



CHARACTERIZATION OF BIOFABRICATION COPPER (II) OXIDE NANOPARTICLES AND INVESTIGATE THE PHOTOCATALYTIC EFFICIENCY

Doaa Domyati^[a]

Article History: Received: 16.12.2021

Revised: 15.01.2022

Accepted: 10.02.2022

Abstract: Photocatalysis utilizes photonic energy to begin the substance response. The absolute most continuous purposes of photocatalytic oxidation responses are contamination decrease, self-cleaning, and self-sanitizing items. Thus in this current review intended to orchestrate the copper (II) oxide nanoparticles utilizing citrus extract with co-precipitation procedures. UV-Vis spec, SEM, HRTEM, XRD, and FTIR examinations were utilized to explore the physicochemical properties of delivered copper (II) oxide nanoparticles in this review. As indicated by the Xrd designs and direct HRTEM estimations, the normal molecule size of copper (II) oxide nanoparticles was around 30-50 nm in the current review. The agglomerated circles were portrayed in surface morphological investigations utilizing SEM and TEM. The presence of copper (II) oxide extending still up in the air by solid tops in the FTIR range, and the absorbance pinnacle of the UV-Vis range uncovered a bandgap energy of 1.58eV. Antibacterial adequacy against *S.aureus* and *E.Coli* is additionally improved, restraining the microbes' development and MB color corruption is accomplished for 100 percent in 100 mins. In light of this review, the copper (II) oxide nanoparticle demonstrated that this material is go about concerning great materials for photocatalytic response and can be use in wastewater treatment in future forthcoming.

Keywords: Photocatalytic, copper (II) oxide Nanoparticles, Antibacterial activity

[a]. Department of Chemistry, College of Science, University of Jeddah, P.O. Box 80327, Jeddah 21589, Saudi Arabia.

Email: dmdomyati@uj.edu.sa

DOI: 10.31838/ecb/2022.11.02.001

INTRODUCTION

Essential effluents depleted from material and different ventures are color effluents (Verma et al., 2021). It likewise has an intricate natural design and a major sub-atomic weight, making it effectively solvent in water (Snetkov et al., 2020). As indicated by the appraisal, the colors utilized in such ventures add up to around 2, 00,000 tons each year, and because of the synthetic construction of the colors' chromophore, this substance emanating is depleted into water without sufficient treatment (Keerthana et al., 2021). The recalcitrant idea of unsafe effluents created from various areas causes eutrophication, which has genuine ramifications for oceanic creatures as well as being mutagenic and cancer-causing to people (Verma et al., 2021; Snetkov et al., 2020; Keerthana et al., 2021). Subsequently, material gushing detoxification is an interesting issue among specialists from one side of the planet to the other (Snetkov et al., 2020; Verma et al., 2021; Keerthana et al., 2021). Numerous physical, synthetic, and natural strategies, like adsorption, film filtration, and ozonation, are accessible for the treatment of material effluents (Behera et al., 2021; Ahmed et al., 2021). Expanding blackmails connected with environmental issues and energy limitations have frustrated human culture's turn of events and perseverance (Raizada et al., 2020). On account of the pervasiveness of inorganic and natural toxins in water because of agrarian, homegrown, and modern exercises, novel innovation has been created to effectively

