University of Sistan and Baluchestan

Challenges in Nano and Micro Scale Science and Technology

Online ISSN: 2821 - 000X

Synthesis of Copper Oxide Nano Particles: Effect of Rosemary and Olive Leaf Extracts as Surface Modifier

Mahdi Shafiee Afarani[1]✉ | Lale Safaei[2]

1 Department of Materials Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan, Iran. Email: shafiee@eng.usb.ac.ir

2 Department of Materials Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan, Iran.

Article Info

Article type:
Research Article

Keywords:
Extracts of planet leaves,
Nanostructure,
CuO,
Precipitation

ABSTRACT

Copper oxide nano particles were synthesized by precipitation synthesis method. Extracts of rosemary and olive leaves were obtained and used as surface modifiers (SMs) during the synthesis process. Results generally showed that melaconite CuO phase was formed. Furthermore, Fourier transform infrared (FTIR) spectra illustrated corresponding bands of Cu-O bonds in all samples. In addition, scanning electron micrographs (SEM) showed that in all samples, highly agglomerated nano particles were synthesized. Moreover, extracts of rosemary and olive leaves caused to decrease of the particle size of copper oxide samples. Also, atomic force micrographs (AFM) and transmission electron micrographs (TEM) illustrated that the size of particles was in nano range dimension. Moreover, AFM and TEM micrographs showed that morphology of particles was mainly rod-like. Band gap value of samples were estimated based on UV-Vis spectra. Considerable band gap broadening of powders in comparison to the bulk one, was observed and confirmed the formation of synthesized nano particles was occurred.

INTRODUCTION

The synthesis of copper oxide nanoparticles has been extensively studied over the past two decades due to their broad range of applications, such as gas sensors [1–3], photovoltaic devices [4], antibacterial material for food packaging, medical and biological applications [5–7], inks for electronics applications [8,9], catalysts/photoacatalyst [10–12], solar cells [13–15] and batteries [16].

Copper oxide nanoparticles were synthesized via several route such as sol–gel method [17–19] , Sonochemical Synthesis method [20], hydrothermal method [21,22], precipitation method [23–25] and thermal decomposition [26,27] Although several researches has been conducted on the effect of surface modifiers on the synthesis of copper oxide [28–31], several of synthesis methods and its different applications highlight the need for further investigation and comparison.

Some researchers synthesized CuO particles in the presence of different SMs. For example Khosravi et al [32] investigated effect of surface modifiers type including acetic acid, D200, SHMP, PVP, CTAB, SDS, urea, and M2P on the microstructure and optical properties of the copper oxide powders. The results showed different morphologies of copper oxide particles in the forms of needle, round, and flake depending on the type of SMs on the morphology of CuO nano particles.

Moreover, many researches were performed on the green synthesis of nano particles using extracts of plants as reductant agents. However, the use of plant extracts as surface modifier is more than scarce [33].

In this regard extracts of rosemary and olive leaves were prepared and used as surface modifiers in the synthesis of CuO nanoparticles by precipitation method. Synthesis process was carried out using NaOH as strong reduction agent in comparison to extracts. So, extracts of leaves do as SMs dominantly. The structure, microstructure, chemical bonds, and optical band gap value of the nanoparticles were studied.

Experimental

Copper sulfate pentahydrate [$CuSO_4.5H_2O$, GHTARAN SHIMI], Sodium hydroxide (NaOH, MERCK), were used as starting materials. Extracts of rosemary and olive leaves were used as surface modifiers. To prepare extracts, the leaves of rosemary and olive were selected from Zahedan, Iran. 50g of dry leaves were added to 200 ml of distilled water in a 500 ml volumetric flask. The mixture remained at room temperature for 24h and then was filtered and

How to Cite this paper: Shafiee Afarani M. Safaei L. Synthesis of Copper Oxide Nano Particles: Effect of Rosemary and Olive Leaf Extracts as Surface Modifier. *Challenges in Nano and Micro Scale Science and Technology*. 2025; 13(1): 50-55. DOI: 10.22111/cnmst.2026.54636.1280

 Publisher: University of Sistan and Baluchestan.
DOI: 10.22111/cnmst.2026.54636.1280

concentrated via evaporation of solvent at room temperature for 24h to obtain final extracts.

