Synthesis and Characterisation of Copper Oxide nanoparticles

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Abstract: Cupric oxide (CuO) nanoparticles were prepared by the chemical route by calcinations at a higher temperature from 300^oC to 400 ^oC. For the comparison transmission electron microscopy (TEM) and x-ray diffraction (XRD) measurements were made through JCPDS. There is good agreement between data produced by spectroscopy and the microscopic measurements.

I. Introduction-

Metal oxide nanoparticles have shown their great interest in field of sensing ,optoelectronics ,catalysis and solar cells due to their unique physical and chemical properties differing from bulk. Among all the metal oxides copper oxide nanomaterials have attracted more attention due to its unique properties.

Cu_2O (Cuprous oxide) and CuO (Cupric Oxide) are two important oxide compounds of copper.

Cuprous oxide is p-type direct band gap II –VI semiconductor (3) with band gap of 2 eV and Cupric oxide has a monoclinic structure and presents p-type semiconductor behavior with a Indirect band gap of $1.21 – 1.51$ eV.

Copper oxide nanomaterials have the advantage of a lower surface potential barrier than that of metals, which affects electron field emission properties. Copper oxide is considered as a potential field emitter, an efficient catalytic agent, as well as a good gas sensing material. It also plays an important role in optoelectronics and solar cell (1-7).
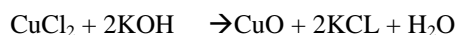
The metal elements are able to form a large diversity of oxide compounds. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic ,semiconductor or insulator character.

Nanomaterials have unique properties in comparison to the same materials in bulk form (2). Particle size is expected to Influence three Important group of basic properties in any material .The first one comprises the structural characteristics, namely the lattice symmetry and cell parameters. Bulk Oxides are usually robust and stable system with well defined crystallographic structures. However, the growing importance of surface free energy and stress with decreasing particle size must be considered: changes in thermodynamic stability associated with size can induce modification of cell parameters and/or structural transformations and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and a high surface free energy. In order to display mechanical or structural stability, a nanoparticle must have a low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. This structural phenomenon has been detected in $TiO_2,$ VO_x, Al_2O_3, or MoO_x oxides.

II. Experimental details

Synthesis of CuO nanoparticles using Cupric Chloride ($CuCl_2$)

The calculated amount of $CuCl_2.H_2O$ (9.7g, 56.9 mmol) and KOH (8 g, 142.9 mmol) were taken in benzene and hexane mixture and it was stirred and refluxed for 2h.The compound was separated out by filtration and filtrate was washed with methanol till the filtrate reaches to pH 7, then it was Oven dried .On calcination at $300^oc,350^oC$ and 400^oC different samples of the black powder were obtained according to calculated yield.

$$CuCl_2 + 2KOH \rightarrow CuO + 2KCL + H_2O$$

The XRD of powdered sample of CuO was recorded using a Philips P.W.1710 diffractometer with 0.15405 nm Cu K_α radiation. The average particle size (d) has been calculated from the line broadening in XRD pattern using Scherrer's formula:

$$d=0.9\lambda/\beta cos\theta$$

where λ is wavelength of X-ray, β is full width of half maximum (FWHM) and θ is Bragg's angle in radians.

The TEM of CuO was performed with E.M.-C.M.-12 (Philips) transmission electron microscope operating at 200KeV. FTIR spectra were recorded in solid phase using the KBr pellets technique.

