

Synthesis and Characterization of Surfactant Capped Copper Nanoparticles Using Natural Vitamin

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Copper nanoparticles (CuNPs) have captivated amazing and renewable interest in recent years due to their fascinating features. In present investigation, CuNPs were produced by reducing copper sulphate with ascorbic acid (vitamin C) in aqueous medium without inert gas insulation at low temperature (80 °C). In present synthetic procedure, a native vitamin C was applied as insulating agent to prevent oxidation of nascent CuNPs during the process and in storage. Triton X-100 was added that worked both as a size controller and as a capping agent. The CuNPs were characterized by UV-visible and FT-IR spectroscopies, powder X-ray diffraction (PXRD) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX). Optical properties of Cu nanoparticles were explored using UV-vis spectroscopy. FT IR was employed to uncover the bonding between copper nanoparticles and Triton X-100. The CuNPs were discerned by PXRD and SEM-EDX Techniques. From the major diffraction peaks, the average particle size is determined using Debye-Scherrer equation and it is found to be about 15 nm. It is hoped that the present results would pave a way for developing plans for the production of nascent CuNPs in the absence of inert gas insulation.

Keywords: Copper nanoparticles, Ascorbic acid, Triton X-100, Powder X-ray diffraction technique, Scanning electron microscopy.

INTRODUCTION

Metal nanoparticles possess unique characteristics which differ from bulk properties [1,2]. Metal nanoparticles are glamorous materials for catalysis with selectivity and specificity. Metal nanoparticles have received remarkable recognition due to their unique features [3,4]. Among various metal particles, copper nanoparticles (CuNPs) possess applications in modern technologies such as metal injection moulding, ceramics, electronics, thin films, biology and medicine. Low-cost of CuNPs have received much attention when compared with costly gold or silver [5,6] nanoparticles. Copper nanoparticles (CuNPs) have been used in non-rigid electronics [7-10], catalysis [11-14], light emitting diodes (LED) [10] and in biology [15,16] and medicine.

Nevertheless, the synthesis of CuNPs is more difficult beneath atmospheric contexts in collation to virtuous metals like gold and silver as copper is susceptible for easy oxidation. Different tactics [17-26] have been used to conquer this problem. The preparation procedure in thermal reduction method is straight forward and the dimension and configuration of CuNPs can be easily tracked. In contrast to traditional techniques, it is much speedy, unstained and less expensive.

Nevertheless, CuNPs prone to be passably tottering in aqueous medium and hence exceptional measures ought to be get hold to circumvent their conglomeration (or condensation) and oxidation during the construction of analogous suspension fragments in aqueous medium. The important strategies to safeguard CuNPs from oxidation during production and reposition are: (i) make use of non-aqueous medium, (ii) employing dilute systems and (iii) operate inert climate [27]. Ascorbic acid acts as reducing agent [28] and considered worthwhile to use as antioxidant of conglomerating copper.

Several surfactants [22-26,29-31] have been employed in the production procedures as spreader or conditioner. These wetters have been used to govern the particle size, its distribution and geometry. These are also known to avert assembling and oxidation. NaBH₄ [3] and NaPO₂H₂ [9] were routinely availed in the creation of CuNPs.

Synthesis of CuNPs have been investigated by divergent reactions [32-39] in solution state. Broadly, methods for the synthesis of Cu-NPs associate with either chemical route or physical methods [40-44]. Lesser reports [45-47] are available in the literature on chemical reduction methods for the synthesis CuNPs. The supremacy of this method is the chance

to produce nanoparticles at ambient temperature and pressures.

Several solvents and reducing agents [48] are monotonously employed in chemical reduction methods. In these methods Cu^{2+} are reduced to Cu^0 . In the light of lacuna identified, it is considered worthwhile to investigate a surfactant safeguarded CuNPs in aqueous medium without inert gas insulation. Triton X-100 (a non-ionic surfactant) is employed to sway the aggregation of nanoparticles and safeguard them to circumvent oxidation. The main objectives of the current investigation are (i) synthesis of surfactant capped CuNPs and (ii) their characterization by employing spectral, powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM).

EXPERIMENTAL

All the synthetics were of AR grade and were utilized as acquired and devoid of further refining. Copper(II) sulphate pentahydrate salt ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was 98.0% pure (Merck) and Triton X-100 (*iso*-octylphenoxypolyethoxyethanol, $\text{C}_{14}\text{H}_{22}\text{O}(\text{C}_2\text{H}_4\text{O})_n$) was 98.1% pure (BDH). Ascorbic acid (Merck; $\text{C}_6\text{H}_8\text{O}_6$) was used as main reducing agent. Purified ethanol ($\text{C}_2\text{H}_5\text{OH}$) was used in the present study.

