

Synthesis of Copper / Copper Oxide nanoparticles in eco-friendly and non-toxic manner from floral extract of *Caesalpinia pulcherrima*

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Abstract: Nanomaterials/nanoparticles are of great interest today due to their small size and amazing properties like large surface area, modified and easily tuneable morphology and shape. Copper nanoparticles (Cu) are of lot interest now days due to their potential applications such as catalysis, cooling fluid or conductive inks the Copper Oxide (CuO) nanoparticle is widely used in Dye sensitized solar cells (DSSCs). Green synthesis is an emerging technique for production of nanoparticles due to many advantages over conventional physical processes and chemical synthesis method. In this study we report cost-effective, stable for long time and reproducible aqueous room temperature synthesis of the Cu/CuO nanoparticles from floral extract of *Caesalpinia pulcherrima* which are natural source of the polyphenol tannins and trace amount of ascorbic acid, where tannins are responsible for reduction and capping whereas ascorbic acid acts as protective agent to prevent the nascent Cu nanoparticles from oxidation during synthesis and storage. The capped polyphenols can be removed from particle surface by simple ethanoic wash. The crystallinity, size and shape of the nanoparticles were characterized by UV-Vis, FTIR, XRD, EDAX and SEM. The Surface Plasmon Resonance peak was observed at 380 nm and amalgamated size from the SEM is on an average to 20 nm. The structure from XRD is found to be monoclinic and confirmed it as CuO complex from EDAX. The Debye-Scherrer particle size is found to be 6 nm.

Keywords: Surface Plasmon Resonance (SPR), Copper nanoparticles, Copper oxide nanoparticles, Eco-friendly and *Caesalpinia pulcherrima*

1 Introduction:

The term "Nanotechnology" has been coined by "Norio Taniguchi", a researcher at University of Tokyo, Japan in 1974.^{1,2} Nanotechnology may be defined as the manipulation of particle with one of its size dimension smaller than 100 nm and having specific properties which can be used in particular applications.³

Nanoparticles are of great interest because they act as bridge gap between the atomic/molecular structure⁴ to the material in bulk as they exhibit completely new or improved properties based on specific characteristics such as size, shape, distribution, ionic strength, capping agent and morphology.^{2,5}

When well characterized bulk material was comparatively studied with Nanoparticles it was observed that nanoparticles due to their extremely small size and large surface area possess^{6,7} many interesting properties (e.g.: Mechanical properties, biological & satirical properties, catalytic activity, thermal & electrical conductivity, optical absorption and melting point) at same chemical composition.⁸⁻¹² Due to this they find novel applications in various areas of electronics, optoelectronic, magnetic, information storage, recording media, sensing devices, catalysis, chemistry, environment, energy, agriculture, medicine and drug delivery, communication technology, aircraft technology, heavy industry and consumer goods etc.¹³⁻¹⁷ So for novel application the focus is very important on design and production of nanoparticles with control on shape and size of synthesized particle at Nano-scale.

The nanoparticles are synthesised by many procedure but can be categorized mainly under physical and chemical technique. The drawback of the physical technique is that resultant nanoparticles have defective surface formation, low production rate, high cost of manufacturing and large

energy requirement.¹⁸⁻²⁰ The chemical method for synthesis of nanoparticles involves usage of toxic chemicals, concentrated reducing agents, high level of radiation²¹ and formation of hazardous by-products and contamination from precursor chemicals²² which is alarming threat in every aspect of flora, fauna and human health. The synthesis provided in this paper is eco-friendly, non-hazardous, non-toxic and also economical in nature.

2 Experimental

2.1 Materials

Copper (II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) of 99.999% was obtained from Sigma-Aldrich Chemicals and were used as obtained. Type 1 Ultrapure Milli-Q water was used throughout the reactions. The glassware's were rinsed thoroughly with dilute Nitric acid (HNO_3) followed with wash of water, and dried in hot air oven. The flowers of *Caesalpinia pulcherrima* was collected from the campus of the Birla College, Kalyan (W).

2.2 Synthesis

The flower petals of *Caesalpinia pulcherrima* was first dried and then powdered by mortar and pestle. 5.0 g of powdered flower petals was then mixed with 100 ml of water and magnetically stirred for 30 min at 60°C. The generated mixture was filtered using Whatman filter paper 1 and then the substrate was centrifuged, the supernatant was taken in further experimental part as flower extract for reduction of copper nitrate to Cu/CuO nanoparticles.

The 1 mM solution of Copper (II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) was prepared by dissolving 0.0187 g in 100 ml of water.

To prepare the copper nanoparticles the flower extract was added drop by drop to the 1 mM solution of the Copper (II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) under magnetic stirrer at

room temperature to have a colour change from blue to green which shows the formation of Cu/CuO nanoparticles which was further ultrasonicated for 20 minute. The solution is then heated in muffle furnace to a temperature of 280°C to have it in powder form which is black in colour.

3 Characterization

3.1 UV – Vis Spectroscopy

To monitor the stability and formation of Cu/CuO nanoparticle the absorption spectra of the synthesized Cu/CuO nanoparticles were recorded against water. Fig. 1 shows the UV–Vis spectra of Cu/CuO nanoparticle forming at room temperature after 24 h.

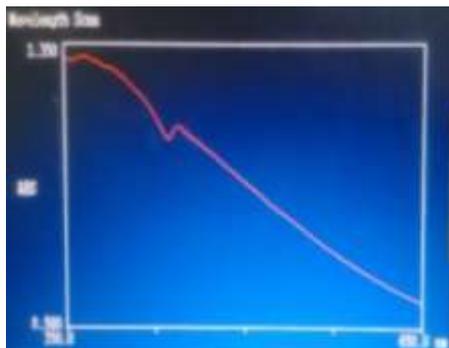


Figure 1: UV–Vis spectra of Cu/CuO nanoparticle at room temperature after 24h.

