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One-pot Low-Temperature Synthesis of High Crystalline Cu Nanoparticles

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ABSTRACT

This research work has developed a classic method to synthesize high crystalline ~50nm copper (Cu) nanoparticles at a low temperature of 80°C. While nanoparticle synthesis is a concern, a rapid chemical reduction method (CRM) was introduced by reducing copper salts and an appropriate capping agent. The capping agent facilities controlled the movement and formation of nanoparticles that were further investigated by X-ray Diffraction (XRD), Thermo-gravimetric Analysis (TGA), Transmission Electron Microscope (TEM), and Selected Area Electron Diffraction (SAED) as well as TEM couple EDS. The such in-depth analysis demonstrates a 100% crystalline phase with having to predominate (111), (200), and (220) planes and 84% purity. The medium and process protocol selection may be adapted to synthesize other nanoparticles for different functional applications.

1. INTRODUCTION

Recently, researchers have profound interest in the field of nanomaterial synthesis and their properties. This is because the nanomaterials essentially consist of particles that are bellow 100 nm in size and these materials show exclusive properties that vary from the regular bulk materials [1]. Nanomaterials have been applied in the fields of chemical manufacturing, energy conversion, envronmental aspets, biotechnology etc. Salavati-Niasari et. al. have stated that reduction in size changes the properties of the materials to follow quantum mechanical rules [1].Nanomaterials are considered to be the connecting link between bulk materials and particles on an atomic level structure [2] [3]. Low cost compared to silver and gold is also another attraction for Cu NPs synthesis [3] For example, an increased catalytic activity can be achieved through a high surface area to volume ratio in nanomaterials [4]. Various synthesis routes to synthesize nanomaterials have gained much attention and these routs allow the precise control of shape and size. Some of these routs include chemical reduction, thermal decomposition, metal vapor deposition, electochemical sythesis, radiolysis etc. [3] [5] . Cu NPs are almost exclusively utilized for their electrical, thermal, surface and catalytic properties [6]. Starch is used for nanomaterial growth control in this process [6]. Khan also found that sodium hydroxide elevates the reduction rate in the synthesis route [6].

Ascorbic acid also lowers the driving force of the reaction and averts the agglomeration of the synthesized Cu NPs [6]. Cu NPs have also found promising application in cooling fluids [7] conductive inks [8] optical switches and photochromic glasses [9]. Dang et. al. stated that the use of ascorbic acid in the reduction process and in storage prevents the oxidation of Cu NPs [9]. Chandra et. al. stated that copper nanowires are being applied in nanoelectronics, magnetic devices, electron emitters etc. [10].

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Cu NPs have been known to exhibit antimicrobial properties which can have an enormous impact on the application of antimicrobial surface coatings. Although Cu NPs can be synthesized by various methods like electrochemical, thermal, laser ablation, chemical reduction etc, chemical reduction method allows a researcher to have superior control over the parametrs and size. Thus this method is highly efficient because of its simplicity, high yield, speed and low-cost [11].

This means that chemical reduction method does not require any complex reaction set up, it produces a large amount of product, it is less time consuming and is a cost effective method. Cu NPs are extremely susceptible to oxidation and this poses a threat during the synthesis process. In this case, the materials are preserved from oxidation by applying a capping agent that rapidly captured the nanomaterials and also decreases the surface energy to control the growth [12].

In this paper, crystalline phase has been investigated on the synthesis of Cu NPs via chemical reduction method. This synthesized nanomaterials have been investigated by XRD, TGA, TEM etc.

2. EXPERIMENTAL

2.1 Materials and Methods

Metanol(CH_3-OH) (Merk,Germany), Copper sulphate pentahydrate ($CuSO_4.5H_2O$) (Merk,Germany), Ascorbic acid (Merk, Germany), Starch(Merk, Germany), Sodium hydroxide (Merk,Germany) used analytical regent grade. DI water collect form Distillation Plant (Water still Merit W4000,UK) with deionization resign plant. CuNPs synthesized by chemical reduction method(CRM).

