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# OPTIMIZATION OF COPPER OXIDE NANOPARTICLES SYNTHESIZED via CO-PRECIPITATION METHOD

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## ABSTRACT

Copper oxide nanoparticles (CuO-NPs) are synthesized for optimization via Co- precipitation method using Copper (II) Sulphate pentahydrate and Sodium Hydroxide for different annealing time. The samples are analysed by X-ray Diffraction (XRD), UV-Vis Spectroscopy, Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX). CuO NP samples are annealed for 3 hrs, 4 hrs and 6 hrs and 4 hr annealed samples exhibit pure CuO peaks. Regardless of the techniques utilized, the synthesised nanoparticles possess spherical shapes and sizes in the nano scale. The average crystallite size of CuO nanoparticles calculated from XRD pattern was 18 nm for the optimized sample is indicative of nanostructure of the sample. SEM images of the samples show spherical nanoparticles with a restricted size distribution. EDX's spectrum shows only elemental copper (Cu) and oxide (O) and no other elemental impurity was observed. The UV-Vis absorption spectrum of CuO nanoparticles shows a strong blue shift compared to that of bulk. Measurements and analysis of the material's absorbance indicated that it had an energy bandgap of 2.67 eV and an absorbance peak at 257 nm. The band gap energy was calculated from the absorption spectra. Overall, the outputs of different synthesis techniques have been highly interesting and remarkable.

**Keywords**: Coprecipitation, Copper oxide Nanoparticles, XRD, SEM, UV-Vis Spectroscopy.

## INTRODUCTION

CuO, a I-VI metal oxide, is a widely investigated material due to their application in superconductors, optical (Dagher et al., 2014), electrical (Bouazizi et al., 2015), nanofluids (Priya et al., 2012), biosensors (Hong et al., 2013) etc. Numerous techniques, including the sonochemical method (Kumar et al., 2000) electrochemical method (Borgohain et al., 2000), sol-gel technique (Eliseev et al., 2000) and microwave irradiation (Wang et al., 2002) are widely accepted techniques for the synthesis of nanoparticles. Due to their low environmental toxicity and abundance in the earth's crust, cuprous and cupric oxides ($Cu_2O$ and CuO) have gained increased attention as promising materials for optoelectronic applications (Paracchino et al., 2012; Golden et al., 1996; Pierson et al., 2003; T Mayuramma et al., 1998) Another important application of CuO nanoparticles is its use as antimicrobial agents. Nanostructured materials have a high antimicrobial effect due to its high surface area to volume ratio. Further, CuO becomes attractive because of various cost-effective methods for its preparation. Co-precipitation technique is one among them.

In the present study, co-precipitation method (Pandey et al., 2012) was chosen because of its simplicity, reaction rates at low temperatures and low cost. In this paper we are presenting the optimization of CuO nanoparticle synthesized via a simple Co- precipitation method based on structural properties, morphological behaviour and optical studies

## MATERIALS AND METHODS

### a. Chemical Reagents

Copper (II) Sulphate pentahydrate and Sodium Hydroxide pellets (Merck, India) are of Analytical grade reagents used without further purification.

### b. Synthesis

The CuO Nanoparticles were prepared by coprecipitation method using Copper (II) Sulphate Pentahydrate solution and sodium Hydroxide as precursors. Copper (II) Sulphate Pentahydrate 0.5 M was dissolved in distilled water. After complete dissolution of copper sulphate 1M of sodium hydroxide solution was added under control stirring, drop by drop touching the walls of the vessels. The reaction is allowed to proceed for 2 hr. the solution was allowed to settle for an overnight and the supernatant solution was then discarded carefully. The precipitate is washed several times with distilled water. For optimization, the washed sample was annealed at 80° C for 3 Hr (CuO:1), 4 Hr (CuO:2) and for 6 Hr (CuO:3).