address water shortage concerns (Snetkov et al., 2020; Verma et al., 2021; Keerthana et al., 2021). Different researchers and analysts are searching for novel and powerful strategies for eliminating poisons from wastewater to assist with tackling this enormous issue (Snetkov et al., 2020; Verma et al., 2021; Keerthana et al., 2021). Nanoscale metal oxide materials have been proposed because of their special size, physical, and compound properties, as well as their forthcoming applications (Raizada et al., 2020; Naseem and Durrani, 2021). Cupric oxide (CuO) is one of the most regularly utilized benchmark photocatalysts in photodegradation since it is financially savvy, non-poisonous, and more effective in retention across a huge segment of the sun powered range (Athanasakou et al., 2018; Raizada et al., 2020; Naseem and Durrani, 2021). CuO NPs, a metal oxide, are displayed to have worked on antibacterial action (Mohammed et al., 2018; Bouafia et al., 2020; Ali et al., 2021). Since nanoparticles are more modest than bacterial openings, they have a stand-out capacity to penetrate the cell layer, as CuO nanoparticles do (Mohammed et al., 2018; Bouafia et al., 2020; Ali et al., 2021). Sometimes, the properties of this metal are better than those of other costlier metals with antibacterial movement, like silver and gold. Subsequently, the point of the exploration was to examine into the combination and portrayal of Copper (II) Oxide nanoparticles, as well as the assessment of photocatalytic color corruption and antimicrobial adequacy.

MATERIALS AND METHODS

All chemical reagents, including copper acetate, ethanol, urea, and sodium hydroxide, were analytical grade and utilised without purification.

Double distilled water is used to make aqueous solution of copper acetate (0.02 mol). 2 M NaOH solutions were added

drop by drop to the aforesaid combination until turbidity was achieved after 3 hours. The bluish gel was then created, and the unreacted ions were removed by washing it four to six times with distilled water. The sample was then dried in an oven at 80°C for 24 hours. The dry powder sample was annealed for 3 hours at 300°C in an air environment. XRD, SEM, TEM and UV Vis spectroscopy was used to characterise the CuO NPs.

Photocatalytic activity (PA) measurements

Methylene Blue was used to assess the PA of the examined materials in terms of the breakdown of organic molecules in water (MB). The experiments were conducted using a halogen lamp as a visible light source. 5 mg CuO nanoparticles were disseminated in a 50 mL aqueous solution of MB (20 mg/L) in a conical flask. The suspension was then exposed to visible light while being constantly stirred. A 4 mL solution was removed from the reaction system at regular intervals and centrifuged at 5000 rpm to remove the photocatalyst particles. At wavelengths stretching from 200 nm to 800 nm, UV Vis is used to measure the cleared solution. The removal rate and degradation efficiency were determined using the UV spectrum and the maximum at 662nm.

Antimicrobial activity of CuO NPs

The antimicrobial activity of CuO NPs were evaluated using *S. aureus* and *E. coli* (obtained from Drs Bio Research Laboratory, Thanjavur, India) and well diffusion method was used to test antimicrobial activity with four different concentrations of 100µl, 150µl, 200µl, and 500µl and Tetracycline (50µl) used as standard drug.

RESULTS AND DISCUSSION

Because of late leap forwards in nanoscience and nanotechnology, metal and metal oxide nanoparticles have a wide scope of uses in an assortment of areas, research associations, and organizations (Akitelu et al., 2020; Danish et al., 2021). CuO-NPs definitely stand out than other metal oxides because of their exceptional properties and applications (Verma et al., 2019; Raizada et al., 2020; Naseem and Durrani, 2021). Physical and substance CuONP unions have been seriously hampered by the significant

expense of reagents, gear, and ecological dangers (Pérez-Hernández et al., 2022). Diminish ecological contamination and produce more modest nanoparticles with great qualities and effectiveness to meet the previously mentioned concerns, this study blended copper (II) oxide nanoparticles utilizing citrus extract and co-precipitation methods, showing that they could be valuable materials for photocatalytic responses and could be utilized in wastewater treatment later on. Since the uses of CuONPs are vigorously dependent on their properties, characterisation is as yet fundamental. The significant portrayal strategies, for example, XRD, SEM, TEM and UV Vis spectroscopy methods are accustomed to deciding the properties blended CuONPs.

