International Journal of Researches In Biosciences, Agriculture & Technology | Feb. 2015 Special Issue-1 | ISSN No. (Online) 2347-517X

$Cu_xZn_{1-X}O$ Nanocrytals: Structural Study and Photo-Catalytic Application

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Abstract:

This study describes synthesis, characterization, various physical parameters and photocatalytic activities of $Cu_xZn_{1-x}O$ (x= 0.0 and 0.02) system prepared by co-precipitation method in aqueous medium. X-ray diffraction (XRD) technique and UV- Visible (UV-vis) spectroscopy have been used for the characterization of synthesized materials. The lattice parameter, volume cell, x-ray density, atomic packing factor, grain size, Williamsons- Hall grain size and strain have been calculated by using XRD data. XRD patterns show that the samples have hexagonal wurtzite structure. The average grain size has been calculated by using Debye-Scherrer formula and Williamson-Hall analysis. The photocatalytic activities of prepared sample have been studied using rhodamine B (RhB) dye solution under UV light illumination.

Keywords: ZnO, Co-precipitation method, grain size, photocatalyticavtivity, rhodamine B.

Introduction:

Nanostructured ZnO semiconductor has attracted widespread attention due to its low cost, high stability, easy synthesis non-toxicity and have many potential application in photocatalysis, solar cell, gas sensors, fuel cells, photovoltaics and antibacterial action [1-9].Various synthesis methods like sol–gel, spray pyrolysis, thermal evaporation, microemulsion, and hydrothermal methods have been carried out to prepare nanostructured ZnO having different morphologies [10-13]. But solution phase techniques are easier and cheaper compared to other methods as they require longersynthesis time and higher temperature [14]

Recently, modified ZnO was prepared by doping with transition metal such as Ag, Mn, Fe, Co, Cr, Al and Pd [15-21]. The results of these transition metal doped ZnO shows that the optical, magnetic and electrical properties changed with the change in concentration of transition metal. Electronic conductivity of Cu is very high and it is cheap and highly available on Earth's crust and so it is important metal for doping [22].

The degradation of organic pollutant in waste water by heterogeneous photocatalysis has attracted great interest. The surface area and surface defects are important parameters in photocatalytic activity of semiconductor metal oxide. Many researchers investigated that ZnO is efficient photocatalyst for the degradation of organic pollutants because of its high surface activity, crystalline size, morphologies and textures [23]. Different morphologies of ZnO have been reported for the degradation of organic dyes [24]. The transition metals doped ZnO has found application in photocatalysis [18].

In this present work, we report the synthesis of undoped and Cu doped ZnO by co-precipitation method in aqueous medium and doping effect of Cu on lattice parameters, volume, grain size, W-H grain size and lattice strain. We have analyzed the photocatalytic activities of undoped and Cu doped ZnO via degradation of rhodamine B under UV light irradiation.

Experimental

Synthesis of Cu doped ZnO

All chemicals used for experimental work were purchased from Merck India and used without further purification.Sample with composition formula $Zn_{1-x}Cu_xO$ (x = 0.0 and 0.2) have been prepared by co-precipitation method in aqueous medium. The appropriate amounts of zinc acetate dihydrate and copper acetate hydrate were dissolved in 50 ml deionized water and stirred for 2h at room temperature. NaOH in 50 ml deionized water was added into the solutions as coprecipitant. This solution again stirred for 2 h at room temperature and precipitates formed were separated from the solution by centrifugation and washed with deionized water in order to remove acetate ion. The wet precipitates were dried in an oven at. 100^{0}C. The calcination of nanocrystalline samples were carried out at 400^{0}C in furnace for 4 h.

Photocatalytic activity

First, 100 mL of RhB solution with a concentration of 20 ppm was prepared. As-prepared samples were weighed (20 mg) and added to 25 ml of the above RhB solutions. The suspension was stirred in the dark for 30 min in order to reach absorption equilibrium and then the mixed solutions were illuminated under UV lamp (250W) in the batch photochemical reactor having cooling system. At different time intervals 10 ml sample was collected and centrifuged to separate the catalyst from the solution. UV–vis adsorption spectra were recorded to monitor the degradation process using a Shimadzu UV- Visible Spectrophotometer (UV-1800). After recording spectra the sample was pour back to original dye solution. All the experiments were carried out at identical condition and at room temperature.