### c. Characterisation

The obtained product was characterized with the aid of XRD, UV–visible, SEM. The structure of the compounds was investigated using X-ray Diffraction (Bruker D8 Advance) with Cu Ká ($\lambda = 1.5406\ A^0$). The average crystallite size was calculated from line broadening using Scherrer's equation. Optical absorption properties of CuO were characterised by UV2600 DRS SHIMADZU UV-Vis Spectrophotometer. The absorption spectra of the sample were recorded in the wavelength range of 200 nm - 800nm. Morphological features were studied by using Scanning Electron Microscopy (Jeol 6390LA).

## RESULTS AND DISCUSSION.

### Structural Properties.

Powder XRD is a quick analytical method that mainly serves to determine the phase of a crystallite material and can reveal details about unit cell dimension. Figure 1(a)-(c) shows the XRD patterns of CuO-NPs annealed at temperatures at $80^0$ C for 3 Hr, 4 Hr and 6 Hr which will be designated as CuO:1, CuO:2 and CuO:3 respectively throughout the manuscript. The peaks in the XRD patterns of CuO-NPs compared with the standard ICDD (00-045-0937) values affirms monoclinic phase of CuO (tenorite) for the lattice.

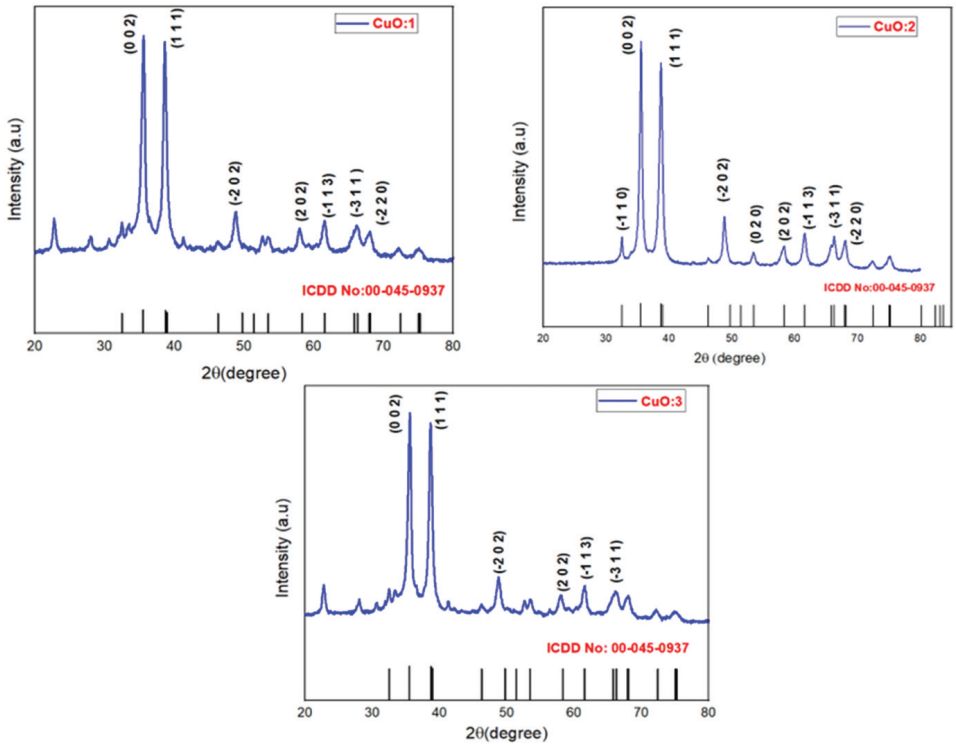


**Figure 1: (a) XRD of CuO:1, (b) XRD of CuO:2, (c) XRD of CuO:3**

XRD pattern of sample CuO:1 exhibits peaks corresponding to CuO lattice with extra peak at 2θ 22.52º (2 0 0) ICDD (01-076-0754) which shows the compound formation is incomplete whereas it is eliminated on annealing the sample for 4 hrs as in sample CuO:2. The intensities and positions of peaks of the sample heated for 4Hr is in good agreement with that of reported values [14]. It was also observed that with increasing the annealing time to 6 hrs (sample CuO:3), the XRD graph does not provide noticeable difference. It is evident from XRD spectra that samples CuO:1 and CuO:3 exhibit undesired peaks that did not correspond to pure CuO NPs. Thus, primarily CuO:2 appears as suitable for further investigation as optimized sample which is annealed for 4 hr. Table 1 illustrates observed 2θ of all samples with standard values and corresponding hkl values.

**Table 1: observed calculated XRD data oxide. The and 20 values of copper**

| Observed 2θ (degrees) | | | Standard Value | h k l values |
|---|---|---|---|---|
| CuO:1 | CuO:2 | CuO:3 | CuO | |
| 22.742 | - | 22.787 | - | |
| 28.018 | - | 28.121 | - | |
| 32.480 | 32.518 | 32.538 | 32.497 | (-1 1 0) |
