

# Photoluminescence Studies of Green Synthesized Copper Nanoparticles

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## ABSTRACT

Copper nanoparticles (CuNPs) are prepared using two stage chemical reduction method. Ocimum Sanctum (OS) leaves extract is used to stabilize the CuNPs. This approach is proved to be an efficient method for preparation of CuNPs at room temperature and without using any inert atmosphere. The resulted powder samples are characterized by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Small Angle X-Ray Scattering (SAXS), UV-Visible Spectroscopy, X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) techniques. The prepared CuNPs are found to be FCC crystalline and monodispersed. The visible photoluminescence from metal nanoparticles is usually due to the interband transition between the sp conduction bands and the d bands. Photoluminescence spectra of CuNPs show an emission peak at 535 nm when illuminated at 325 nm. The fluorescence of molecules in direct contact with the metal gets enhanced. Here adsorbed natural extract on the surface of CuNPs can enhance the emission peak.

Keywords: Green synthesis, Copper, Nanoparticles, Photoluminescence, Ocimum Sanctum

## 1. INTRODUCTION

The study of nanoparticles is of great interest due to their wide range of applications in various fields like textiles, renewable energy, environment, biomedical and healthcare etc. Nanosized metal particles are one of the main objectives of present scientific field because of their physical and chemical properties, which are quite dissimilar from those of bulk materials (1-2). The toxicity free metal nanoparticles are produced by increasing the use of eco-friendly materials in the preparation (3).

CuNPs are preferred over silver and gold as they show high conductivity and catalytic properties. However, aggregation and oxidation are the main problems concerned to copper nanoparticles. These

problems can be rectified by usage of a suitable separate stabilizing agent in the preparation (4).

Different preparation methods such as Laser ablation, electrochemical reduction, thermal decomposition, chemical reduction etc. have been used for the synthesis of nanomaterials. Among these methods, chemical reduction is highly preferred method as it is simple and economical (5).

There is great interest in the preparation of stable CuNPs and in their emission spectra. The electronic structure of copper can explain its photoluminescence behavior where 3d valence and 4sp conduction electrons play the role for fluorescence. In the present study, we have tested the capping behavior of Ocimum Sanctum (OS) leaves extract to surround CuNPs and also the impact of OS extract in enhancing the photoluminescence behavior of CuNPs.

## 2. EXPERIMENTAL

The raw materials of analytical reagent grade such as copper chloride, L-Ascorbic acid, NaOH and Hydrazine Hydrate (HH) were used in the preparation of CuNPs. All the solutions were made with Millipore water. Ocimum Sanctum (OS) leaves extract was the natural stabilizer used for the capping of produced CuNPs. 20 grams of fresh young OS leaves were washed several times with Millipore water to remove dust particles and then leaves were cut and grounded with a mortar and a pestle. The finely grinded OS paste was transferred into a 100 mL round bottom flask and then stirred with 50 mL of Millipore water at room temperature for 3 hours and then allowed to stay for 1 hour. The OS extract was decanted gently and filtered to remove the solid undissolved residues of OS leaves. This filtrate was used as stabilizing agent for CuNPs preparation.

### 2.1. Nanoparticle Synthesis

In the present study, copper chloride (precursor, 0.04M) and L-Ascorbic acid (anti-oxidant agent, 0.001M) solutions were prepared separately

using Millipore water. The solutions of OS extract and L-Ascorbic acid were added to copper chloride solution under stirring. Then the solutions of HH (reducing agent, 1M) and NaOH (catalyst, 0.01M) were added to the mixed copper chloride solution under stirring. Eventually the initial blue colored solution changed to brown-black color. Stirring was continued for another 1 hr. to complete the reaction. The precipitate was washed twice and then dried to obtain copper nanopowders.

## 2.2. Characterization

Morphology and size of the CuNPs were investigated using Transmission Electron Microscope (TEM-Phillips equipment) and Scanning Electron Microscope (SEM-Hitachi S-3400N equipment). Small Angle X-Ray Scattering (SAXS) data were collected using Panalytical X-ray Generator (PW 3830) having SAXS 896986 Anton Paar mounted on it. The UV-Visible spectrometer (Lab India Instruments Pvt. Ltd, Lab India UV- 3000+) is used to study the surface plasmon peak of colloidal dispersion of CuNPs. All spectra are corrected against the background spectrum of water as reference. The X-Ray Diffraction (XRD) pattern of CuNPs was recorded using Philips X-ray diffractometer coupled with graphite monochromator. The Crystallite size of the CuNPs was calculated using Williamson – Hall equation given as following.

$$\beta_{hkl} \cos \theta = \frac{K\lambda}{D} + 4\varepsilon \sin \theta \quad (1)$$

Here  $\lambda$  is the wavelength of X-rays,  $\beta_{hkl}$  is the full width at half maximum of X-ray profile,  $D$  is the diameter or crystallite size of the particle,  $\varepsilon$  is the lattice strain,  $K$  is the constant (0.89) and  $\theta$  is the Bragg angle. The Fourier Transform Infrared Spectroscopy (FTIR) spectra of CuNPs were recorded by KBr pellet method using FTIR spectrometer (Bruker Optics, Germany, Tensor 27).

