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Solid State Synthesis Of CuO Nanoparticles For Photo Catalytic Application

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Abstract: Copper oxide (CuO) nanoparticles were synthesized by solid-state reaction method and annealed at 350°C and 800°C. Copper chloride and sodium hydroxide were ground together and Poly Ethylene Glycol (PEG-400) was added in the grinded powder which acts as a surfactant agent. Synthesized salts were annealed at 350°C and 800°C and the structural, morphological and optical properties were studied. X-ray diffraction analysis shows that the CuO compound belongs to monoclinic crystal system. The direct band gap calculated from the UV-Vis absorption spectrum of CuO annealed at 350°C is 1.67 eV and CuO annealed at 800°C is 2.73 eV. Photo catalytic activity of CuO annealed at 350°C is relatively higher when comparing to that of CuO annealed at 800°C.

Keywords: Solid State Reaction, CuO, XRD, FESEM, and UV-Vis-absorption

Introduction

Semiconducting nanoparticles are the important functional materials because they have large number of charge carriers (holes and electrons). Semiconducting materials are important for photo catalytic application. Electron oxidations and reductions are important functions in the photo catalytic reaction. Copper oxide (CuO) is p-type semiconducting material with a narrow band gap 1.6 eV¹. The narrow band gap range enhances the photo catalytic activity². Mostly titanium compounds are widely used in the studies of photocatalytic activity^{3,4} and some other materials reported are CuO/Ag⁶ and Cu-FeO₂⁷. CuO nanoparticles are also known for production of H₂O₂⁸ and bacteria inactivation⁹. Methods employed to synthesis of CuO nanoparticles are, chemical co-precipitation method¹⁰, hydrothermal method^{11, 12}, thermal decomposition method¹³, aqueous solution process¹⁴, self assembled synthesise method¹⁵, chemical reaction method¹⁶ and polyol method¹⁷. In the present work solid state reaction method is used to prepare CuO nanoparticles because this method is simple, environmental friendly and not required any high cost of instruments.

Experimental

Copper oxide nanoparticles were synthesized by solid state reaction method. 5 g of copper chloride (CuCl_2) and 3 g of sodium hydroxide (NaOH) were used as precursors. They were grounded separately in agate mortar. 6 ml of poly ethylene glycol (PEG-400) was added to the prepared powder which acts as the surfactant agent and further grained for 30min. The resulted colloidal salt was washed with distilled water and ethyl alcohol by ultrasonic bath to remove PEG-400. Finally, the obtained product was annealed at 350°C and 800°C for 3 hours. The structural properties of the annealed CuO nanoparticles were studied using X-pert powder XRD system using $\text{Cu-K}\alpha$ radiation ($\lambda=1.5406\text{\AA}$) in Bragg-Brentano ($\theta/2\theta$ coupled) geometry. The morphology of synthesized nanoparticles was studied by scanning electron microscope (SEM) using FEI quanta FEG200. Optical transmittance of the nanoparticles was recorded using UV-Vis absorption spectrum.

Results and Discussion

Structural Analysis

X-ray diffraction (XRD) analysis confirms the formation of CuO nanoparticles. The observed XRD peaks of CuO annealed at 350°C (Fig. 1a) are $2\theta = 35.51^\circ, 38.68^\circ, 48.81^\circ, 53.37^\circ, 58.34^\circ, 61.51^\circ, 66.07^\circ$ and 68.12° correspond to the characteristic reflection of (110), $(\bar{1}11)$, (111), $(\bar{2}02)$, (202), $(\bar{1}13)$, $(\bar{3}11)$ and (200) planes of the monoclinic CuO structure well matched with JCPDS card no. 89-5895. For CuO annealed at 800°C , XRD peaks (Fig. 1b) are observed at $2\theta = 32.67^\circ, 35.72^\circ, 38.92^\circ, 48.87^\circ, 53.67^\circ, 58.47^\circ, 61.67^\circ, 65.97^\circ, 66.37^\circ, 68.22^\circ, 73.37^\circ$ and 75.37° well correspond to the characteristics reflection of (110), $(\bar{1}10)$, (111), $(\bar{2}02)$, (020), (202), $(\bar{1}13)$, (022), $(\bar{3}11)$, (113), (221) and (004) planes of the monoclinic CuO structure match well with corresponding value of JCPDS card no. 65-2309. Crystalline size was calculated by Debye-Scherrer formula: $D = k\lambda/\beta\cos\theta$ where k is 0.9, β is full width at half maximum of the XRD peak and θ is Bragg's angle. The average crystalline size of the CuO annealed at 350°C is 17.95nm which is smaller compared to the average crystalline size of 45.42nm obtained from CuO nanoparticles annealed 800°C . Crystalline size increases with increase in the annealed temperature. The predominant peaks of CuO annealed 350°C are slightly shifted towards the higher value of 2θ when compared with the corresponding XRD peaks of CuO annealed at 800°C .

