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Research Article

Optimization of the cupric oxide nanoparticles synthesis by novel *spondias mombin* peel extract exhibited excellent peroxidase activity

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ABSTRACT

This study describes a straightforward protocol for synthesizing cupric oxide nanoparticles from the peel extract of *Spondias mombin*. The CuO NPs were produced in a basic H_2O solution as cubic-shaped, homogenous nanoparticles with excellent peroxidase activity without taking any special precautions. The influence of the concentration of the peel extract, temperature as well as the synthesis medium on CuO NPs production has been investigated extensively. The typical UV-visible absorption maxima observed at wavelengths of 279 and 383 nm observed in spectrophotometry confirmed the formation of CuO NPs. Moreover, the homogeneity, shape (cubic), and size (approximately averaged ~31nm (29nm~38nm)) of the synthesized CuO nanoparticles under optimum conditions were confirmed through the SEM technique. Besides, its elemental compositions, capping agent, and crystallinity were investigated through EDS, FT-IR and XRD. Finally, in the presence of hydrogen peroxide (H_2O_2), the as-prepared CuO NPs demonstrated excellent peroxidase activity against 3,3',5,5'-tetramethylbenzidine (TMB).

Introduction

Recently, copper oxide nanoparticles (CuO NPs) have received much interest, particularly due to their antibacterial and biocide properties (Nations et al., 2015; Perreault et al., 2012 and Nguyen, 2014), distinctive electrical). Being in nano size and semiconducting character with narrow bandgap, super thermal conductivity, photovoltaic properties, high stability, potent antimicrobial activity (Tran, optical, and magnetic properties and has been employed in a wide range of applications, including catalysis (Yecheskel et al., 2013), energy conversion, and storage (Kumar et al., 2013), magnetic storage (Rashad et al., 2013), gas sensors (Aslani and Oroojpour, 2011; Yang et al., 2011; Li et al., 2008), thermites (Wang and Xu, 1999), as well as optoelectronics (Gupta et al., 2018). Copper oxide nanoparticles demonstrated excellent performance as nanofluids in heat transfer applications. For instance, it has been found that adding of 4% CuO improves water's thermal conductivity by 20% (Lee et al., 1999) and photoconductive and photothermal applications (Rakhshni, 1986). Besides, it has diverse applications in dye removal (Phang et al., 2021), photovoltaic devices (Jiang et al., 2015), waste-water treatment (Das et al., 2018), batteries (Zhao et al., 2016), agriculture (Dimkpa et al., 2012), textiles (Shaheen et al., 2021), food preservation (Kazemian et al., 2019). Therefore, it is highly desirable to synthesize copper oxide nanoparticles with defined, controllable size, shape, and morphology.

The fabrication of copper and copper oxide nanoparticles (CuO NPs) has been reported using a

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variety of methods until now, including chemical vapor deposition (Eisermann et al., 2012), chemical reduction method (Sarker et al., 2021), electrochemical methods (Zhang and Hua, 2014), photochemical (Nishino et al., 2017; Jung et al., 2011), solvothermal route (Sarker et al, 2022a, b), and polyol (Ramyadevi et al., 2012). Most of those methods negatively impact the environment since they utilize harsh, hazardous, and poisonous substances. They are also costly and do need expensive reaction conditions. According to Akintelu et al. (2020), additional research is needed to reduce the toxicity of the CuO NPs process of production while retaining and/or enhancing their performance in environmental or healthcare applications. Therefore, eco-friendliness, ease of synthesis, safety, time efficiency, non-toxicity, and versatile applications have established green chemistry or biological pathways of synthesis as a research focus.

According to literature, CuO NPs have been synthesized by different biological species such as fungi (Saravanakumar et al., 2019), algae (Bhattacharya et al., 2019), etc. and green plants such as *Catha edulis* leaf (Gebremedhn et al., 2019), *Calotropis gigantea* leaf (Sharma et al., 2015), *P. acerifolium* (leaf) (Saif et al., 2016), *gum karaya* (gum) (Padi and Černík, 2013), *Gundelia tournefortii* (stems) (Nasrollahzadeha et al., 2015a), *Thymus vulgaris L* (leaf) (Nasrollahzadeha, 2016), *Citrus lemon* (juice) (Mohan et al., 2015), *Gloriosa superba L* (leaf) (Naika et al., 2015), *Tinospora cordifolia* (leaf) (Udayabhanu et al., 2015), *Punica granatum* (peels) (Ghidan et al., 2016), *Carica papaya* (leaf) (Sankar et al., 2014), *Anthemis nobilis* (flowers) (Nasrollahzadeh et al., 2015b), Tamarix gallica (leaf) (Nasrollahzadeh et al., 2015c), *Coffee Powder* (beans) (Fardood, and Ramazani 2016), *Bifurcaria bifurcate* (alga) (Abboud et al., 2014), *Aloe barbadensis* (leaf) (Gunalan et al., 2012), *Aloe vera* (leaf) (Kumar et al., 2015), *Tea and Coffee* (leaf) (Sutradhar et al., 2014) etc.

According to the literature report on the phytochemical contents of *S. mombin* leaves and their feasibility towards nanoparticle synthesis, Recently, our research team investigated the phytochemical constituents of *S. mombin* peel extract and found its suitability as well (Njoku, and Akumefula 2007, Mohammad et al., 2014, Engels et al., 2012). And we used *S. mombin* peel extract successfully for Pd NP synthesis (Akanda et al., 2021). Our research group recently compared the synthesis of CuO nanoparticles by *S. mombin* peel extract in a buffer system Vs an H_2O system and investigated the synthesis in a PBS buffer system (Akanda et al., 2022). To the author's knowledge, no studies have been conducted on the facile synthesis of CuO NPs in the H_2O system by *S. mombin* peel extract. Additionally, according to Yugandhar et al. (2017), the green extract's ascorbic acid is principally responsible for the production of CuO NPs, while the yellowish part of ripe *S. mombin* contains a significant amount of ascorbic acid (de Carvalho et al., 2015). Therefore, ripe *S. mombin* was harvested for this study, and its yellowish peel was chosen for extract preparation and CuO NPs production in H_2O.