2.2 Synthesis of Cu-NPs

Calculated amounts of precursor Copper sulphate pentahydrate were dissolved in 250 ml of Methanol. Starch was dispersed in 120 ml (1.2%) of boiling DI waterand added to the precursor solutions dropwise as a capping agent. Then 50 ml of 0.2 M ascorbic acid was prepared in DI water and added to the mixture of precursor and starch very slowly and dropwise to reduce the Cu^{+2} ions. Finally 30 ml of 1.0 M NaOH solution was prepared in DI water and added to the previous solution dropwise at 80°C the reaction was allowed to carry out for 2 hours. The color of the solution turned from light blue to ocher and brown. The solution was kept overnight (20 hours) and then the residue was separated by centrifuging (UniCeM, D-69168 Wlesloch, Herolab, Germany) with DI water and with ethanol at 7000 rpm for 20 minutes to remove the impurities. Afterwards it was dried in a desiccator for 24 hours and then stored in a glass vial covered with aluminium foil. In this chemical reduction process, the reducing agent ascorbic acid generates semidehydro-ascorbate acid radical which then reduces $Cu(OH)_2$ into Cu_2O and then finally into metallic copper(Cu)

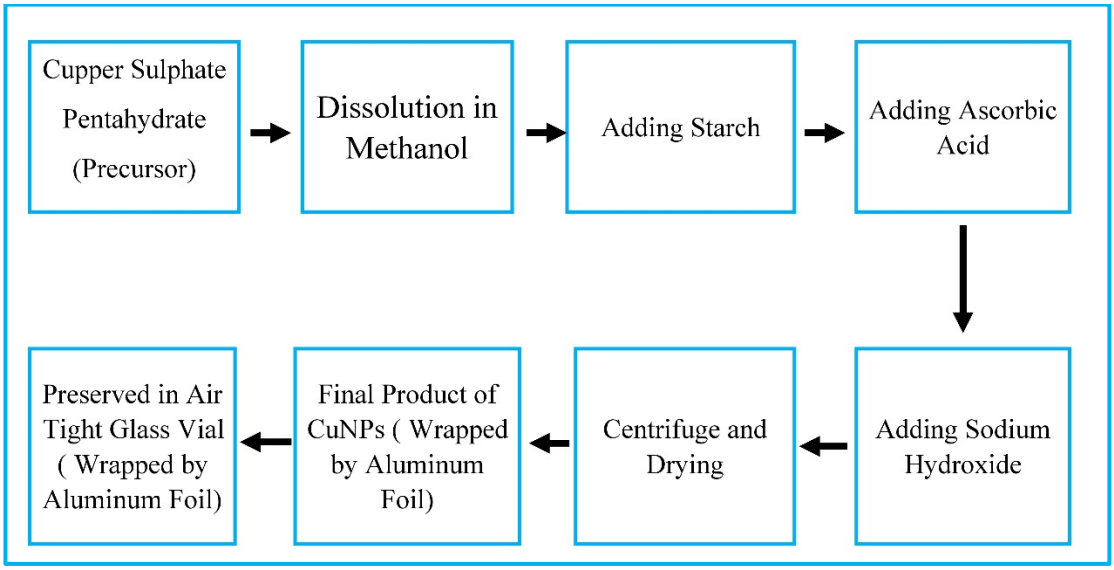


Fig. 1. Synthesis pathway from Precursor to Copper Nanoparticles

2.3 Characterization

2.3.1 X-ray Diffraction (XRD)

X-ray diffractogram were obsereved in Multipurpose X-ray diffractometer (SmartLab SE), (Brand: Rigaku, Japan) with a source of 2.00 kW (40KVx50mA) and K_β filter $Ni_{(28)}$. The process was carried out a step size 0.01°(speed 20°/Min) by HyPix-400 (1D) detector with Standard Operation Mode (SOM). The data was analysed by SmartLab Studio II (Brand: Rigaku, Japan). In XRD analysis, the crystallographic properties of a material is determined by irradiating the material with incident X-rays and measuring the diffraction angles and intensities of the X-rays that leaves the material. The investigation was made on the powder sample at room temperature 25°C. To determine the crystal structure of Cu NPS, X-Ray diffraction is used. From XRD analysis, Debye-Scherrer equation has been applied for crystal size determination.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Here λ is the wavelength of X-ray (λ=0.1541 nm), D is the crystal size, β is the full width at half maximum(FWHM) and θ is the diffraction angle.