The synthesis of copper oxide was performed based on the work of M. Vaseem et.al [9]. First, an aqueous solution (0.02M) was prepared by dissolution of 0.4994 g copper sulfate in 100 ml distilled water in a volumetric flask. Then, 0.015 g of extract was added to the solution. After that, resultant solution was heated up to 70°C and 0.5g NaOH was immediately added into the solution under stirring for 10 min. Finally, the black gained precipitates were washed by distilled water and dried at 80°C for 1h.

Molecular studies were performed using Fourier transform infrared spectroscope (FTIR, Bruker TENSOR II) which was equipped with platinum ATR accessory with the robust diamond crystal. Structural characterization of samples was performed using XRD (XRD, Philips PW1730) method. Microstructure analyses of samples were performed using field emission scanning electron microscope (FESEM, KYKY EM8000F), Atomic force microscope (AFM, Ara Research - Brisk) and transmission electron microscope (TEM, Philips CM120). UV-visible absorption spectra were measured using a UV–Vis spectrophotometer (Agilent, Carry 60). Band gaps of samples were estimated by plotting $(\alpha h\nu)^2$ versus hν, based on the Tauc equation according to [34], where α is absorption coefficient, h is Plank constant and ν is frequency (s^{-1}).

RESULTS AND DISCUSSIONS

X-ray diffraction (XRD) pattern of the CuO sample synthesized without SMs is represented in figure 1. As illustrated, sample exhibit dominate phase of melaconite CuO (Card No. 00-041-0254), with no detectable secondary phases, indicating high phase purity. The broadening of these peaks is due to nanocrystalline nature of particles.

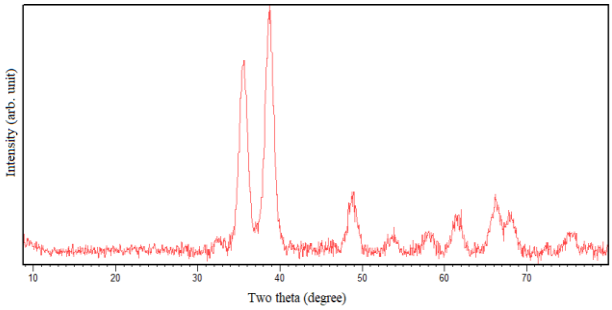

Fig. 1. XRD pattern of the CuO sample synthesized without SMs

Figure 2 shows the FTIR spectra of the CuO samples which were synthesized without SMs and in the presence of extracts of rosemary and olive leaves.

The main bands at about 415-430 and 588-593 cm^{-1} are associated with Cu-O bonds. The main bands at about 404 is attributed to bending Cu-O bonds. Moreover, the bands at about 500 and 608 cm^{-1} are associated with stretching Cu-O bonds. Other bands are attributed to the absorbed water, and functional groups of surface modifiers.

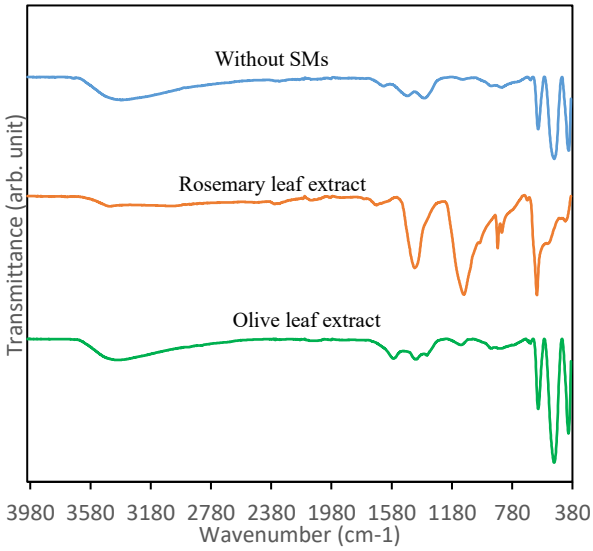

Fig. 2. FTIR spectra of the CuO samples which were synthesized without SMs and in the presence of extracts of rosemary and olive leaves.