The peel extract of *S. mombin* fruits in H_2O was employed as the green reductant in this work, while $CuSO_4.5H_2O$ was used as the precursor. The peel extract functioned both as a capping agent and a reducing agent. The peel extract prepared at room temperature was employed for the synthesis of our CuO NPs. Furthermore, a thorough investigation of the effects of peel extract concentration, solvent system medium, and temperature on the synthesis of CuO NPs was undertaken systematically. CuO NPs produced a maintained cubic shape, appeared homogenous and crystalline, and under optimal settings demonstrated high peroxidase activity.

Materials and Apparatus

Chemicals and reagents

S. mombin peels were obtained from Shahbagh, Dhaka, Bangladesh. From Scharlau, Spain, we purchased copper sulfate ($CuSO_4.5H_2O$), di-Sodium monohydrogen phosphate dihydrate ($Na_2HPO_4.2H_2O$),

and H_2O_2. We received sodium hydroxide pellets & mono-sodium dihydrogen phosphate dihydrate ($NaH_2PO_4.2H_2O$) from Duksan. China's Hangzhou Xinhua Paper Industry supplied the double-ring filter paper. The experiment was carried out entively with distilled water.

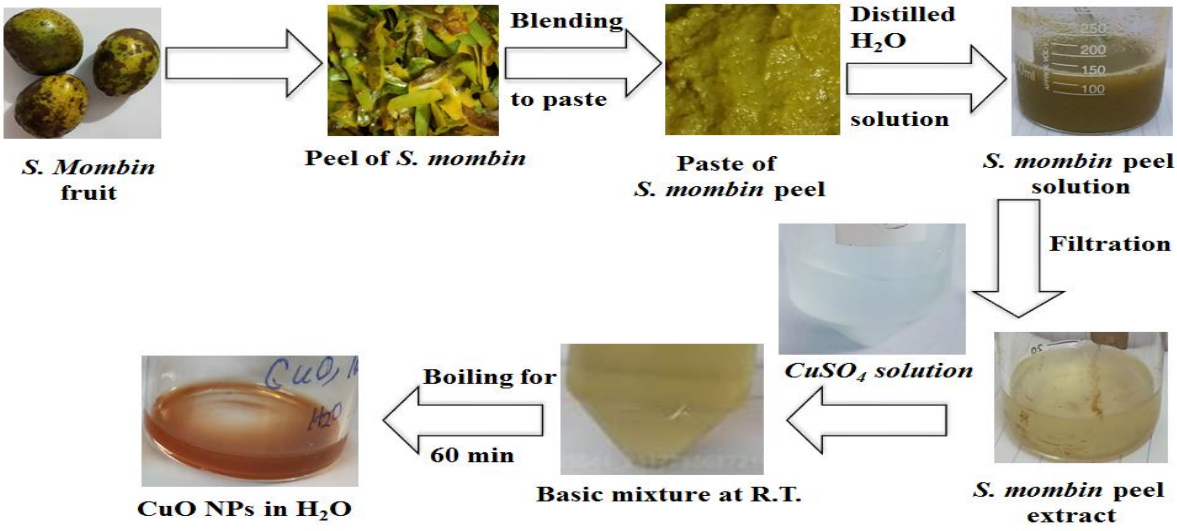
Instrumentation

The UV-1800 model double-beam spectrophotometer came from Shimadzu of Japan. The magnetic stirrer was manufactured by Daihan Labtech of Korea, (model LMS-1003). Distilled water plant we used (Basic/PH4 Pure-HIT still type) was provided by Glassco in the UK. The Energy-dispersive X-ray spectroscopic (EDS) instrument (model (SUPRA 55)-CARL ZEISS) and the scanning electron microscopic (SEM) system (model JSM-7600F) were both made by JEOL, Japan.

preparation of peel extract of *S. mombin* and synthesis of CuO nanoparticles

Ripe *S. mombin* fruits were obtained from a nearby market, thoroughly cleaned using distilled water, and allowed to air dry for a couple of hours. The fruit peel was then removed and washed once more. The peels were then mashed with distilled water to make a paste.

Following that, 10 g of the peel paste was diluted by adding to 20 mL of distilled water in a 100 mL beaker and stirred using a magnetic stirrer for 10 min at room temperature. The extract was then filtered and collected with double filter paper; after that, it was stored at 4 °C for subsequent experiments. In our previous study, the phytochemical contents of peel extract were also determined. We found that the total phenolic content of peel extract was calculated to be approximately 26.035 g/mL GAE per mg of plant material, the total flavonoid content was estimated at 76.871 g/mL, and the total condensed tannin amounted to approximately 21.581 g/mL QE per mg of plant material, respectively (Akanda et al., 2021). Although the particular reducing agent for the formation of CuO NPs from peel extract is uncertain, it was proposed that the ascorbic acid of the peel extract (which was not determined) was accountable for NPs production (Yugandhar et al., 2017). The precursor $CuSO_4.5H_2O$ solution for the production of CuO NPs was prepared in water in a beaker. A 0.01 M 10 mL $CuSO_4.5H_2O$ solution was prepared in a different beaker using distilled water. In a different beaker, 10 mL of 0.01 M $CuSO_4.5H_2O$ solution was transferred before 10 mL of the peel extract was quickly added. The Cu^{2+} concentration in the solution has been determined to be at a final concentration of 2.5 mM, and the solution's color changed to a brownish color.



Scheme. Schematic representation for forming CuO NPs from *S. mombin* peels extracts in the water system.

CuO NPs were generated by heating the resultant solution to boiling for 60 minutes while vigorously stirring. The generation of CuO NPs was confirmed by the solution's deep reddish color following heating. The **scheme** provides a brief schematic depiction of the whole process.

