ENHANCED STRUCTURAL AND OPTICAL PROPERTIES OF COPPER OXIDE FOR SOLAR CELL APPLICATIONS

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The cuprous and coper oxides were prepared by many techniques such as thermal oxidation, co-precipitations template-based sol-gel, simple hydrolysis, simple solutions and electrochemically. CuO nanoparticles with an average size of xrd 13.81 to 18.75nm have been successfully prepared by Co-Precipitation technique, using copper chloride dehydrate and sodium hydroxide as the precipitate agent. The CuO nanoparticles are characterized by using techniques such as X-ray diffraction, UV–Visible absorption spectroscopy (UV), Scanning electron microscopy (SEM) and IR spectrum (FTIR). The as-prepared CuO nanoparticles have irregular flake like shapes, nonuniform distribution and high purity. The band gap is estimated to be 2.03, 2.05 and 2.15 eV according to the results of the optical measurements of the CuO nanoparticles.

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1. Introduction

In recent year's nanomaterials and nanotechnology gained considerable interest due to their physical properties which depend on the size and shape of the nanoparticles [1]. The scientific community have been very interested in nanostructure of metal oxides because of their great applications in many fields and morphologically based characteristics in recent years [2]. Nanoparticles has many applications in gas sensors dye sensitized solar cells [3] and also had applications Included in coatings, fabrics and textiles as an antimicrobial, anti-fouling, antibiotic and anti-fungal agent [4]. The cuprous and coper oxides were prepared by many techniques such as thermal oxidation [5], co-precipitations template-based sol-gel [6], simple hydrolysis [2], simple solutions [7] and electrochemically[8]. Additionally, the arrangement of copper oxide or cuprous oxide nanostructure such as 2D and 3D can be excellently promoted by the adding of surfactants [9, 10]. Among the numerous nanomaterials of metal oxides semiconductor recently CuO. P-type semiconductor with its exclusive properties and large applications has attracted with great attention. The properties of copper oxide include photo chemically and high thermal stabilities cost-effective fabrications, non-toxicity, high temperature superconductivity, electrochemical activity and so on. Coper oxide is a semiconductor monoxide with narrow band gape [11]. The heterogeneous and low electric resistance can also be used in many chemical processes e.g.

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hydrocarbons, nitrous oxide degradation and phenol in water and also be in practical application such as lithium batteries [12], active catalysts[13], optical switches[14], solar cells [15], magnetic storage media [16] and gas sensor [17] because of their photoconductive and photochemical characteristics [18]. In recent years nanocrystalline semiconductor particles have attracted considerable attention such as electronic properties, unique optical properties, large surface volume ratio and increased activities as compare to the bulk materials. Copper oxide has tremendous physical and chemical characteristics that vary from micro or bulk counterparts because of their wide surface area and potential side effects [19]. In its ground state copper oxide has an electronic structure ($3d^9$) acts as an antiferromagnetic substance. The conductivity of copper oxide decreases because of exposure of reducing gas species. CuO nanostructure can also be synthesized by many methods that are solution method, wet chemical route, pluse laser ablation, vapor deposition, co-precipitations and sol gel method. In this present work, the CuO nanoparticles are also prepared by using co-precipitation method. Copper chloride is used as starting material in this method and sodium hydroxide is used as a reducing precipitate agent. The large number of nanomaterials are form in this way. There are many applications of copper oxide nanoparticles used in many fields. Keeping this in mind, we have designed this study to synthesize CuO nanoparticles with different Cu precursor concentration and studied its effect on the structural, morphological and optical properties.

2. Experimental Detail

During experiment, Copper chloride dehydrate ($CuCl_2.2H_2O$), sodium hydroxide (NaOH) pellets and distilled water was used. All analytical grade samples used in the preparation of material were purchased from (Merck and Sigma Aldrich through local suppliers) in pure form without any need of further purification. A standard procedure was adopted to synthesize CuO nanoparticles. During synthesis (0.001, 0.002, 0.003) grams of Copper chloride dehydrate ($CuCl_2.2H_2O$) were used for synthesized of CuO and required amount of NaOH pellets were dissolved in distilled water. In the current research work, CuO nanoparticles were synthesized via Co-precipitation method. At room temperature, in solution of $CuCl_2.2H_2O$, NaOH was added dropwise under constant stirring. The solution was mixed with precipitating agent (NaOH) to obtained less chemically dispersed nanoparticles.