The d-spacing values (interplanar distance between atoms) are calculated using the Bragg's law.

$$d = \frac{\lambda}{2\,\mathrm{Sin}\theta} \qquad (2)$$

The details of crystal size and d-spacing value determined by equation (1) and equation (2) are listed in Table-1.

2.3.2 Thermo-gravimetric Analysis (TGA)

TGA was performed with Simultaneous Thermal Analyzer (STA) 449 F5 Jupiter (NETZSCH, Germany) with a TGA resolution of 0.025 μg and N_2 atmosphere (maintain inert condition) at a heating rate of 5 °C/min. In TGA, mass loss is determined of Cu NPs with the increase of temperature in different process (isothermal or dynamic). Activation energy of Cu NPs (the minium amount of energy required for the activation of chemical species to undergo chemical reactions) was calculated on the basis of Coats Redfren method by using the plot of $\ln[-\ln(1-\alpha)/T^2]$ vs. 1000/T(1/K).

2.3.3 Transmission Electron Microscope (TEM) and Energy Dispersive X-ray Spectroscopy (EDS)

Internal morphology of Nanoparticles was observed by TEM. The dispersion of CuNPs sample into Ethanol medium onto the Copper grid is used and left to dry completely at room temperature. In this study the sample of Cu NPs is preperd at room temperature at 25°C. The presence of elemental Copper was conformed through EDS. Energy Dispersive Spectometer depends on the photon nture of light in X-Ray range. A single photon of energy is just sufficient to produce a measure singnal X-Ray. Silicon Drift Detector (semiconductor material) is used to detect the X-Ray along with processing electronics to analyse the spectrum. EDS observations were carry out by instrument copled with TEM. TEM and EDS was carried out by JEM 2100 Plus (Brand:JEOL, Japan) with LaB_6 (lanthanum hexaborate) filament under a voltage of 200 Kv, Very low (micro unit) current, Filament Current: 101.5 to 106.5 μA and Botton Mount Camera (Charge Couple Device) detector. EDS used as 200KV and data was detected by SDD detector. Selected Area Electron Diffraction (SAED) was performed at low magnification to conformed the crysatl palne of the Cu NPs. TEM utilizes transmitted electrons to generate information (i.e. crystal structure) about the inner structure of CuNPs.