Results and discussions

Confirmation and optimization of the CuO NPs synthesis

Fig. 1 illustrates the UV-Visible spectra of CuO NPs produced from *S. mombin* peel extract and 0.0025M $CuSO_4$ solution. The generated CuO NPs were dispersed in an alkaline H_2O system, subsequently sonicated to ensure uniform dispersion, and then sent straight away for UV-Visible spectrophotometric studies. The spectrum shows typical CuO NP absorption maxima at wavelengths of 279 and 383 nm, which is evident from the curve in Fig. 1A (green curve) and Fig. 1B and is not present in the curves of the other components of Fig. 1A. The electronic transitions via the intrinsic band-gap of CuO are what cause this pattern of absorption (Zak et al., 2012 and 2013). As the concentration of *S. mombin* peel extract is raised, Fig. 1B demonstrates rising absorbance while keeping the same band-gap as a sign of the higher peel extract concentration. Additionally, the existence of sharp peaks denotes a state that is evenly distributed and stable. For this work, 10 mL (0.1250 g/mL) of the peel extract from Fig. 1B's (blue curve) peel was taken into account since a concentration of peel extract that is too high might inhibit the activity of CuO NPs by obstructing their active sites.

Optimization of medium and temperature conditions for CuO NPs synthetic

We have studied the optical study by the addition of 0.1250 g/mL peel extract in 0.0025M precursor solution to realize the effect of medium and temperature. Fig. 2A and B show the optical images of the precursor $CuSO_4.5H_2O$ and peel extract respectively. The reaction system's medium was controlled by adding hydrochloric acid, and sodium hydroxide, respectively, and the medium was confirmed through pH in all three mediums. It was found that only the basic medium showed color changes (Fig. 2C). Indicating reaction can occur in the basic medium only. The mixed solution was left at room temperature, 60 ^{0}C, and boiling temperature to confirm synthesis Fig. 2D.

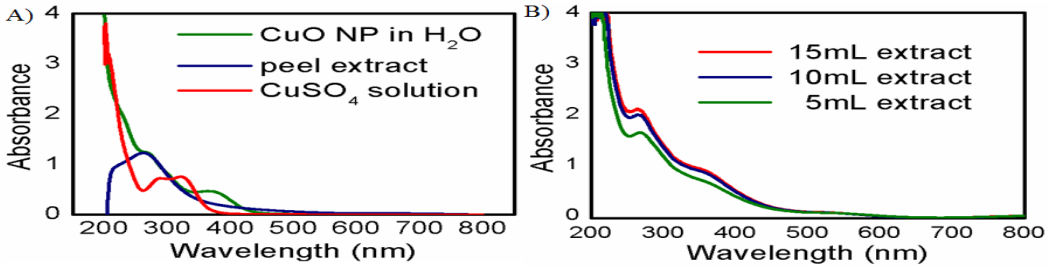


Fig. 1. (A) UV-Visible spectra of the synthesized CuO NPs in H_2O (green curve), precursor 0.0025M $CuSO_4.5H_2O$ (red curve) and 0.1250 g/mL peel extract (blue curve) and (B) UV-Visible spectra of the synthesized CuO NPs on 5mL (0.1875 g/mL-red curve), 10 mL (0.1250 g/mL-blue curve) and 15mL (0.0625 g/mL-green curve) concentration of peel extract, respectively, in H_2O.

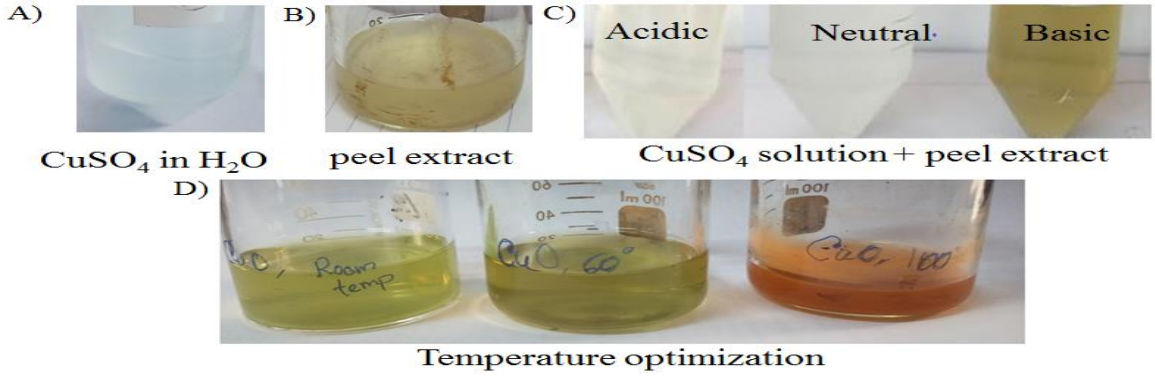


Fig. 2. Optical image of (A) 0.0025M $CuSO_4$ solution, (B) 0.1250 g/mL *S. mombin* peel extract in water systems (C) reaction of 0.0025M $CuSO_4$ solution with 0.1250 g/mL *S. mombin* peel extract in acidic, neutral and basic medium respectively and (D) temperature effect nanoparticles formation.

It was found that only boiling temperature can synthesize CuO NPs. Thus, basic medium and boiling temperature was considered the optimum conditions for the synthesis of CuO NPs.

Characterization of the synthesized CuO NPs in the basic water system

CuO nanoparticles were synthesized and characterized by SEM and EDS study after optimizing the synthetic conditions as shown in Figure 3(A-C). The SEM data was analyzed, and it was revealed that Fig. 3A, where the magnification is 50,000, appears to have few aggregations but a mostly homogeneous synthesis of nanoparticles. The produced CuO NPs appear to have a cubic shape in Fig. 3B, which has a magnification of 100,000. Their average size is around 31 nm (29 nm–38 nm). Most greenly synthesized CuO NPs are spherical (Amin et al., 2021, Alhalili, 2022), but quasi-spherical (Okpara et al. 2021) and rod-shaped CuO (Tavakoli et al., 2019) are also found. It is anticipated that an increased number of edges, corners, and faces on cubic-shaped CuO NPs might be responsible for their excellent peroxidase activity (Ni and Wang, 2015). Importantly the elemental composition of CuO NPs was validated by its EDS analysis, which is shown in Fig. 3C. The existence of the green species on artificially generated CuO NPs as a capping agent and stabilizing agents was confirmed through its FT-IR analysis in Fig. 4(A).