| 35.586 | 35.545 | 35.534 | 35.496 | (0 0 2) |
| 38.592 | 38.715 | 38.660 | 38.731 | (1 1 1) |
| 48.818 | 48.798 | 48.761 | 48.727 | (-2 0 2) |
| - | 53.44 | - | 53.453 | (0 2 0) |
| 58.001 | 58.308 | 58.016 | 58.337 | (2 0 2) |
| 61.58 | 61.601 | 61.490 | 61.535 | (-1 1 3) |
| 66.141 | 66.264 | 66.065 | 66.25 | (-3 1 1) |
| 68.023 | 68.084 | - | 68.091 | (-2 2 0) |

**nanoparticles.**

According to ICDD data (00-045-0937), for the sample CuO:2, the exhibited diffracted peaks at 2θ = 31.51 (-1 1 0), 35.54 (0 0 2), 38.75 (1 1 1), 48.79 (-2 0 2), 53.44 (0 2 0), 58.308 (2 0 2), 61.601 (-1 1 3), 66.26(-3 1 1) and 68.08(-2 2 0) corresponds to monoclinic phase of CuO NP. For the samples CuO:1 and CuO:3 they exhibit diffracted peaks at 2θ = 22.52 (2 0 0) and 28.254 (0 2 0) which corresponds to peaks of Copper Oxide Sulphate ($Cu_2O_2S$) ICDD (01-076-0754) given in Table 1. The lattice parameters of CuO sample are calculated from XRD data using the equation of d-spacing

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2 sin^2\gamma} + \frac{k^2}{b^2 sin^2\gamma} - \frac{2hk\cos\gamma}{absin^2\gamma} + \frac{l^2}{c^2} \quad \text{--------- (1)}$$

The average crystallite size has been calculated using Debye Scherrer equation

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \text{-------- (2)}$$

where D is the crystallite size, $\lambda$ is the wavelength (1.5406 A°) of the X-ray radiation, â is the full width at half maximum FWHM of the peaks at the diffracting angle è. Crystallite size is calculated from the prominent peaks is found to be nearly 13 nm, 18 nm and 14 nm for CuO:1, CuO:2 and CuO:3 respectively.

Micro strain, and dislocation density are calculated using formula (3) & (4) and tabulated along with evaluated cell parameter in Table 2.

$$\text{Micro strain, } \varepsilon = \frac{\beta}{4\tan\theta} \text{ ------ (3)}$$

$$\text{Dislocation density, } \delta = \frac{1}{D^2} \text{ -------(4)}$$

**Table 2: Lattice parameter, Crystallite size, microstrain and dislocation density of CuO nanoparticles.**

| Sample | a ($A^0$) | b ($A^0$) | c ($A^0$) | Crystallite size D (nm) | Micro strain $(\varepsilon) \times 10^{-3}$ | Dislocation Density $\delta \times 10^{-3}(nm^{-2})$ |
|---|---|---|---|---|---|---|
| CuO:1 | 4.0949 | 3.7223 | 5.044 | 13.63 | 7.281 | 9.734 |
| CuO:2 | 4.6216 | 3.4278 | 5.0496 | 18.2118 | 4.917 | 3.4095 |
| CuO:3 | 4.0894 | 3.42 | 5.0511 | 14.6203 | 6.5424 | 5.3504 |