Results and Discussion:

XRD study

The crystal structure of $Zn_{1-x}Cu_xO$ samples with concentration x = 0.0 and 0.02 shown in figure 1 were determined by X-ray diffractometer (Bruker D8 Advance Diffractometer) with CuKα radiations (λ = 1.5416A^o) in the range of 20^o to 80^o at room temperature. The sharp intense peak obtained in all the samples at 2θ ≈ 30.80, 34.22, 35.38, 46.70, 54.88, 62.02, 67.12 & 68.23 corresponds to the lattice plane (100), (002), (101), (102), (110), (103), (112) and (201) respectively confirms that the prepared samples are good crystalline in nature with wurtzite hexagonal structure and are agree with the JCPDS data (01-075-1533).

The structural data such as lattice parameter, volume of unit cell, x-ray density, atomic packing fraction, c/a ratio, grain size, W-H grain size and strain

obtained from XRD pattern of $Zn_{1-x}Cu_xO$ samples with concentration x = 0.0 and 0.02 is tabulated in the table 1.

The volume of unit cell can be determined by using well known formula,

$$V = 0.866\, a^2 c \qquad \text{---------- (1)}$$

It is observed that the volume of unit cell decreases by doping 2% Cu ion into ZnO.

The X-ray density of ZnO sample was calculate using the formula [25].

$$D_x = \frac{nM}{N_A V} \qquad \text{---------- (2)}$$

Where, D_x is X-ray density, n is the number of atoms per unit cell, M is the molecular weight of the sample, N_A is Avagadro,s number and V is the volume of unit cell. It is observed that the x-ray density depend on mass of the sample as well as volume of the unit cell.

It is observed from the table1 that the average atomic packing fraction (APF) of the samples is ≈ 0.74 which is in good agreement with the standard wurtzite hexagonal structure. The c/a ratio shows that the isotropic nature of the prepared materials.

A definite line broadening of the diffraction peak (101) of pure and Cu doped ZnO samples is an indication that the synthesized materials are in nanometer range. The crystallite size (D) was calculated from line broadening of the major XRD peak (101) using the Scherrer's formula [26].

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad \text{---------- (3)}$$

where, , K is the shape factor, which is a constant taken as 0.9, λ is the wavelength of the X-ray radiation (λ = 1.5416A°), β is the full-width at half-maximum (FWHM) in radians, θ is the Bragg's angle in degree. The crystallite size of the pure and Cu doped ZnO sample obtained from eq (3) are listed in table 1. It is found that the samples synthesized by co-precipitation route in aqueous medium have grain size between 23 - 33 nm.

In order to understand the peak broadening with lattice strains, various peaks appeared in the XRD pattern were used. The Stokes and Wilson formula given in equation (4) were used to calculate the strain induced broadening of the Bragg's diffraction peak.

$$\varepsilon = \frac{\beta_{hkl}}{4\tan\theta} \qquad \text{---------- (4)}$$

The W-H plot of $\beta_{hkl}\cos\theta$ versus $4\sin\theta$ for $Zn_{1-x}Cu_xO$ samples with concentration x = 0.0, and x = 0.02 is shown in figure 2. It is well known that, in the absence of strain in broadening of peak, the $\beta_{hkl}\cos\theta$ versus $4\sin\theta$ plot is expected to be a horizontal line parallel to the 4sinθ axis and in the presence of strain in broadening of peak, it should have a non – zero slope. The obtained values of grain size and strain induced in the broadening of the peak are tabulated in table 1. It is observed that the strain value increases by doping 2% Cu.

The UV-vis spectra of pure and Cu doped ZnO samples in the wavelength range 300-1100 nm at room temperature. The band gap was calculated by plotting the absorption plot $(ah\upsilon)^2$ versus (Energy, E) shown in figure 3.The values of energy band gap of pure and Cu doped ZnO calculated from figure 6 s are in the range 3.66 - 3.51 eV. It is observed that band gap decrease with increasing Cu concentration.

Photodegradation with undoped and Cu doped ZnO

The potential of undoped and Cu doped ZnO nanoparticles towards degradation of 20 ppm RhB solution were carried out at pH = 3 under atmospheric pressure and at room temperature . No measurable dye degradation was observed under UV light without catalyst and with catalyst in dark condition. Figure 4shows the absorption spectra of RhB solution with undopedZnO and 2% Cu doped ZnO respectively, under UV light irradiation. By observing these spectra it is clear that undopedZnO is more effective photocatalyst as compared to 2% Cu doped ZnO. The photocatalytic efficiency of ZnO nanoparticles decreases after doping with Cu towards the degradation of RhB dye solution would be due to increased of charge carrier recombination rate, which is accordance with the results obtained by K. Milenova[27].

