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Eco-Friendly Synthesis of Copper Oxide Nanoparticles via Plant-Based Precursors: its Applications in Bio-medicine and Toxicity

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ABSTRACT: Nanomaterials, characterized by their nanoscale dimensions (1–100 nm), possess unique properties such as high surface area, catalytic reactivity, thermal conductivity, magnetic susceptibility, and chemical stability. Among these, Zinc Oxide (ZnO) nano particles (NPs) are prominent due to their applications in gas sensing, bio sensing, cosmetics, and biomedicine, including anti-diabetic and antimicrobial treatments. Their luminescent properties and radiation resistance make them valuable in space applications. Various chemical and green synthesis methods have been employed for metallic oxide nano particles, particularly ZnO and Copper Oxide (CuO) NPs. ZnO NPs exhibit desirable semiconductor properties and have been synthesized using techniques like sol-gel, co-precipitation, and green synthesis, often employing plant-based precursors. Similarly, CuO NPs have been synthesized using co-precipitation, thermal decomposition, and microwave-assisted green methods. The latter involves eco-friendly precursors such as banana peel ash and plant extracts (e.g., teak, spinach, lettuce, and banyan leaves) combined with microwave heating. Characterization using techniques like XRD and FESEM confirms the nano-range dimensions and uniformity of synthesized particles, with spherical shapes offering enhanced catalytic activity due to increased surface area. This study demonstrates the efficacy and sustainability of green synthesis techniques for CuO NPs including their medicinal applications, evalution of toxicity and highlighting their cost-effectiveness, simplicity, and rapid production. The findings underline the potential of nanotechnology in advancing green and sustainable development across industries.

Keywords: Copper Oxide NPs, Banana Peel, Nanoparticles, toxicity, medicinal applications, sustainable.

INTRODUCTION

Nanomaterials are particles having very minute size having a size range between 1-100 nm. Due to their high surface area, they offer significant catalytic reactivity. Because of their large surface area to volume ratio, they posses some magical property which include high thermal conductivity, large magnetic susceptibility, semiconducting property, non-linear optical performance and chemical steadiness (Jeevanandam *et al.*, 2018). Due to these multidimensional properties associated with nano particles they have been widely used in the area of food, feed, space, chemical, cosmetics industry, bio-medical science and material science division and thereby meet the criteria to achieve green and sustainable development (Pareek *et al.*, 2017). ZnO NPs are very much important due to their utilization in gas sensor, biosensor, cosmetics, etc. ZnO NPs have been used for anti-diabetic treatment (Nakahara *et al.*, 2001). Moreover, ZnO NPs shows excellent luminescent properties. ZnO is resistance to radiation damages make it useful in various space applications.

1. Synthetic method of nano particles. In general, two approaches have been employed for the synthesis of nano particle which include bottom up and top-down approach. The top-down approach involves milling or attrition of large macroscopic particle mostly done by the physicist. It involves synthesizing large-scale patterns initially and then reducing it to nano scale level through plastic deformation. Top-down technique cannot be employed for large scale production of nanoparticles because it is a costly and slow process. Inter ferometric Litho- graphic (IL) is the most common technique which employs the role of top-down approach for nano material synthesis (Teragundi and Nanjundeswaraswamy 2018) . The bottom-up method has been used by the chemist for the production of large scale and uniformly size distributed nano materials. Bottom-up approach is just reverse to top-down approach which manufactures the nano material from atomic or molecular species with the help of chemical reactions, allowing for the precursor particles to grow in size (bottom-up). Both top down and bottom-up approaches could be employed in different phases such as in gaseous, liquid, supercritical fluids, solid states, or in a vacuum (Tokumoto *et al*., 2003). The biological activity of nano particles depends on factors like surface chemistry, size distribution, particle morphology, and functionality is essential for various biomedical applications. The ZnO NPs occurring in a very rich variety of size and shape provides a wide range of properties. Nano particles preparation mainly includes chemical precipitation method, solid-state pyrolytic method, solution-free mechano chemical method, sol-gel method and biosynthesis method.