Fluorescence spectra were obtained on a Fluorolog 3-11 Spex – Jobin Yvon spectrofluorometer. Xenon lamp source was used for excitation. Excitation and emission slit width was 2 nm; the acquisition interval was 1 nm and the integration time was maintained at 0.1 s for the total luminescence spectra and 0.05 s in the synchronous scan method. Individual spectra were corrected for the wavelength response of the system. The emission spectra in the total luminescence method were collected between 200 to 700 nm in the range from 250–550 nm at excitation wavelengths, spaced by 10 nm intervals in the excitation domain.

## 3. RESULTS AND DISCUSSION

The size and morphology of OS extract stabilized CuNPs are studied by using TEM and SEM. The TEM images of the CuNPs samples are shown in Figure 1. During TEM analysis, it is observed that the CuNPs have been formed with spherical morphology and with average particle size of 12 nm.

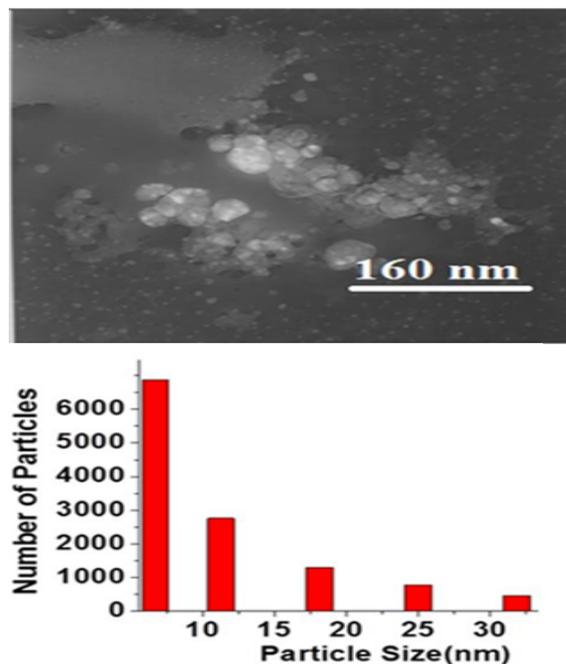


Figure 1: TEM image and particle size distributions of OS extract stabilized CuNPs

The SEM images of prepared CuNPs are shown in Figure 2. These images show the spherical morphology of CuNPs which is in agreement with TEM results. The average particle size determined SEM image is 15 nm.

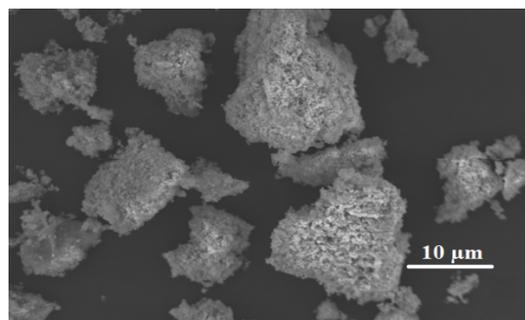


Figure 2: SEM image of OS extract stabilized CuNPs

SAXS measurements were performed using Mo and Cr radiations with three different configurations to cover wide q-range. SAXS profiles are fitted with diluted spherical model and log-normal size distribution. The SAXS profile of prepared CuNPs is shown in Figure 3, which reveals that the particle size is on the order of nanometers. The average particle size of prepared CuNPs is 14 nm.

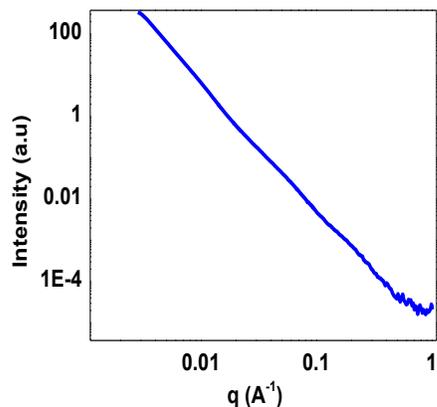


Figure 3: SAXS image of OS extract stabilized CuNPs

The UV-Visible absorption spectrum of prepared CuNPs is shown in Figure 4. The CuNPs have displayed an absorption peak at around 558 nm. This peak can be assigned to the absorption of CuNPs and it confirms Cu phase in the prepared samples.