Synthesis of copper nanoparticles: Ascorbic acid suspension was made by solvating 1.0 g of L-ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$) in 25 mL of distilled water. A $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution (0.01 M) was prepared by solvating 0.395 g of the brine alone in distilled water and this was combined to the ascorbic acid solution under powerful magnetic stirring. A 1.0 mL of Triton X-100 was dissolved in 5 mL of ethanol.

Copper sulphate solution was taken in a 250 mL round bottom flask and heated on a mantle. To the hot solution of copper sulphate a mixture of ascorbic acid and Triton X-100 is added drop-wise with constant stirring. The reaction mixture changes colour from blue \rightarrow yellow and then yellow \rightarrow orange red and finally turned to brown colour indicating the formation of copper nanoparticles. The colour changes are demonstrated in Fig. 1. The brown coloured solid is collected by filtration washed with distilled water and dried in vacuum.

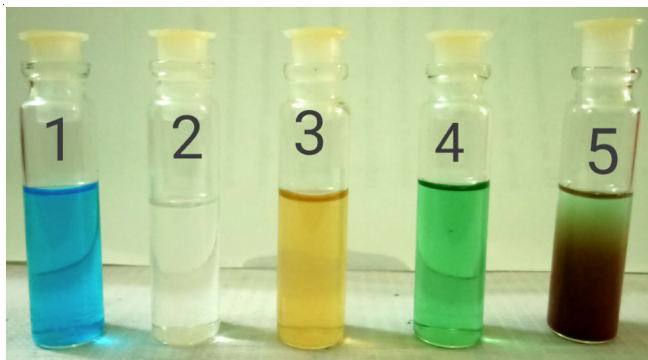


Fig. 1. Colours of reactants and products (1) copper sulphate solution, (2) Triton X-100, (3) ascorbic acid, (4) mixture of reactants (1 + 2 + 3) at room temperature and (5) formation of brown coloured CuNPs after heating the reaction mixture (4) at 80 °C for 1 h

Characterization: The synthesized sample was studied by employing ELICO double beam (SL 210) UV-visible

spectrophotometer in the wavelength range 200-1100 nm. The geometry of newly prepared nano particles was analyzed with XRD (D8-Advance, Bruker AXS) with a $\text{CuK}\alpha$ radiation source ($\lambda = 0.154056 \text{ nm}$) XRD patterns were documented from 20° to 80° with scanning step of 0.01. The infrared spectrum was recorded in the range 4000-400 cm^{-1} using Perkin-Elmer spectrum 100 spectrometer in KBr discs. The configuration and synthetic constitution of the CuNPs were examined by scanning electron microscopy (SEM; JEOL, IT500 LA) provisioned with an energy-dispersive X-ray spectrometer (EDX) (6490 LA). EDX was accomplished at an acceleration voltage of 20.0 kV.

RESULTS AND DISCUSSION

The UV-visible spectrum of CuNPs in ethanol solvent is given in Fig. 2. The compound shows absorption peak in the visible region. It is more familiar that the location and appearance of plasmon absorption of metal nanoparticles are very reliant upon the shape of particles. As mentioned in Mie's hypothesis [49], spherical nanoparticles show single SPR peak, while anisotropic shape particles could give two or more SPR peaks based on the shape of the particle. Since a single peak is observed in the visible region, the present CuNPs are proposed to have spherical shape.