2 Review literature for synthesis of Metallic oxide nano particles

Metallic oxide nanoparticles commonly used are ZnO NPs and CuO NPs. Agarwal *et al.* (2017) reported the synthesis of metal oxides such as TiO_2, CuO and ZnO where it was observed that among this synthesis of ZnO is economic compared to others. It is observed that ZnO is a good semiconductor because of its good band gap and hence it can be used as cosmetics like sunscreen lotions, anti-cancer, anti-diabetic, antibacterial, antifungal because of its UV filtering properties. (Karam *et al.,* 2018) performed an experiment and reported that when TiO_2 is coated with ZnO nano crystals the change of the total active surface area is uniform and single way for PS 5 microns. But, it is seen that for PS 1 microns, the uniformity is broken because the active surface depends on how much quantity of TiO_2 NPs is added for layer thickness.

(Kumari *et al*., 2015) reported the synthesis of ZnO NPs by chemical precipitation method, where undoped and N doped ZnO nanoparticles were synthesized and reported the conclusion that the formation of impurity free wurtzite phase for undoped and N doped samples was uncertain through XRD analysis, the crystallite size found increasing with increase in N doping concentration.

Rochman and Akwalia (2017) reported the synthesis of ZnO nanoparticles by Sol-Gel method. In the experiment the variation in pH as the parameter was taken, and concluded that greater the pH of the sol-gel that will increase the agglomeration of particle and vice-versa. Datta *et al*. (2017) reported the synthesis of ZnO

NPs from *Parthenium hysterophrous* leaf extracts for their anti-microbial properties. And after SEM and TEM analysis it was conferred that the particles were spherical and cylindrical in shape with average particle size ranging between 16-45 nm.

Sutradhar and Saha (2016) reported the green synthesis of ZnO NPs by thermal method under microwave irradiation. It was observed that the preparation under microwave irradiation eliminates the toxic chemicals for the production of Nanoparticles. And the synthesized nanoparticles can be successfully used for preparation of nano-composites for photovoltaic application.

Mohan and Renjanadevi (2016) reported the synthesis of ZnO NPs by using two methods: (i) conventional method (ii) preparation using surfactants. And after the analysis it was conferred that ZnO NPs were formed with or without surfactants, but, ZnO nanoparticles formed in conventional method was in micron range *i.e.*, preparation was highly affected by particle agglomeration. And the ZnO NPs prepared using surfactants was in nano meter's range.

Ahmed (2017) performed the synthesis of ZnO NPs by solid-state reaction method, where synthesis deals with Mn doped ZnO sample. And the study reveals that Mn doped Zn nano-powders have been successfully synthesized and UV-v measurements conferred that the band gap decreases due to decrease in incorporation of Mn.

Thaweesaeng *et al.* (2013) reported the synthesis of pure ZnO and Cu-doped ZnO NPs by co-precipitation method. It was found that the synthesis by this method was successful and confirmed the result by XRD analysis with an average crystallite size of 25-27 nm.

Khalil *et al.* (2014) reported the synthesis of ZnO NPs by thermal decomposition of a binuclear Zn (II) curcumin complex. It was concluded that NPs with a size ranging from 117± 4 nm were obtained from an easily prepared organic moiety consisting metal complex precursor and such a type of precursors has potential for synthesizing metal oxide nanoparticles.

Sutradhar and Saha (2015) Synthesis of zinc oxide nanoparticles using tea leaf extract and its application for solar cel, reported the synthesis of ZnO NPs and its composites with natural graphite (NG) powder for application in solar cells working. It was reported that the synthesis using green tea leaf extract as non-toxic reducing material under microwave irradiation and successfully reveals the production of thin film of ZnO/NG composite material for photovoltaic application.

