Copper Nanoparticles: Green Synthesis and Characterization

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Abstract – Present work describes the synthesis of copper nanoparticles using papaya extract as a capping agent. The preparation of copper nanoparticles by using papaya extract has desired quality with low cost and convenient methods. The papaya extract was mixed with copper salt solution by heating to a temperature of 50-60˚C and the reduction reaction was studied by observing the color change. The resulting copper nanoparticles were characterized by UV Visible Absorption Spectrometer, X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) experiments. X-ray diffraction analysis shows that the particles are FCC crystalline in nature. The FTIR spectrum analysis has confirmed the presence of functional groups of stabilizer papaya in capping the copper nanoparticles. SEM and TEM results display the formation of copper nanoparticles with an average size of 20 nm. Copper nanoparticles exhibit an absorption peak at around 560 nm.

Index Terms - Papaya, Copper Nanoparticles, Reduction Reaction, Green Synthesis, Capping Agent, XRD, FTIR

1 INTRODUCTION

Noble metal nanoparticles have been the subject of focused research due to their unique optical, electronic, mechanical and chemical properties that are significantly different from those of bulk materials. For these reasons, metallic nanoparticles have found uses in many applications in different fields, such as catalysis, photonics, and electronics. Preparation of copper nanoparticles has attracted considerable attention due to their diverse properties and uses, like catalysis, antimicrobial and antibacterial activities, and surface-enhanced Raman scattering (SERS) [1], [2].

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For the last few years, many efforts have been made on the synthesis of metallic copper nanoparticles in condensed phases with shape, size and growth control. Several methodologies have been proposed with interesting approaches to control the nanomaterial properties such as size and shape; these include metal vapor deposition, electrochemical reduction, thermal decomposition, radiolytic reduction and chemical reduction etc. [3], [4].

Most of these methods are extremely expensive and also involve the use of toxic, hazardous chemicals. This may pose potential environmental and biological risks. Since noble metal nanoparticles are widely applied to areas of human contact, there is a growing need to develop environmentally friendly processes for nanoparticle synthesis that do not use toxic chemicals. Sometimes the synthesis of nanoparticles using plants or parts of plants can prove advantageous over other biological processes by eliminating the elaborate processes of maintaining microbial cultures [5], [6].

2 EXPERIMENTAL

2.1 Materials

All chemicals used were of analytical reagent grade. The copper chloride, copper sulphate, copper nitrate, L-Ascorbic acid, NaOH, Hydrazine Hydrate (HH) was used as received. All solutions were made with millipore water.

2.2 Synthesis of Copper Nanoparticles

In the present method, copper salts were used as basic precursors, papaya extract as stabilizer, HH as reducing agent, L-Ascorbic acid as an anti-oxidant agent. NaOH was used as a catalyst and also to adjust the pH to 12. Copper chloride solution was prepared separately. L-Ascorbic acid was dissolved in Millipore water. Papaya extract and the solution of L-Ascorbic acid were added to copper chloride solution by heating to a temperature 50-60˚C under rapid stirring. Then the solutions of HH and NaOH were added to the mixed copper salt solution under stirring. The initial blue color of the reaction mixture eventually turned to brown-black color. Stirring was continued for another 1 hr to complete the reaction. The precipitate was washed twice with methanol after filtration and then dried and then the powder was obtained. Following same procedure, copper nanoparticles were also prepared using the other copper salts, copper sulphate and copper nitrate.

2.3 Characterization

XRD patterns of copper nanoparticles were recorded using Philips X-ray diffractometer coupled with graphite monochrometer. The scanning was done using Cu Kα radiation in the range of 2θ from 0° to 80°. Crystallite size was calculated using Scherrer's formula given by equation (1).

$$D = \frac{0.89\lambda}{\beta\cos\theta} \qquad (1)$$

where λ is wavelength of X-rays, β is the full width at half maximum of X-ray profile and θ is the Bragg angle.

The FTIR spectra were recorded using FTIR spectrometer. A known amount of sample was ground with KBr and the pellet form of the samples was analyzed with FTIR instrument. The green synthesis of copper nanoparticles was monitored by UV-Vis spectroscopy. All spectra were corrected against the background spectrum of water as reference. Morphology and size of copper nanoparticles were investigated using scanning and transmission electron microscopes (SEM and TEM).

3 RESULTS AND DISCUSSION

3.1 XRD

XRD patterns of copper nanoparticles (CuNPs) synthesized using different copper salts and papaya extract as stabilizer are shown in Fig. 1.

Three main characteristic diffraction peaks for Cu were observed at around 2θ = 43°, 50°, 74° which correspond to the (111), (200), (220) crystallographic planes of face-centered cubic (fcc) Cu phase (JCPDS No.04-0784). A small peak is also observed at around 29° indicates that a small amount of copper is oxidized and converted into copper oxide.