### 3.2. Morphology and Energy dispersive Spectroscopy Analysis.

Figure 2 (a)-(c) represent SEM images of as-prepared CuO samples. For the sample CuO:1 in which formation of pure CuO is not complete, the particles appear to be agglomerated significantly. But on increasing annealing time it is noted that the particles are spherically distributed and well-aligned. The morphology of the synthesized CuO NPs indicate that on increasing annealing time from 3hrs to 6hrs, the surface becomes more uniform without voids. But at 6hr annealing, the sample CuO:3 exhibits a tendency for further agglomeration which is not a desirable factor. Thus, morphologically also, sample CuO:2 is found more suitable for further investigation.

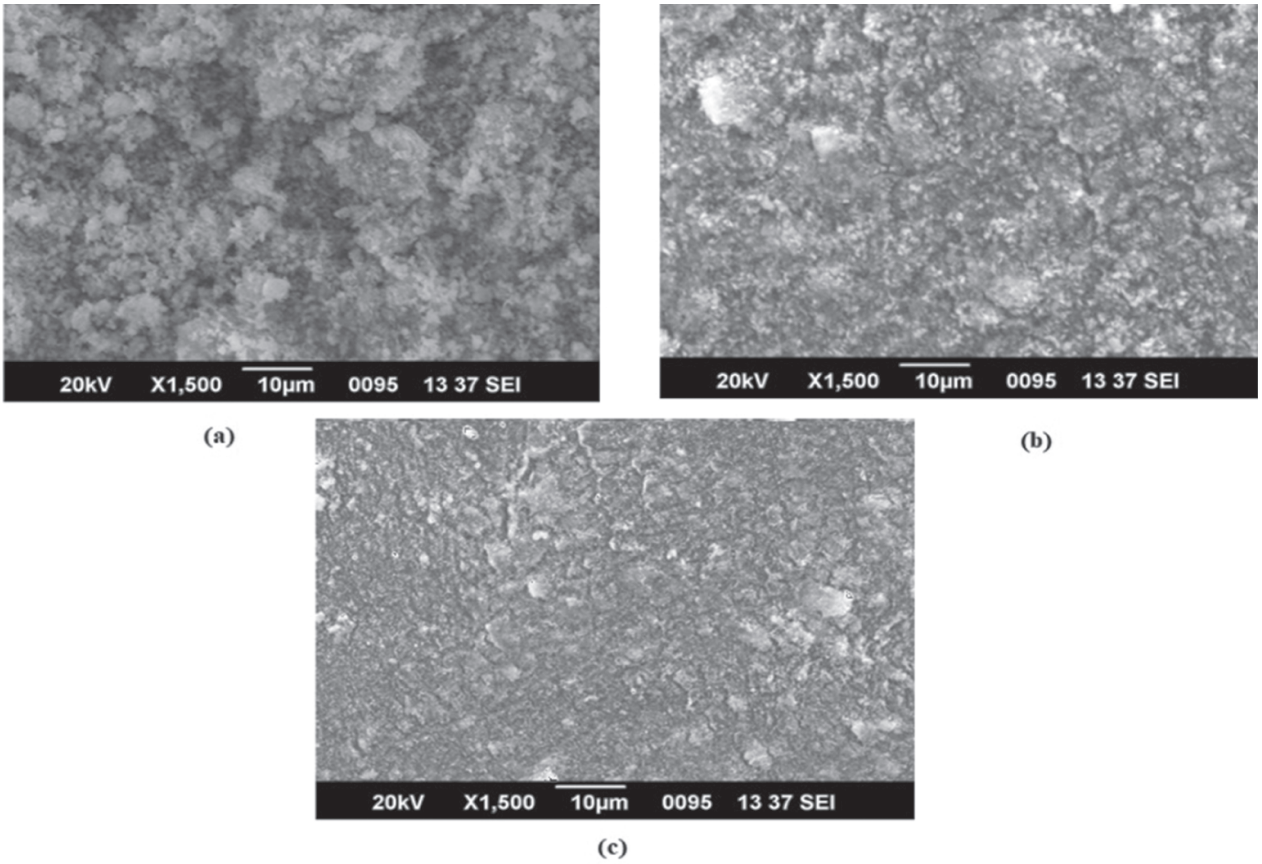


**Figure 2: (a) SEM of CuO;1, (b) SEM of CuO:2, (c) SEM of CuO:3**

Figure 3(a)-(c) showed the EDX spectra of CuO-NPs. The Energy dispersive spectra EDAX used to provide elemental identification and quantitative compositional information. Results revealed the presence of elemental copper (Cu) and oxygen (O) in CuO-NPs indicating the nearly stoichiometric distribution of the elements. The EDX result showed the presence of nearly uniform distribution of copper to oxygen with atomic ratio of 1:1 in CuO. This result confirmed the formation of pure CuO-NPs.[15] The elemental analysis of the sample shows that the prepared sample was copper oxide, which is in concordance with the results of XRD.