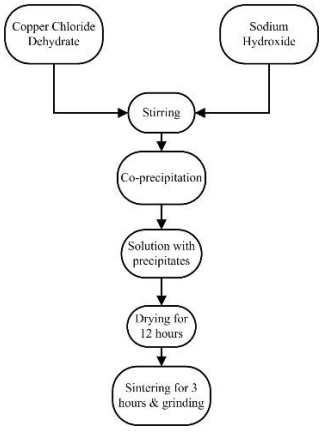


Fig. 1. Schematic flow chart of CuO via Co-Precipitation method.

The pH 11 was maintained throughout the reaction. The solution color was gradually changed green to bluish green and finally black while the reaction proceeded. Furthermore, black precipitate (copper hydroxide) was filtered and washed several times with distilled water to remove the impurities. After that, precipitates were dried in the oven at 70℃ overnights. In order to obtain crystalline CuO nanoparticles the dried samples were calcinated in furnace at 700℃ temperature for 2 hours. Then the calcinated samples were grinded with pestle and mortar to

obtain powder sample. The schematic flow chart of CuO nano-particles (NPs) as shown in figure 1. All prepared samples of CuO Nano-particles have characterized by X-ray diffraction, UV-vis spectroscopy to study their UV spectra, Scanning electron microscopy, particle structure and morphology and FTIR spectrum, functional groups respectively.

3. Results and discussions

Crystalline size (D) is calculated in nano-meter. Lambda (λ) is the X-ray wavelength having a typical value of about 1.54Å. Shape factor (K) having a typical value of approximately (0.9-0.99) fluctuate with the definite shape of the crystallites.

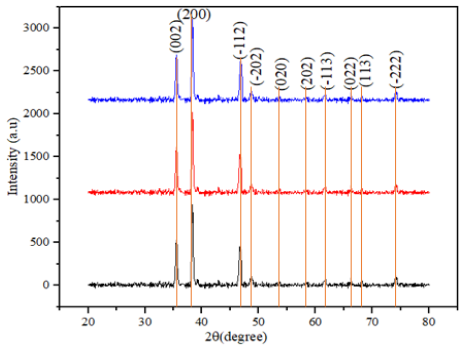


Fig. 2. XRD Pattern of CuO having Concentration (0.01, 0.02, 0.03).

Crystalline size and particle structure of obtained nanoparticles was examined by using XRD analysis. The diffraction peaks justify the formation of nano-sized CuO particles. Fig. 2 shows the XRD diffraction of CuO for different concentrations. In above XRD pattern of diffraction peaks at (002), (200), (-112), (-202), (020), (-113), (022), (113) and (-222) indicates the presence of CuO nanoparticles with Monoclinic structure with JCPDS data (Card#45-0937). The peaks at 2θ values of about 35°, 38°, 46°,48°,53°,58°,61°,66°,68° and 74° also correspond to the CuO. Broader peaks in XRD measurement suggest small particles diameter in the powder. The highest intensity peak at 2Θ equal to 38° corresponds to the (200) plane of the CuO crystal structure. All the patterns show well defined but broad diffraction peaks indicating the formation of nanocrystalline materials. Figure1. shows that all the major crystalline planes of CuO are present.

The average crystalline size was calculated from the Full Width Half Maximum (FWHM) of the diffraction peaks using the Debye formula.

$$D = \frac{K\lambda}{\beta Cos\Theta} \tag{1}$$

where "ʎ" is the X-ray wavelength, "β" is full width half maxima and "Θ" is the angle of X-ray diffraction.

It is clearly observed that the crystallinity of CuO nanoparticles increase with the increase of Cu concentrations. Above discussion suggested that the crystallinity of CuO Nano powders is significantly affected by Cu dopant.