Controlling particle size, shape, and morphology is critical in the creation of nanoparticles (Kumaran et al., 2017; Xiao et al. 2018). The most essential tool utilised in nanomaterials science is XRD (Theivasanthi and Alagar, 2010). As a result, this work presents the simple and low-cost synthesis of Copper nanopowder as well as its XRD examinations. In this present study, the XRD pattern of the prepared sample was shown in the Figure -1. The positions of the observed diffraction strong peaks at $2\theta = (32.57^\circ, 35.65^\circ, 38.79^\circ, 48.94^\circ, 53.52^\circ, 58.34^\circ, 61.64^\circ, 66.42^\circ, 68.12^\circ, 72.45^\circ, \text{ and } 75.17^\circ)$ were assigned to $(1\ 1\ 0)$, $(0\ 0\ 2)$, $(1\ 1\ 1)$, $(0\ 2\ 0)$, $(2\ 0\ 2)$, $(1\ 1\ 3)$, $(3\ 1\ 1)$ and $(2\ 2\ 0)$ are highly consistent with JCPDS standard no. 01-080-0076 of CuO NPs with a monoclinic phase. The XRD patterns not showed any sign of extra peaks corresponding to impurities or secondary phases. In addition, no changes in the diffraction angles or in the relative intensities can be recognized. Consequently, the calcination process leads to high phase purity with desired compositions. Furthermore the sharp and intense peaks show the high degree of crystallinity with average crystallite size of 20.27nm. The structural crystallinity was manually assessed, while the average particle size was calculated using Debye- Scherrer's formula.

$$D = K\lambda/\beta \cos\theta$$

where, D is 'crystallites size (nm)', K is 'Scherer constant (0.9)', λ is 'wavelength of X-rays source', β is 'full width at half maximum of reflection peaks (radians)' and θ is 'peaks position (radians)'.

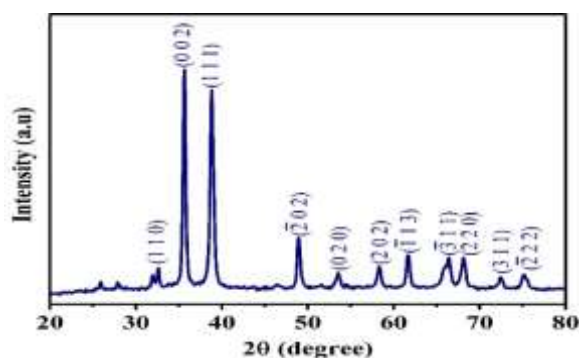


Figure 1. XRD pattern of CuO Nanoparticles

The FTIR assessment is an essential tool for determining the significance of functional groups in metal particle interactions (Li et al., 2019). The particle production can be effectively measured using FTIR spectroscopy (Vijayaraj et al., 2019). The width and intensity of peaks in an IR spectrum are found to be explicitly dependent on particle size (Li et al., 2019). The peak's width narrows as particle size increases, while the intensity rises (Amaro-Gahete et al., 2019). CuO

nanoparticles have a large frequency band at 3430 cm^{-1} in their FT-IR spectra (Figure 2), which corresponds to the hydroxyl (OH) functional group of water molecules absorbed from the surface moisture content. Along with this, three characteristic bands at 465, 560, and 740 cm^{-1} revealed the formation of CuO (Subbulekshmi and Subramanian, 2017). The higher frequency mode at 740 cm^{-1} can be linked to the Cu-O stretching vibration along the direction (Sherif et al.,

2007), The peak at 497 cm^{-1} , on the other hand, could be due to Cu-O stretching vibrations along the direction (Ethiraj and Kang, 2012). Therefore, it is confirmed through the FTIR

spectrum results that synthesized CuO nanoparticles have crystallised in monoclinic phase.