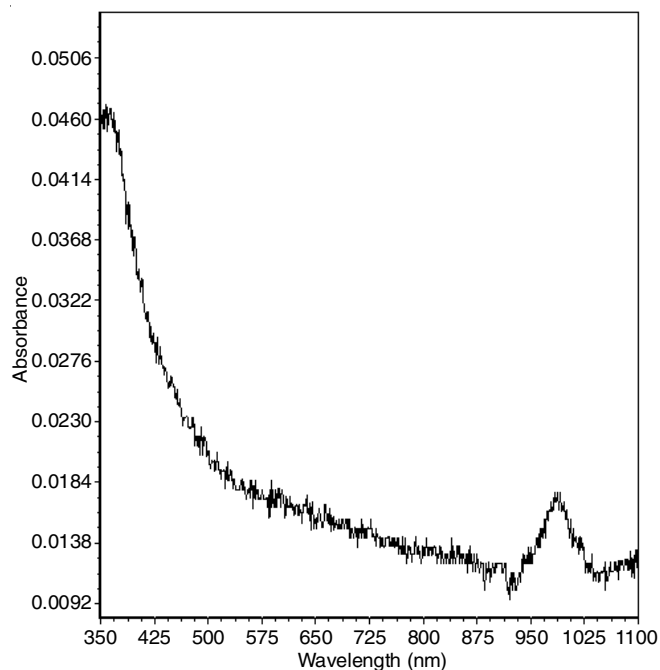


Fig. 2. UV-Visible spectrum of CuNPs

IR spectrum of copper nanoparticles is shown in Fig. 3. The broad bands centered at 2897 cm^{-1} is connected with the asymmetric (ν_{asym}) and symmetric (ν_{sym}) stretching vibrations of methylene ($-\text{CH}_2$) group. The band at 1512, 1376 cm^{-1} arises from C=C skeletal vibration of phenyl group. These changes in the positions of peaks suggest the binding of functional lot of Triton X-100 with CuNPs.

X-ray diffraction studies: The phase analysis of CuNPs was explored by the powder X-ray diffraction measurement in the 2θ range 20-100° using PANalytical Empyrean diffracto-