UV- Visible spectra of the samples synthesized without SMs and in the presence of extracts of rosemary and olive leaves are shown in figure 3. Generally, for estimating of band gap value, the curve of $(\alpha h\nu)^n$ versus hν should be plotted, where n =2 and 0.5 for direct and indirect transitions, respectively. Since CuO has direct transition, band gaps of the samples were estimated based on the spectra and Tauc equation by plotting $(\alpha h\nu)^2$ versus hν (figure 4) as 2.8, 2.95 and 3.05 eV for, without SMs, olive leaves extract and rosemary leave extracts, respectively. In comparison with bulk CuO band gap, i.e. 1.2 eV, these value resulted in great band splitting, band gap increase and nano size particles. Such increase of band gap values using SMs were reported by Piri et al [35].

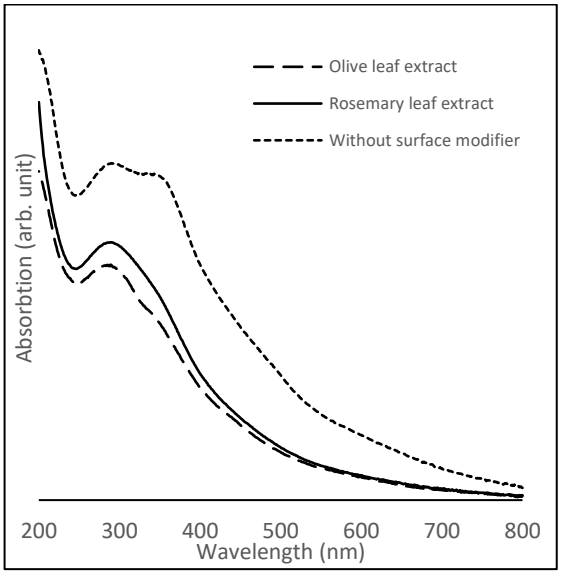

Fig. 3. UV- Visible spectra of the CuO samples which were synthesized without SMs and in the presence of extracts of rosemary and olive leaves.

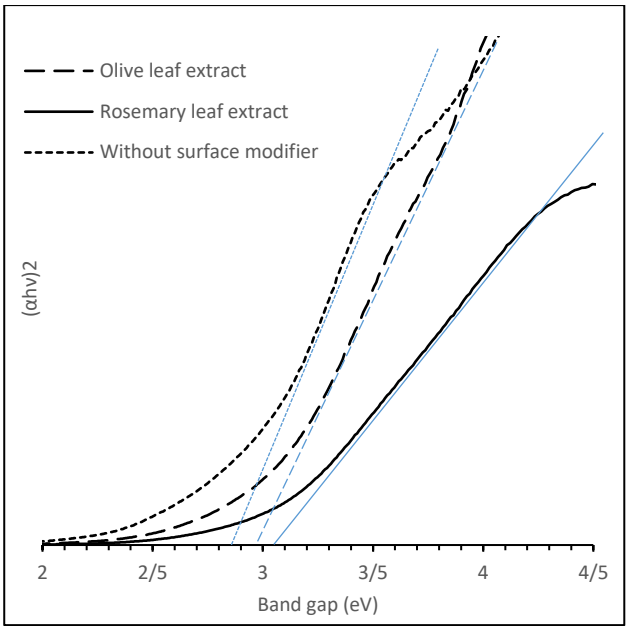

Fig. 4. $(\alpha h\nu)^2$ versus hν of the samples synthesized without SMs and in the presence of extracts of rosemary and olive leaves