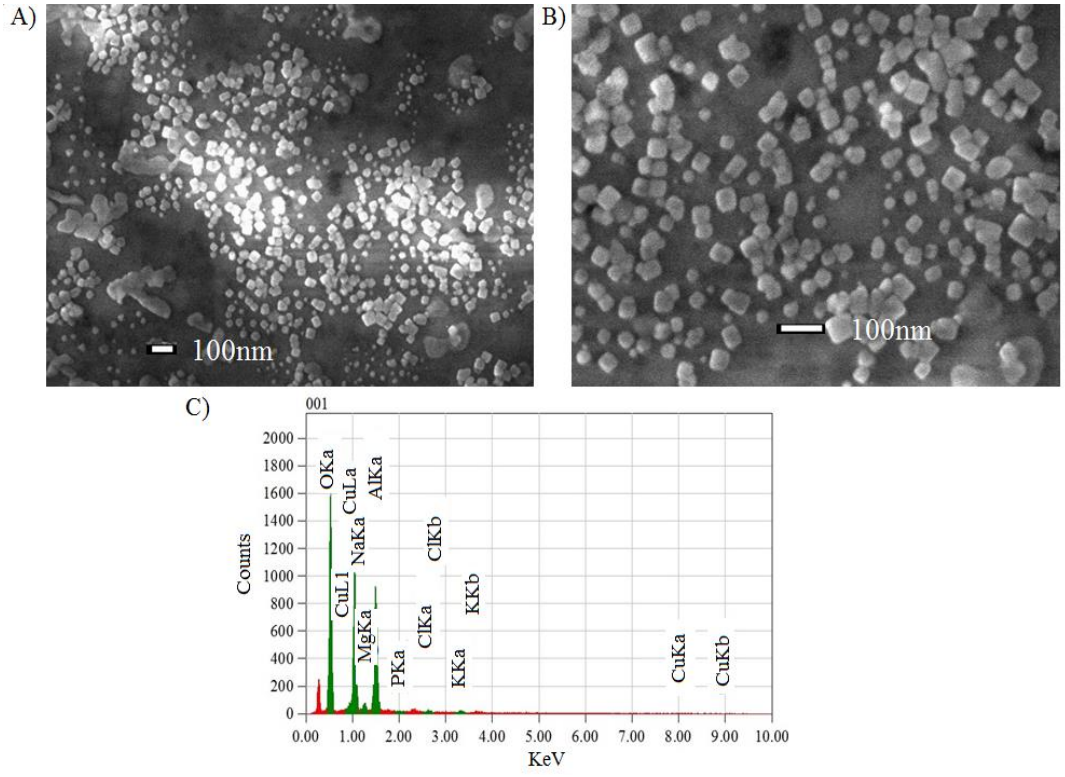


Fig. 3. SEM images of the synthesized CuO NPs in 100 nm scale bar with (A) x50,000, (B)x100,000 magnification from the mixture of 0.0025 M $CuSO_4.5H_2O$ and 0.1250 g/mL peel extract in basic H_2O system. And (C) EDS, spectra of the as-synthesized CuO NPs from the mixture of 0.0025 M $CuSO_4.5H_2O$ and 0.1250 g/mL peel extract in a basic H_2O system.

The O-H groups of phenols cause a broad and strong peak to arise at around 3450 cm^{-1}. Stretching of the C-H caused the band at 2860 cm-1. The stretching vibration of the C-O group of primary and secondary phenols (C-O) was responsible for the absorption peak at 1074.0 cm-1, whereas the aromatic bending vibration of the C-H group was responsible for the smaller peaks at 1722 and 1475 cm-1. The above analysis confirmed that these functional groups were from peel extract as a stabilizing as well as a capping agent for the nanoparticles. Additionally, a prominent peak in the spectra at 484.13 cm-1 is seen due to the characteristic properties of Cu-O bond formation in CuO. (Khan et al., 2011) Furthermore, the absence of a peak at 610 cm^{-1}, the frequency mode caused by Cu_2O in Fig. 4(A), further demonstrates that the as-prepared nanoparticles consist entirely of the CuO phase with no traces of Cu_2O. (Botsa et al., 2018). In Fig. 5, the self-assembled CuO sample's characteristic XRD pattern was displayed. Its cubic shape and crystallinity were confirmed by the detection of three diffraction peaks that correspond to the (-111), (111), and (002) lattice planes. These results were congruent with published values (JCPDS 80-1268). (Gou et al., 2012). We assume that pure CuO nanostructures were produced since no observable contaminant signals were observed. It discovered several other crystalline peaks that it was unable to identify. Additional crystallinity is believed to promote high peroxidase activity.

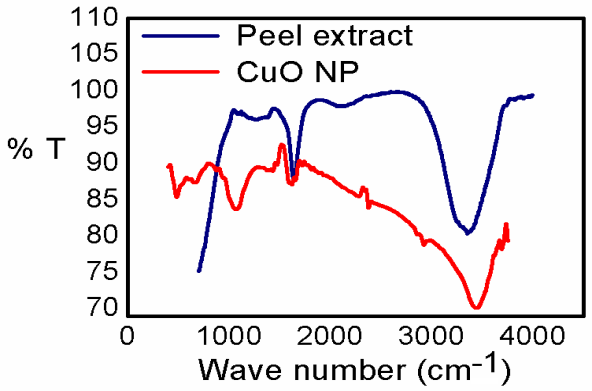


Fig. 4. FT-IR spectra of the synthesized CuO NPs from the mixture of 0.0025 M $CuSO_4.5H_2O$ and 0.1250 g/mL peel extract in basic H_2O system.