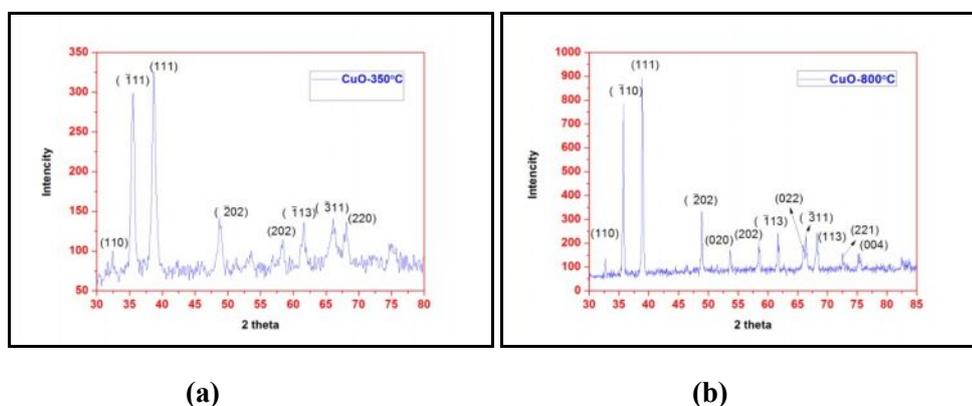


Fig.1. XRD peaks of CuO annealed at (a) 350°C and (b) 800°C

Morphology Analysis

Surface morphology of the synthesized nanoparticles was analyzed using Scanning Electron Microscope (SEM). CuO nanoparticles annealed at 350°C are spherical in shape and surface of nanoparticles discloses the vesicular morphology and the average particle size is 37.5nm as shown in Fig 2a. SEM studies on the synthesized CuO by chemical co-precipitation method using oxalic acid as template and hydrazine hydrate as reducing agent at 650°C disclosed vesicular morphology¹⁰. SEM image of the surface of the CuO annealed at 800°C nanoparticles shows pebbles shaped nanoparticles of size $2.19\mu\text{m}$ and it reveals improvement of the crystalline size and formation of step like structure as has been observed in Fig. 2b.

Optical Analysis

UV-Visible absorption spectrophotometer is used to record absorption spectrum and optical band gap energy (E_g) of the prepared CuO nanoparticles annealing at different temperature. Figs. 3a, b show the

absorption peak of annealed CuO nanoparticles at 350°C and 800°C in the range of 380 nm and 381 nm respectively. Direct band gap of CuO nanoparticles annealed at 350°C and 800°C was calculated from UV-Vis absorption spectrum. From the graph plotted between $(\alpha h\nu)^2$ and $(h\nu)$ the band gap of the copper oxide nanoparticles was estimated. Fig.3c shows the calculation of direct band gap of the copper oxide nanoparticles annealed at 350°C and band gap value is 1.67 eV. The direct band gap value for copper oxide nanoparticles annealed at 800°C is 2.73eV (Fig. 3d).