SEM micrographs of the samples synthesized without SMs and in the presence of extracts of rosemary and olive leaves are shown in figures 5a to c, respectively. As shown, all samples were formed from nano particles, and were agglomerated irregularly. Moreover, extracts of rosemary and olive leaves acted as surface modifiers and decreased particle slightly. Based on SEM micrographs, particle size distributions of synthesized samples were plotted in figure 5d. As illustrated all powders were in nano size scale range. Mean particle size of the samples synthesized without SMs and in the presence of extracts of rosemary and olive leaves were calculated as 57, 32 and 22 nm, respectively. As expected, extracts of leaves caused to narrower particle size distributions and smaller in size. Since extract of plant leaf is composed from various components, it is very difficult to determine the mechanism of function of each of them. Generally, fatty acid components are in the extracts of plants which have many ionic groups and organic chains in turn act as surface modifiers and cause to decrease of particle size.

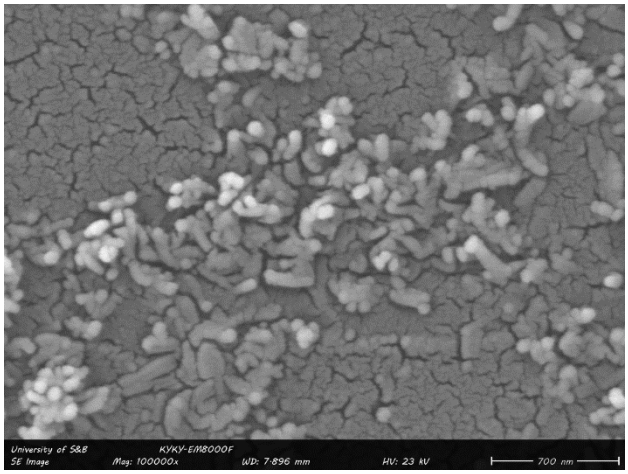

Fig. 5a

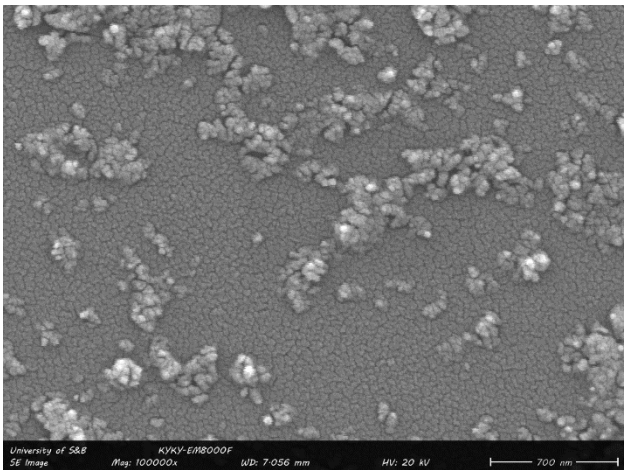

Fig. 5b

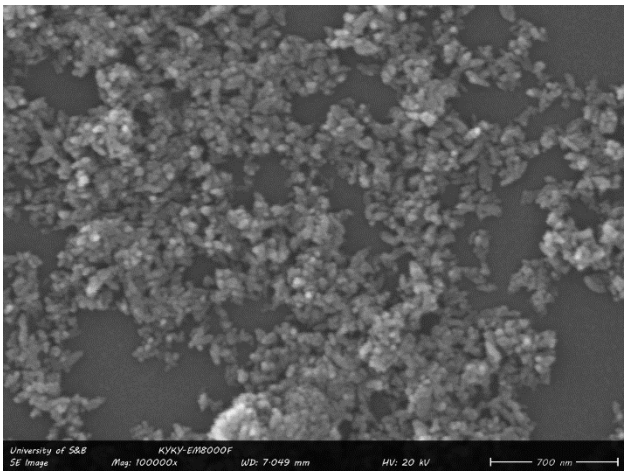

Fig. 5c

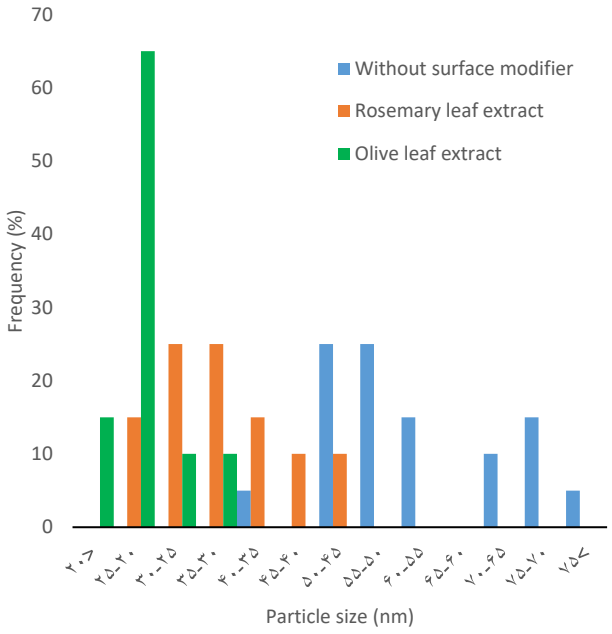

Fig. 5d

Fig. 5. SEM micrographs of samples synthesized a) without SMs and in the presence of extracts of b) rosemary, c) olive leaves and d) corresponded particle size distributions

Figures 6a to c showed AFM micrographs and corresponded profiles of samples synthesized without SMs and in the presence of extracts of rosemary and olive leaves, respectively. Considering x-y profiles illustrated that all samples were formed in rod-like morphology.

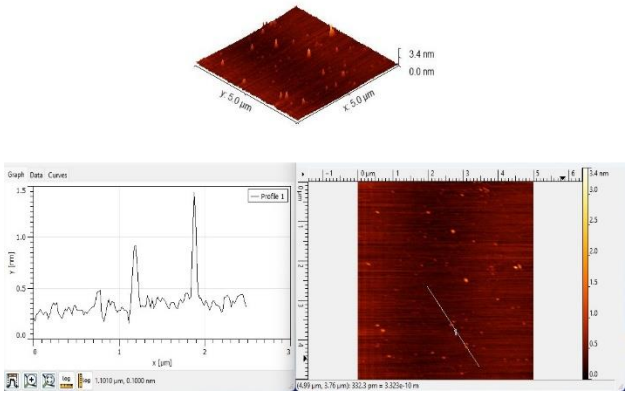

Fig. 6a

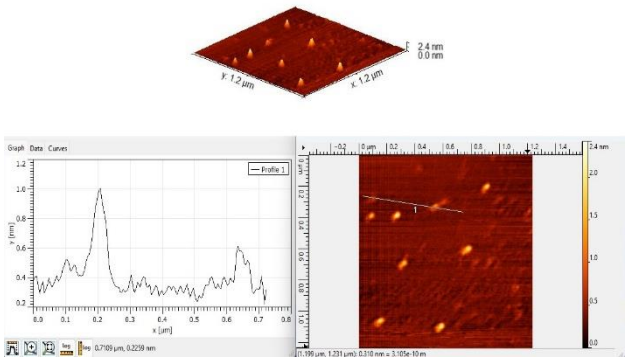

Fig. 6b

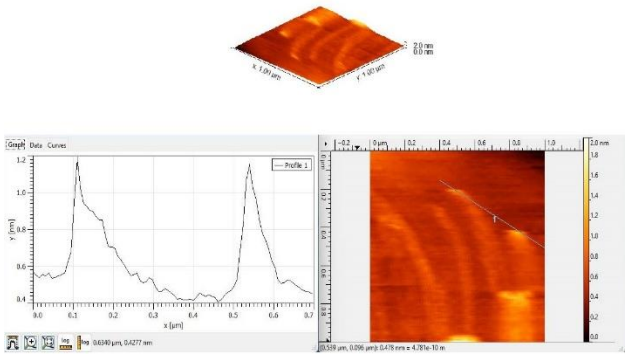

Fig. 6c

Fig. 6. AFM micrographs and corresponded profiles of samples synthesized a) without SMs and in the presence of extracts of b) rosemary and c) olive leaves

TEM micrograph of the sample synthesized without SMs is shown in figure 7. As illustrated, rod like particles were formed in nanoscales which were highly agglomerated.