Peroxidase activity of the synthesized CuO NP

It is known from the literature that if the synthesized NPs are in CuO form in H2O, it shows peroxidase activity (Chen et al., 2011 and 2012). Therefore, the TMB oxidation in the presence of H2O2 has been applied using the as-synthesized CuO NPs under optimal basic H2O operating conditions to test its peroxidase activity. Interestingly, no green method-mediated produced CuO NPs have had their peroxidase activity tested up to now. As a result, the study's findings are extremely significant. TMB was found to not be oxidized with H2O2 alone but to be easily oxidized when CuO NPs were added, demonstrating its peroxidase activity. This is shown schematically in Fig. 6A. The addition of CuO NPs to a mixed solution of TMB solution (red curve), H2O2 (blue curve), and oxygen (UV-visible spectra in Fig. 6B) resulted in the creation of oxidized TMB (purple curve, peak at 652 nm) (green curve). The peak of the oxidized TMB (purple curve) at 652 nm represents the oxidation kinetics of TMB with a single electron transfer (Dahal et al., 2015). Interestingly, optimization of the basic H2O systems for CuO NPs synthesis shows significant peroxidase activity and is completed within 10 minutes. In this instance, additional prolongation of time did not result in any alteration of absorbance (data not shown). The reaction was extremely sluggish and finished in 30 minutes compared to prior studies on un-optimized basic H2O-assisted produced CuO NPs (Akanda et al., 2022). Therefore, it can be claimed that the CuO NPs produced under optimized conditions were more homogeneous, had single (cubic) morphologies, and were approximately the same size.

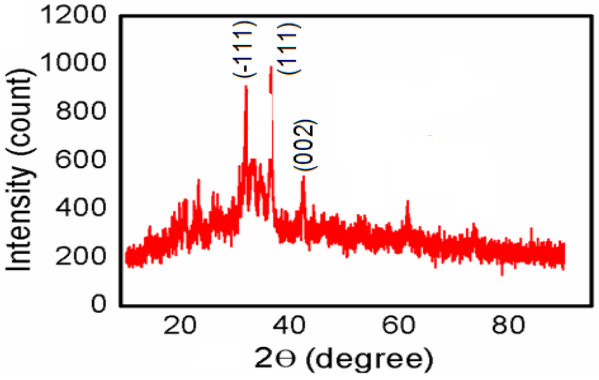


Fig. 5. XRD spectra of the synthesized CuO NPs from the mixture of 0.0025 M $CuSO_4.5H_2O$ and 0.1250 g/mL peel extract in Basic H_2O system.

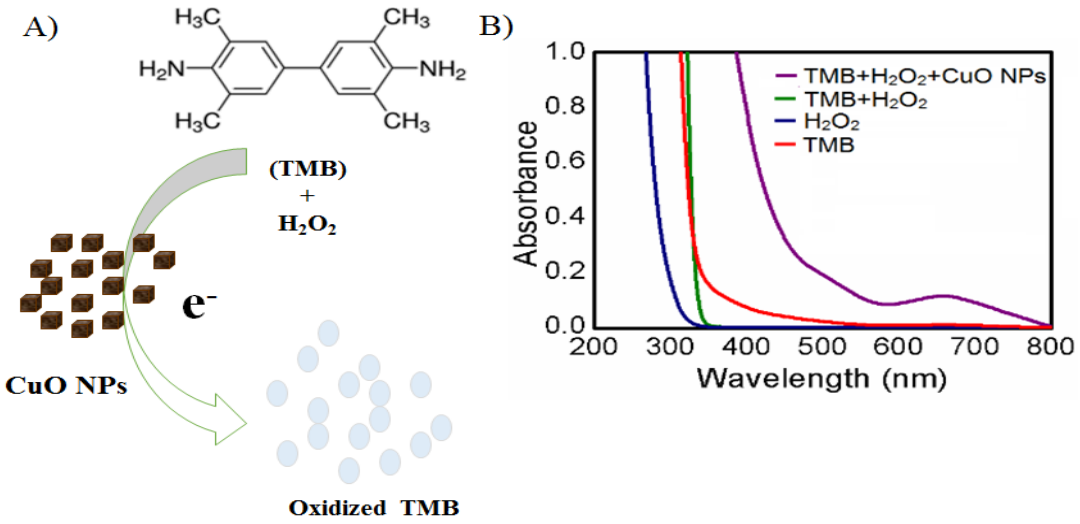


Fig. 6. (A) Schematic representation of TMB oxidation by CuO NPs in the presence of H_2O_2. (B) UV-Visible spectra of the synthesized CuO in basic H_2O with 0.00208M TMB and 0.1M H_2O_2.

Conclusion

We conclude that the basic method of synthesizing CuO NPs with H_2O was thoroughly optimized in this study, and their superiority over unoptimized methods has been proved. The basic H_2O-assisted synthetic conditions were optimized with regard to the temperature, medium of the synthesis, and concentration of *S. mombin* peel extract. CuO NPs of about 31 nm in size were produced under optimal conditions for a basic H_2O-assisted system.

These NPs were homogeneous, well-dispersed, single-shaped (cubic), and well-stabilized. The remarkable peroxidase activity found in this study within the shortest amount of time (10 minutes) when applied to TMB oxidation is very beneficial for the bio-medicine industry. As a consequence, biomedical and green technology applications will be significantly impacted by the findings of this study.

Acknowledgments

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Conflict of Interest The authors declared that they have no conflict of interest.

Author's contribution

M.R. Akanda contributed to the conceptualization, supervision, and manuscript drafting, U.M. Ema and M. Hasan carried out the whole experiment, M.A. Haque contributed to the conceptualization, and MA Miah contributed to data collection and preliminary drafting.