The change in the color indicates change in the Surface Plasmon Resonance (SPR). The Surface Plasmon Resonance peak is observed at 380nm. Formation of sharp narrow shape of SPR band indicating the formation of spherical and homogeneous distribution of nanoparticles.

3.2 FTIR Spectroscopy

To have FTIR measurements the small amount of 0.1g of nanoparticles was mixed with KBr and hydro pressed to form a pallets/disk. Fig. 2 shows the FTIR spectra of Cu/CuO nanoparticle. The peaks observed are in range of 400-550 cm^{-1} which clearly indicates that the sample is metallic in nature. The major bonds observed at 414, 431, 458, 475, 486 cm^{-1} which corresponds to Cu-O stretch also peak around 528 cm^{-1} is present which indicates the Cu-O stretch and absence of peak around 610 cm^{-1} clearly shows absence of Cu_2O phase in sample and is clear indication that the sample comprises of pure Cu/CuO phase.

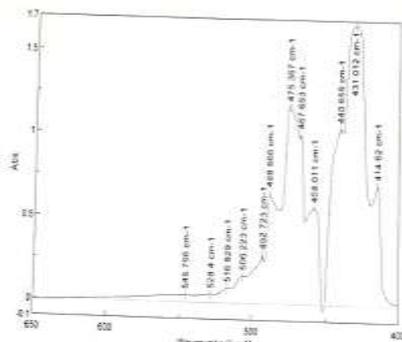


Figure 2: FTIR spectra of Cu/CuO nanoparticle at room temperature after 24h

3.3 SEM and EDAX

The SEM image shows predominately spherical nanoparticles. Fig. 3 shows the SEM image of Cu/CuO nanoparticle. The amalgamated size of the observed nanoparticles is found to be in range of 18-20nm average. The EDAX result shows the dominant peaks of Copper (Cu) and Oxygen (O) with complex as CuO.

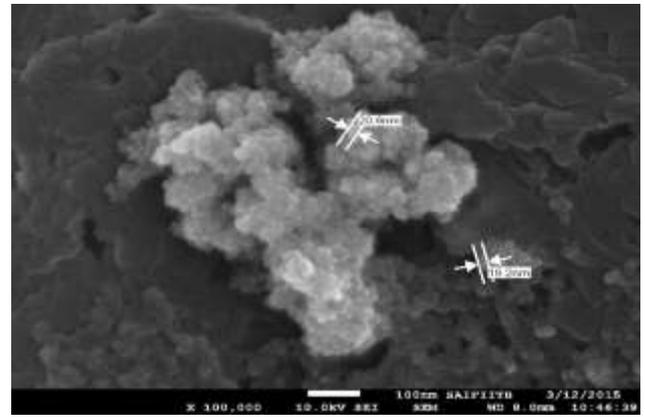


Figure 3: SEM image of Cu/CuO spherical nanoparticles with size 18-20nm

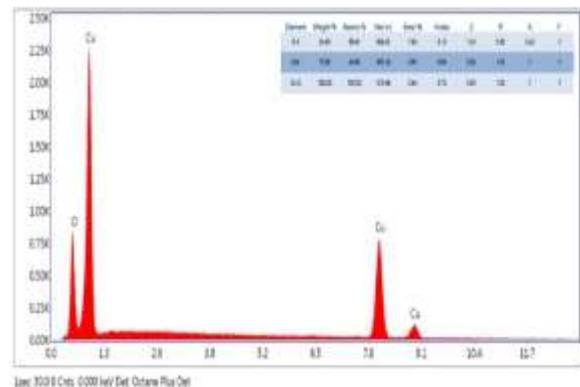


Figure 4: EDAX spectra of CuO nanoparticle.

3.4 XRD spectroscopy

The X ray diffraction shows the sample as the Monoclinic in nature matching the COD reference no. 96-101-1195. The unit cell parameters calculated are $a = 4.6700 \text{ \AA}$, $b = 3.4300 \text{ \AA}$, $c = 5.1200 \text{ \AA}$. The Debye-Scherrer particle size calculated is 6 nm for the sample.

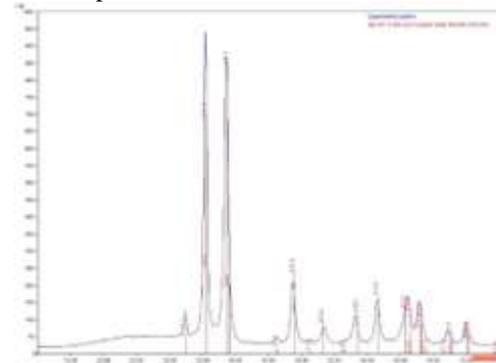


Figure 4 : XRD spectra of CuO nanoparticle at room temperature with hkl planes

3.5 Conclusion

Successful synthesis of Copper / Copper Oxide NPs using *Caesalpinia pulcherrima*. Method is eco-friendly, non-toxic and Economical. The amalgamated size of NPs obtained from SEM are in range of 18-20nm and are of high purity. The Surface Plasmon resonance peak is observed at 380 nm. The structure from XRD is found to be monoclinic with COD reference no. 96-101-1195 which is same for Copper oxide (Tenorite). The Debye-Scherrer particle size is found to be 6nm. The EDAX results show the high purity of the sample and showed the peaks of Copper and Oxygen in 75:25 wt%. The check for the oxide composition also showed there that sample is purely 100% CuO.

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