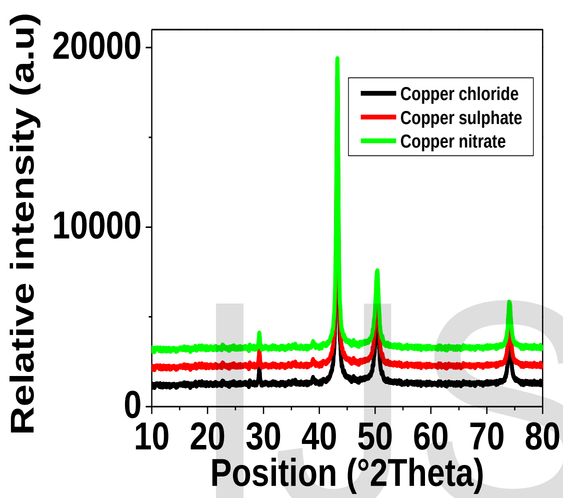

Fig.1. XRD patterns of CuNPs

The lattice parameter 'a' has been calculated by using these profiles and the average value of lattice parameter is found to be in the range 3.61 A° - 3.63 A°. These values not only agree with each other but also in agreement with reported value 3.615 A° in literature ([7]). In general, the width of XRD peaks is related to crystallite size. Crystallite size of copper nanoparticles was calculated using the Scherer's equation (1), and found to be around 10 nm.

3.2 FTIR

FTIR measurement was carried out to identify the possible molecules responsible for capping and reducing agent for the copper nanoparticles synthesized using papaya extract stabilizer. FTIR spectra of copper nanoparticles synthesized using different copper salts stabilized by papaya extract are shown in Fig. 2. The broad bands observed at around 3480 cm^{-1} and 617 cm^{-1} illustrates the stretching frequency of hydroxyl group (OH group) present in the surface of the copper nanoparticle.

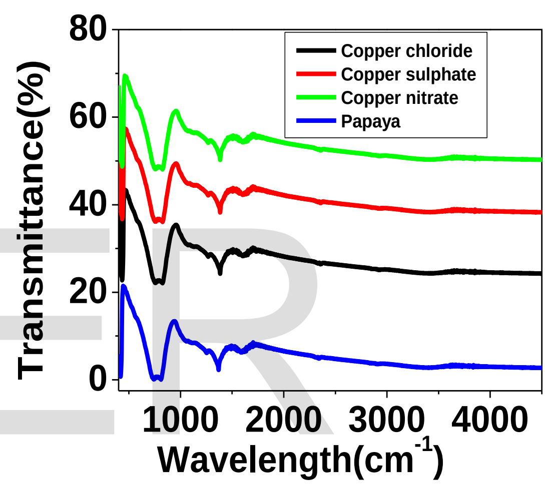

Fig.2. FTIR spectra of CuNPs

3.3 UV-Vis Spectra Analysis

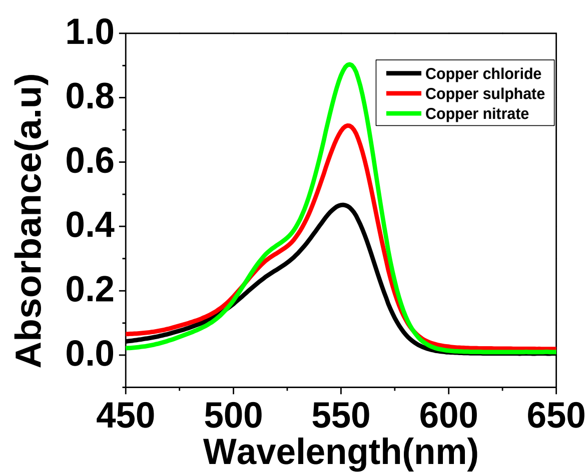

Fig.3. UV Visible spectra of CuNPs

UV-Vis absorption spectra of the copper nanoparticles are shown in Fig. 3. The copper nanoparticles prepared using different copper salts and papaya extract stabilizer display an absorption peak at around 560 nm. This peak can be assigned to the absorption of copper nanoparticles. The broadness of the absorption peak probably stems from the wide size distribution of nanoparticles.