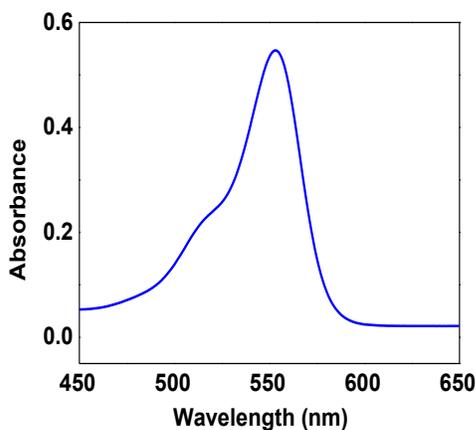


Figure 4: UV visible absorption spectrum of OS extract stabilized CuNPs

XRD pattern of prepared CuNPs is shown in Figure 5. Three main characteristic diffraction peaks for Cu are observed at around  $2\theta = 43^\circ, 50^\circ, 74^\circ$  correspond to (111), (200), (220) crystallographic planes of face-centered cubic (FCC) Cu crystals (JCPDS No.04-0784). The lattice parameter 'a' has

been calculated by using these profiles and the average value of lattice parameter is found to be in agreement with reported value  $3.615 \text{ \AA}$  in literature [6]. The average crystallite size of all CuNPs sample is determined using equation (1) and it is found to be 10 nm.

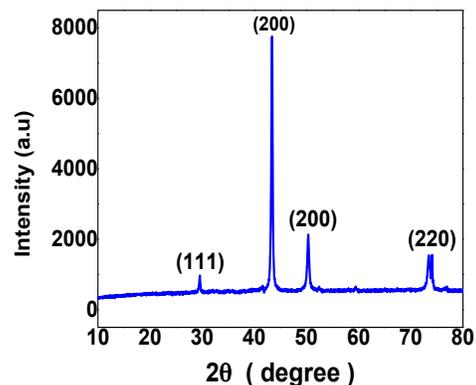


Figure 5: XRD pattern of OS extract stabilized CuNPs

The FTIR spectrum of OS extract stabilized CuNPs is obtained and this is compared with the FTIR spectrum of corresponding OS extract. The FTIR spectra of both samples are shown in Figure 6. The broad and strong bands are observed in these spectra at around  $3460 \text{ cm}^{-1}$  and  $628 \text{ cm}^{-1}$  corresponding to the O-H stretching frequency. The absorption peak that appeared at around  $1562 \text{ cm}^{-1}$  is due to O-H bending. It is clear from the Figure 6 that the peaks in the range  $650\text{-}1000 \text{ cm}^{-1}$  of OS extract are shifted slightly to higher wave numbers when compared with the FTIR spectrum of OS extract stabilized CuNPs. These differences indicate that the thin layer of natural extract molecule is developed on the surface of the CuNPs.

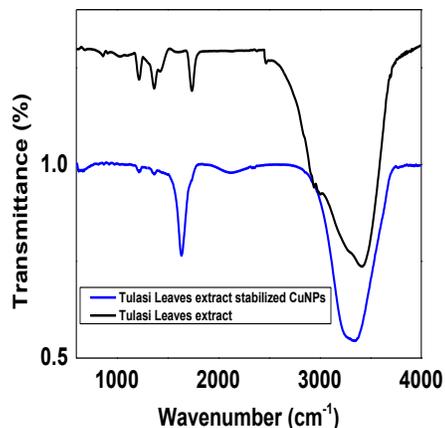
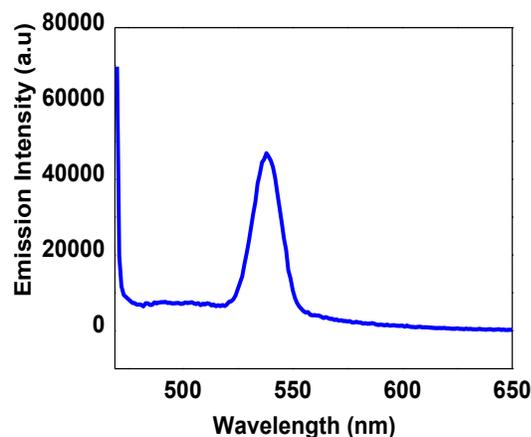


Figure 6: FTIR spectrum of OS extract stabilized CuNPs

Figure 7 shows the photoluminescence spectrum of OS leaves extract stabilized CuNPs. It is clear from the figure that the luminescence peak observed at around 535 nm is attributed to the radiative recombination of electron hole pair between d-band and sp-conduction band followed by initial electronic relaxation. Here, the excitation at around 325 nm from Xenon laser leads to the excitation of d-band electrons into sp-conduction band due to interband transition. It is known that the emission properties of the fluorescent molecules near a metal nanoparticles change significantly and the adsorbed OS extract on the surface of CuNPs can enhance the emission peak.



**Figure 7. Photoluminescence Spectrum of OS extract stabilized CuNPs**

#### 4. CONCLUSIONS

The green route of preparing CuNPs in aqueous solution at room temperature without using any inert atmosphere is reported. The prepared CuNPs are coated with a natural OS extract layer on the particle surface which controls the particle size. The photoluminescence spectra of OS extract stabilized CuNPs shows peak at 535 nm. The impact of OS extract present on the CuNPs surface is understood as there is enhancement in the emission peak. This is a cost effective method and scaling up is possible.

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