The lattice parameters for monoclinic structured of CuO nanoparticles are calculated from the following equation.

$$\frac{1}{d^2} = \frac{1}{\sin^2 B}\left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 B}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right) \tag{2}$$

where "d" is the de-spacing, "h, "k", l" is the miller indices, "a" ,"b","c" is the length of crystal.

The volume unit cell of monoclinic structure can also be calculated from the following

formula:

$$V = abc\sin\beta$$

For Monoclinic Structure

where 'v' is the volume of unit cell and 'a, b and c are the lattice constant of monoclinic structure.

X-ray density 'ρ_x' is estimated using the following equation;

$$\rho_{x} = \frac{n M_W}{V N_A} \quad (3)$$

M_w, n and N_A in equation designates molecular weight of compound, number of atoms present in a unit cell of hexagonal structure and Avogadro's Number respectively.

Dislocation density has been calculated from the following formula.

$$\rho = \frac{1}{D^2} \quad (4)$$

where "D" is the average crystalline size.

The dislocation density is known as the length of dislocation lines per unit volume of the crystal. A dislocation is a crystallographic defect or irregularity in the crystal structure. The presence of dislocation strongly influences many of the properties of materials.

Here, we can calculate the number of unit cell from the following equation.

$$n = \pi \times \left(\frac{4}{3}\right) \times \left(\frac{D}{2}\right) \times \left(\frac{1}{V}\right) \quad (5)$$

where "n" is the number of unit cell, "D" is the average crystalline size and "V" is the volume of the unit cell.

Morphology index can also be calculated from the following relation

$$M.I = \frac{FWHM_h}{FWHM_h + FWHM_p} \quad (6)$$

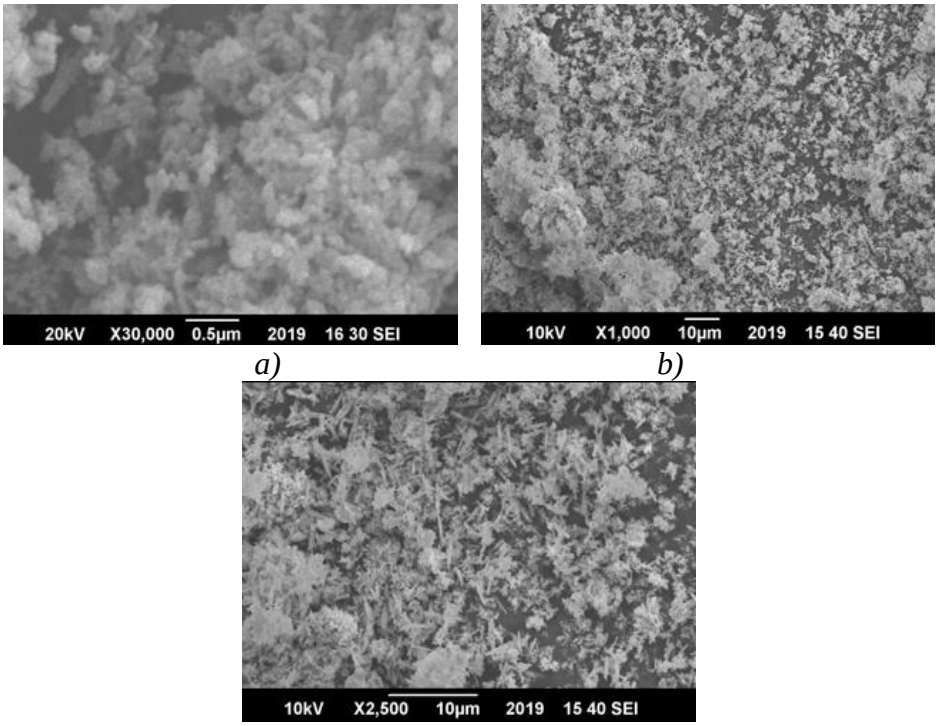
where (M.I) is morphology Index, $FWHM_h$ is the high peak and FWHMp is the particular peaks.

