Nano World Journal

https://doi.org/10.17756/nwj.2022-s1-011

Research Article

Open Access

Effect of pH on Facile Synthesized Copper Nanoparticles

Lokesh[1], Rashi Nathawat[1*] Shivani Dhall[2], and Satyapal S. Rathore[3]

[1]*Department of Physics, Manipal University Jaipur, Rajasthan, India*

[2]*DAV College, Jalandhar, India*

[3]*Cluster University Jammu, Jammu, India*

[*]Correspondence to:
Rashi Nathawat
Manipal University Jaipur, India
E-mail: rashi.nathawat@gmail.com

Received: August 23, 2022
Accepted: October 13, 2022
Published: October 15, 2022

Citation: Lokesh, Nathawat R, Dhall S, Rathore SS. 2022. Effect of pH on Facile Synthesized Copper Nanoparticles. *NanoWorld J* 8(S1): S54-S58.

Published by United Scientific Group

Abstract

Copper (Cu) was one of the first metals to be excavated and used by humans. Cu NPs have a lot of attention due to their high electrical conductivity, high melting point, low electrochemical migration, and low cost. It also demonstrated antiviral activity such as a recent study showing that the coronavirus survives for several days on glass, plate, and stain-less steel, but dies within a few hours on Cu. It was observed that controlling particle size expands the range of innumerable applications. Several methods have been employed for the synthesis of Cu NPs such as physical, chemical, biological, and green synthesis. In the present work, NPs were successfully synthesized by a facile electrochemical deposition method. In which, copper sulfate pentahydrate ($CuSO_4.5H_2O$), was used as a precursor and sodium hydroxide (NaOH) used to maintain pH during the deposition in deionized water (DI) as a solvent. The structural and optical characterization of NPs were performed by X-ray diffraction (XRD), field effect scanning electron microscope (FESEM), and Ultraviolet-Visible (UV-Vis) Spectroscopy. The face-centered cubic (FCC) structure of Cu NPs has been analyzed by XRD and the size varies from 65 nm - 30 nm by controlling pH of electrolyte solution. In the optical studies, it was observed that the bandgap was varying in the range of 2.98 eV to 4.97 eV, calculated by Tauc's plot.

Keywords

Nanoparticles, Electrodeposition, X-ray diffraction, field effect scanning electron microscope, Bandgap

Introduction

Cu is the most attractive material because of its high natural abundance in nature and cost-effective [1]. This metal found as a native metal and in the mineral's cuprite, malachite, azurite, chalcopyrite, and bornite [2]. Cu metal exhibited excellent electrical conductivity, high meting temperature, low electrochemical migration behavior, low coast, and excellent solderability [3-5]. These characteristics are frequently influenced by their size, shape, composition, crystallinity, and structure, it is generally acknowledged. Therefore, one of the most efficient approaches to get desired qualities is to carefully manage the synthesis of nanomaterials with precise shape and consistent size. Cu have been used for electromagnetic devices [6]. It also demonstrates extra ordinary performance as antibacterial and antimicrobial agent [7, 8]. NPs size and shape is important for electronic, catalytic, magnetic, sensing, and biological applications [9-10]. Cu particles exhibits novel physical and chemical properties due to their nano size. Various synthesis techniques have been employed for preparing NPs. In which most of the methods, require high-end equipment and the production