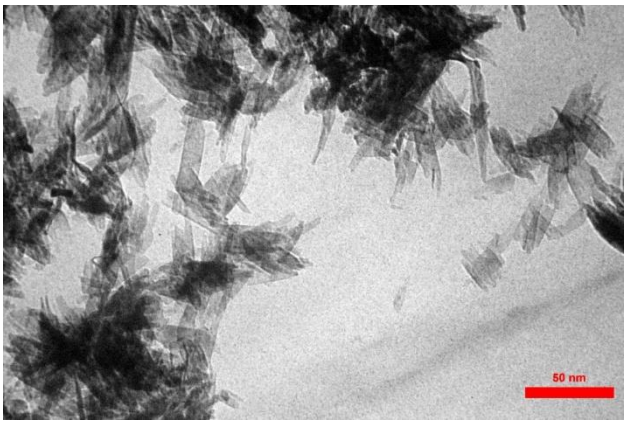

Fig. 7. TEM micrograph of the sample synthesized without SMs

CONCLUSIONS

The present work focused on the precipitation synthesis of copper oxide nanoparticles without/ in the presence in the presence of extracts of rosemary and olive leaves. XRD patterns showed that nano CuO with no minor phase were synthesized. FTIR spectra confirmed the presence of characteristic Cu–O bond bands in all samples. SEM, AFM and TEM micrographs revealed that all samples consisted of highly agglomerated, rod-like nanoparticles. The considerable broadening of the band gap in the powders confirms the nanoscale nature of the synthesized particles which is higher than the bulk CuO.

REFERENCES

[1] Zhang M, Lv X, Wang T, Pei W, Yang Y, Li F, et al. CuO-based gas sensor decorated by polyoxometalates electron acceptors: From constructing heterostructure to improved sensitivity and fast response for ethanol detection. Sens Actuators B Chem. 2024;415:136016. doi:10.1016/j.snb.2024.136016.

[2] Steinhauer S. Gas sensors based on copper oxide nanomaterials: A review. Chemosensors. 2021;9:51. doi:10.3390/chemosensors9030051.

[3] Bhat N, Ukkund SJ, Ashraf M, Acharya K, Ramegouda NJ, Puthiyillam P, et al. GO/CuO nanohybrid-based carbon dioxide gas sensors with an Arduino detection unit. ACS Omega. 2023;8:32512–32519. doi:10.1021/acsomega.3c02598.

[4] Lakshmanan A, Alex ZC, Meher SR. Recent advances in cuprous oxide thin film based photovoltaics. Mater Today Sustain. 2022;20:100244. doi:10.1016/j.mtsust.2022.100244.

[5] Gopinath K, Sathishkumar G, Xu L. An overview of the copper oxide nanofillers integrated in food packaging systems. Coatings. 2024;14:81. doi:10.3390/coatings14010081.

[6] Gunaki MN, Masti SP, D'Souza OJ, Eelager MP, Kurabetta LK, Chougale RB, et al. Fabrication of CuO nanoparticles embedded novel chitosan/hydroxypropyl cellulose bio-nanocomposites for active packaging of jamun fruit. Food Hydrocoll. 2024;152:109937. doi:10.1016/j.foodhyd.2024.109937.

[7] Gvozdenko AA, Siddiqui SA, Blinov AV, Golik AB, Nagdalian AA, Maglakelidze DG, et al. Synthesis of CuO nanoparticles stabilized with gelatin for potential use in food packaging applications. Sci Rep. 2022;12:12843. doi:10.1038/s41598-022-16878-w.

[8] Rahman MK, Lee JS, Kwon KS. Fine conductive line printing of high viscosity CuO ink using near field electrospinning (NFES). Sci Rep. 2023;13:17668. doi:10.1038/s41598-023-45083-6.