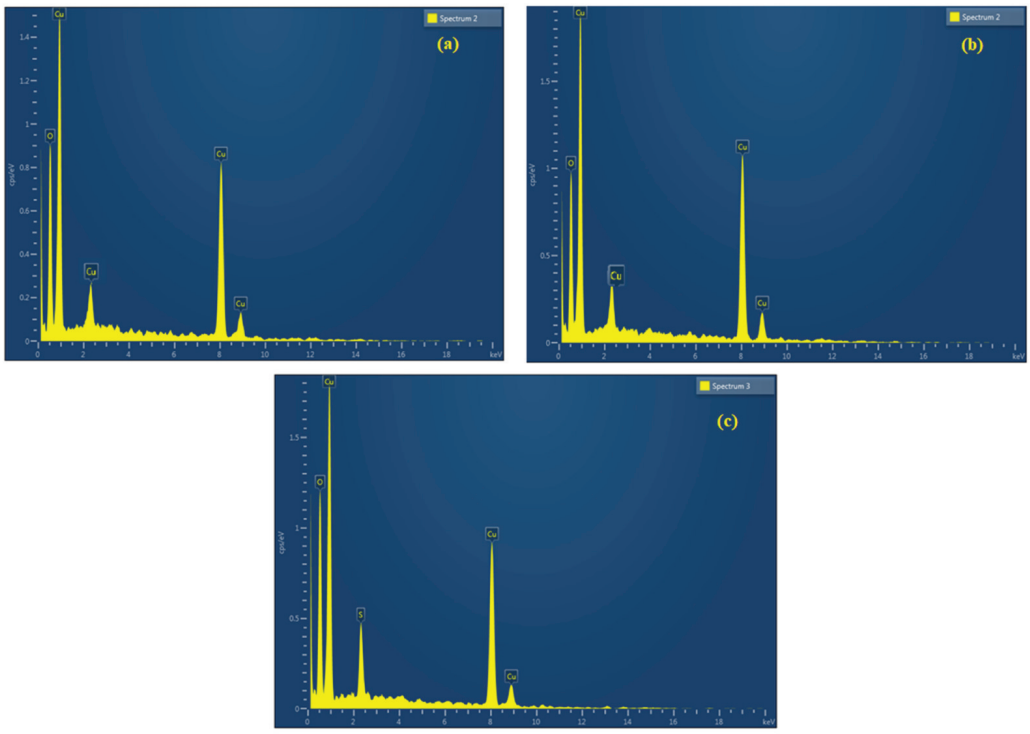


**Figure 3: (a) EDAX of CuO;1, (b) EDAX of CuO:2, (c) EDAX of CuO:3**

## Optical Properties.

UV-vis spectroscopy is one of the most widely used technique to investigate the optical properties of the particles [16]. Optical properties of CuO nanoparticles have been studied by UV-Vis spectrum and absorbance graph of all CuO NP samples are shown in Figure 4. The absorption coefficient peaks are observed at 230.7 nm, 257 nm and 243 nm for CuO:1, CuO:2 and CuO:3 respectively. It shows high absorbance for the samples in the visible region of the spectrum with a slight decrease exhibited by the sample CuO:1.

The optical band gap energy of ($E_g$) of the obtained CuO nanoparticles is estimated from the Tauc's relation and is illustrated in Figure 5.

$$(\alpha h\vartheta)^{\gamma} = A(h\vartheta - E_g) \text{ ————(5)}$$

The energy band gap of as-prepared CuO NPs is estimated from the energy intercept of the extrapolation of the linear portion of the curve. Of the samples, CuO:1 exhibits larger energy bandgap of 3.71eV whereas as annealing time increases, there occurs noticeable decrease in bandgap. The values of bandgaps are displayed in the Tauc plot. The red shift in the bandgap energy is attributed to the quantum confinement effect brought on by the reduction in the dimensional structure and size of the nanoparticles [17]. The optical bandgap energy of the sample CuO:2 with a 4-hour annealing period is comparable to previously published values [18] corresponding to CuO NP. On further increasing annealing time for 6 hrs, it does not show noticeable difference in Bandgap energy. For the same reason, the sample CuO:2 becomes the favourable candidate for further studies.

