



## Preparation of CuO/ZnO Nano-Particles Using Sol-Gel Technique and Studying the Characterization

Doaa A.Yassen<sup>a\*</sup>, Farhad M. Othman<sup>a</sup>, Alaa A. Abdul Hamead<sup>b</sup>

<sup>a</sup>, Materials Engineering Dept., University of Technology-Iraq, Alsina'a Street, 10066 Baghdad, Iraq.

<sup>b</sup> Building & Construction Engineering Dept., Al-Mustaqbal University College, Babylon, Iraq.

\*Corresponding author Email: [doaa.ahmad@mustaqbal-college.edu.iq](mailto:doaa.ahmad@mustaqbal-college.edu.iq)

### HIGHLIGHTS

- The sol-gel technique was used to make Nano composite particles NCPs of ZnO-CuO.
- FESEM scans revealed nanoparticles incorporated in the ZnO-CuO matrix with particle sizes ranging from 60.76 to 145.1 nm.
- The density of the aforesaid samples was 0.1382, 0.1418, and 0.1469 g/cm<sup>3</sup> in that order, increasing as the calcined duration increased.
- This promotes crystal formation, and CuO/MgO has strong catalytic activity for advanced applications.

### ABSTRACT

Copper oxide (CuO) and zinc oxide (ZnO) are two of the most promising oxides under development right now. The sol-gel technique was used to make Nano composite particles NCPs of ZnO-CuO. The copper (II) nitrate rehydrate 0.1M and zinc nitrate hex hydrate 0.1M liquids were mixed in a 1:1 ratio, and the gel was formed at 80 °C, then dried and calcined for various times 500 °C (3, 5, and 7 hours). Particle size analyzer (PZA), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and apparent density were used to characterize the CuO/MgO particles. The x-ray diffraction results showed that the phases of the composite particles were pure. FESEM scans, on the other hand, revealed nanoparticles incorporated in the ZnO-CuO matrix with particle sizes ranging from 60.76 to 145.1 nm. The density of the aforesaid samples was 0.1382, 0.1418, and 0.1469 g/cm<sup>3</sup> in that order, increasing as the calcined duration increased. This promotes crystal formation, and CuO/MgO has strong catalytic activity for advanced applications.

### ARTICLE INFO

**Handling editor:** Jawad K. Olewi

**Keywords:** Nano composite particles, Copper oxide, Zinc oxide, and Sol-gel.

## 1. Introduction

Because of their unique physical and chemical features, innovative materials have sparked a surge in interest in recent years. The particle size of these materials is dictated by the conditions under which they were prepared in the lab. As a result, various experimental procedures have been used in the synthesis of nanoparticles, including the sol-gel technique and liquid-solvent techniques. [1], as well as others. For the first time in history, sol-gel processing techniques have been applied for decorative and building materials; numerous new uses have been developed in the recent century. Sol-gel techniques are now reaching their maximum potential, allowing new generations of advanced materials to be prepared that are not readily accessible by other techniques while still using moderate, low-energy conditions[2]. Initially, based on empirical evidence, but later on, a more scientific basis as modern characterization techniques became available. Sol-gel techniques are now reaching their maximum potential, allowing new generations of advanced materials to be prepared that are not readily accessible by other techniques while still using moderate, low-energy conditions. Individual properties of transition metal oxides (TMO) such as MnO<sub>2</sub>, RuO<sub>2</sub>, TiO<sub>2</sub>, ZnO, BaTiO<sub>3</sub>, ReO<sub>3</sub>, NiO<sub>2</sub>, CuO, and others have resulted in numerous technical applications. These applications include microelectronics, bio and gas sensors, batteries, solar cells, fuel cells, super capacitors, pigments, and multiferroics. These materials have unique and useful electrical and magnetic properties. The TMO mixing produces sophisticated compounds with a wide range of characteristics. [3-7] Transition metal oxides are particularly interested in copper oxide nanoparticles because of their usefulness as Nano fluids [8], antibacterial applications [10], catalysis[11], superconductors[12], energy storage systems[13], and anti-cancer agents[14]. To date, mechanical, physical, biological, and hybrid approaches have been used to make copper oxide nanoparticles [15]. ZnO.NPS has been used in various technologies and industries, including optoelectronics,