Table 1. Cu Concentration, Crystalline size (Dnm), Parameters (Å), (Volume (V), Dislocation density (ρ), Number of atoms (n), Morphology Index (M.I), X-ray density (ρ_x) calculated from XRD of different samples.

Contents (Cu)	Crystalline Size (Dnm)	Parameters (Å)			Volume (nm^3)	X-ray density (ρ_x)	Dislocation density (ρ)	number of unit cell (n)	Morphology index (M.I)
		A	b	c					
0.01	13.81	5.45	3.42	5.97	94.35	6.86×10^{-24}	0.00524	0.3064	0.5227
0.02	13.19	5.56	3.45	5.95	96.70	6.70×10^{-24}	0.00574	0.2855	0.5220
0.03	18.75	5.59	3.49	5.59	98.52	6.57×10^{-24}	0.00284	o.398	0.5313

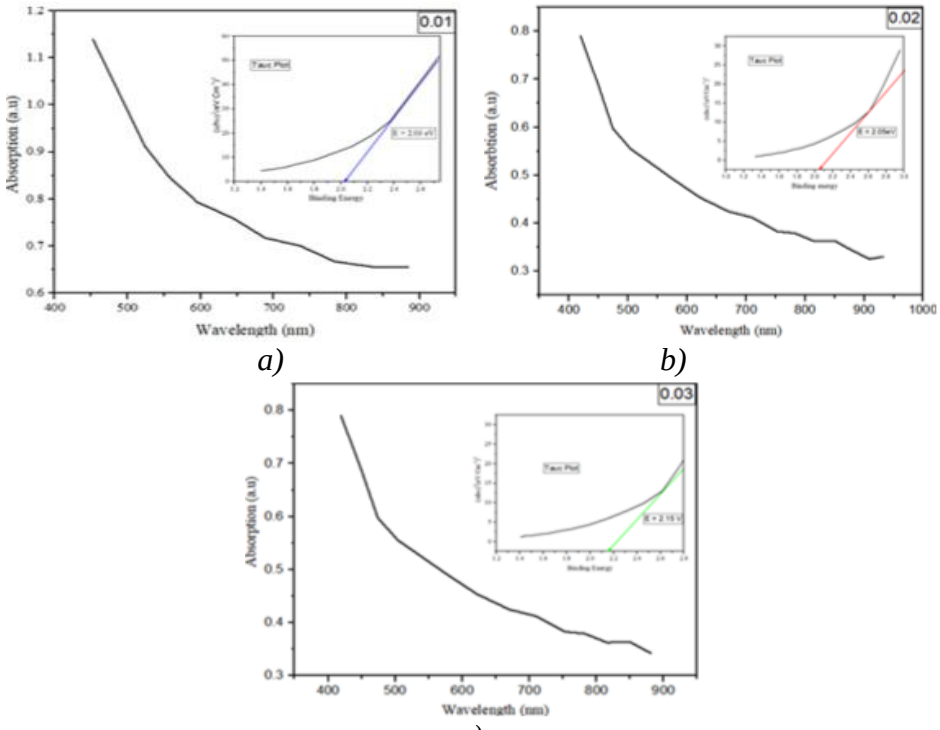
SEM is an important tool for interpreting information and grain size analysis of nanoparticles. CuO nanoparticles at different concentrations (0.01, 0.02 and 0.03) were studied by using SEM as shown in Fig. 3. These images reveal that the shape and morphology of CuO nanoparticles highly depend on the concentration of Cu. In Fig. 3. the morphology of 0.02 of CuO nanoparticles shows good homogeneity and uniform distribution due to increased substitution of v arious cupper ions. In CuO nanoparticles increasing the Cu loading content greater than 0.03 increases the size of particles and their shape tends to be in irregular flake like shapes. The SEM shows the non-uniform grains distributions for all compositions. This feature implies the phase

transformation of the compounds strongly depending on cupper content. The corresponding particle size distribution of CuO nanoparticles was in agreement with the results calculated from the XRD analysis. The morphological overview of SEM results suggest that one can obtain particles with less aggregation from this method.



a) *b)* *c)*

Fig. 3. SEM Images of CuO for a) 0.01; b) 0.02, c) 0.0.



a) *b)* *c)*

Fig. 4. Uv-Visible Pattern of CuO for a) 0.01; b) 0.02, c) 0.0.