Table. 1-

Sample	Lattice parameter in (A°)		Volume in $(A°)^3$	X-ray density D_x (kg/cm³)	Atomic packing factor	c/a ratio	Grain size D in nm (high intensity peak)	Avg.Grain size (D) of all peaks	W-H grain size (G)	Strain ε
	A	C								
X=0.00	3.3063	5.4120	51.2342	5.2782	74%	1.6369	24.17	22.78	32.78	0.00137
X= 0.02	3.3050	5.4147	51.2195	5.2797	74%	1.6383	18.392	17.014	23.38	0.00152

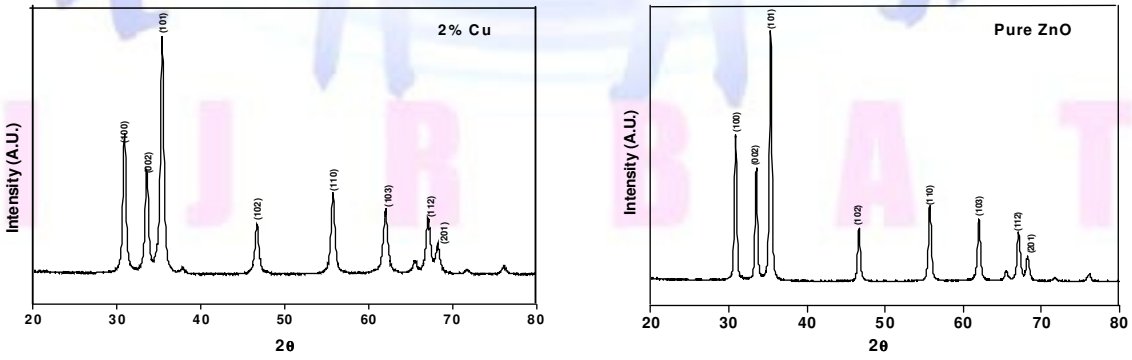

Figure. 1- XRD pattern of $Zn_{1-x}Cu_xO$ samples with concentration x = 0.0(pure) and 0.02(2%Cu)

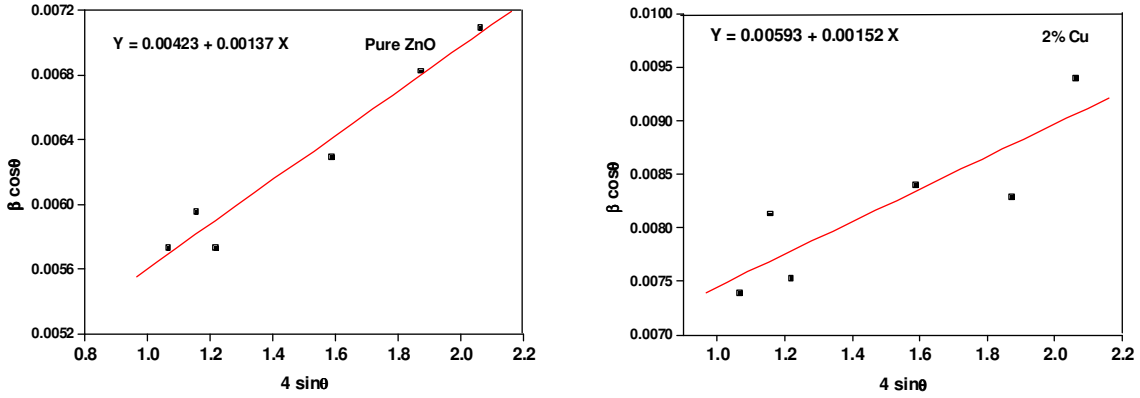

Figure. 2- The W-H plot of $\beta_{hkl}cos\theta$ versus 4 $sin\theta$ for $Zn_{1-x}Cu_xO$ samples.