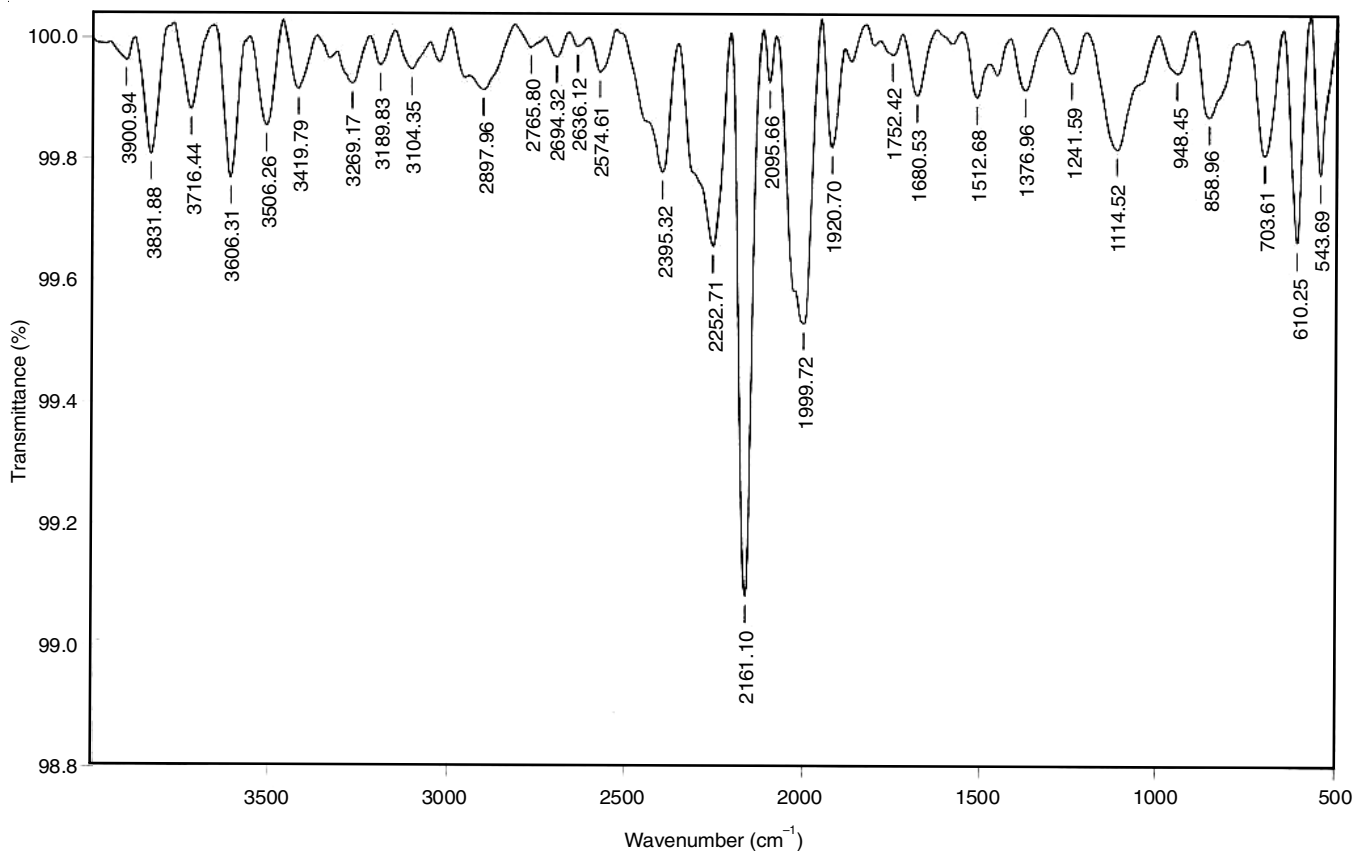


Fig. 3. IR spectrum of CuNPs in KBr discs

meter with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and nickel filter, operated at 45 kV and 30 mA. Fig. 4 shows the XRD patterns of (a) standard copper (JCPDF Card No. 85-1326) and (b) indexed CuNPs. All diffraction peaks could be indexed to the face centered cubic phase with Fm-3m (No. 225) space group, which were in accordant with the JCPDF Card No. 85-1326. Absence of extra peaks in XRD pattern indicates the formation of single phase of CuNPs.

The synthesized CuNPs are analyzed using Goniometer Ultima 3 (theta-theta gonio, below 40 kV/30 mA-X-ray, $2\theta/\theta$ -scanning mode, fixed monochromator). Diffractogram was recorded with a step of 0.02° in the 2θ range of 10 to 80° .

Indexing operation for powder diffractogram was completed and in the first step Miller indices (h k l) to each peak was allocated. Indexing has been done (Table-1) and data are compared with standard values as given in Table-2.

The data in the 3rd column are approximately considered as integers. In this experiment the constant is calculated as 45.4 (181.5-136.1). High intense peak is observed for (1 1 1) reflection for the sample under investigation. It indicates that

Peak position, 2θ	$1000 \times \sin^2 \theta$	$1000 \times \sin^2 \theta/46$	Reflection	Remarks
43.307	136.147	2.99	(1 1 1)	$1^2 + 1^2 + 1^2 = 3$
50.440	181.554	3.99	(2 0 0)	$2^2 + 0^2 + 0^2 = 4$
74.110	363.103	7.99	(2 2 0)	$2^2 + 2^2 + 0^2 = 8$

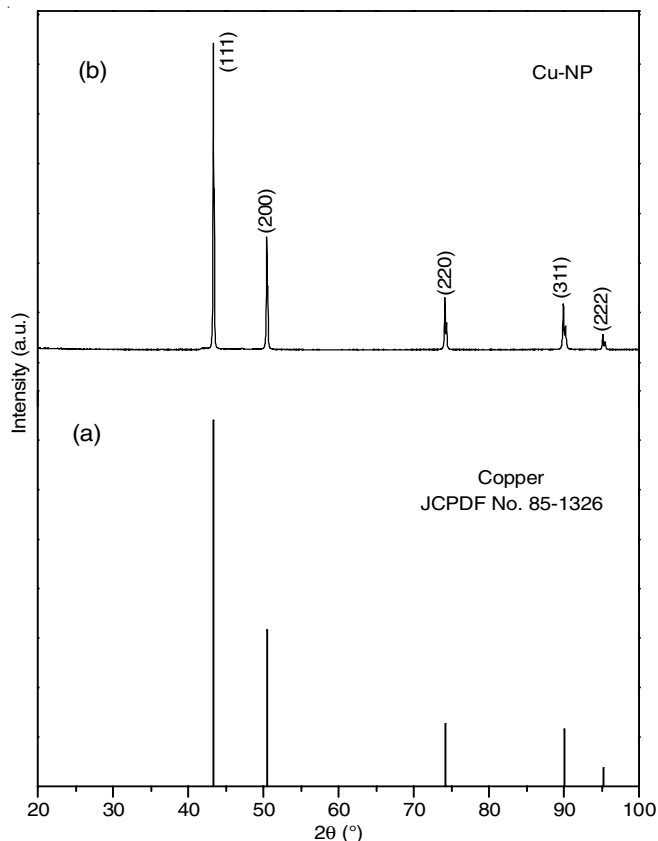


Fig. 4. Powder XRD pattern for (a) standard [copper JCPDF No. 86-1326] (b) indexed CuNPs

TABLE-2
EXPERIMENTAL AND STANDARD
DIFFRACTION ANGLES OF CuNPs

Experimental values	[2θ in °] JCPDS Copper: 04-0836 (Reference values)
43.307	43.297
50.440	50.433
74.110	74.130

the material has FCC crystal lattice. The three peaks at (2θ values of) 43.307, 50.440 and 74.110° correspond to (111), (200) and (220) planes of CuNPs. The values were matched with the calibrated powder diffraction card of JCPDS, copper file No. 04-0836. Thus the XRD experiment uncovered the crystal lattice of present CuNPs.