III.   Results

The typical XRD pattern of theCuO nanoparticles annealed at 300°C is shown in Figure 1. The peak positions of the sample exhibited the monoclinic structure of CuO which was confirmed from the ICDD card No 801916. Further, no other impurity peak was observed in the XRD pattern, showing the single phase sample formation. The crystalline size was calculated using the Scherrer formula, $D = 0.9 \lambda / \beta \cos\theta$, where λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the peaks at the diffracting angle θ. Crystallite size calculated by the Scherrer formula was found to be 16 nm. Lattice parameters of unit cell of CuOare found to be a = 4.691 Å, b = 3.432 Å, c = 5.138 Å. These values are in good agreement with the standard values reported by the ICDD Card No 801916. In order to investigate the effect of temperature on CuO nanoparticles, samples were further annealed at 350°C, and 400°C. Figures 1, 2& 3 exhibits the XRD spectra of CuO nanoparticles annealed at different temperatures. It is clear from these Figures that the intensity of crystalline peaks increases with temperature, indicating an improvement in the samples crystallinity. Simultaneously, the peaks become narrower as the temperature increases resulting in the increase of crystallite size. The variation of crystallite size and lattice parameters with temperature was calculated and the results are presented in Table 1. It can be seen from Table 1 that crystallite size and lattice parameters increase with the increase in annealing temperature. The increase in crystallite size with temperature can be attributed to atomic diffusion. Figure 4 shows the TEM micrograph of CuO nanoparticles sintered at 300°C. Average particle sizes obtained from TEM images were found to be 16 ± 1.26 nm for the samples sintered at 300°C.The average particle sizes determined by TEM are closely matched to the crystallite size calculated from XRD results.
FTIR spectra were recorded in solid phase using the KBr pellets technique in the range of 3500–400 cm^{-1}. FTIR spectra of CuO nanoparticles treated at 300°C is shown in Figure 5. FTIR spectra exhibit only three vibrations: occurring at approximately 480 cm^{-1}, 530 cm^{-1}, and 580 cm^{-1} for the sample, which can be attributed to the vibrations of CuO, confirming the formation of highly pure CuO nanoparticles.

Table-1 Variation of Crystallite size and lattice parameters with annealing temperature.

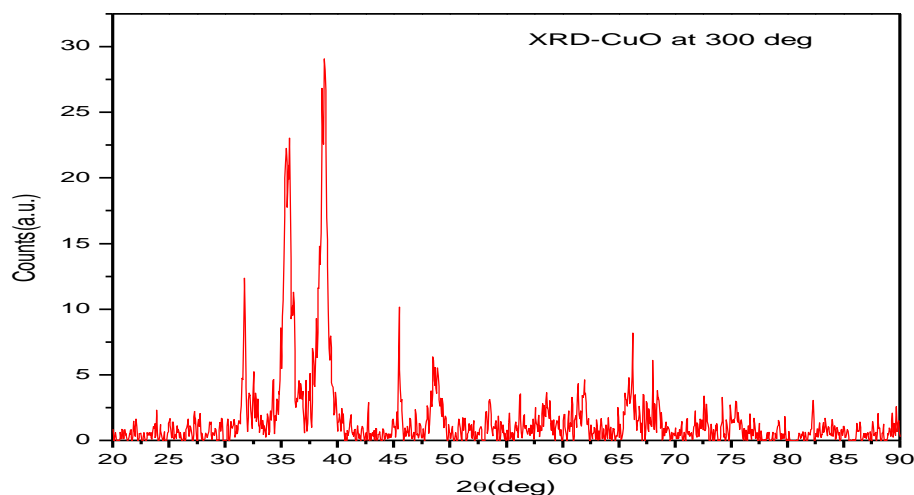| Temperature (^{O}C)	a (Å)	b (Å)	c (^{A})	Crystallite size (nm)
300	4.691	3.432	5.138	16
350	4.695	3.436	5.143	21
400	4.698	3.439	5.147	24