UV-Visible absorption spectrum of CuO with different concentrations of Cu shown in Fig 4. The effect of doping on the optical absorption, band gap energies and the optical properties of CuO nanoparticles were investigated by UV-Visible spectroscopy. The absorption spectrum generally depends on factors such as band gap ,oxygen deficiency, grain size, lattice strain, impurity centers and surface roughness. Band gap of CuO nanoparticles is calculated through tauc plot. The coefficient of optical absorption near the band edge is calculated from Tauc relation using following equation:

$$\alpha h\nu = A(h\nu - E_g) \tag{7}$$

where *'α'* is the absorption coefficient, '*h'* is the Plank's constant, '*v'* is the frequency of the incident photon, '*A'* is a constant, '*n'* depends on the nature of transition (*n* = 1 for direct transition) and 'E_g'is the optical energy direct band gap.

The *α* is calculated by formula is:

$$a = 2.303\left(\frac{Ab}{t}\right) \tag{8}$$

Band gap can be calculated by the intercept of tangent of $(\alpha h\nu)^2$ and the (hν) is photon energy. Calculated band gap of CuO nanoparticles is 2.03, 2.05 and 2.15 respectively.

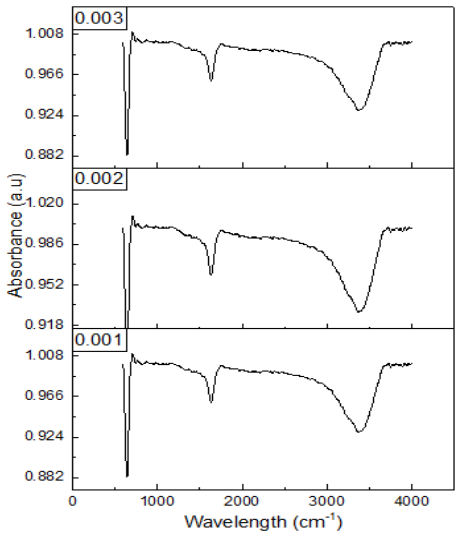


Fig. 5. FTIR Spectra of CuO for (0.01, 0.02, 0.03).

Fourier transform infrared (FTIR) spectroscopy investigated the compositional properties of the prepared CuO nanoparticle. Fourier transform infrared spectra (FT-IR) is an analysis used to generate an infrared radiation absorption spectrum of a material. In figure 4. FT-IR spectra CuO monoclinic structure is reported in the region of $4000 - 500\ cm^{-1}$. Fig 4 shows the FTIR peaks of the Sample. The peak at 624cm^{-1} relate to M−O(CuO) bond vibrational frequency that support the presence of monoclinic phases. It ranging to Cu− O vibrations and formation of CuO nanoparticles. Another peak at 1619cm-^{1} may be corresponds to Co^{2-} vibrations. Absorption peak at 3406cm^{-1} of CuO could be correlated to the bending and stretching vibrations of adsorbed water and surface hydroxyl group.

4. Conclusion

Crystalline size and particle structure of obtained nanoparticles was examined by using XRD analysis. CuO nanoparticles has Monoclinic structure. The average crystalline size was calculated from the Full Width Half Maximum (FWHM) of the diffraction peaks using the Scherrer Debye formula.The morphology of 0.02 of CuOnanoparticles shows good homogeneity and uniform distr ibution due to increased substitution of various cupper ions. The absorption spectrum generally depends on factors such as band gap ,oxygen deficiency, grain size, lattice strain, impurity centers and surface roughness. Band gap of CuO nanoparticles is calculated through tauc plot. Fourier transform infrared (FTIR) spectroscopy investigated the compositional properties of the prepared CuO nanoparticle.

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