Hasnidawani *et al.* (2016) reported the synthesis of ZnO NPs by using sol-gel method. Spanhel and Anderson (1991) reported the synthesis of ZnO NPs by sol-gel method**,** which involve the following reaction:

Chemical reactions:

$Zn(CH_3COO)_2.\ 2H_2O + 2LiOH \quad Zn(OH)_2 + 2CH_3COOLi + 2H_2O$

$Zn(OH)_2 + 2H_2O + Zn(OH)_4^{2-} + 2H^+$

$Zn(OH)_4^{2-} \leftrightarrow ZnO + H_2O + 2OH^-$

3. Literature Review For The Synthesis Of Copper Oxide Nanoparticles

Singh *et al.* (2016) reported the synthesis of CuO NPs by co-precipitation method using $CuSO_4$, Hydroxylamine and NaOH as precursors.

$2CuSO_4 + 2NH_2OH.HCl + 6NaOH \rightarrow Cu_2O + N_2 + 2NaCl + 2Na_2SO_4 + 7H_2O$ (1)

$Cu_2O \rightarrow CuO$ (2)

- Wongpisutpaisan *et al.* (2011) reported the synthesis of CuO NPs by sono-chemical method followed by calcinations at 600-700°C.
- Ghane *et al.* (2010) reported the CuO NPs synthesis by thermal decomposition method.
- Zhu *et al.* (2011) reported the synthesis of CuO NPs by wet chemical method.
- Jayalakshmi (2014) reported the synthesis via simple sol gel method which reveals that the water soluble CuO NPs are stable over wide range of pH and temperature.

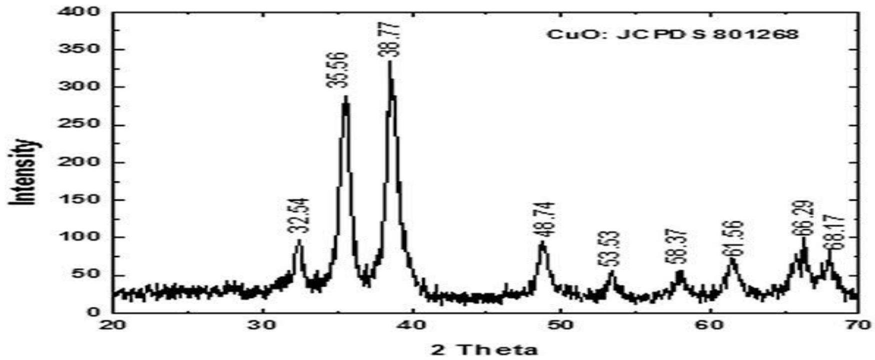


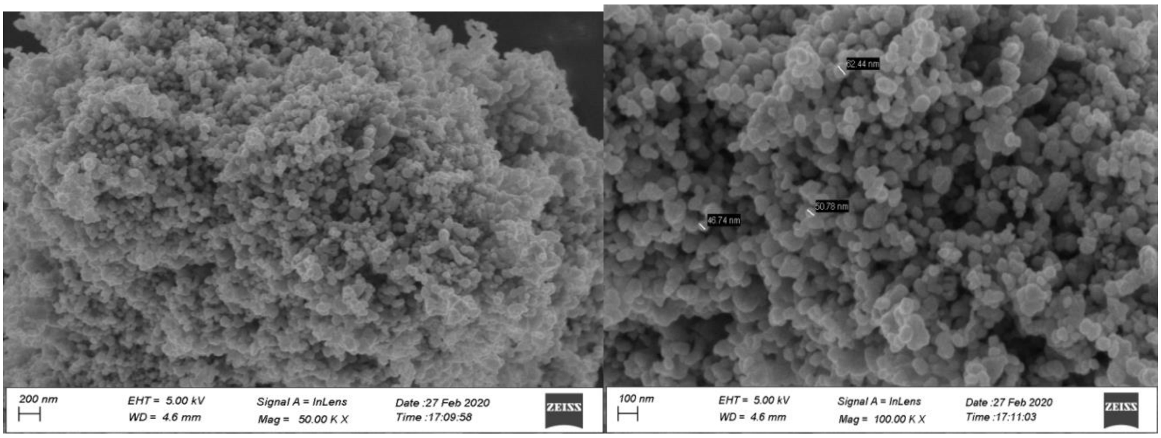
Fig. 1. XRD of Copper oxide nanoparticles.