piezoelectric and magnetic sensors, diagnostics, bio labeling, ceramic and rubber processing, and the atmosphere [16–18]. It can represent a wide range of bio-safe, non-toxic, and biocompatible nanostructures. ZnO has a lot of OH groups on its surface, which allows it to dissolve slowly in both acidic (like tumor cells and the tumor microenvironment) and strong basic environments. Biomedical researchers have taken notice of ZnO.NPS because of this property [19]. Because of their expanding usage in medicine as anti-angiogenesis, anti-platelet agents, anti-inflammatory drugs, dental products, cosmetics, narcotics, and gene transfer, ZnO.NPs have emerged as a prospective anti-cancer agent [20-21]. Composite materials are solids that comprise two or more separate constituent materials or phases of greater size than the atomic scale. Properties such as the elastic modulus are markedly different from those of a homogeneous material [22]. In terms of physicochemical qualities, CuO/ZnO Nano composites outperform pure ZnO and CuO nanostructures [23]. The optical and electrical properties of the CuO/ZnO hetero junction are also improved, making it a viable photocatalysis candidate [24]. Inorganic antimicrobials have been promoted for pollution control because they offer benefits similar to natural antimicrobials, such as decreased host disruption, more stable bacteria tolerance, and high selectivity [25]. Inorganic nanoparticles with antibacterial action and metal oxide nanoparticles are well-known. Metal oxides have rapid synthesis pathways that may be utilized to modify the size and shape of nanoparticles, and they are less expensive than metal nanoparticles such as silver and gold. Organic antibacterial alternatives such as zinc and copper oxides are thought to be effective [26].

This study aims to use the sol-gel process to manufacture (MgO – ZnO) Nano composite particles with good mechanical properties.

## 2. Experimental section

### 2.1 Materials

Analytical grade copper (II) nitrate rehydrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ], extra pure with Mol. Wt. 241.60 from HIMEDIA (GRM1363-500G), Zinc nitrate hex hydrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], purified with Mol. Wt.: 297.49 from HIMEDIA (GRM691-500G) were used as starting materials; double distilled water was used as a solvent. Citric acid AR monohydrate ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ ) with Mol. Wt. 210.14 From ALPHA (Sr.No:AL1238) was taken as a chelating agent.

### 2.2 Procedures

50 ml double distilled water was mixed with 0.1M copper (II) nitrate rehydrate [ $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ] and 0.1M zinc nitrate hex hydrate [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] for the manufacture of CuO/MgO NCPs by sol-gel. 0.025 M citric acid was diluted into beakers separately in 50 ml distilled water. They used a magnetic stirrer to stir for 60 minutes. Citric acid was added drop-wise to the aforementioned mixture at room temperature. At a temperature of 80 °C and continual stirring, a gel forms after 3 hours. The gel is cured for 4 hours in an electric oven at 130°C. At a different time, the dry gel is claimed at 500 °C (3, 5, and 7 hours). The CuO/ZnO Nano composite particles processes are shown in Figure 1.

### 2.3 Characterization

A powder X-ray Diffract meter (Shimadzu 7000; using Cuka radiation ( $k = 1.5418$ ) in the range of 10–79 in steps of 0.0500 at a scan speed of 1/min) is used to study particle-phase purity and crystallinity. The morphological features and particle size were examined using scanning electron microscopy (FESEM), TESCAN (Czech Republic). We used the bettersize2000 laser particle size analyzer as a particle size analyzer. First, the apparent density of the particle was calculated. Then, the density of solid powders (CD, CuO/ZnO) that do not dissolve in water was measured using a pycnometer. To begin, weigh the pycnometer and the weight of the pycnometer with solid powder. Water was then added, and the weight of the water (Mw) was calculated [27].

## 3. Results and Discussions

### 3.1 Particle Size Analyser and Density Results

Figure 2-(a, b, and c) shows the particle size of CuO/ZnO with a ratio of 1:1 after 3 hours, 5 hours, and 7 hours, which are 0.647, 0.622, and 0.732 m, respectively. Because of the agglomerations of the particles, this assay could not identify the Nano scale in the size of the NCPs. Therefore, FESEM was used to measure the results. The density of the aforesaid samples was 0.1382, 0.1418, and 0.1469  $\text{g}/\text{cm}^3$  in order, with the density increasing as the claimed duration increased [28]. This is due to the elimination of superfluous holes and spaces, which drive crystal development.