of yield were very less. The preparation of Cu NPs by chemical method is more challenging compared to other noble metals because, it's easily oxidized at ambient temperature. In most of the wet chemical processes for synthesizing metallic NPs, utilized chemicals are toxic and flammable. Whereas in the electrodeposition method chemicals as well as procedure are non-toxic, easy, and cost effective [11]. The size and shape of Cu NPs depends on the synthesis processes and chemicals. The various shapes of Cu NPs are reported like cubic, prism, and spherical due to different techniques and parameters. The Cu NPs size is measured from 20 nm to 7 µm while preparing electrodeposition method [12], but the particle size found is 70 nm while using the same method on applying voltage on electrodes as 8 volts, for 4 ms and 8 ms plus on time and plus off time, respectively [13]. By this method, the particle size was also found to be 24 nm with electrode power of 15 volt at 6A [10]. The size of Cu NPs was found to be 1.5 nm using the polyol method by combining ethylene glycol, copper chloride, polyvinylpyrrolidone, sodium citrate, and ascorbic acid all in one solution [14]. Ultrafine Cu NPs prepared from an organic solvent whose particle size can be controlled down to 1 nm using poly (N-vinylpyrrolidone) (PVP) as a stabilizer and sodium borohydride as a reducing agent in an alkaline ethylene glycol (EG) solvent [15]. The average size was 20 nm when soybean was used as a chelating agent. These NPs had a spherical form and were not aggregated [16]. Therefore, a size of 40 nm is necessary for synthesis using the polyol technique [17]. These NPs are used as light-collecting NPs and conductive ink. In the present study, we have optimized the synthesis of Cu NPs through an electrodeposition method. NPs were deposited on Cu-tape without any template. We have investigated that, by changing voltages and pH of solution, the size of Cu NPs can be controlled.

Materials and Methods

Copper sulfate pentahydrate ($CuSO_4.5H_2O$) and sodium hydroxide (NaOH) were procured from Rankem and used for electrodeposition without any further purification. Electrodeposition setup (Figure 1) was carried out with a conventional two electrode system. Cu strip used as an anode electrode and Cu tape used as a cathode electrode. Both electrodes kept in beaker with 5 cm distance and connected with power supply. The electrolyte solutions with different molar concentration were prepared in DI water. The optimized $CuSO_4.5H_2O$ aqueous electrolyte solutions were prepared with two molar concentration 0.1 M (solution C_1) and 0.05 M (solution C_2). Another, two more electrolyte solutions were prepared with adding NaOH 2 M in C_1 and C_2 and called CN_1 and CN_2. All four electrolyte solutions were used for electrodeposition process. Varying voltage 0.2 V- 0.4 V applied on electrodes to deposit Cu NPs. After deposition of NPs, Cu tape was removed from the solution and clean several times by DI water. As-synthesized NPs were characterized by FESEM, XRD, and UV-Vis spectroscopy for their structural and optical studies.

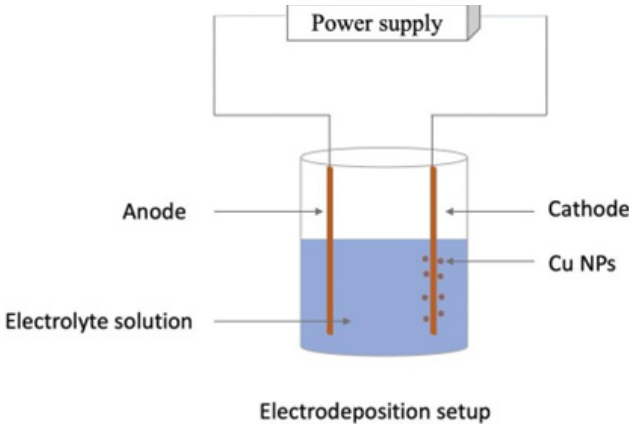

Figure 1: Electrodeposition set-up.

Results and Discussion

X-Ray diffraction

The XRD patterns were recorded on a Rigaku, Cu Kα = 0.154 nm by X-ray diffractometer. The XRD peaks of Cu NPs appeared at 43.3°, 50.4°, 74°, 89.9°, 116.8°, 117.3°, and 136.4° correspond plane (111), (200), (220), (311), (222), (400) and (331) planes of FCC crystal structure (JCPDS 04-0836) of metallic Cu, respectively (as shown in Figure 2). The sharp diffraction peak (200) reveals that Cu NPs highly orientated and crystalline in phase [18, 19]. The crystallographic planes of FCC phase matched with JCPDS No 04-0836 and ASTM 03-1005 standard powder diffraction card. These diffraction peaks are in good agreement with reported literatures [16, 20-22]. The intensity of peaks reflects the high degree of crystallinity of the Cu NPs. This crystalline size was calculated by Debye Scherrer formula as follow in equation number (1).