[9] Vaseem M, Hong AR, Kim RT, Hahn YB. Copper oxide quantum dot ink for inkjet-driven digitally controlled high mobility field effect transistors. J Mater Chem C. 2013;1:2112. doi:10.1039/c3tc00869j.

[10] Raizada P, Sudhaik A, Patial S, Hasija V, Parwaz Khan AA, Singh P, et al. Engineering nanostructures of CuO-based photocatalysts for water treatment: Current progress and future challenges. Arab J Chem. 2020;13:8424–8457. doi:10.1016/j.arabjc.2020.06.031.

[11] Sibhatu AK, Weldegebrieal GK, Sagadevan S, Tran NN, Hessel V. Photocatalytic activity of CuO nanoparticles for organic and inorganic pollutants removal in wastewater remediation. Chemosphere. 2022;300:134623. doi:10.1016/j.chemosphere.2022.134623.

[12] Assaouka HT, Daawe DM, Fomekong RL, Nsangou IN, Kouotou PM. Inexpensive and easily replicable precipitation of CuO nanoparticles for low temperature carbon monoxide and toluene catalytic oxidation. Heliyon. 2022;8:e10689. doi:10.1016/j.heliyon.2022.e10689.

[13] Ahmmed S, Aktar A, Tabassum S, Rahman MH, Rahman MF, Ismail ABMd. CuO based solar cell with V2O5 BSF layer: Theoretical validation of experimental data. Superlattices Microstruct. 2021;151:106830. doi:10.1016/j.spmi.2021.106830.

[14] Benaissa N, Garmim T, El Boughdadi M, El Jouad Z, Louardi A, Hartiti B, et al. Experimental and numerical simulation studies of CuO thin films based solar cells. Eng Res Express. 2023;5:045038. doi:10.1088/2631-8695/ad05b3.

[15] Akter S, Sikdar TT, Sultana M, Ahmed S, Bashar MS, Rahman MK. Enhancing the performance of CuO thin film in solar cell by introducing optimum amount of Ni doping. J Mater Sci Mater Electron. 2024;35:1299. doi:10.1007/s10854-024-13053-x.

[16] Singh J, Lee S, Tomar A, Zulkifli, Kim J, Rai AK. Surfactant-mediated synthesis of novel mesoporous hollow CuO nanotubes as an anode material for lithium-ion battery application. ChemistrySelect. 2023;8:e202203755. doi:10.1002/slct.202203755.

[17] Wang F, Li H, Yuan Z, Sun Y, Chang F, Deng H, et al. A highly sensitive gas sensor based on CuO nanoparticles synthetized via a sol–gel method. RSC Adv. 2016;6:79343–79349. doi:10.1039/C6RA13876D.

[18] Dörner L, Cancellieri C, Rheingans B, Walter M, Kägi R, Schmutz P, et al. Cost-effective sol-gel synthesis of porous CuO nanoparticle aggregates with tunable specific surface area. Sci Rep. 2019;9:11758. doi:10.1038/s41598-019-48020-8.

[19] Mai XT, Duong TM, Nguyen DN, To TH, Luc HH, Tran PD, et al. Sol–gel synthesis of CuO nanoparticles and its use as catalyst for electrochemical CO_2 reduction. Energy Technol. 2025;13:2401486. doi:10.1002/ente.202401486.

[20] Silva N, Ramírez S, Díaz I, Garcia A, Hassan N. Easy, quick, and reproducible sonochemical synthesis of CuO nanoparticles. Materials (Basel). 2019;12:804. doi:10.3390/ma12050804.

[21] Pană IO, Ciorîță A, Boca S, Guțoiu S, Kacso I, Miclăuș MO, et al. Interaction of manganese-doped copper oxide nano-platelets with cells: Biocompatibility and anticancer activity assessment. Biomimetics (Basel). 2025;10:203. doi:10.3390/biomimetics10040203.