References

Abboud Y, Saffaj T, Chagraoui A, El Bouari A, Brouzi K, Tanane O, and Ihssane B. Biosynthesis, characterization and antimicrobial activity of copper oxide nanoparticles (CONPs) produced using brown alga extract (*Bifurcaria bifurcata*). *Appl. Nanosci.* 2014; 4(5): 571-576.

Akanda MR, Ema UH, Hauqe MA and Hasan MH. Comparative study on cupric oxide nanoparticles synthesis in saline buffer versus basic water by *Spondias mombin* peel extract for biocatalysis. *Inorg. Nano-Met. Chem.* 2022. https://doi.org/10.1080/24701556.2022.2068587.

Akanda MR, Hasan MH, Ema UH and Haque MA, Optimization of *Spondias mombin* peel extract mediated synthesis of palladium nanoparticles as nanozyme exhibits potent multienzyme activity. *J. Iran. Chem. Soc.* 2021; 18: 3407-3415.

Akintelu SA, Folorunso AS, Folorunso FA, and Oyebamiji AK. Green synthesis of copper oxide nanoparticles for biomedical application and environmental remediation. *Heliyon* 2020; 6: e04508.

Alhalili Z. Green synthesis of copper oxide nanoparticles CuO NPs from *Eucalyptus globulous* leaf extract: Adsorption and design of experiments. *Arab. J. Chem.* 2022; 15: 103739.

Amin F, Fozia, Khattak B, Alotaibi A, Qasim M, Ahmad I, Ullah R, Bourhia M, Gul A, Zahoor S and Ahmad R. Green synthesis of copper oxide nanoparticles using *Aerva javanica* leaf extract and their characterization and investigation of in vitro antimicrobial potential and cytotoxic activities. *Evid. Based Complement. Altern. Med.* 2021; 2021: 5589703.

Aslani A and Oroojpour V. CO gas sensing of CuO nanostructures, synthesized by an assisted solvothermal wet chemical route. *Phys. Rev. B Condens. Matter*. 2011; 406(2): 144-149.

Bhattacharya P, Swarnakar S, Ghosh S, Majumdar S and Banerjee S. Disinfection of drinking water via algae mediated green synthesized copper oxide nanoparticles and its toxicity evaluation. *J. Environ. Chem. Eng.* 2019; 7(1): 102867.

Botsa SM, Ramadevi D and Basavaiah K. A Facile synthesis of copper oxide nanorods for photocatalytic degradation of organic pollutant and inactivation of pathogens. *J. Nanosci. Tech.* 2018; 4(5): 467-470.

Chen W, Chen J, Feng YB, Hong L, Chen QY, Wu LF, Lin XH and Xia XH. Peroxidase-like activity of water-soluble cupric oxide nanoparticles and its analytical application for detection of hydrogen peroxide and glucose. *Analyst*, 2012; 137: 1706-1712.

Chen W, Chen J, Liu A-L, Wang L-M, Li G-W and Lin XH. Peroxidase-like activity of cupric oxide nanoparticle. *Chem. Cat. Chem*, 2011; 3:1151-1154.

Dahal E, Curtiss J, Subedi D, Chen G, Houston JP and Smirnov S. Evaluation of the catalytic activity and cytotoxicity of palladium nanocubes: The role of oxygen. *ACS Appl. Mater. Interfaces* 2015; 7(18): 9364-9371.

Das P, Ghosh S, Ghosh R, Dam S and Baskey (Sen) M. *Madhuca longifolia* plant mediated green synthesis of cupric oxide nanoparticles: A promising environmentally sustainable material for waste water treatment and efficient antibacterial agent. *J. Photochem. Photobiol. B: Biol.* 2018; 189: 66-73.

de Carvalho JM, Maia GA, da Fonseca AVV, de Sousa PHM and Rodrigues S. Effect of processing on physicochemical composition, bioactive compounds and enzymatic activity of yellow mombin (*Spondias mombin L.*) tropical juice. *J. Food Sci. Technol.*, 2015; 52(2): 1182-1187.

Dimkpa CO, McLean JE, Britt DW, and Anderson AJ. Bioactivity and biomodification of Ag, ZnO, and CuO nanoparticles with relevance to plant performance in agriculture. *Ind. Biotechnol.* 2012; 8(6): 344-357.

Eisermann S, Kronenberger A, Laufer A, Bieber J, Haas G, Lautenschläger S, Homm G, Klar PJ and Meyer BK. Copper oxide thin films by chemical vapor deposition: Synthesis, characterization and electrical properties. *Phys. Status Solidi A* 2012, 209(3), 531-536.

Engels C, Gräter D, Esquivel P, Jiménez VM, and Gänzle MG, Characterization of phenolic compounds in jocote (Spondias purpurea L.) peels by ultra high-performance-liquid chromatography/ electrospray ionization mass spectrometry. *Food Res. Int.* 2012; 46: 557-562.

Fardood ST and Ramazani A. Green synthesis and characterization of copper oxide nanoparticles using coffee powder extract. *J. Nanostruct.* 2016; 6(2): 167-171.

Gebremedhn K, Kahsay MH and Aklilu M. Green synthesis of CuO nanoparticles using leaf extract of *Catha edulis* and its antibacterial activity. *J. Pharm. Pharmacol.* 2019; 7: 327-342.

Ghidan AY, Al-Antary TM and Awwad AM. Green synthesis of copper oxide nanoparticles using *Punica granatum* peels extract: Effect on green

peach Aphid. *Environ. Nanotechnol. Monit. Manag.* 2016; 6: 95-98.

Gou L, Tong F, Liu H, Yang H and Li J. Shape-controlled synthesis of self-assembly cubic CuO nanostructures by microwave. *J. Mater. Lett.* 2012; 71: 32-35.

Gunalan S, Sivaraj R and Venckatesh R. Aloe barbadensis Miller mediated green synthesis of mono-disperse copper oxide nanoparticles: optical properties. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 2012; 97: 1140-1144.

Gupta D, Meher SR, Illyaskutty N and Alex ZC. Facile synthesis of Cu_2O and CuO nanoparticles and study of their structural, optical, and electronic properties. *J. Alloys Compd.*, 2018; 743: 737-745.