$$D = \frac{0.89\lambda}{\beta}\cos\theta \qquad \text{..... (1)}$$

Where λ is wavelength, θ is diffraction angle, β is full width half maxima (FWHM) and D is crystalline size [23]. The details of FWHM, d-spacing, lattice parameter and crystallite size was tabulated in Table 1 and 2 for sample C1 and CN1, respectively. It has been observed that Cu NPs syn-

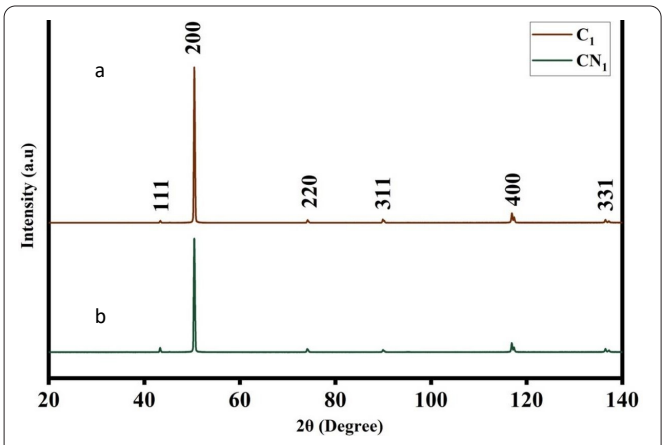

Figure 2: XRD pattern of Cu NPs (a) use electrolyte C1 (b) use electrolyte CN_1.

thesized by chemical method when pH was increased then observed grain size also increased [24]. The theoretical lattice parameter of Cu is 3.615Å [25]. This value was calculated by the formula given in equation number (2).

$$a = \frac{4}{\sqrt{2}} \text{ r} \quad \text{.....(2)}$$

Where r is the radius of Cu atom 0.128 nm and a is lattice constant, the calculated value for lattice parameter is 3.6211 Å. Both theoretical and experimental observed values of lattice constant are comparable.

Field emission scanning electron microscopy

The surface morphology of nanoparticles was observed by FESEM as shown in Figure 3. The pH variation on particle size of all four types of samples were prominent (Table 3). As per the observation, when pH was increased, particles size was decreased [26]. On applying 0.4 V on electrodes with same molar concentration (0.1 M $CuSO_4.5H_2O$), particle size decreased from 65 nm to 30 nm in C1 and CN1, respectively. Similarly, the particle size decreased from 64 nm to 52 nm in C2 and CN2, respectively. The pH plays an important role to control size of the particle [12, 26]. Cu NPs were found to be spherical in shape as reported by another researcher [23].

Ultraviolet-visible spectroscopy

The optical characterization performed by Shimadzu UV-2600 spectrometer ranges between 200 nm to 800 nm. The absorption peak of synthesize Cu NPs were observed between 220 and 310 nm. NPs absorption peak observed at 587 nm prepared by other physical methods [23, 27]. Band gap of NPs were calculated by Tauc's plot on linear fitting. The formula used for the optical band gap calculation given in equation (3).

$$ah\upsilon = \text{A}(\text{h}\vartheta - \text{E}_g)^n \quad \text{.....(3)}$$

Where, A is a constant, hυ is photon energy, Eg is the allowed energy gap, for allowed indirect transition, n = 2. It has been calculated that band gap decrease with increasing pH of electrolyte solution (4.63 eV to 2.98 eV) as shown in Figure 4. The calculated band gap was having higher value than the reported study on Cu NPs [20]. Because, in current synthesis process, the electrolyte solution was solidified on the Cu tape with the deposition of Cu NPs on Cu tape.

Table 1: Details of Sample C_1.