4. Extraction of Banana peels Ash*:* Banana peels were collected from the ripe banana and washed thoroughly with water. Then the peels were dried for about 2-3 days, and were burnt. The ashes obtained were taken in a beaker and water was added. Finally, the solution was filtered (using whatman42 filter paper). Filtrate was directly used for synthesizing CuO NPs.

MATERIAL AND METHODS

1. Synthesis: For synthesizing CuO NPs, firstly we have prepared $CuSO_4$ solution by dissolving 1g of $CuSO_4.5H_2O$ in 10 ml of distilled water. In a separate vessel 0.1gm of starch was prepared in 10 ml of water and was heated for about 10 min. 0.5 g of NaOH was prepared in 20 ml of water in another separate beaker. In the aqueous $CuSO_4$ solution, the warm starch solution was first added slowly and then gradually aqueous NaOH solution was added drop-wise over a period of 10 minutes with constant stirring. The colour of the mixture appeared to be bluish. Then the reaction mixture was finally heated in microwave condition in 300w for 10 min. Finally, the reaction mixture turned into black colloidal solution, which indicates the formation of CuO NPs. The solid CuO nanoparticle was separated by either centrifugation or filtration. Residue was washed for several times with water and ethanol, so that no external impurity remains with the CuO NPs. The synthesized CuO nanoparticles was first dried at room temperature for about 24 h and then heated at around 300-400°C for around 4h. Similar procedure was employed for synthesizing CuO NPs with the various leaf extract. Only instead of starch we have used the different leaf extract (about 5-10 ml) for the synthesis of NPs.

Picture 1. Pictorial representation to show the synthesis of CuO nanoparticles.



Picture 2. FESEM analysis of the synthesized CuO NPs using starch.

Characterization of CuO Nanoparticles by FESEM analysis: The synthesized CuO nanoparticles using starch stabilizers were characterized by FESEM.

Application of CuO NPs. In modern days, nanoparticles have been used in day to day life such as cosmetics, textiles, agriculture, and in heavy industries as catalysts. Besides this the application of NPs has been extensively used in health care for preparation of pharmaceutical products. NPs also used in food packaging industries which are harmful for human being. Study reveals that CuO NPs can be used in treating diseases caused by microbes, fungal, work against cancer, and anti-inflammatory agents and therapeutic agents for wound healing and cuts.

Antibacterial Studies have revealed that The Cu/CuO NPs have the ability to retarded growth effects against both types of bacteria Gram-negative and Gram-positive. Biosynthesis of Cu NPs effective against in treating diseases caused by Gram-negative bacteria in urinary tract infection, kidney infection such as Escherichia coli (*E. coli*), *Enterococcus* sp., *Proteus* sp., and *Klebsiella* sp. CuO NPs have been used widely in preparation of ulcers related issue in human. This indicate the potential of these NPs in treating such infection. The banana peel NPs can also inhibit K. pneumonia, which is harm if spread to other organs of the body. Cu and CuO NPs have also shown a suppressive effect against the growth of Gram-positive bacteria such as Staphylococcus aureus (*S. aureus*), Bacillus subtilis (*B. subtilis*), and Streptococcus pyrogenes (*S. pyrogenes*). *S. aureus* which is known as a pathogen to cause respiratory and dermal infections, while *B. subtilis* can cause diarrhea and dysentery. Whereas, *S. pyrogenes* infects humans, causing various infections such as rheumatic fever and scarlet fever etc.