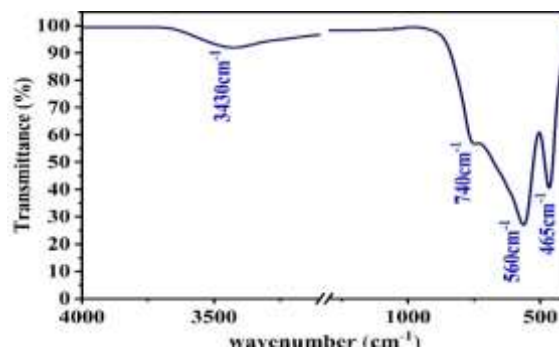


Figure 2. FTIR spectra of CuO Nanoparticles

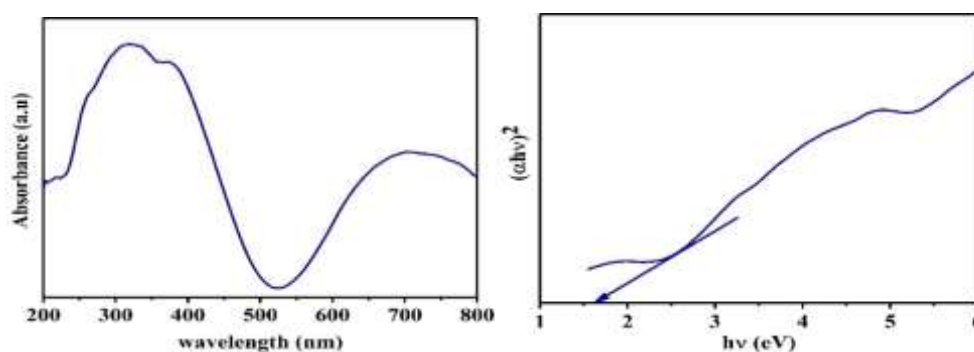


Figure 3. UV-Vis spectra of CuO NPs (left side) tauc plot (Right side)

The electrical and optical characteristics of nanomaterials are largely controlled by surface atoms (Bolshakov *et al.*, 2019). Because the valence and conduction band boundaries of surface atoms are not abrupt, and the tail states confuse the determination of the genuine optical gap, estimating the energy band gap in nanostructural semiconductors is problematic (Thota *et al.*, 2018). In this study, photocatalysis of the transition-metal oxide's optical band gap is critical for determining light harvesting ability. In the UV-vis spectral range, (Figure - 3) plots, CuO particles have shown broad absorption in the range of ~ 250 to $\sim 490\text{ nm}$ with minor humps at ~ 290 and $\sim 390\text{ nm}$. In general, decreasing nanoparticles reduces charge diffusion length, which minimises charge

recombination due to rapid charge transfer, resulting in increased photocatalytic efficiency (Xiao *et al.*, 2019). The Tauc plot (Figure 3b) was utilised to estimate the optical energy band gap of CuO nanoparticles, where the $(\alpha h\nu)^2$ against $h\nu$ plot can be employed in the equation below.

$$(\alpha h\nu)^2 = K(E_{\text{photon}} - E_g)^2$$

where α is the retention coefficient, $E_{\text{photon}} = h\nu$ is the photon energy, K is a steady, and E_g is the optical energy band hole. The assessed optical energy band hole ($E_g = 1240/\lambda_{\text{edge}}$) of CuO nanoparticles was about $\sim 1.20\text{ eV}$, which is a lot bigger than that of mass CuO ($\sim 1.20\text{ eV}$) precious stones.

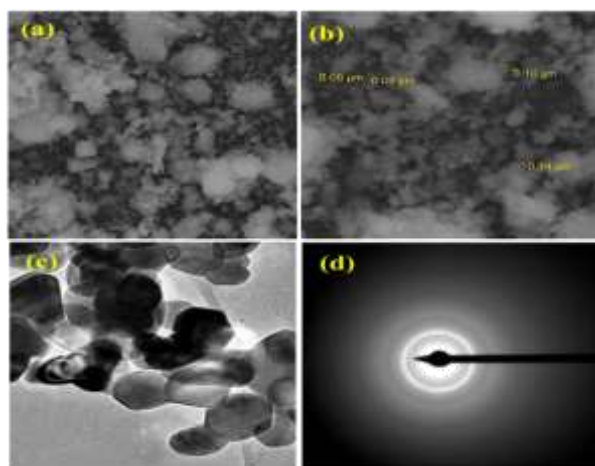


Figure 4. (a) & (b) SEM images of CuO nanoparticles (c) TEM image and (d) SAED example of CuO nanoparticles