### 3.2 Scanning electron microscopy (FESEM) results

Figure 3- (a,b, and c) depicts typical FESEM images of CuO/ZnO in various calcined at 500 °C at various times (3, 5, and 7 hours). The particle size of CuO/ ZnO Nano composites with small agglomeration was discovered to be around 73.80–120.3 nm after 3 hours of calcination, confirming fully nodular shaped particles CuO/ ZnO Nano composites with minor agglomeration. Particles size were 60.76–145.1 nm after 5 hours of claiming, and 64.60–133.5 nm after 7 hours of calcining. The production of nanoparticles in CuO/ MgO may be seen in FESEM pictures at all calcined periods. These findings are in line with material science discoveries, which show that grain size, temperature, and time are linked by an Arrhenius-type equation:

$$D^n - D_0^n = k_0 \exp(-Q/RT) (t-t_0) \quad (1)$$

Where  $D$  represents the ultimate grain size at time  $t$ ,  $D_0$  represents the initial grain size at a time  $t_0$ ,  $k_0$  represents a pre-exponential factor,  $Q$  represents the activation energy, and  $T$  represents the temperature in Kelvin [30].



Figure 1: The preparation of CuO/ZnO NCPs

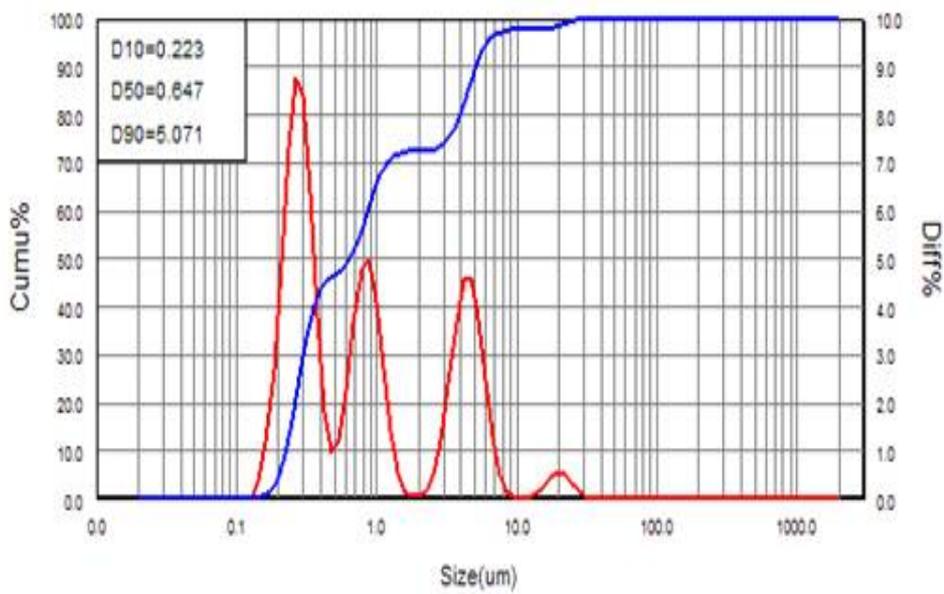


Figure 2: A Particle size of CuO/ ZnO NCPs calcined at 500 °C for 3 hours

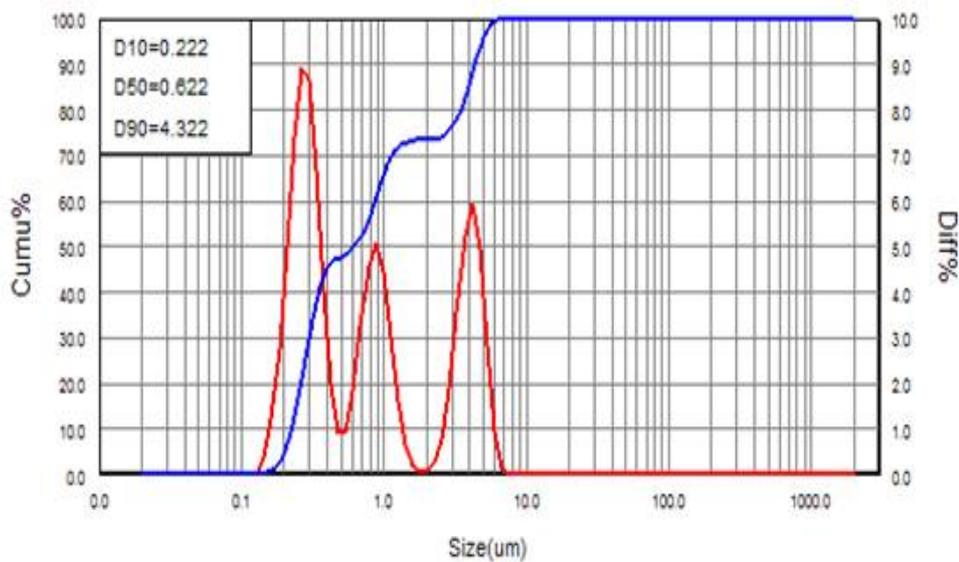


Figure 2: B Particle size of CuO/ ZnO NCPs calcined at 500 °C for 5 hours

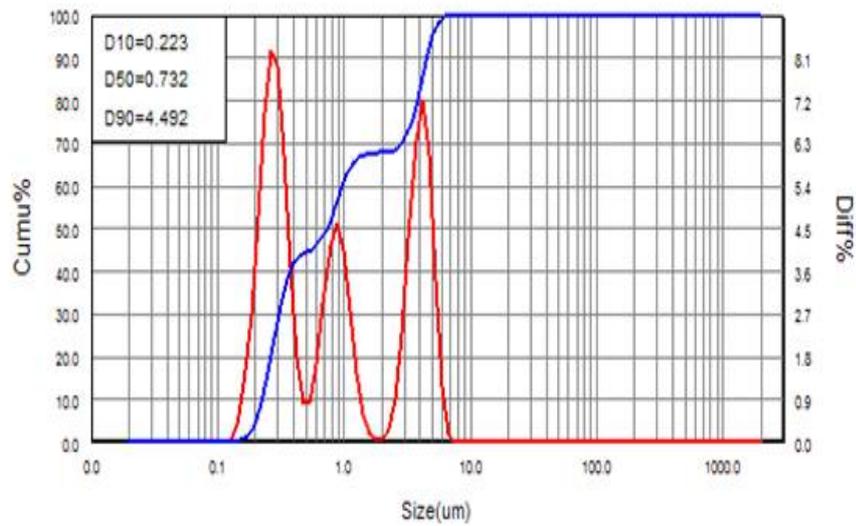


Figure 2: C Particle size of CuO/ ZnO NCPs calcined at 500 °C for 7 hours

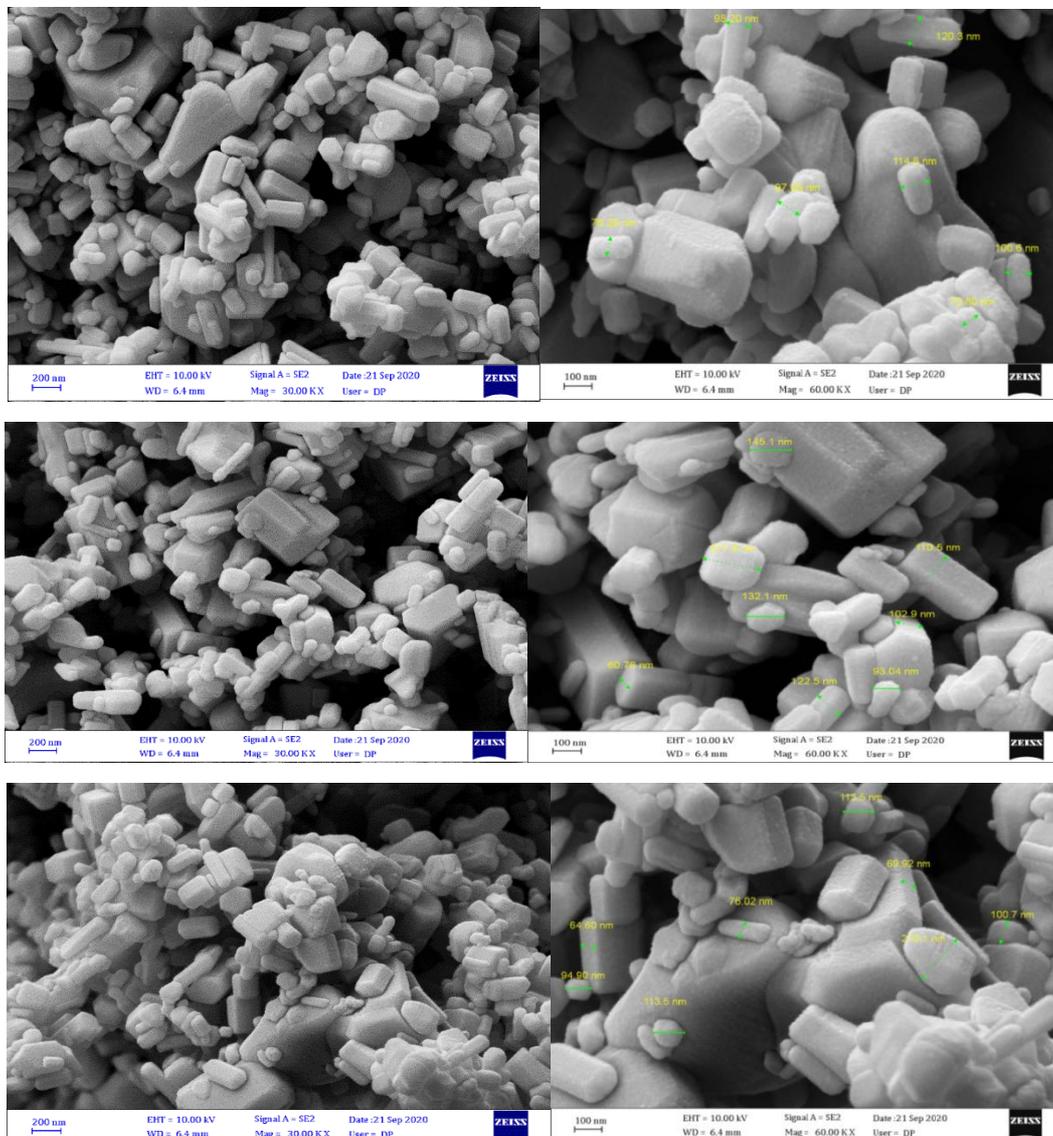


Figure 3: (A) FESEM image of CuO/ZnO NCPs calcined at 500 °C for 3 hours, (B) FESEM image of CuO/ZnO NCPs calcined at 500 °C for 5 hours, (C) FESEM image of CuO/ZnO NCPs calcined at 500 °C for 7hours

### 3.3 X-ray diffraction (XRD) results

Figure 4 depicts the XRD pattern. The spectrum shows that doped CuO Nano samples have high crystallinity. CuO and ZnO have a simple phase difference in Figure 4, demonstrating that both CuO and ZnO exist. In addition, CuO's diffraction profiles were reported at two values:  $32.52^\circ$  (110),  $36.04^\circ$  (011),  $48.5^\circ$  (202) (JCPDS44-0706), and ZnO's diffraction profiles were reported at two values:  $31.82$  (100),  $34.50$  (002), and  $36.32$  (101) (JCPDSno.36-1451) [31]. CuO monoclinic phase is indicated by the diffraction peak. CuO/ZnO Nano composites also showed a small peak at  $38.8^\circ$ , attributed to the CuO. (111). When ZnO was added to CuO, the diffraction intensities and angles improved considerably. According to the results of the X-ray investigation, the substance is crystalline and has a small granular size and a small pore size, which confirms the FESEM [32-34] results.