It suggested that diverse size and characteristics of Cu/CuO NPs are required to treat various pathogenic infections based on the type of bacterial agent involved and their characterization.

Study Shown that NPs derived from sugarcane-juice are effective against in treating *E. coli* compared to Gram-positive bacteria *B. subtilis* and *S. aureus*. However, a comparative study between Gram-negative bacteria, *E. coli* and *P. aeruginosa*, and gram-positive bacteria, *S. aureus* and *B. cereus*, with the treatment of CuO NPs synthesized using fruit extract that the minimal inhibitory concentration (MIC) is higher in Gram positive bacteria compared to Gram-negative bacteria. Predicted Mechanism for Antibacterial Activity The banana peel extract derived Cu/CuO NPs have an antibacterial effect tend to have antioxidant properties. It was found that C. vitiginea-mediated Cu NPs have antioxidant factors, which contributes to growth inhibition of urinary tract infection disease.

Fungal infection in human can be caused by direct touch or contact. *A. flavus* is a pathogenic fungus for human that causes liver cancer when spoiled food is consumed. A. fumigates produces airborne spores, which can cause chronic lung disease if inhaled or consumed. *C. albicans*, which is found in our body at the mouth and vagina, can cause infectious if there is high growth. Cu/CuO NPs have antifungal properties, suggesting their potential in treating fungal infection.

A study has highlighted that the Cu NPs synthesized using *A. eriophyllum* Boiss leaf extract is more resistant against fungi such as *C. guilliermondii* and *C. krusei* compared to bacteria. The fungus has numerous layers of lipids in its cell wall, which makes it challenging for the entry of NPs into the organism. A recent study noted that the green synthesis of CuO NPs triggered damage to the cell wall and accumulated ROS in A. flavus to demonstrate an antifungal effect. In addition, the CuO NPs synthesized from A. sativum extract also exhibited an antioxidant activity that may contribute to the antifungal property. The limited data implies that the CuO NPs can induce antifungal properties via different mechanisms.

In addition to antibacterial, antifungal effects, plant-mediated Cu/CuO NPs synthesized biologically possess unique properties, including high surface reactivity and biocompatibility, making them effective in treating inflammatory diseases. CuO NPs inhibit key pro-inflammatory pathways such as NF-κB and MAPK. By neutralizing ROS, CuO NPs reduce oxidative stress and associated inflammation. They modulate cytokine levels, decreasing pro-inflammatory cytokines (e.g., IL-6, TNF-α) and increasing anti-inflammatory cytokines (e.g., IL-10). CuO NPs can inhibit enzymes like COX-2, which are involved in inflammation. CuO NPs reduce joint inflammation and oxidative stress in arthritis models. Topical formulations help manage skin conditions like dermatitis. CuO NPs show promise in reducing inflammation in neurodegenerative diseases. Potential to reduce endothelial inflammation and oxidative damage in cardiovascular diseases. Reduced cytotoxicity compared to chemically synthesized NPs. Uses natural resources without harmful chemicals. Easier surface modification for targeted delivery. Scaling up biosynthesis methods while maintaining consistency is challenging. The exact interaction mechanisms with biological systems need further elucidation. Despite biosynthesis, potential long-term effects must be studied. Combining biosynthesis with other methods to enhance properties. Designing CuO NPs with specific targeting ligands for precision therapy. More comprehensive studies to validate anti-inflammatory effects in humans.

Toxicity Evaluation. Although Cu/CuO NPs have multiple medical effects, the toxicity of these NPs against normal cells and vital organs in humans can cause damage to the organ. This is the reason for which aspect should be evaluated thoroughly before utilizing these NPs in medicine.