3.4 SEM

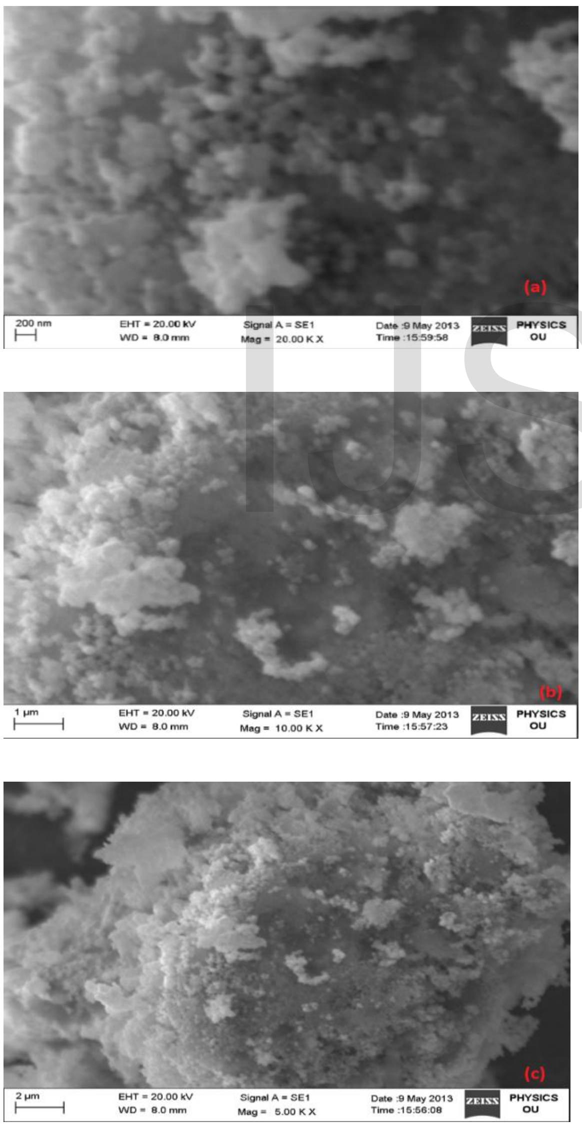

Fig.4. SEM images of CuNPs prepared using different copper salts, (a) Copper chloride (b) Copper sulphate (c) Copper nitrate

SEM images of copper nanoparticles stabilized by papaya extract prepared using copper chloride, copper sulphate and copper nitrate are shown in Fig.4 (a-c). Copper nanoparticles by this method show nearly monodispersed distribution of particle sizes. The average particle size of the Cu nanoparticles is around 20 nm. The composition of copper nanoparticles was further probed by energy-dispersive X-ray (EDX) analysis. Fig. 5 shows the EDX pattern of CuNPs prepared using copper sulphate, which indicates the presence of Cu and small amount of oxygen.

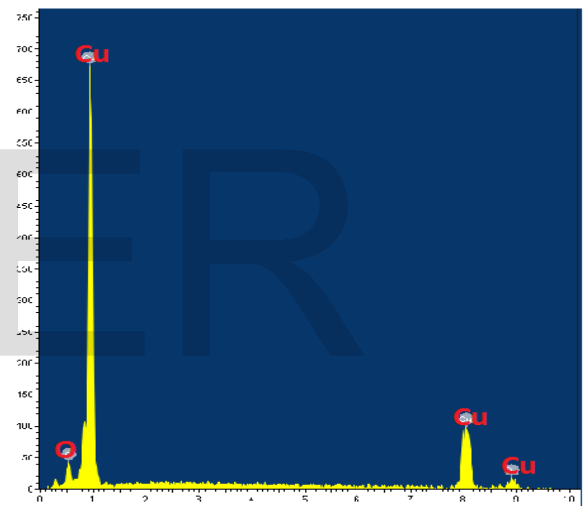

Fig.5. EDX pattern of CuNPs prepared using copper sulphate

3.5 TEM

Transmission electron microscopy (TEM) has been employed to characterize the size, shape and morphology of synthesized copper nanoparticles. Copper sulphate is found to be the best precursor that gives better result among other salts used for the synthesis of CuNPs, i.e., good particles size control along with papaya extract as capping agent. The TEM image of copper nanoparticles synthesized using copper sulphate stabilized by papaya extract is shown in Fig. 6. The average size of copper nanoparticles is around 20 nm. The sample studied reveal monodispersity of the metal particles.

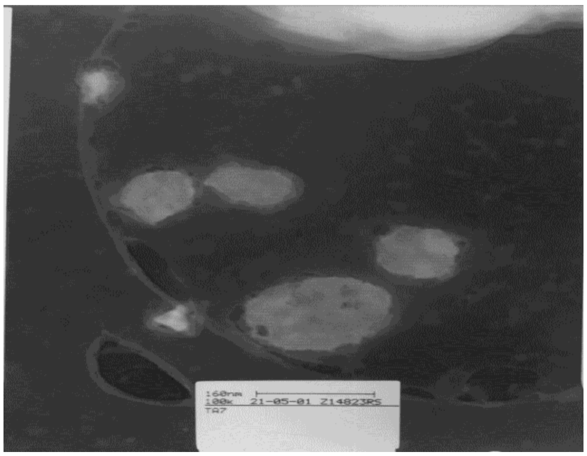

Fig.6. TEM image of CuNPs prepared using copper sulphate

4 CONCLUSIONS

A novel green approach for the synthesis of Cu nanoparticles using papaya extract has been presented. This is a simple, green and efficient method to synthesize copper nanoparticles at room temperature without using any harmful chemicals. It has been concluded that the green synthesized copper nanoparticles are nearly spherical and crystalline. The average particles size of copper nanoparticles is around 20 nm.

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