Calculation of particle size: The average particle size is determined by using Debye-Scherrer formula [41-43]. The equation is given below:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where, λ = wavelength of X-ray (0.1541 nm), β = full width at half maximum (FWHM), θ = diffraction angle and D = particle diameter.

On substituting the values and on calculation, the particle size is found to be about 15 nm.

SEM-EDX analysis: Further, the synthesis of CuNPs is ascertained by SEM-EDX analysis. The CuNPs, which are surfactant capped seem to have a spherical agglomerate morphology (Fig. 5). The EDX spectroscopy has been used to quantify elements and constitution of newly prepared materials. The spectrum of the sample is manifested in Fig. 6. It confirms the existence of C, O and Cu in the sample. The analysis shows a signal, which correspond to significant percentage (81.7) of copper (Fig. 6), with only 3.47% oxygen indicating the formation of metallic Cu-NPs. The apex at about 0.5 KeV pertains to the binding energy of oxygen (OK_{α}). The crests appeared at 0.85, 0.94, 8.04 and 8.94 KeV are assigned to CuL_1 , CuL_2 ,

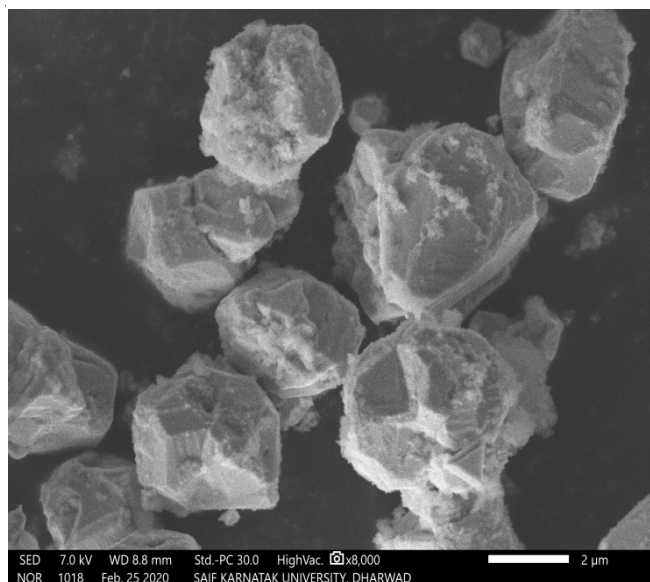


Fig. 5. SEM image of copper nanoparticles

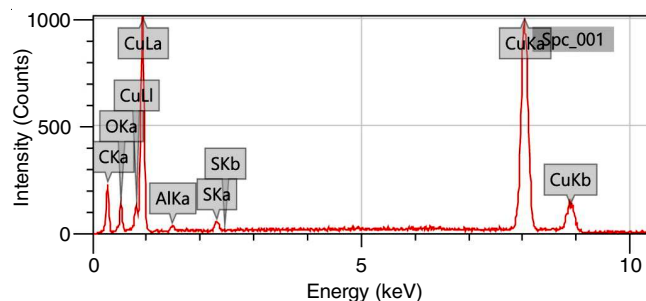


Fig. 6. EDX Spectrum of copper nanoparticles

CuK_{α} and CuK_{β} , respectively. Apex due to CK_{α} is also observed at 0.27 KeV. The present spectrum (Fig. 6) is very akin to that reported before by Kooti and Matouri [50] and Khan *et al.* [51].

The weight percentage of Cu, C, O, S and Al from EDS analysis is specified in Table-3.

TABLE-3
EDS ANALYSIS OF COPPER NANOARTICLES

Element	Cu	C	O	S	Al
Wt.%	81.7	13.87	3.47	0.59	0.36

Conclusion

The present work focuses on the formation of copper nanoparticles (CuNPs) by using reduction procedure. The study demonstrates low-cost and environmental friendly synthetic route. The nanomaterial can be prepared using simple laboratory equipment under ambient conditions. The formation of CuNPs are successfully characterized by employing spectral (UV-visible, FT-IR), powder XRD and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDX).

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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