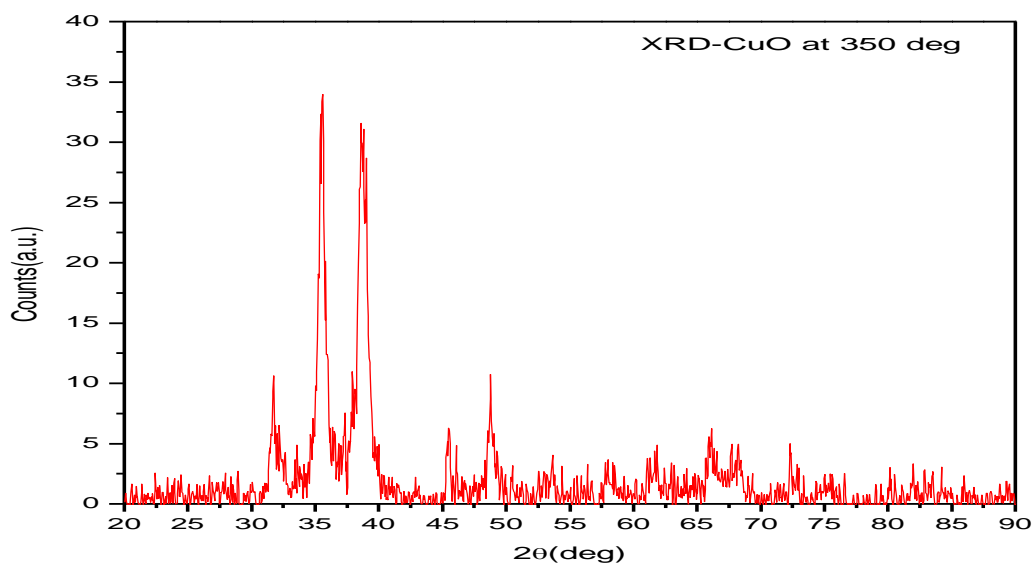Fig 1 : XRD of CuO NPs at 300 ^{o}C

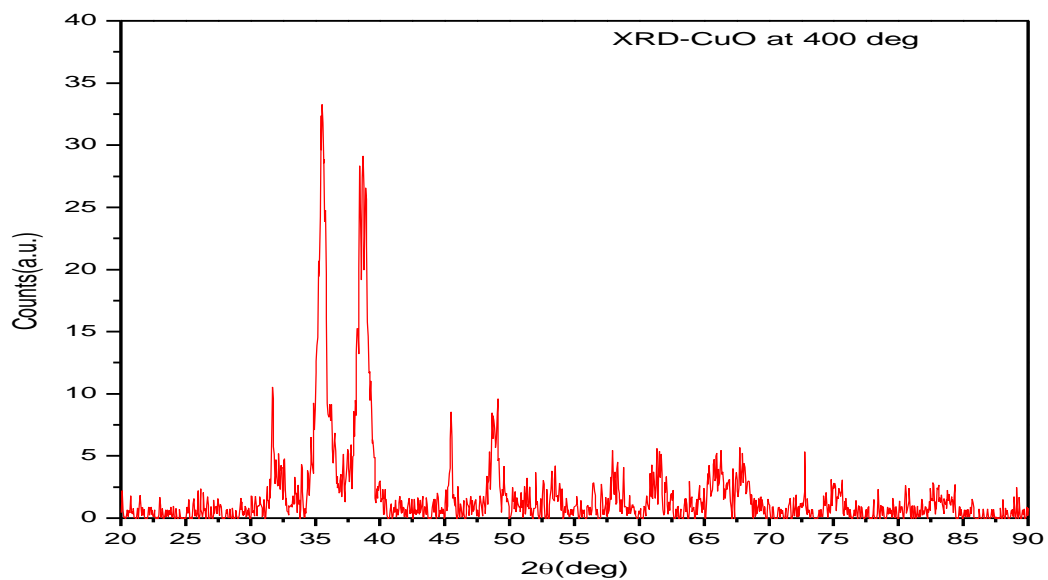Fig 2: XRD of CuO NPs at 350°C
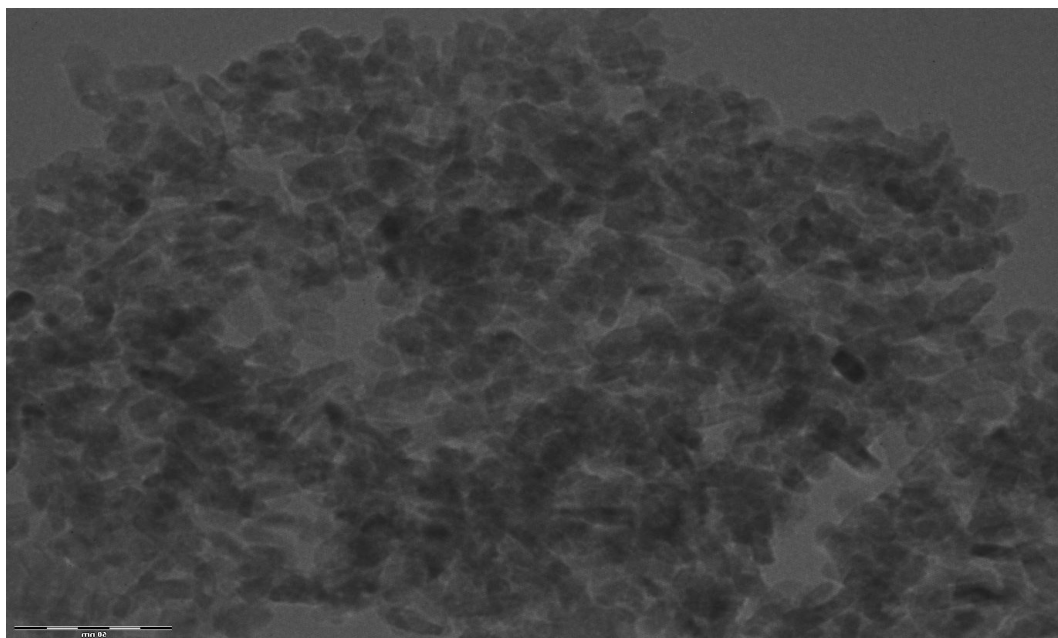