SEM and TEM, as well as single-molecule research, are utilized to explore surface morphology, molecule size circulation, molecule, gem structure, agglomeration of nanoparticles, and surface functionalization (Xu, 2018; Quast et al., 2021). In this review, the underlying morphologies of the CuO nanoparticles were inspected by SEM and TEM. As uncovered in the low amplification SEM pictures show the agglomerated circles (Figure - 4). The as-gotten CuO nanoparticles shows a common round morphology with high agglomeration likewise affirmed in TEM moreover. Particles are all around dissipated in nature, as confirmed by SEM and TEM photos. The SAED design obviously shows the brilliant back to back rings of the significant planes uncover the high glasslike nature of the examples.

Photocatalytic corruption and toxin decrease impetuses in light of CuO NPs have been broadly utilized (Sahu et al., 2019). In all actuality, dull adsorption is an initial phase in the photocatalysis instrument and perhaps the main part

(Rafique et al., 2020). CuO NPs were utilized to concentrate on how cationic colors, for example, MB and MR fall apart within the sight of daylight. To accomplish an adsorption-desorption harmony between the CuO NPs and color particles, the MB and MR arrangements were unsettled in obscurity for 1 hour within the sight of light. The photocatalytic debasement tests were completed within the sight of apparent light, and the MB cycle was picked as the toxin color particle of premium in this examination. The framework was disturbed for a couple of moments before the photoreaction to accomplish the surface assimilation balance in obscurity. The MB fixation quickly diminished as the photocatalytic response advanced because of the debasement response. Shortly, CUO nanoparticles eliminate generally 50.78 percent of the MB color particles. The CuO nanoparticle's high photocatalytic action could be a suitable method for eliminating natural toxins from water and wastewater treatment frameworks on a wide scale.

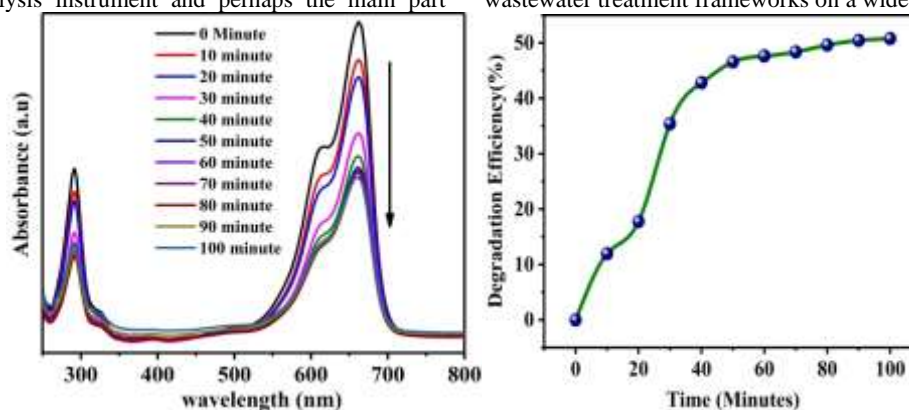


Figure 5. Dye Degradation and degradation efficiency of CuO NPs

CuO nanoparticles' higher visible-light driven photocatalytic activity can be attributed to their increased photo-generated charge carrier separation. Meanwhile the optimized band gap led to high adsorption of visible light. The Reactive Oxygen Species ((ROS) (O₂^{•-}, H₂O₂, and OH[•])) is responsible for the breakdown of organic contaminants by semiconductors in aqueous medium and photogenerated hole (h⁺) during light irradiation. The relevant reaction path can be described as follows