2θ	(*h k l*)	FWHM	Crystallite size	d-spacing	Lattice parameter
43.35	110	0.336	25.15997518	2.08517	2.949
50.44	200	0.31	28.01216209	1.8076	3.615
74.168	220	0.288	34.1933739	1.27746	3.613
89.885	311	0.24	46.24564951	1.0904	3.616
116.9167	400	0.288	52.14470141	0.9038	3.615
136.47	331	0.384	55.17354585	0.82941	3.615
			Avg. Lattice parameter		3.3488 Å

Table 2: Details of Sample CN1.

2θ	(h k l)	FWHM	Crystallite size	d-spacing	Lattice parameter
43.28	111	0.312	27.0887862	2.08859	2.9537
50.31	200	0.096	90.4076915	1.8121	3.6242
74.05	220	0.336	29.2858275	1.27919	3.618
89.928	311	0.384	28.9143612	1.09	3.6151
116.86	400	0.288	52.1027065	0.9041	3.6164
136.486	331	0.336	63.0775404	0.82938	3.6151
			Avg. Lattice parameter		3.50708 Å

Table 3: Details of particle size distribution of C1, C2, CN1, and CN2.

Sample	Electrolyte Solutions	Concentration (M)	Voltage (Volt)	Particle size (nm)
C1	$CuSO_4.5H_2O$	0.1	0.4	65
C2	$CuSO_4.5H_2O$	0.05	0.4	64
CN1	$CuSO_4.5H_2O$+NaOH	0.1	0.4	30
CN2	$CuSO_4.5H_2O$+NaOH	0.05	0.4	52

Conclusion

In conclusion, a simple and cost-effective technique have been used to synthesize Cu NPs by electrodeposition method at room temperature. The synthesized NPs were spherical in shape and could be used for various applications in pure or

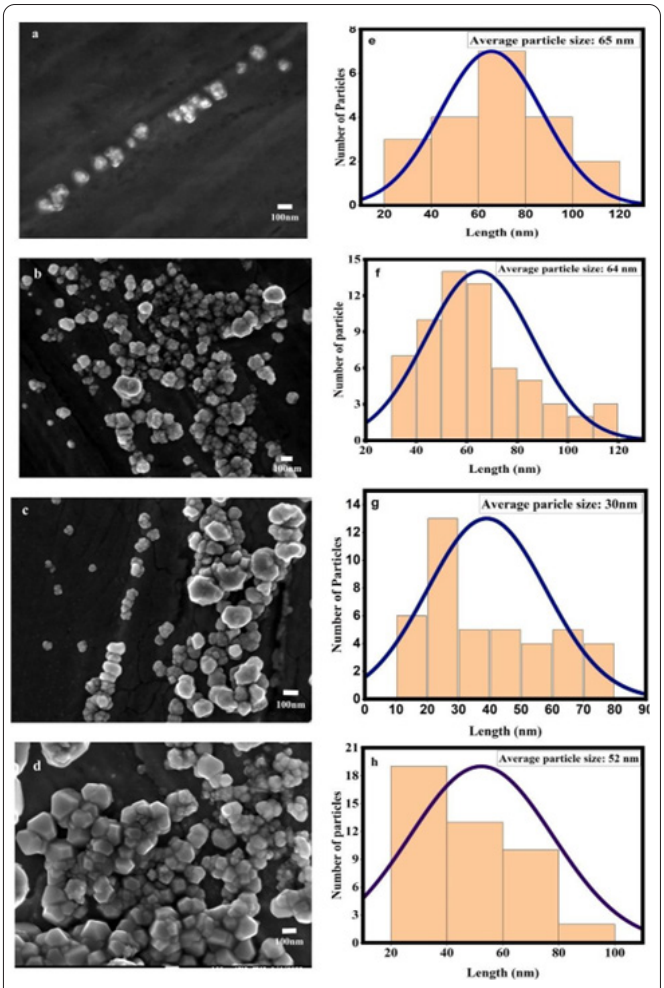

Figure 3: Surface morphology of synthesized Cu NPs (a) electrolyte C_1, (b) C_2, (c) CN_1 and (d) CN_2. Particle size distribution of (e) C_1, (f) C_2, (g) CN_1 and (h) CN_2.

composite form. The size and shape of NPs can be controlled by electrolyte solution concentration and applied voltage on electrodes. The structural and optical characterization shown prominent results by varying pH of the electrolyte solution. It has been also observed that agglomeration was decreasing with increasing pH value.

