751     |
| 68.24                       | 34.12                       | 0.168                          | 57.3                       | 1.3743         | (20)  | CuO      | 0.06198    |

Particle size calculation: The existence of sharp peaks indicates that the synthesized nanoparticles are polycrystalline in nature [31]. One can calculate the values of average crystallite size Debye - Scherer formula (D) from eq (1), d-Spacing the value of d (the inter planar spacing between the atoms) is calculated from equation (2) and microstrain (ε) from equation (3) formation XRD spectrum using the following equations:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \]  
(1)

Bragg’s Law: \( 2d \sin \theta = n\lambda \)  
(2)

\[ d = \lambda \]  
(3)

Wavelength \( \lambda = 1.5418 \text{ Å} \) for Cu Ka

\[ \epsilon = \frac{\beta}{4 \tan \theta} \]  
(3)

The calculated d-spacing and micro strain details are in Table 2.
Eco Friendly Synthesis, Spectroscopic Investigation of Copper and Its Oxide Nanoparticles with Excellent Electrical Conductivity

Cyclic voltammetry

Figure 4 shows cyclic voltammogram (CV) the instructor will familiarize the students with the operation of the computer program interfaced to the CV and the proper procedure for introducing and removing solutions from the cell. Set the Copper Nanoparticles was recorded in DMSO with 0.1 M tetrabutylammonium perchlorate as supporting electrolyte in the initial potential +2 V and –2 V. The scan should be initiated in a positive direction with a scan rate of 50 mV/s with a conventional three electrode system composed of a platinum auxiliary, Glassy carbon working electrode and Calomel (Saturated KCl) reference electrode. The reductive peaks correspond to Cu (II)/Cu (I) and Cu (0) i.e CuO $\rightarrow$ Cu. After the deoxygenating is complete switch on the working electrode and wait for approximately 10 s until the current has reached a constant value. Initiate the potential scan and a background CV of the supporting electrolyte is obtained. This scan with a wide potential range provides the operational limits of potential at which the experiment can be run, i.e. the potential window of the electrolyte. The redox potential values obtained from the cyclic voltammogram for the Copper and its oxide Nanoparticles were quasi-reversible and the electron flow was sluggish (Table 3).

Data from Cyclic voltammetric measurements; $E_{1/2}$ is calculated as average of anodic (Epa) and cathodic (Epc) peak potentials $E_{1/2} = \frac{1}{2} (Epa+Epc)$

Table 3: Redox Potentials of Copper and its oxide nanoparticles in DMSO solution at 298K.

| Compound | $E_{pc}$ (V) | $E_{pa}$ (V) | $\Delta E$(V) | $E_{1/2}$ | $i_{pc}$ (µA) | $i_{pa}$ (µA) | $i_{pa}/i_{pc}$ |
|----------|--------------|--------------|--------------|-----------|--------------|--------------|----------------|
| P2       | -1.0901      | 0.9035       | 1.9936       | 0.0933    | 1.612X10$^{-4}$ | 7.782X10$^{-5}$ | 0.4827         |
| B3       | -0.8354      | -0.5376      | 0.2978       | -0.6865  | 7.993X10$^{-4}$ | 2.162X10$^{-6}$ | 0.2704         |

SEM & AFM analysis for Copper and Its Oxide nanoparticles

The morphology of the product is examined by SEM. Figure 5 depicts the SEM pictures of a sample of Copper and its oxide Nanoparticles. From the micrograph, it was observed that the Nanoparticles are agglomerated. The Atomic force microscopic (AFM) photographs of the product are given in Figure 6. These sizes are nearly cubic (fcc). The area roughness and RMS are in the range 160 to 487 nm which indicates its conducting nature. We may consider that when the reaction was carried out at 473 K, most organic molecules decomposed. Copper and its oxide nano have rod like, loose solid morphologies.
Eco Friendly Synthesis, Spectroscopic Investigation of Copper and Its Oxide Nanoparticles with Excellent Electrical Conductivity

Conclusion

In summary, a facile and rapid route has been developed for synthesizing uniform crystal Copper and its oxide nanoparticles by a microwave assisted method. This method is highly efficient and is scalable for large scale synthesis. The prepared Copper and its oxide nanoparticles have an average diameter of 50 nm, 10 μ and lengths of longer than 10 mm, i.e., an aspect ratio of greater than 300. Moreover, the Copper and its oxide nanoparticles show outstanding conductivity, comparable with electrospun copper nanofibers. Our experimental results demonstrate that this novel and simple route can produce high quality crystalline Copper and its oxide Nanoparticles of nanostructures.

Acknowledgment

Authors are grateful thank to Principal, Muthurangam Govt. Arts College (Autonomous), Vellore, for providing facilities to undertake this work. We also thank Center for nanotechnology, VIT Vellore for AFM analysis.

Conflict of Interest

None.