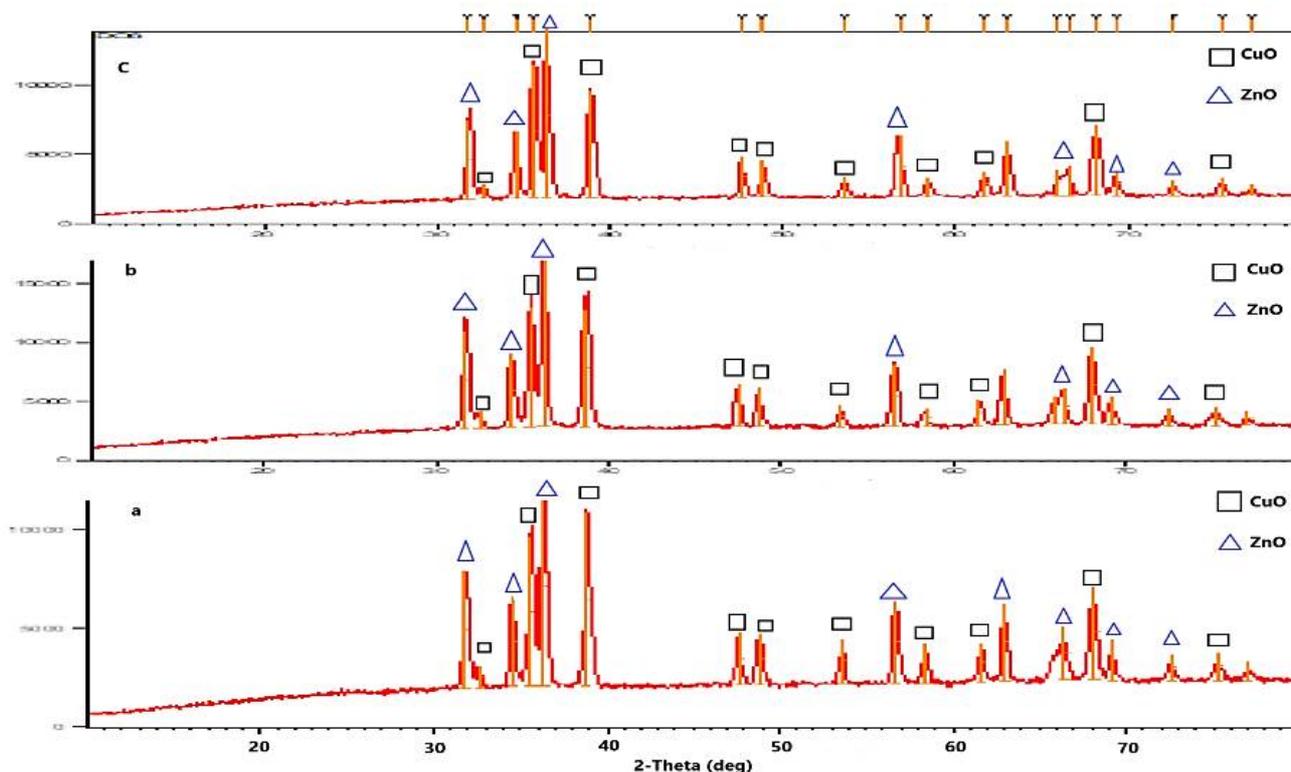


Figure 4: XRD image of CuO/ZnO NCPs calcined at  $500^\circ\text{C}$  for (a) 3 hours, (b) 5 hours, and (c) 7 hours

## 4. Conclusions

Based on this study's tests' results, XRD data showing CuO and ZnO oxides, it is safer, easier to do, and more cost-effective. The peak of diffraction indicates CuO's monoclinic phase. In addition, it was observed that the diffraction profiles that correspond to ZnO are less owing to a lesser compositional ratio attributable to CuO's diffraction. From the X-ray examination results, the structural perfection and the growth features of the synthesized crystals were studied to eliminate excess pores and voids. The quality of the NCPs was visualized by observing the surface morphology using SEM studies. It can be observed that the particle size of CuO/ ZnO is about  $60.76 - 145.1\text{nm}$ , and it shows the nodular-shaped particles of CuO/ ZnO Nano composites with small agglomeration. The FESEM images of CuO/ ZnO prove the formation of nanoparticles at all calcined times. The SEM and particle size analyzer results showed the size and size distribution control. The synthesized NCPs could be promising materials for modern materials design due to all these properties.

### Author contribution

All authors contributed equally to this work.

### Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

### Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

### Conflicts of interest

The authors declare that there is no conflict of interest.

## References

- [1] D.M. Fernandes, R. Silva, A.A.Winkler Hechenleitner, E. Radovanovic, M.A. Custodian Melon, and E.A. Gomez Pineda, Synthesis and characterization of ZnO, CuO and a mixed Zn and Cu oxide, *Mater. Chem. Phys.*, 115 (2009) 110–115. <https://doi.org/10.1016/j.matchemphys.2008.11.038>