Fig.3: XRD of CuO NPs at 400°C
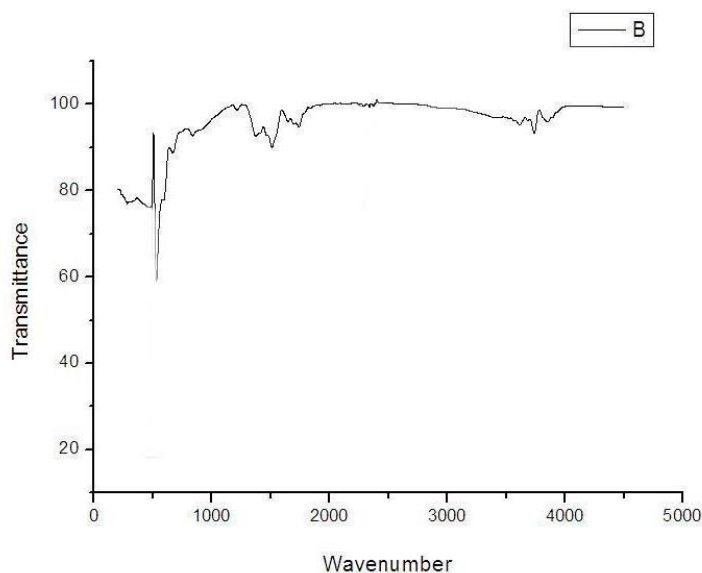
Fig 4: TEM image of CuO NPs

Fig 5: FTIR of CuO nanoparticles

IV.   Conclusion

We have successfully synthesized CuO nanoparticles using a sol gel combustion route. XRD spectra confirmed the formation of single phase CuO nanoparticles. Crystallite size was found to increase with the increase in annealing temperature. Minimum crystallite size of 16 ± 1.26 nm was observed in the case ofCuO nanoparticles annealed at 300°C. TEM results corroborate well with XRD results. FTIR spectra also validated the purity of CuO nanoparticles.

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