Acknowledgements

The Authors would like to acknowledge Sophisticated Analytical Instrument Facility (SAIF) and Central Analytical Facilities (CAF,) Manipal University Jaipur, for the provisions of XRD, FESEM and UV-Vis facilities, respectively for characterization. RN also acknowledges the award of the Enhanced Seed Grant Project No. (EF/2019-21/QE04-03) to her by Endowment Fund Committee under Directorate of Research at Manipal University Jaipur. One of the authors (SSR) acknowledge the Science and Engineering Research Board (SERB), Government of India for financial support under sanctioned project no. ECR/2017/002691. The first author would like to acknowledge Human Resource Development Group Council of Scientific & Industrial Research, India for supporting junior research fellowship.

References

1. Gawande MB, Goswami A, Felpin FX, Asefa T, Huang X, et al., 2016. Cu and Cu-based nanoparticles: synthesis and applications in catalysis. *Chem Rev* 116(6): 3722-3811. https://doi.org/10.1021/acs.chemrev.5b00482
2. Kettanah YA. 2019. Copper mineralization and alterations in Gercus Basalt within the Gercus formation, northern Iraq. *Ore Geol Rev* 111: 102974. https://doi.org/10.1016/j.oregeorev.2019.102974
3. Yabuki A, Arriffin N. 2010. Electrical conductivity AR of copper nanoparticle thin films annealed at low temperature. *Thin Solid Films* 518(23): 7033-7037. https://doi.org/10.1016/j.tsf.2010.07.023
4. Khodashenas B, Ghorbani HR. 2014. Synthesis of copper nanoparticles: an overview of the various methods. *Korean J Chem Eng* 31(7): 1105-1109. https://doi.org/10.1007/s11814-014-0127-y
5. Din MI, Rehan R. 2017. Synthesis, characterization, and applications of copper nanoparticles. *Anal Lett* 50(1): 50-62. https://doi.org/10.1080/00032719.2016.1172081
6. Lin CH, Hwang CC. 2016. Multi objective optimization design for a six-phase copper rotor induction motor mounted with a scroll compressor. *IEEE Trans Magn* 52(7): 1-4. https://doi.org/10.1109/TMAG.2016.2517665
7. Raha S, Mallick R, Basak S, Duttaroy AK. 2020. Is copper beneficial for COVID-19 patients? *Med Hypotheses* 142: 109814. https://doi.org/10.1016/j.mehy.2020.109814
8. Ramyadevi J, Jeyasubramanian K, Marikani A, Rajakumar G, Rahuman AA. 2012. Synthesis and antimicrobial activity of copper nanoparticles. *Mater Lett* 71: 114-116. https://doi.org/10.1016/j.matlet.2011.12.055
9. Carbon nanotubes - growth and applications. [https://www.intechopen.com/books/180]
10. Tamilvanan A, Balamurugan K, Ponappa K, Kumar BM. 2014. Copper nanoparticles: synthetic strategies, properties and multifunctional application. *Int J Nanosci* 13(2): 1430001. https://doi.org/10.1142/S0219581X14300016
11. Theivasanthi T, Alagar M. 2011. Nano sized copper particles by electrolytic synthesis and characterizations. *Int J Phys Sci* 6(15): 3662-3671. https://doi.org/10.5897/IJPS10.116
12. Anand V, Harshavardhan, Srivastava VC. 2015. Synthesis and characterization of copper nanoparticles by electrochemical method: effect of pH. *Journal of Nano Research* 31: 81-92. https://doi.org/10.4028/www.scientific.net/JNanoR.31.81.
13. Jain NK, Pathak S, Alam M. 2019. Synthesis of copper nanoparticles by pulsed electrochemical dissolution process. *Ind Eng Chem Res* 58(2): 602–608. https://doi.org/10.1021/acs.iecr.8b03146
14. Boita J, Nicolao L, Alves MCM, Morais J. 2017. Controlled growth of metallic copper nanoparticles. *New J Chem* 41(23): 14478-14485. https://doi.org/10.1039/c7nj03056h
15. Zhang HX, Siegert U, Liu R, Cai WB. 2009. Facile fabrication of ultrafine copper nanoparticles in organic solvent. *Nanoscale Res Lett* 4(7): 705-708. https://doi.org/10.1007/s11671-009-9301-2
16. Guajardo-Pacheco MJ, Morales-Sánchez JE, González-Hernández J, Ruiz F. 2010. Synthesis of copper nanoparticles using soybeans as a chelant agent. *Mater Lett* 64(12): 1361-1364. https://doi.org/10.1016/j.matlet.2010.03.029
17. Park BK, Kim D, Jeong S, Moon J, Kim JS. 2007. Direct writing of copper conductive patterns by ink-jet printing," *Thin Solid Films* 515(19): 7706-7711. https://doi.org/10.1016/j.tsf.2006.11.142
18. Dhas NA, Raj CP, Gedanken A. 1998. Synthesis, characterization, and properties of metallic copper nanoparticles. *Chem Mater* 10(5): 1446–1452. https://doi.org/10.1021/cm9708269
19. He W, Duan XC, Lei Z. 2009. Characterization of ultrafine copper powder prepared by novel electrodeposition method. *J Cent South Univ Technol* 16: 708-712. https://doi.org/10.1007/s11771-009-0117-0
20. Kadam SL. 2016. Synthesis and characterization of copper nanoparti-