- [2] Wright, J. D. and A. N.J.M. Sommerdijk, Sol-Gel materials: chemistry and applications, CRC Press, Boca Raton, 1st edition, USA, 2001.
- [3] G. Bodurov, T. V and K. Gesheva, Technology and application of transition metal oxide of W-V-O as functional layers and NiO thin films as counter electrode material in electro chromic smart windows, Phys. Procedia., 46 (2013) 149–58. <https://doi.org/10.1016/j.phpro.2013.07.057>
- [4] D. Guo, G.Liu, X .Li, X .Tang, J.Zhang, X .Zhu, and S. Jiang, Transition metal oxide hierarchical nanotubes for energy applications Nanotechnology, J. Bionanosci, 9 (2015) 325-329.
- [5] I. Hasa, D .Buchholz, S. Passerini and J. Hassoun, A comparative study of layered transition metal oxide cathodes for application in sodium-ion battery, ACS Appl. Mater. Interfaces, 7 (2015) 5206–5212. <https://doi.org/10.1021/am5080437>
- [6] Z. He, L. Dai, S .Liu, L .Wang and C .Li, Mn<sub>3</sub>O<sub>4</sub> anchored on carbon nanotubes as an electrode reaction catalyst of V (IV)/V(V) couple for vanadium redox flow batteries, Electrochim. Acta., 176 (2015) 1434–1440. <https://doi.org/10.1016/j.electacta.2015.07.067>
- [7] V. Subramanian, S.C. Hall, S. P. Rambabu, Mesoporous anhydrous RuO<sub>2</sub> as a super capacitor electrode material, J. Solid State Ion, 175 (2004) 511–5. <http://dx.doi.org/10.1016/j.ssi.2004.01.070>
- [8] A. D. Manasrah, I. W. Almanassra, N. N. Marei, U.A. Al-Mubaiyedh, T. Laoui and M. A. Atieh, Surface modification of carbon nanotubes with copper oxide nanoparticles for heat transfer enhancement of Nano fluids , RSC Adv., 8 (2018) 1791–802. <https://doi.org/10.1039/C7RA10406E>
- [9] S .Chaudhary, D .Rohilla, V.Umar, K.N. Shanavas, Synthesis and characterizations of luminescent copper oxide nanoparticles: toxicological profiling and sensing applications, Ceram. Int., 45 (2019) 15025–15035. <https://doi.org/10.1016/j.ceramint.2019.04.239>
- [10] S. El. Hassan , A. Fouda , A. A. Radwan , S. S. Salem , M.G. Barghoth , M.A Awad , A.M Abdo , and M. S .El-Gamal, Entophytic actinomycetes Streptomyces sap mediated biosynthesis of copper oxide nanoparticles as a promising tool for biotechnological applications, J. Biol. Inorg. Chem., 24 (2019) 377–393. <https://doi.org/10.1007/s00775-019-01654-5>
- [11] R. Kanwar, R. Bhar, and S. Mehta, Designed meso-macroporous silica framework impregnated with copper oxide nanoparticles for enhanced catalytic performance, J. Chem Cat Chem., 10 (2018) 2087–95. <https://doi.org/10.1002/cctc.201701630>
- [12] M.A. Kumar, N. A. Kumar, D. A.Kumar, and P. Debabrata, Microwave-assisted solvothermal synthesis of cupric oxide nanostructures for high-performance super capacitor, J. Phys. Chem. C., 122 (2018) 11249– 11261. <https://doi.org/10.1021/acs.jpcc.8b02210>
- [13] A. Ch. Nwanya, M. M. Ndipingwi, N. Mayedwa,L.C. Razanamahandry,Ch. O. Ikpo,T Waryo,S.K.O. Ntwampe, E. Malenga, E. Fosso-Kankeu, F. I. Ezema, E. I. Iwuoha, and M. Maaza, Maize (Zea mays L.) Fresh husk mediated biosynthesis of copper oxides: Potentials for pseudo capacitive energy storage, J. Electro him Acta., 301 (2019) 436– 448. <https://doi.org/10.1016/j.electacta.2019.01.186>
- [14] R. D Preeth, M .Shairam, N .Suganya, R .Hootan, R .Kartik, K .Pierre, and S. Rajalakshmi, Green synthesis of copper oxide nanoparticles using sinapic acid: an underpinning step towards antiangiogenic therapy for breast cancer, J. Biol. Inorg. Chem., 24 (2019) 633–645. <https://doi.org/10.1007/s00775-019-01676-z>
- [15] D.Renuga, J .Jeyasundari,A.S. S. Athithan andY. B. A. Jacob, Synthesis and characterization of copper oxide nanoparticles using Brassica oleracea var. italic extract for its antifungal application, J. Mater. Res. Express., 7 (2020) 045007. <https://doi.10.1088/2053-1591/ab7b94>
- [16] L. Theodore, Nanotechnology: basic calculations for engineers and scientists, IEEE Electr. Insul. Mag., 22 (2006) 50–51.
- [17] X. Wang, J. Lu, M. Xu, and B. Xing, Sorption of pyrene by regular and nanoscaled metal oxide particles: influence of adsorbed organic matter, J Environ. Sci. Technol., 42 (2008) 7267–7272. <https://doi.org/10.1021/es8015414>
- [18] C. Dagdeviren, S. W. Hwang, Y. Su, S. Kim, H. Cheng, O. Gur, R. Haney, F. G. Omenetto, Y. Huang, and J. A. Rogers, Transient biocompatible electronics and energy harvesters based on ZnO, Small, 9 (2013) 3398–3404. <https://doi.org/10.1002/sml.201300146>
- [19] D. Liu, W. Wu, Y. Qiu, S. Yang, Si Xiao, Qu. Wang, Lu Ding, and J. Wang, Surface functionalization of ZnO Nano tetrapod's with photoactive and electro active organic monolayers, J. Langmuir., 24 (2008) 5052–5059. <https://doi.org/10.1021/la800074f>
- [20] G. Bisht, and S. Rayamajhi, ZnO nanoparticles: a promising anti-cancer agent, Nano Biomed., 3 (2016) 9–20. <https://doi.org/10.5772/63437>
- [21] S. Sonia, L.J. Kumari, H. Ruckmanib, K. Sivakumara, Antimicrobial and antioxidant potentials of biosynthesized colloidal zinc oxide nanoparticles for a fortified cold cream formulation: a potent Nano cosmeceutical application, Mater. Sci. Eng. C., 79 (2017) 581–589. <https://doi.org/10.1016/j.msec.2017.05.059>