3. RESULTS AND DISCUSSIONS

3.1 X-ray diffraction (XRD)

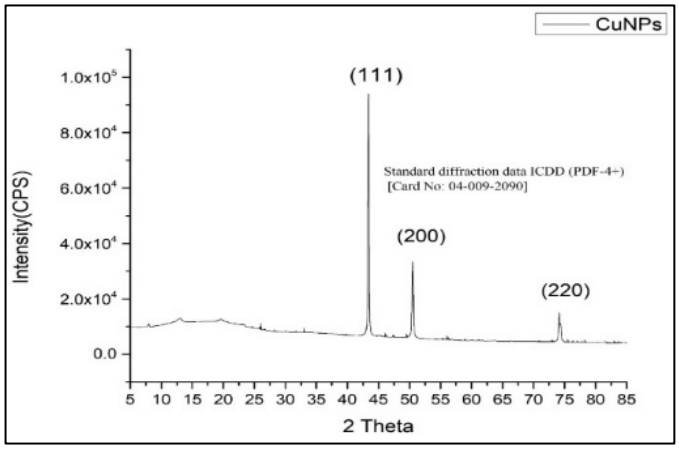


Fig. 2. The X-ray diffractogram of copper nanoparticles

From Figure:2, it can be observed that three main peaks were at 2θ=43.38 (111), 50.49 (200), 74.15 (220). Three main peaks were observed the near value of 43.00, 51.00 and 74.00. By the equation (1) crystal sizes were calculated as 61.80, 45.40, 51.10nm. Copper in cubic crystal system with pure crystalline phase of Cu NPs has been found [ICDD Card No: 04-009-2090].

From Table:1 its shows that the intensity values in CPS unit is 13865, 6186, 2968. The highest intensity was observed in the theta value is 21.69 as well as lowest intensity in theta value is 37.08. The average size of copper nanoparticles was calculated from major three diffraction peaks by Debye-Scherrer formula in equation (1). The average crystal size is 52.63nm. The particles onto the crystal plane are arranged with more uniformity where the crystal size decreases. It expressed the increase of surface area to volume ratio, so properties like photocatalytic activity, crystallinity, conductivity, antimicrobial activity are increased.

Table 1. Grain Size Calculation of Synthesized copper nanoparticles

2θ of the intense peak (deg)	θ of the intense peak (deg)	FWHM of intense peak (radians)	Crystal size, D (nm)	hkl	d-spacing (nm)	Intensity, I (cps°)
43.38	21.69	0.002521	61.80	(1 1 1)	0.208	13865
50.49	25.25	0.002523	45.40	(2 0 0)	0.180	6186
74.15	37.08	0.003560	51.10	(2 2 0)	0.128	2968

Table 2. Peak Indexing

Peak position (2θ)	θ	1000×sin²θ	1000× sin²θ/51	Reflection	Remarks
43.38	21.69	137.072	3	(1 1 1)	$1^2+1^2+1^2=3$
50.49	25.25	182.499	4	(2 0 0)	$2^2+0^2+0^2=4$
74.15	37.08	363.859	8	(2 2 0)	$2^2+2^2+0^2=8$

From table:2 shows the comparison between the experimental and standard data from ICDD (PDF-4+) [Card No: 04-009-2090] The values of diffraction angles of synthesized Cu NPs is (43.38, 50.49, 74.15) are mostly similar to those of standard data (43.37973, 50.52385, 74.24562) [ICDD Card No: 04-009-2090] which confirmed the synthesis of purer crystalline phase of metallic copper nanomaterial. Three main peaks were observed the plane of (1 1 1) (2 0 0) (2 2 0) which completely similar to the standard data [ICDD Card No: 04-009-2090] crystal plane.

From table:3 the d-spacing values in nm unit of prepared Cu NPS calculated is 0.208, 0.180, 0.127nm. The d-spacing values (interplanar distance between atoms) are determined using the Bragg's law by equation (2). The values of prepared Cu NPS completely similar to the standard data (0.208424, 0.180500, 0.127633) [ICDD Card No: 04-009-2090] which defined the well uniformity of the Cu NPs particle onto the plane.

Table 3. Peak Indexing from Inter-Planar Distance

Peak position (2θ)	Inter-Planar Distance d (Å)	1000/d²	(1000/d²)/77.32	hkl
43.38	2.08	231.14	2.989	(1 1 1)
50.49	1.80	308.64	3.99	(2 0 0)
74.15	1.27	620.00	8.0	(2 2 0)