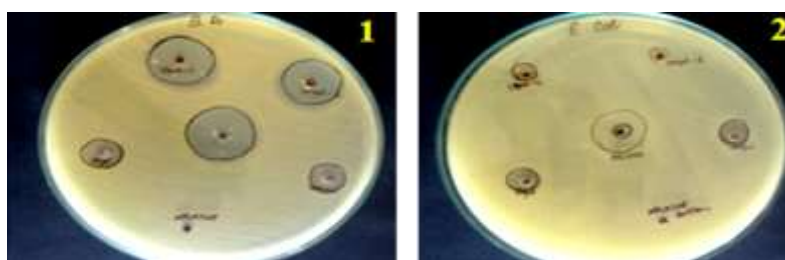
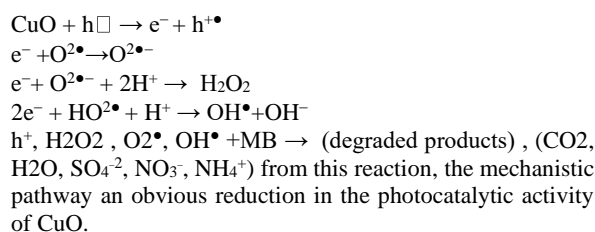


Figure 6. Antimicrobial activity of CuO NPs (1. S. aureus; 2. E. coli)

Table 1. Antimicrobial activity of CuO NPs

Pathogen	Standard drugs (Tetracycline)	CuO NPs			
	Concentrations (µg/mL)				
	50µl	100µl	150µl	200µl	500µl
Zone of inhibition (mm)					
<i>S. aureus</i>	26	14	15	23	24
<i>E. coli</i>	31	7	9	13	12

Nanomaterials have for quite some time been known for their antibacterial properties against microbes, microorganisms, and different creatures, both gram positive and gram negative. Metal oxide nanoparticles work as antibacterial specialists because of their enormous surface region (Vijayaraj and Kumaran, 2017; Kumaran et al., 2017; Sathiyavimal et al., 2018; Niranjana et al., 2022). In this review, the antimicrobial action of CuO NPs successful antimicrobial movement against *S.aureus* (24 mm) at the convergence of 500µl when contrasted with Standard medications, Tetracycline. In light of these discoveries, it tends to be surmised that CuO NPs incorporated showed intense antibacterial activity against microscopic organisms from both Gram classes (Dulta et al., 2022). In light of their huge surface region, CuO NPs have a significant antibacterial impact, permitting them to contact all the more intimately with microorganisms (Bulut Kocabas et al., 2021). By cross-connecting inside and between nucleic corrosive strands, copper particles delivered later can tie with DNA atoms, causing helical underlying interruption (Bulut Kocabas et al., 2021; Dulta et al., 2022). Biochemical exercises in bacterial cells are routinely modified by copper particles (Mehrotra et al., 2021; Priyadarshane and Das, 2021). The specific instrument is obscure and will require further examination. Gram negative microorganisms had all the earmarks of being more impervious to CuO NPs than Gram positive microbes specifically. It was recently seen that the connection between Gram positive microbes and NPs was more grounded than that between Gram negative microorganisms and NPs because of varieties in cell dividers between Gram positive and Gram negative microscopic organisms (Mehrotra et al., 2021; Priyadarshane and Das, 2021). The CuO NPs made have a significant degree of activity against Gram positive microorganisms *S. aureus*, as indicated by the examination, and could be utilized to control risky microorganisms in the climate.

CONCLUSION

The impetus in this study was CuO NPs with a little bandgap and close infrared light awareness, which were made using a basic wet synthetic precipitation strategy. Research shows that the high glasslike monoclinic period of CuO NP s was framed with round morphology. Because of the light reaction and interfacial charge move capacity, it was found that CuO NPs have a bandgap in the district of 1.55eV, which may successfully help synergist execution by 50.78 percent in a short time against methylene blue color. It likewise has antibacterial properties against *E. coli* and *S. aureus*. In view of this review, the copper (II) oxide nanoparticle showed that CuO-NPs exhibited productive photocatalytic debasement of methylene blue, and they could be utilized as an impetus in the future to diminish colors, other poisonous materials, and modern effluents.

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