UV-Vis Study

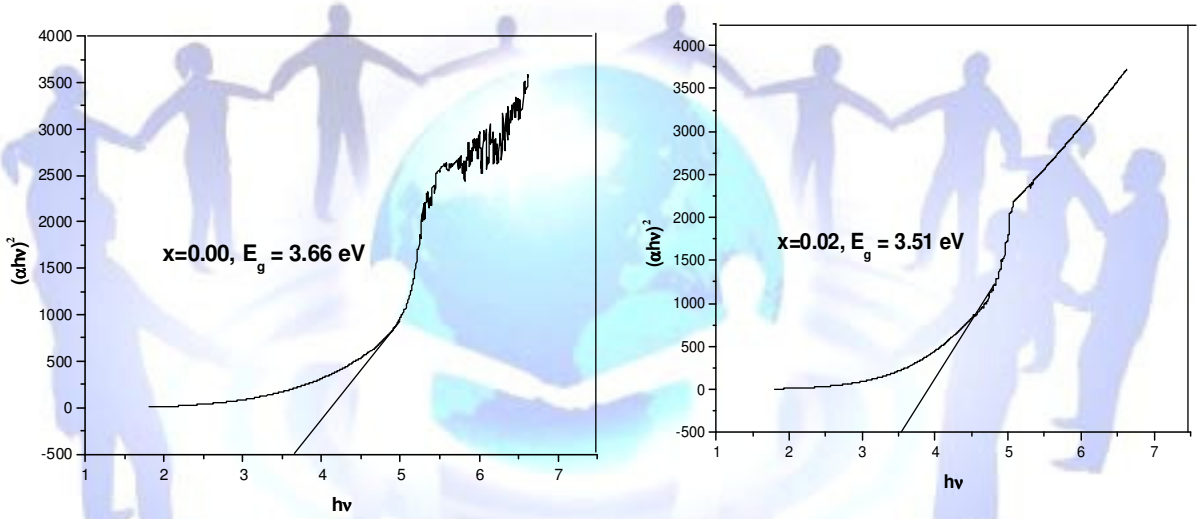

Figure. 3- absorption plot $(ah\upsilon)^2$ versus (Energy, E)

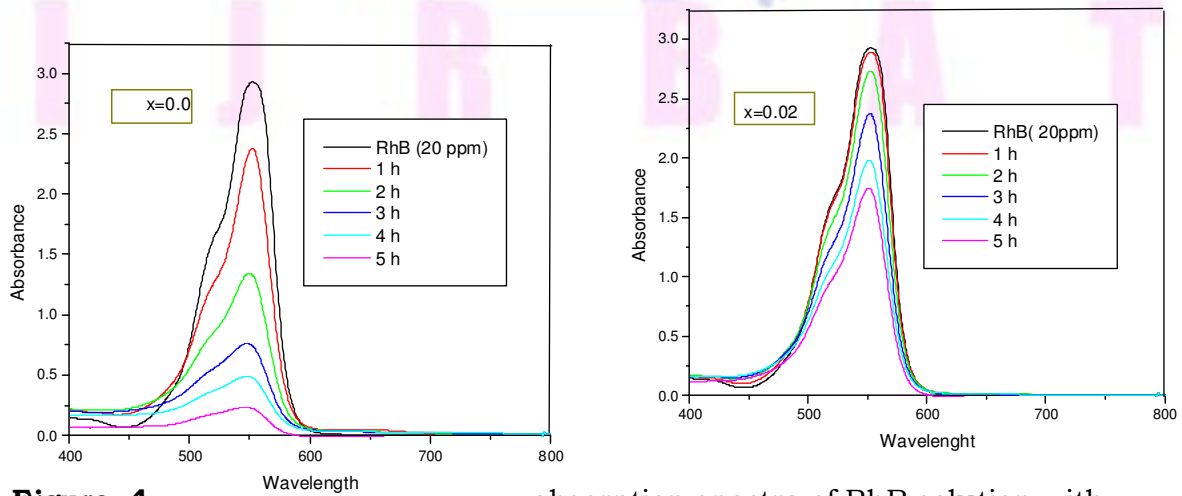

Figure. 4- absorption spectra of RhB solution with undopedZnO and 2% Cu doped ZnO

Conclusion

The crystal structure of $Zn_{1-x}Cu_xO$ samples with concentration x = 0.0 and 0.02 have been synthesized by co-precipitation method in aqueous medium at room temperature. XRD data reveals that undoped and doped samples are in wurtziteZnO structure. It is found that the x-ray density depend on mass of the sample as well as volume of the unit cell. The grain size of nanocrystalline samples have been computed by Debye Scherer's equation and Williamson- Hall analysis. The photocatalytic properties of undoped and Cu doped ZnO nanoparticles have been investigated with RhB dye solution. Pure ZnO was found to be more effective than 2% Cu doped ZnO towards degradation of RhB under UV light illumination.

Acknowledgments:

P. K. Labhane would like to thank University Grants Commission, New Delhi, for financial support through research project 47-815/13 (WRO) and UDCT, North Maharashtra University, Jalgaon for providing characterization facilities.

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