Jiang T, Wang Y, Meng D, and Yu M. Facile synthesis and photocatalytic performance of self-assembly CuO microspheres. *Superlattice. Microst.* 2015; 85: 1-6.

Jung S, Jeon S and Yong K. Fabrication and characterization of flower-like CuO–ZnO heterostructure nanowire arrays by photochemical deposition. *Nanotechnology* 2011; 22: 015606.

Kazemian S, Zarrinnia V, Khosroshahli M and Hasanzadeh N. Investigation on the control effects of green copper oxide (CuO) nanoparticles on the tomato gray mold disease caused by *Botrytis cinerea*. *Iranian J. Med. Arom. Plants* 2019; 35: 54-67.

Khan MAM, Kumar S, Ahamed M, Alrokayan SA, and AlSalhi MS. Structural and thermal studies of silver nanoparticles and electrical transport study of their thin films. *Nanoscale Res. Lett.* 2011; 6: 434.

Kumar PPNV, Shameem U, Kollu P, Kalyani RL and Pammi SVN. Green synthesis of copper oxide nanoparticles using *Aloe vera* leaf extract and its antibacterial activity against fish bacterial pathogens. *J. Bio. Nano. Sci.* 2015; 5(3): 135-139.

Kumar V, Masudy-Panah S, Tan CC, Wong TKS, Chi DZ, and Dalapati GK. Copper oxide based low cost thin film solar cells. *Proceedings of the IEEE 5th International Nanoelectronics Conference (INEC '13)*, 2013; 443-445.

Lee S, Choi US, Li S and Eastman JA. Measuring thermal conductivity of fluids containing oxide nanoparticles. *J. Heat Transfer* 1999; 121: 280-289.

Li Y, Liang J, Tao Z, and Chen J. CuO particles and plates: Synthesis and gas-sensor application. *Mater. Res. Bull.*, 2008; 43(8-9): 2380-2385.

Mohammad NAN, Arham NA, Jai J, and Hadi A. Plant extract as reducing agent in synthesis of metallic nanoparticles: A review. *Open J. Adv. Mater. Res.*, 2014; 832: 350-355.

Mohan S, Singh Y, Verma DK, and Hasan SH. Synthesis of CuO nanoparticles through green route using *Citrus limon* juice and its application as nanosorbent for Cr (VI) remediation: Process optimization with RSM and ANN-GA based model. *Process Saf. Environ. Prot.* 2015; 96: 156-166.

Naika HR, Lingaraju K, Manjunath K, Kumar D, Nagaraju G, Suresh D and Nagabhushana H. Green synthesis of CuO nanoparticles using gloriosa superba L. extract and their antibacterial activity. *J. Taibah Univ. Sci.* 2015; 9(1): 07-12.

Nasrollahzadeh M, Sajadi SM, Rostami-Vartooni A and Hussin SM. Green synthesis of CuO nanoparticles using aqueous extract of *Thymus vulgaris L.* leaves and their catalytic performance for N-arylation of indoles and amines. *J. Colloid Interface Sci.* 2016; 466: 113-119.

Nasrollahzadeha M, Maham M, and Sajadi SM. Green synthesis of CuO nanoparticles by aqueous extract of *Gundelia tournefortii* and evaluation of their catalytic activity for the synthesis of N-monosubstituted ureas and reduction of 4-nitrophenol. *J. Colloid Interface Sci.* 2015a: 455: 245-253.

Nasrollahzadeh M, Sajadi SM and Vartooni AR. Green synthesis of CuO nanoparticles by aqueous extract of *Anthemis nobilis* flowers and their catalytic activity for the A3 coupling reaction. *J. Colloid Interface Sci.* 2015b; 459: 183-188.

Nasrollahzadeh M, Sajadib SM, and Maham M. *Tamarix gallica* leaf extract mediated novel route for green synthesis of CuO nanoparticles and their application for N-arylation of nitrogen-containing heterocycles under ligand-free conditions. *RSC Adv.* 2015c; 5(51): 40628-40635.

Nations S, Long M, Wages M, Maul JD, Theodorakis CW, and Cobb GP. Subchronic and chronic developmental effects of copper oxide (CuO) nanoparticles on *Xenopus laevis*. *Chemosphere* 2015; 135: 166-174.

Ni B. and Wang X. Face the Edges: Catalytic active sites of nanomaterials. *Adv. Sci.* 2015; 2: 1500085.

Nishino F, Jeem M, Zhang L, Okamoto K, Okabe S and Watanabe S. Formation of CuO nano-flowered surfaces via submerged photo-synthesis of crystallites and their antimicrobial activity. *Sci. Rep*. 2017; 7: 1063.

Njoku PC and Akumefula MI. Phytochemical and nutrient evaluation of *Spondias mombin* leaves. *Pakistan J. Nutr*. 2007; 6(6): 613-615.

Okpara EC, Ogunjinmi OE, Oyewo OA, Fayemi OE and Onwudiwe DC. Green synthesis of copper oxide nanoparticles using extracts of *Solanum macrocarpon* fruit and their redox responses on SPAu electrode. *Heliyon* 2021; 7: e08571.

Padi VVT and Černík M. Green synthesis of copper oxide nanoparticles using gum karaya as a biotemplate and their antibacterial application. *Int. J. Nanomed.* 2013; 8: 889-898.

Perreault F, Melegari SP, Da Costa CH, Rossetto ALdOF, Popovic R, and Matias WG. Genotoxic effects of copper oxide nanoparticles in Neuro 2A cell cultures. *Sci. Total Environ.* 2012; 441: 117-124.

Phang YK, Aminuzzaman M, Akhtaruzzaman M, Muhammad G, Ogawa S, Watanabe A and Tey LH. Green synthesis and characterization of CuO nanoparticles derived from papaya peel extract for the photocatalytic degradation of palm oil mill effluent (POME). *Sustainability* 2021; 13(2): 796.

