SYNTHESIS AND CHARACTERIZATION OF COPPER OXIDE NANOPARTICLES USING RAMBUTAN PEEL EXTRACT VIA GREENER ROUTE

L. Ragunath¹, J. Suresh^{1,✉}, M. Sankaran², R. Suresh Kumar³,
A. I. Almansour³ and N. Arumugam³

¹Department of Chemistry, Sri Ramakrishna Engineering College, N.G.G.O Colony,
Coimbatore-641 022, Tamil Nadu, India

²Department of Chemistry, School of Sciences, Bharathiar University,
Coimbatore-641 046, Tamil Nadu

³Department of Chemistry, College of Science, King Saud University,
P.O. Box 2455, Riyadh 11451, Saudi Arabia

✉Corresponding Author: suresh.j@srec.ac.in (Joghee Suresh)

ABSTRACT

An efficient, greener, simple approach to synthesize copper oxide nanoparticles using aqueous extract of rambutan peel as a precipitant and reducing agent. Green synthesis of copper oxide nanoparticles was found via hydroxide precipitation using rambutan peel wastes. The successful formation of copper oxide nanoparticles was confirmed by UV-Visible, XRD, SEM, TEM and SAED studies. UV-Visible confirms the absorption spectrum of copper oxide around 360nm. X-Ray Diffraction results found the highest intense peak (111) and the average crystallite size calculated as 35.74nm using debye scherrer's formula. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) images confirm the formation of copper oxide nanoparticles looks flake-like structures and shows the particle size range between 20-50nm. Further Selected Area Electron Diffraction (SAED) pattern also confirms the crystalline nature of copper oxide nanoparticles. Further, a possible formation mechanism was proposed for CuO nanoparticles using rambutan peel wastes.

Keywords: Rambutan Peel, Copper Oxide, Biosynthesis, XRD, SEM, TEM

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INTRODUCTION

Nowadays, we compare existing biological, physical and chemical methods, plant extract-based synthesis shows greener and eco-friendly alternative methods to synthesize biocompatible nanoparticles.¹⁻³ Recently, synthetic strategies employing biological plant extract⁴⁻⁶, enzymes⁷ and microorganisms⁸ play a vital role in forming nanoparticles. Among the transition metal oxides, copper oxide nanoparticles have potential industrial applications in catalysis, sensors, biocidal activity and superconductivity.⁹⁻¹³ Various conventional methods are available for the synthesis of copper oxide nanoparticles. Some of them are sol-gel, chemical vapor deposition, precipitation, pyrolysis, sonochemistry, electrochemistry, one-step solid-state reactions, cathodic vacuum arc and solvothermal reactions.¹⁴⁻²¹ The above-said methods are expensive and environmentally hazardous and they can apply in biological and clinical applications. So due to environmental concerns, the green synthetic approach for the synthesis of nanomaterials is given more importance nowadays. The utilization of plants extracts, microorganisms, or plant biomass has been a recent research topic for the formation of nanoparticles over physical and chemical methods.²²⁻²⁴ Recently, many groups successful to synthesized nanoparticles using unicellular organisms and plant extracts such as neem leaves, lemongrass, geranium leaves, aloe vera etc.,²⁵⁻³⁷ This new green chemistry approach is also in consequence with its simplicity, eco-friendly, inexpensive price and environmentally acceptable nature. In this present work, we choose rambutan fruit peels as one of the biological waste materials. We have to synthesize copper oxide nanoparticles and using the rambutan peel extract and it can be characterized by

different techniques like UV - Visible, XRD, SEM and TEM analysis. To the best of our knowledge, it is the first report on the synthesis of CuO nanoparticles using rambutan fruit peel extract and no other attempts have been made earlier so far.

EXPERIMENTAL

Materials

The rambutan fruit peels were collected from a fruit stall at Coonoor, Tamil Nadu, India. $\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$, ethanol were purchased from Merck chemicals Ltd, India.

Preparation of the Extract

Rambutan fruit peels were separated manually and washed thoroughly with running water. Then it is cut into small pieces and then placed in a circulating oven for drying purposes. About 3 g of finely dried rambutan peels were boiled with a mixture of ethanol and double distilled water (1:2 ratio) for 10 min. Then the obtained extract is filtered and collected in a 250ml flask and stored in the refrigerator.