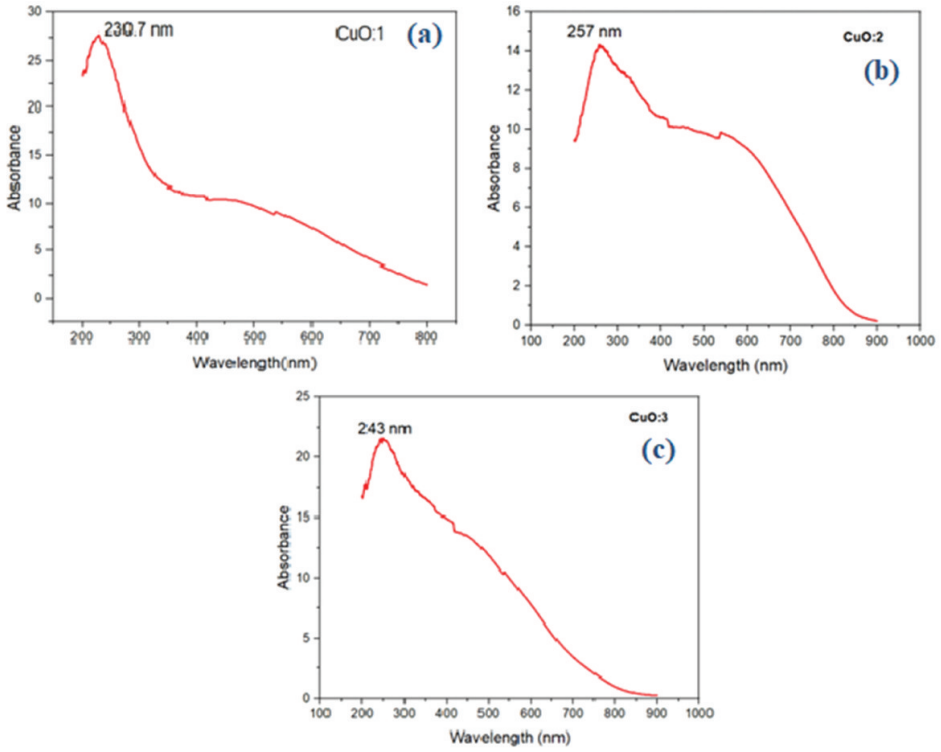


**Figure 4: Optical absorption spectrum of (a) CuO:1, (b) CuO:2, (c) CuO:3**

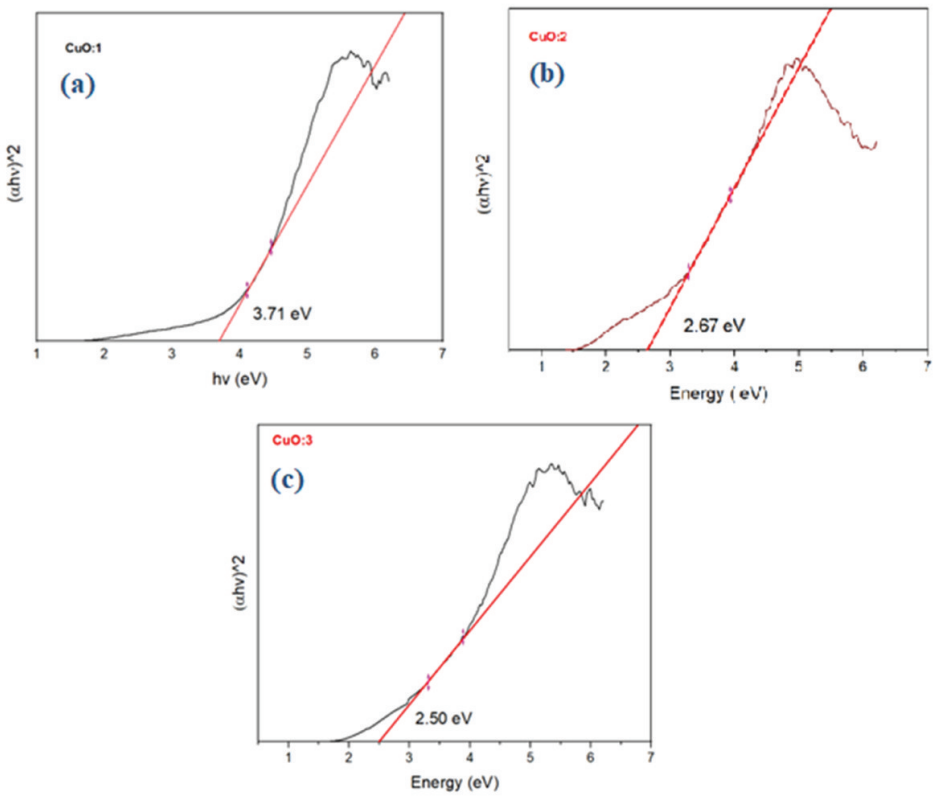


**Figure 5: Band gap energy of (a) CuO:1, (b) CuO:2, (c) CuO:3**

## CONCLUSION

In the present study, CuO nanoparticles with monoclinic structure have been synthesized and optimized by co-precipitation technique. CuO NPs annealed at 4 hrs possess the optimized properties of the sample. Structural properties using XRD diffractograph of the samples affirms the formation of pure CuO NPs for an annealing time of 4 hrs at 80ºC. The crystallite size determined is indicative of nanostructure of the particles. SEM images exhibit gradual evolution of smooth surface on increasing annealing time. Elemental composition verified from EDS spectrum illustrates the most comparable composition of Cu and O for annealing time of 4 hrs. Bandgap energy estimated from Tauc plot illustrate a red shift on increasing duration of annealing time and shows reported values for 4hr annealing time. Thus the sample CuO:2 NPs annealed for 4 hrs has been chosen as optimized sample for further investigation.

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