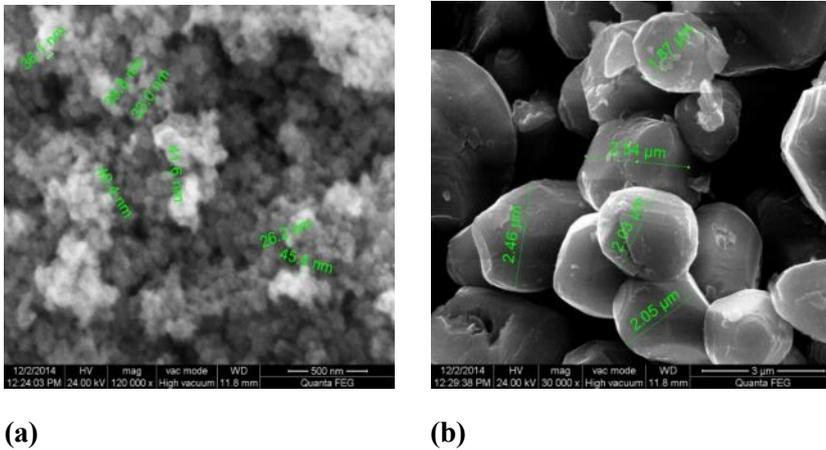


Fig.2. SEM image of CuO annealed at (a) 350°C and (b) 800°C

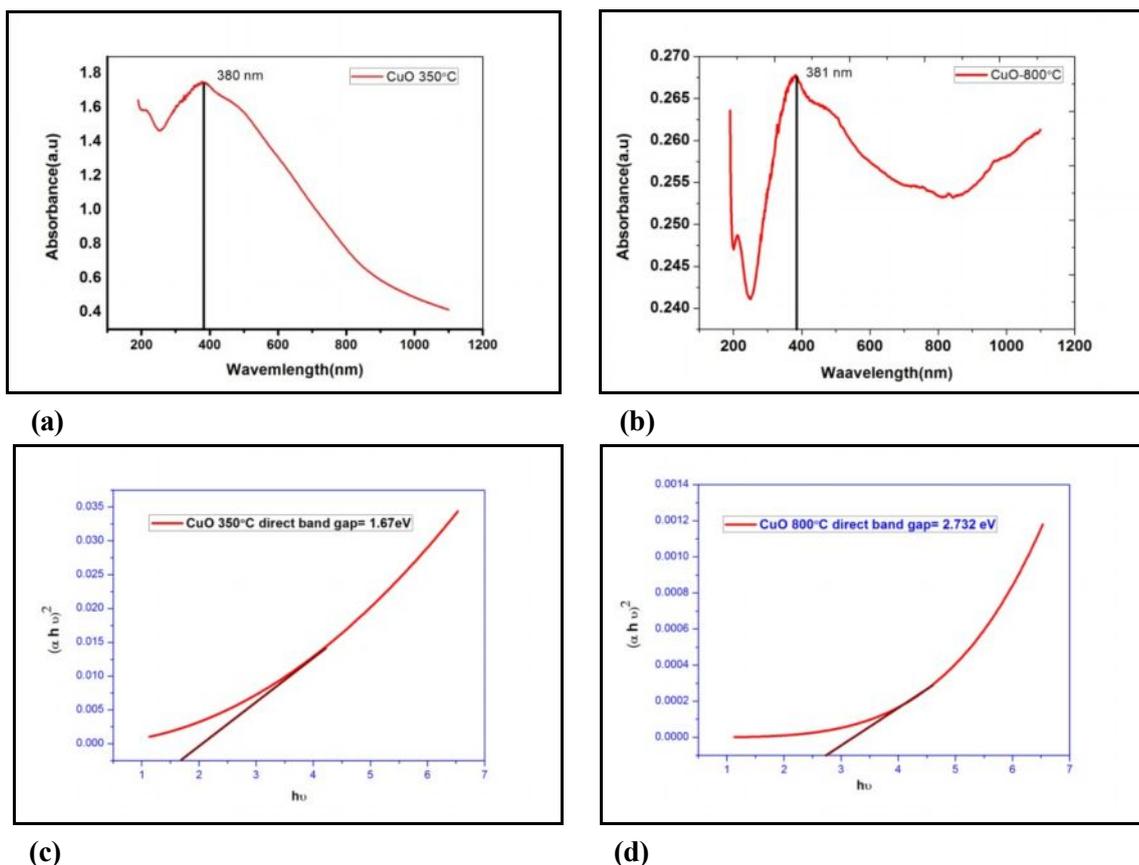


Fig. 3 Optical absorption Spectrum of (a) CuO-350°C, (b) CuO-800°C and (c) Plot of $(\alpha h\nu)^2$ vs $(h\nu)$ CuO-350°C and , (d) Plot of $(\alpha h\nu)^2$ vs $(h\nu)$ CuO-800°C