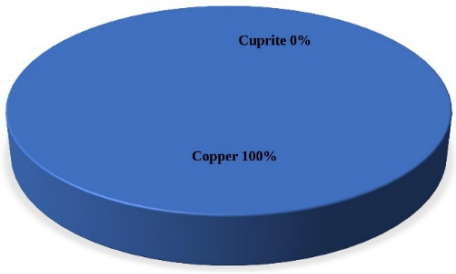


Fig. 3. Quantitative analysis (crystalline phase percentage) of copper nanoparticles by WPPF method

The pure crystalline phase also confirmed by the quantitative analysis by WPPF (Whole Powder Pattern Fitting) method and SmartLab Studio II software, Japan, which is shown in Figure:3. The crystalline percentage of metallic copper is 100% in the cubic crystals system. This is explained that the availability of an exact amount of $Cu(OH)_2$ produce and its reduced to Cu^{2+} ions into Copper (I) oxide and then finally to metallic copper (Cu) by the reducing agent ascorbic acid. This is why pure crystalline metallic phase is formed by CRD method. Here, semidehydro-ascorbate acid radical is formed through which the reduction reaction proceeds.

3.2 Thermo-gravimetric Analysis (TGA)

On the basis of TGA data, the activation energy of the synthesized Cu NPs have been determined by the Coats-Redfern method. The process is stated bellow:

The value of activation energy can be calculated from the slope of the plot of $\ln[-\ln(1-\alpha)/T^2]$ vs. 1000/T(1/K).

$$\alpha = (W_i-W_t)/(W_i-W_f) \quad (3)$$

[W_i is the weight of sample before degradation, W_t is the weight after time, t and W_f the weight after degradation]

$$\text{slope} = (-E_a)/(R) \quad (4)$$

here, E_a is the activation energy and R is the molar gas constant (= 8.314 J/K.mol)

T is the temperature in Kelvin.

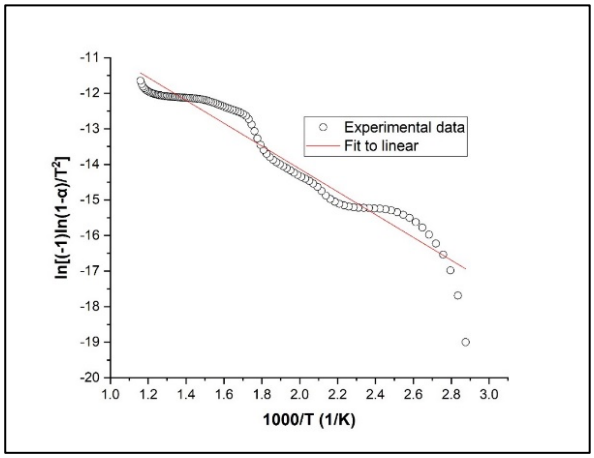


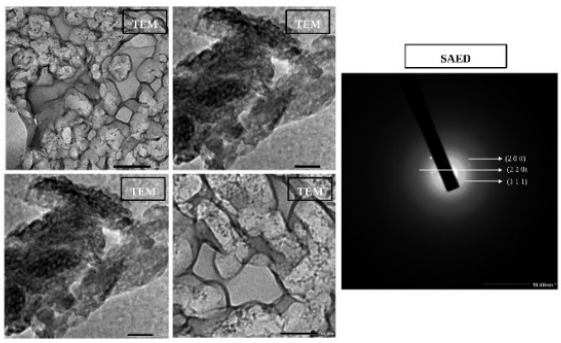
Fig. 4. Curve the energy of activation of copper nanoparticles

For the calculated value of slope from (4), Ea is 26.68 KJ/mol. So, the activation energy of synthesized Cu NPs indicates that the particle will be more thermodynamically stable, less prone to degradation reactions, compatible with coating materials, less affected by medium etc. so, this nanoparticle can be used for antimicrobial coating substrates, tableware, electronic appliance etc.