- [22] A. H. Waleed , K. H. Abbas, A. S. Hayder, Ceramic filled polymer matrix composite used for bio-medical application, Eng. Technol. J., 29 (2011) 1766-1767.
- [23] S. Kuriakose, D. K. Avasthi, S. Mohapatra, Effects of swift heavy ion irradiation on structural, optical and photo catalytic properties of ZnO–CuO Nano composites prepared by carbothermal evaporation method, Beilstein J. Nanotechnol., 6 (2015) 928–937. <https://doi.org/10.3762/bjnano.6.96>
- [24] R. Saravanan, S. Karthikeyan, V.K. Gupta, G. Sekaran, V. Narayanan, A. Stephen, Enhanced photo catalytic activity of ZnO/CuO Nano composite for the degradation of textile dye on visible light illumination, J. Mater. Sci. Eng., 33 (2013) 91–98. <https://doi.org/10.1016/j.msec.2012.08.011>
- [25] T. A. Saleh, G. Fadillah, and O. A. Saputra, Nanoparticles as components of electrochemical sensing platforms for the detection of petroleum pollutants: a review, TrAC, Trends Anal. Chem., 118 (2019) 194-206. <https://doi.org/10.1016/j.trac.2019.05.045>
- [26] V. Apalangya, Y. D. Bensah, and E. Annan, Synthesis and characterization of zinc and copper oxide nanoparticles and their antibacterial activity, Res. Mater., 20 (2020) 30041-8.
- [27] J. Oremusová and M. Vojteková, Density determination of liquids and solids, Manual for laboratory practice, UK, 1999.
- [28] A. A. Abdul Hamead, Fabrication and AFM characterization of selenium recycled Nano particles by pulse laser evaporation and thermal evaporation, J. Mater. Res. Express., 6 (2020) 12. <https://doi.10.1088/2053-1591/ab6a50>
- [29] H. A. Sallal, A. A. Abdul Hamead, and F. M. Othman, Preparation of Al<sub>2</sub>O<sub>3</sub>/MgO Nano-composite particles for bio-applications. Eng. Technol, J., 38 (2020) 586-583. <https://doi.10.30684/etj.v38i4A.290>
- [30] H. Marco, B. Alfons, Differences in grain growth of calcite: a field-based modeling approach, Contrib. Mineral. Petrol., 145 (2003) 600–611. <http://dx.doi.org/10.1007/s00410-003-0473-y>
- [31] R. Lamba, A. Umar, S. K. Mehta, S. K. Kansal, Sb<sub>2</sub>O<sub>3</sub>–ZnO Nano spindles: A potential material for photo catalytic and sensing applications, J. Ceram. Int., 41 (2015) 5429–5438. <https://doi.org/10.1016/j.ceramint.2014.12.109>
- [32] A. M. Abdul Majeed, I. F. Hussein, R. O. Abd Al-Jalil, Fabrication of high responsively for MgO NPs/PSi heterojunction device by sol-gel technique, Springer, 12 (2019) 1007–1010. <https://doi.org/10.1007/s12633-019-00188-4>
- [33] G. S. Campos, D. C. German, J. A. G. Valenzuela, M. C. Leal, J. L. F. Rios, M. M. Gil, H. Hu, and M. S. Lerma, Controlled synthesis of Mg(OH)<sub>2</sub> thin films by chemical solution deposition and their thermal transformation to MgO thin films, Ceram. Int., 45 (2019) 10356-10363. <https://doi.org/10.1016/j.ceramint.2019.02.093>
- [34] P. A. Tran, L. Sarin, R. H. Hurt, and T. J. Webster, Differential effects of Nano selenium doping on healthy and cancerous osteoblasts in culture on titanium, Int. J. Nanomedicine., 5 (2010) 351–358. <https://doi.org/10.2147/IJN.S7289>