Photocatalytic Activity

The photocatalytic activities of the as-prepared CuO with different annealed temperature were investigated by the degradation of dye Rhodamine-B (Rh-B) under visible-light irradiation shown in Figs. 4a,b and the values are given in the Table.1. The Figs. 4a,b show the time dependent absorption spectra of the dye solution in the presence of CuO annealed at 350°C and 800°C temperatures as used catalytic. It can be seen that

the absorbance peak at 555 nm is reduced significantly showing the degradation of the Rh-B dye molecules. After 120 minute the CuO annealed at 350°C and 800°C yields the 25.58 and 20.64 percentage of degradation respectively. As the morphologies and the exposed high energy surfaces can affect the properties of metal oxide nanostructures¹⁸ the catalytic activity of materials is related to the surface area of a catalys. Rh-B molecules adsorption is more active sites in high surface area¹⁹. SEM image shows the morphology difference in CuO annealed at 350°C and 800°C temperature. The enhancement on photo degradation of Rh-B in spherical shaped CuO nanoparticles annealed at 350°C is relatively more active than the pebble shaped CuO annealed at 800°C. Thus the higher surface area influences in the photo degradation activities.

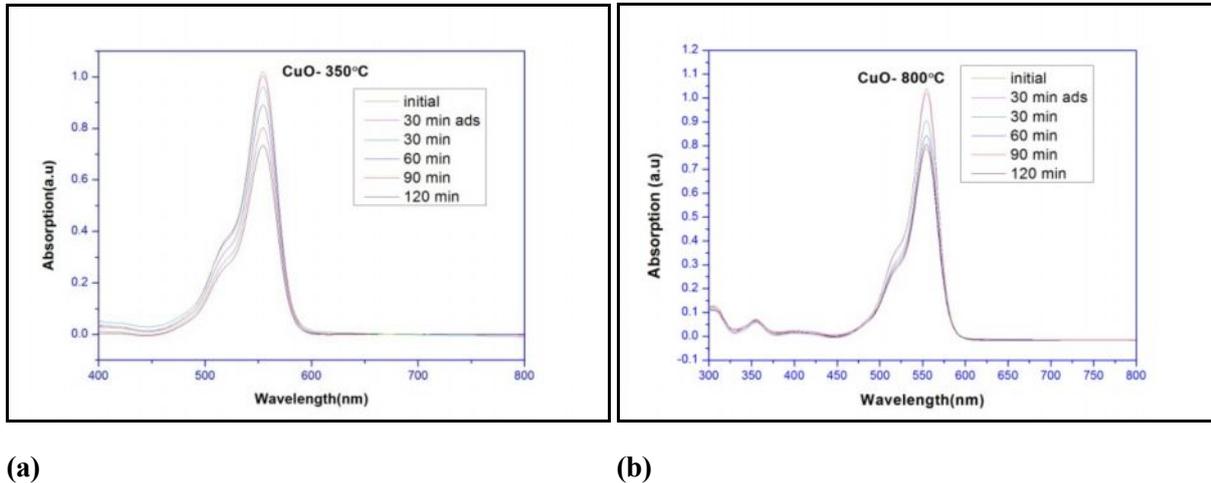


Fig. 4 photo catalytic reaction of (a) CuO-350°C and (b) CuO-800°C

Table 1- Photo catalytic reaction of CuO-350°C

S.No	Irradiation time	CuO annealed at 350°C		CuO annealed at 800°C	
		Observed peak	% of degradation	Observed peak	% of degradation
1.	Initial	1.017	-	1.0855	-
2.	30-min Ads	0.993	2.359	1.03	5.11285
3.	30 min	0.974	1.8199	0.9206	10.03871
4.	60 min	0.891	10.0303	0.8593	15.72547
5.	90 min	0.768	22.0362	0.8206	19.27223
6.	120 min	0.732	25.5761	0.806	20.63565

Conclusion

Copper oxide nanoparticles were synthesized by solid state reaction method and annealed at 350°C and 800°C. The XRD pattern revealed the formation of copper oxide with monoclinic structure. The calculated average crystalline size of the synthesized nanoparticles is 17.95 nm (350°C) and 45.25 nm (800°C) respectively. SEM images indicate that spherical in shape and surface of the nanoparticles discloses the vesicular morphology for 350°C annealed CuO and pebbles shaped structure was observed in CuO annealed at 800°C. The direct band gaps was calculated for the prepared CuO with different annealed temperature using UV-Visible absorption spectroscopy. The photo catalytic studies show that CuO annealed at 350°C has relatively good catalytic activity.

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