cles by using electrochemical method. *International Journal of Scientific & Engineering Research* 7(11): 1067- 1069.

21. Gonçalves RV, Wojcieszak R, Wender H, Dias CSB, Vono LLR et al. 2015. Easy access to metallic copper nanoparticles with high activity and stability for CO oxidation. *ACS Appl Mater Interfaces* 7(15): 7987–7994. https://doi.org/10.1021/acsami.5b00129
22. Mandke MV, Pathan HM. 2012. Electrochemical growth of copper nanoparticles: structural and optical properties. *J Electroanal Chem* 686: 19-24. https://doi.org/10.1016/j.jelechem.2012.09.004
23. Raja M, Shuba J, Ali FB, Ryu SH. 2008. Synthesis of copper nanoparticles by electroreduction process. *Materials and Manufacturing Processes* 23(8): 782-785. https://doi.org/10.1080/10426910802382080
24. Yadav S, Bajpai PK. 2017. Synthesis of copper sulfide nanoparticles: pH dependent phase stabilization. *Nano-Structures and Nano-Objects* 10: 151-158. https://doi.org/10.1016/j.nanoso.2017.03.009
25. Mott D, Galkowski J, Wang L, Luo J, Zhong CJ. 2007. Synthesis of size-controlled and shaped copper nanoparticles. *Langmuir* 23(10): 5740-5745. https://doi.org/10.1021/la0635092
26. Dang TMD, Le TTT, Fribourg-Blanc E, Dang MC. 2011. Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method. *Adv Nat Sci Nanosci Nanotechnol* 2(1): 015009. https://doi.org/10.1088/2043-6262/2/1/015009
27. Jain S, Jain A, Kachhawah P, Devra V. 2015. Synthesis and size control of copper nanoparticles and their catalytic application. *Transactions of Nonferrous Metals Society of China* 25(12): 3995-4000. https://doi.org/10.1016/S1003-6326(15)64048-1