CuO NPs have a high surface area-to-volume ratio, which enhances their reactivity. They can release copper ions (Cu^{2+}) in biological environments, contributing to toxicity. CuO NPs can generate reactive oxygen species (ROS), leading to cellular damage, lipid per oxidation, and DNA damage. Exposure to CuO NPs can trigger inflammation by activating signaling pathways in immune cells. Copper ions can bind to proteins and enzymes, disrupting normal cellular functions. The accumulation of CuO NPs in cells can impair mitochondrial function, affecting energy production. Inhalation of CuO NPs may cause lung inflammation, fibrosis, and oxidative stress. Nanoparticles can enter the bloodstream, potentially causing endothelial dysfunction, coagulation issues, and inflammation. Ingestion can result in gastrointestinal inflammation, damage to intestinal cells, and altered gut microbiota. CuO NPs may cross the blood-brain barrier, leading to neurotoxicity, oxidative stress, and neuronal damage. Studies suggest potential effects on fertility and embryo development due to oxidative damage. Higher doses and prolonged exposure generally result in increased toxicity. Smaller nanoparticles are more likely to penetrate cells and tissues. Coatings can reduce or enhance reactivity and toxicity. pH, ionic strength, and the presence of biomolecules affect the behavior of CuO NPs.

RESULT AND DISCUSSIONS

From FESEM it was observed that the synthesized particles are in the nano range where average sizes are around 40-60 nm. Morphology of the particles was studied by SEM and it was observed that the synthesized particle using starch is spherical in shape. Spherical shape particles can offer greater catalytic activity due to their larger surface area. The biosynthesis of copper oxide nanoparticles (CuO NPs) using banana peel extract proved to be an efficient, eco-friendly, and sustainable method for nanoparticle production. Characterization through techniques such as UV-Vis spectroscopy, XRD, and SEM confirmed the formation of CuO NPs with sizes ranging from 10–50 nm, high purity, and crystalline structure. The banana peel extract acted as a natural reducing and capping agent, minimizing toxic byproducts and supporting green chemistry principles.

Antimicrobial activity tests demonstrated significant efficacy of CuO NPs against bacterial strains like *E. coli* and *S. aureus* and fungal pathogens such as *Candida albicans*, showcasing their potential in combating infections. The nanoparticles disrupted microbial cell membranes, leading to enhanced therapeutic applications in wound healing and infection prevention.

Anticancer studies revealed promising cytotoxic effects of CuO NPs against specific cancer cell lines. The nanoparticles induced reactive oxygen species (ROS) production and mitochondrial dysfunction, triggering apoptosis in cancer cells while minimizing toxicity in normal cells. This highlights their potential for targeted cancer therapies.

The antifungal properties of CuO NPs further expand their applicability, demonstrating the ability to inhibit fungal growth effectively. This positions CuO NPs as a potential solution in addressing resistant fungal infections.

The use of banana peel for nano particle synthesis not only provides a value-added approach to agricultural waste but also aligns with sustainable and cost-effective biomedical advancements. The findings emphasize the versatile applications of CuO NPs in antimicrobial, antifungal, and anticancer treatments, underscoring their importance in modern medicine. Further studies should focus on in vivo efficacy, biocompatibility, and scaling up production to establish their clinical relevance. This green synthesis approach paves the way for innovative and sustainable therapeutic solutions in biomedicine.

CONCLUSIONS

The synthesis of CuO NPs do not requires any expensive ingredients. Synthesizing of CuO NPs using green precursor is cost effective as well as eco-friendly. This microwave assisted method is very simple. Most importantly NPs could be synthesized in short interval of time. SEM image of CuO NPs shows that the particles are spherical. Morphology of the particles analyzed by FESEM also confirmed the uniformity of synthesized particles.

FUTURE SCOPE

The nano scale dimensions (1–100 nm), possess unique properties, catalytic reactivity, thermal conductivity, magnetic susceptibility, and chemical stability which can be further identified and exploited and can several field including medical sector.

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Conflict of Interest. None.

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