[22] Gounder Thangamani J, Khadheer Pasha SK. Hydrothermal synthesis of copper oxide nanoparticles with highly enhanced BTEX gas sensing performance using chemiresistive sensor. Chemosphere. 2021;277:130237. doi:10.1016/j.chemosphere.2021.130237.

[23] Rahnama A, Gharagozlou M. Preparation and properties of semiconductor CuO nanoparticles via a simple precipitation method at different reaction temperatures. Opt Quant Electron. 2012;44:313–322. doi:10.1007/s11082-011-9540-1.

[24] Nahar B, Chaity SB, Gafur MA, Hossain MZ. Synthesis of spherical copper oxide nanoparticles by chemical precipitation method and investigation of their photocatalytic and antibacterial activities. J Nanomater. 2023;2023:1–10. doi:10.1155/2023/2892081.

[25] John AS, Gurumurthy K. Synthesis and characterization of CuO nanoparticles from bioleached copper through modified and optimized double precipitation method. ACS Omega. 2025;10:10193–10198. doi:10.1021/acsomega.4c09064.

[26] Abdel-Monem YK, Emam SM, Okda HMY. Solid state thermal decomposition synthesis of CuO nanoparticles from coordinated pyrazolopyridine as novel precursors. J Mater Sci Mater Electron. 2017;28:2923–2934. doi:10.1007/s10854-016-5877-3.

[27] Abdelghany MM, Ahmed IS, Dessouki HA, Abdelrahman EA. Facile synthesis of CuO and Ag nanoparticles by thermal decomposition of novel Schiff base complexes. J Inorg Organomet Polym Mater. 2021;31:4281–4299. doi:10.1007/s10904-021-02032-y.

[28] Mandal S, Hazra C, Joshi N, Kumar P, Sen R, Das S, et al. Comparative insights of bio and chemical surfactants in CuO nanoparticle synthesis: Unveiling the superior antibacterial efficacy of biosurfactants. J Ind Eng Chem. 2025;147:566–583. doi:10.1016/j.jiec.2024.12.046.

[29] Siddiqui H, Qureshi MS, Haque FZ. Surfactant assisted wet chemical synthesis of copper oxide (CuO) nanostructures and their spectroscopic analysis. Optik. 2016;127:2740–2747. doi:10.1016/j.ijleo.2015.11.220.

[30] Ravishankar TN, Vaz MdO, Teixeira SR. The effects of surfactant in the sol–gel synthesis of CuO/TiO_2 nanocomposites on its photocatalytic activities under UV-visible and visible light illuminations. New J Chem. 2020;44:1888–1904. doi:10.1039/C9NJ05246A.

[31] Singh Z, Singh I. CTAB surfactant assisted and high pH nano-formulations of CuO nanoparticles pose greater cytotoxic and genotoxic effects. Sci Rep. 2019;9:5880. doi:10.1038/s41598-019-42419-z.

[32] Khosravi MD, Ghahari M, Shafiee Afarani M, Arabi AM. Synthesis of CuO and CuO/ZnO composite powders for antibacterial, photocatalytic and pigment-related applications. Adv Ceram Prog. 2022;8(1):1–8. doi:10.30501/acp.2022.329820.1082.

[33] Nieto-Maldonado A, Bustos-Guadarrama S, Espinoza-Gomez H, Flores-López LZ, Ramirez-Acosta K, Alonso-Nuñez G, et al. Green synthesis of copper nanoparticles using different plant extracts and their antibacterial activity. J Environ Chem Eng. 2022;10:107130. doi:10.1016/j.jece.2022.107130.

[34] Abbasian AR, Shafiee Afarani M. One-step solution combustion synthesis and characterization of $ZnFe_2O_4$ and $ZnFe_{1.6}O_4$ nanoparticles. Appl Phys A. 2019;125:—. doi:10.1007/s00339-019-3017-7.

[35] Piri F, Shafiee Afarani M, Arabi AM. Synthesis of copper oxide quantum dots: Effect of surface modifiers. Mater Res Express. 2019;6:125006. doi:10.1088/2053-1591/ab548d.