Synthesis of Copper Oxide Nanoparticles

0.1 M of copper sulphate pentahydrate ($\text{Cu}(\text{SO}_4)_2 \cdot 5\text{H}_2\text{O}$) was prepared in 50 mL double distilled water and add 10 mL of rambutan peel extract was added slowly. Then the mixture was kept under magnetic stirring at 80°C for two hours and it formed a copper hydroxide precursor. The light green precipitate is formed and then centrifugation for 15 minutes. Further, the separated light green precipitate dried in an oven for four hours, followed by grinding using mortar and pestle. Then finally, the powdered sample undergoes calcination around 450°C to get pure copper oxide nanoparticles.

RESULTS AND DISCUSSION

UV-Visible Absorbance Studies

Figure-1a and b show the UV-Vis spectra recorded for the pure natural extract and the synthesized copper oxide nanoparticles. The spectrum of pure extract does not show any characteristic absorption peak, which confirms organic compounds present in the rambutan peel extract. The UV-Visible absorption spectrum of CuO nanoparticles shows a broad absorption peak around 370 nm. The obtained continuous rise from wavelength 600 nm confirms the characteristic optical absorption of CuO nanoparticles.

Fig.-1: UV Visible Spectrum of (a) Rambutan Extract, (b) Synthesized Copper Oxide Nanoparticles

XRD Analysis

Figure-2 shows the XRD spectrum of CuO nanoparticles and it's clearly observed the presence of sharp peaks as well as broad peaks suggesting the formation of the resulting CuO products were of mixed-phase of an amorphous and crystalline state. The diffraction peaks at $2\theta = 32.06^\circ, 35.48^\circ, 38.74^\circ, 48.71^\circ, 61.53^\circ$ and 66.07° are assigned to (110), (111), (200), (202), (113) and (311) crystal planes

of cubic phase CuO and it match with JCPDS data card (89-2529). The crystallite size of the CuO nanocrystals was estimated from a higher intense peak of the XRD spectrum using Debye Scherrer's equation. The average crystallite size of the higher intense plane of (111) was 35.74 nm.

Fig.-2: X-ray Diffraction Pattern of Copper Oxide Nanoparticles

SEM and TEM Analysis

Figure-3 (a and b) shows the SEM image of copper oxide nanoparticles at different magnifications. The SEM images showed a flake-like structure and nanoparticles were distributed in the form of aggregation of small individual nanocrystallites of about 20–50 nm in size. Figure-4 (a and b) shows the representative TEM images of CuO nanoparticles. The uniform weak agglomeration of CuO nanoparticles with reasonable distribution has evidence from the obtained TEM images. The average crystallite size obtained from TEM images was around 40 nm which agrees well with the size calculated from XRD analysis. Figure-4c shows the electron diffraction (SAED) pattern of the selected area and its confirmed diffraction rings and hallow patterns, apparently indicating the obtained mixed phase of an amorphous and crystalline state of the Copper oxide grains, which is also evident from the XRD pattern.

Fig.-3:(a) and (b) SEM Images of Copper Oxide Nanoparticles at Different Magnification

Possible Mechanism of CuO Nanoparticles

In rambutan peel extract, the active ingredients, polyphenolic compounds such as ellagic acid, corilagin and geranin are present as major components with high proportion. These natural phenolic antioxidant compounds have favorable effects for the synthesis of copper oxide nanoparticles and also have anti-carcinogenic in nature.³⁸ Scheme 1. shows the possible mechanism of copper oxide nanoparticles using rambutan peel extract. When a metal complex is formed in the initial step. Then

after complexes undergo hydrolysis to precipitate metal ions as metal hydroxide or metal oxide, depending upon the reaction pH, the pH value varies depending upon the metal ions. In our synthesis, rambutan peel extract permits the copper sulphate to precipitate the copper hydroxide at pH 5-7. The precursor copper hydroxide undergoes calcining at 450°C yields copper oxide nanoparticles.

Fig.-4: TEM Images of Copper Oxide Nanoparticles (a & b) and (c) SAED Pattern

Scheme-1: Possible Mechanism of CuO Nanoparticle Formation using Rambutan Peel Extracts

CONCLUSION

Copper oxide nanoparticles were synthesized using a simple, eco-friendly, inexpensive, greener route using rambutan peel extract. The synthesized nanoparticles were confirmed by UV Visible, XRD, SEM, TEM analysis. Further, we discussed the formation mechanism of copper oxide nanoparticles. More importantly, this present work can be extended to other metal oxide nanoparticles and this type of transition metal oxides have various more attention in biomedical applications.

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