References

1. Moulton B, Zaworotko MJ (2001) From molecules to crystal engineering: supramolecular isomerism and polymorphism in network solids. Chem Rev 101(6): 1629-1658.
2. Kitagawa S, Kitaura R, Noro SI (2004) Functional porous coordination polymers. Angew Chem Int Ed Engl 43(18): 2334-2375.
3. Janiak CJ (2003) Engineering coordination polymers towards applications. Dalton Trans 14: 2781.
4. James SL (2003) Metal-organic frameworks. Chem Soc Rev 32(5): 276-288.
5. Carlucci L, Ciani G, Proserpio D (2003) Polycationization, polythreading and polynknotting in coordination network chemistry. Coor Chem Rev 246: 247-289.
6. Wong KT, Lehn JM, Peng SM, Lee GH (2000) Nanoscopic molecular organometallo wires containing diruthenium cores. Chem Commun 22: 2259.
7. Bunn AG, Carroll PJ, Wayland BB (1992) Coordination polymers of tetracyanoethylene with metal hexafluoroacetacetates: formation and X-ray crystal structure. Inorg Chem 31(7): 1297-1299.
8. Caneschi A, Gatteschi D, Lalotti N, Sangregorio C, Sessoli R, et al. (2001) Cobalt(II)-nitryl nitrooxide chains as molecular magnetic nanowires. Angew Chem Int Ed Engl 40(9): 1760-1763.
9. Tanatani A, Moli MJ, Moore JS (2001) Chain length-dependent affinity of helical foldamers for a rodlike guest. J Am Chem Soc 123(8): 1792-1793.
10. Fujita M, Kwon YJ, Washizu S, Ogura KJ (1994) Preparation, clathration ability, and catalysis of a two-dimensional square network material composed of cadmium (II) and 440-bipyridine. J Am Chem Soc 116(3): 1151-1152.
11. Jin R, Cao Y, Mirkin CA, Kelly KL, Schatz GC, et al. (2001) Photoinduced conversion of silver nanospheres to nanoprisms. Science 294(5548): 1792-1793.
12. Koch CC (2002) Nanstructured materials: processing, properties and applications. Williams and Wilkins, Norwicht, UK, pp. 397.
13. Jun YW, Seo JA, Oh SJ, Cheon J (2005) Recent advances in the shape control of inorganic nano-building blocks. Coord Chem Rev 249(17-18): 1766-1775.
14. Kim F, Connor S, Song H, Kuykendall T, Yang PD (2004) Platonic gold nanocrystals. Angew Chem Int Ed Engl 43(28): 3673-3677.
15. Lv S, Li P, Sheng J, Sun W (2007) Synthesis of single-crystalline BaCO3 nanostructures with different morphologies via a simple PVP-assisted method. Mater Lett 61(21): 4250-4254.
16. Li Y, Liang J, Tao Z, Chen J (2008) CuO particles and plates: synthesis and gas-sensor application. Mater Res Bull 43(8-9): 2380-2385.
17. Zhang H, Zhang M (2008) Synthesis of CuO and its oxide nanoparticles with application as electrode materials for capacitors. Mater Chem Phys 108(2-3): 184-187.
18. Arbusov T, Ghezhevski B, Naumov S, Korolev A, Arbusov V, et al. (2003) Temporal changes in magnetic properties of high-density CuO nanoceramics. J Magn Magn Mater 258: 342-344.
19. Gao P, Chen Y, Lu H, Li X, Wang Y, et al. (2009) Synthesis of CuO nanoribbon arrays with noticeable electrochemical hydrogen storage ability by a simple precursor dehydration route at lower temperature. Int J Hydrogen Energ 34(7): 3065-3069.
20. Maruyama T (1998) Copper oxide thin films prepared by chemical vapor deposition from copper dipivaloylmethanate. Sol Energ Mater Sol 56(1): 85-92.
21. Yao M, Tang Y, Zhang L, Yang H, Yan J (2010) Photocatalytic activity of CuO towards HER in catalyst from oxalic acid solution under simulated sunlight irradiation. Trans Nonferrous Met Soc China 20(10): 1944-1949.
22. Chen JT, Zhang F, Wang J, Zhang GA, Miao BB, et al. (2008) CuO nanowires synthesized by thermal oxidation route. J. Alloys Compd 456(1-2): 268-273.
23. Yu L, Zhang G, Wu Y, Bai X, Guo D (2008) Cupric oxide nanoflowers synthesized with a simple solution route and their field emission. J. Cryst Growth 310(12): 3125-3130.
24. Zhu J, Bi H, Wang Y, Wang X, Yang X, et al. (2007) Synthesis of flower-like CuO nanostructures via a simple hydrolysis route. Mater Lett 61(30): 5236-5238.
25. Dinesh karthik A, Geetha K (2014) Synthesis and characterization of copper and copper oxide nanoparticles by thermal decomposition method. Int J NanoDimens 5(4): 321-327.
26. Dinesh karthik A, Geetha K (2013) Synthesis of copper precursor, copper and its oxide nanoparticles by green chemical reduction method and its antimicrobial activity. Journal of Applied Pharmaceutical Science 3(5): 016-021.
27. Zhang H, Li S, Ma X, Yang D (2008) Controllable growth of dendrite-like CuO nanostructures by ethylene glycol assisted hydrothermal process. Mater Res Bull 43(5): 1291-1296.
28. Nakamoto K (1997) Infrared and raman spectra of inorganic and coordination compounds. (5th edn), John Wiley and Sons, New York, USA.
29. Teng F, Yao W, Zheng Y, Ma Y, Teng Y, et al. (2008) Synthesis of flower-like CuO nanostructures as a sensitive sensor for catalysis. Sensors Actuat B 134(2): 761-768.
30. Song X, Yu H, Sun S (2005) Single-crystalline CuO nanobelts fabricated by a convenient route. J Colloid Interf Sci 289(2): 588-591.
31. Cullity Addison BD (1978) Elements of X-Ray Diffraction. Wesley Pub co USA, p. 4-47.