3.3 Transmission Electron Microscope (TEM) and SAED

TEM images show the internal morphology of the synthesized Cu NPs. These nanoparticles are spherical in shape and uniformly distributed in inner core of the samples. the particles show more consistent distribution into the crystal plane. The particles are finely distributed with poor agglomeration. These images also show that the particles are below 50 nm in size which has been previously confirmed by

XRD analysis. These images show that the nanomaterials are spherical with a regular in shape of the internal morphology with a narrow size distribution. The majority of the nanoparticles are nearly spherical with a small percentage of elongated particles.



SAED images show that the Cu NPs are aligned in the planes (111), (200) and (220) which proves the data analyzed by XRD [18] [19]. Including three planes, there are no more crystal planes is observed in SAED patterns which conform the pure metallic copper crystal phase is present in the cubic crystal system of the synthesized nanomaterial.

3.4 Energy Dispersive X-ray Spectroscopy (EDS)

EDS report confirmed the elemental composition of synthesized Cu NPs. EDS analysis utilized carbon coated copper grid. EDS spectra clearly show the Copper signal along with Oxygen signal. No other signal was observed in the pictogram without Copper and Oxygen. The elements detected were carbon (due to the grid used to increase the conductivity).

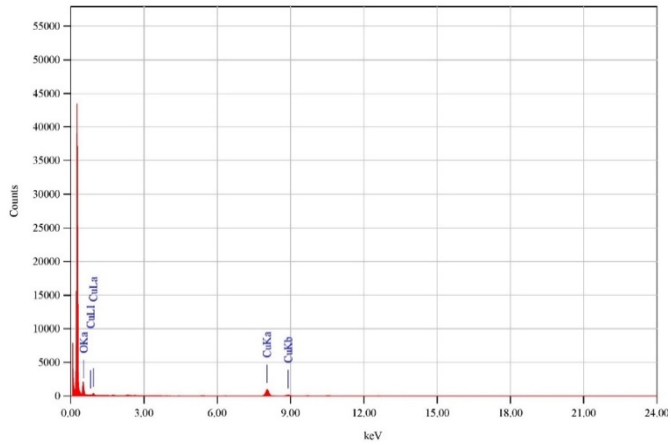


Fig. 6. Energy Dispersive X-ray Spectroscopy pattern of copper nanoparticles

By the Table:4, EDS pattern show that the atomic mass percent of synthesized Cu NPs is 84.00% Copper and 16.00% is Oxygen. So, the purity of the synthesized Cu NPs is 84%. As the analysis was done three weak after the powder preparation, an aerial oxidation might have taken which led to the formation of copper oxide.

Table 4. Elemental Composition of synthesized copper nanoparticles

Element	Atomic Mass (%)
Copper (Cu)	84.00
Oxygen (O)	16.00
Total=	100.00

CONCLUSION

The XRD analysis yields the pure crystalline phase of Cu NPs synthesis via chemical reduction method and phase plane (111), (200), (220) was observed as well as the crystallite size is 52.63 nm. TGA shows the activation energy is 26.5KJ/mol . No significant phase change upon the application of heat was observed. TEM shows the internal morphology of the particles are in spherical shape which size below 50 nm. SAED pattern also conform the crystille phase plane (111), (200), (220). EDS follow the presence of copper in the synthesized nanomaterial. Overall the pure metalic copper crystalline phase of Cu NPs has been investigated by this work. These synthesized nanoparticles will be further investigated for antimicrobial activity.

STATEMENT AND DECLARATION

The author declares that this document has neither been submitted elsewhere nor under consideration in any other journal.

AUTHOR CONTRIBUTION

Md. Ashraful Alam designed the experiment, analyzed the data, and wrote the original document. Mobashsara Tabassum and Raton Kumar Bishwas cooperate in the synthesizing of Cu NPs. Sabrina Mostofa assistance in performing the TEM analysis. Debasish Sarkar assistance to the intellectual knowledge for this research. Shirin Akter Jahan supervised the overall work and assisted in writing the document.

COMPETING INTERESTS

The author has no financial interest to disclose.

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