Rakhshni AE. Preparation, characteristics and photovoltaic properties of cuprous oxide-a review. *Solid State Electron.* 1986; 29: 7-17.

Ramyadevi J, Jeyasubramanian K, Marikani A, Rajakumar G and Rahuman AA. Synthesis and antimicrobial activity of copper nanoparticles. *Mater. Lett.* 2012; 71: 114-116.

Rashad MM, Rayan DA, and Ramadan AA. Optical and magnetic properties of $CuO/CuFe_2O_4$ nanocomposites. *J. Mater. Sci.: Mater. Electron.* 2013; 24(8): 2742-2749.

Saif S, Tahir A, Asim T, and Chen Y. Plant mediated green synthesis of CuO nanoparticles: comparison of toxicity of engineered and plant mediated CuO nanoparticles towards daphnia magna. *Nanomaterials* 2016; 6(11): 205.

Sankar R, Manikandan P, Malarvizhi V, Fathima T, Shivashangari KS and Ravikumar V. Green synthesis of colloidal copper oxide nanoparticles using *Carica papaya* and its application in photocatalytic dye degradation. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 2014; 121: 746-750.

Saravanakumar K, Shanmugam S, Varukattu NB, Ali DM, Kathiresan K and Wanga M-H. Biosynthesis and characterization of copper oxide nanoparticles from indigenous fungi and its effect of photothermolysis on human lung carcinoma. *J. Photochem. Photobiol. B: Biol.*, 2019; 190: 103-109.

Sarker MZ, Rahman MM, Minami H., Suzuki T, Rahman MA, Khan A, Hoque SM, and Ahmad H. Magnetite incorporated amine-functional SiO_2 support for bimetallic Cu-Ni alloy nanoparticles produced highly effective nanocatalyst. *Colloids Surf. A Physicochem. Eng.* 2022a; 647: 129044.

Sarker MZ, Rahman MM, Minami H., Suzuki T., and Ahmad H. Amine functional silica–supported bimetallic Cu-Ni nanocatalyst and investigation of some typical reductions of aromatic nitro-substituents. *Colloid Polym. Sci.* 2022b; 300: 279-296.

Sarker MZ, Rahman MM, Minami H., Suzuki T., Hossain MK, and Ahmad H. Mesoporous amine functionalized SiO_2 supported Cu nanocatalyst and a kinetic-mechanistic degradation study of azo dyes. *Colloids Surf. A Physicochem. Eng.* 2021; 617: 126403.

Shaheen TI, Fouda A, and Salem SS. Integration of cotton fabrics with biosynthesized CuO nanoparticles for bactericidal activity in the terms of their cytotoxicity assessment. *Ind. Eng. Chem. Res.* 2021; 60(4): 1553-1563.

Sharma JK, Akhtar MS, Ameen S, Srivastava P and Singh G. Green synthesis of CuO nanoparticles with leaf extract of *Calotropis gigantea* and its dye-sensitized solar cells applications. *J. Alloys Compds.* 2015; 632: 321-325.

Sutradhar P, Saha M and Maiti D. Microwave synthesis of copper oxide nanoparticles using tea leaf and coffee powder extracts and its antibacterial activity. *J. Nanostruct. Chem.* 2014; 4: 86.

Tavakoli S, Kharaziha M and Ahmadi S. Green synthesis and morphology dependent antibacterial activity of copper oxide nanoparticles. *J. Nanostruct.* 2019; 9(1):163-171.

Tran TH and Nguyen VT. Copper oxide nanomaterials prepared by solution methods, some properties, and potential applications: A brief review. *Int. Sch. Res. Notices*, 2014;2014: 856592.

Udayabhanu, Nethravathi PC, Kumar MAP, Suresh D, Lingaraju K, Rajanaika H, Nagabhushana H, and Sharma SC. *Tinospora cordifolia* mediated facile green synthesis of cupric oxide nanoparticles and their photocatalytic, antioxidant, and antibacterial properties. *Mater. Sci. Semicond. Process.* 2015; 33: 81-88.

Wang X and Xu X. Thermal conductivity of nanoparticle-fluid mixture. *J. Thermophys. Heat Trans.*, 1999; 13(4): 474-480.

Yang M, He J, Hu X, Yan C and Cheng Z. CuO nanostructures as quartz crystal microbalance sensing layers for detection of trace hydrogen cyanide gas. *Environ. Sci. Technol.* 2011; 45(14): 6088-6094.

Yecheskel Y, Dror I, and Berkowitz B. Catalytic degradation of brominated flame retardants by copper oxide nanoparticles. *Chemosphere*, 2013; 93(1): 172-177.

Yugandhar P, Vasavi T, Devi PUM and Savithramma N. Bioinspired green synthesis of copper oxide nanoparticles from *Syzygium alternifolium (Wt.) Walp*: characterization and evaluation of its synergistic antimicrobial and anticancer activity. *Appl. Nanosci.* 2017; 7(7): 417-427.

Zak AK, Majid WHA, Mahmoudian MR, Darroudi M, and Yousefi R. Starch-stabilized synthesis of ZnO nanopowders at low temperature and optical properties study. *Adv. Powder Technol.* 2013; 24: 618-624.

Zak AK, Yousefi R, Majid WHA, and Muhamad MR. Facile synthesis and X-ray peak broadening studies of Zn1-xMgxO nanoparticles. *Ceram. Int.* 2012; 38: 2059-2064.

Zhang Q and Hua Y. Electrochemical synthesis of copper nanoparticles using cuprous oxide as a precursor in choline chloride-urea deep eutectic solvent: nucleation and growth mechanism. *Phys. Chem. Chem. Phys.* 2014; 16: 27088-27095.

Zhao Y, Mu S, Sun W, Liu Q, Li Y, Yan Z, Huo Z and Liang W. Growth of copper oxide nanocrystals in metallic nanotubes for high performance battery anodes. *Nanoscale* 2016; 8: 19994-20000.