COBALT DOPED ZINC OXIDE NANOPARTICLES FOR PHOTOCATALYTIC APPLICATIONS

S. KALPANA[a*], S. S. KRISHNAN[a], T. S. SENTHIL[b], S.V. ELANGOVAN[c]
[a]*Department of Physics, Sri Venkateswara College of Engineering, Chennai*
[b]*Department of Physics, Erode Sengunthar Engineering College, Erode*
[c]*Department of Chemistry,Velalar College of Engineering and Technology,Erode*

Pure and cobalt doped Zinc Oxide nanoparticles were prepared by mixing zincsulphateheptahydrate(0.6M) and sodium hydrogen carbonate(0.6M) as starting material by Co-precipitation method. The prepared nanoparticles were centrifuged and annealed at 450°C for one hour. The effect of addition dopant cobalt at different concentrations (0.05,0.075 and 0.1%) on structure, optical property and photocatalytic activity for Co doped nanocrystals was measured. Photo catalytic degradation by using Co doped ZnO nanocrystals was measured in terms of different parameters like contact time and pH using Methylene blue dye as a model. The results were interpreted in view with the crystallite size and influence of Co dopant metal.

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1. Introduction

In recent years, the use of nanomaterials due to their outstanding chemical and physical properties compared to bulk materials by researchers was intensively increased. The different type of Nanomaterials can added an additional values to stronger, lighter, cleaner and smarter surfaces and systems [1]. Now a days, nano-structured materials used in the making of crack-resistant paints and anti-corrosion coatings for walls,scratch proof glasses for eyes, transparent sunscreens, stain-repellent fabrics, self-cleaning articles like ceramic coatings for solar cells [2].The development of different type of new materials for a suitable application is also an other important part of research [3]. Zinc oxide is an inorganic compound which has its own specific values due to its wide range of applications in the various fields of sensors like gas sensor, chemical sensor, biosensor, cosmetics, storage, optical and electrical devices for displays, solar cells, and drug delivery[4]. ZnO is a suitable alternative material for TiO_2 due to its short-wavelength optoelectronic applications owing to its wide band gap energy 3.37 eV, high bond strength, and large exciton bonding energy (60 meV) at room temperature and the missing absorbance of visible light makes this material one of the best transition metal oxide nanomaterials so far [5]. ZnO is a wide band gap material, so it is used in solid state blue to ultraviolet (UV) Opto-electronics, including laser developments [6]. By using ZnO nanoparticles, it is easy to alter the optical and electrical properties in a wide range [7].In addition, due to its non-centrosymmetric crystallographic phase, the structural, morphological and optical properties of ZnO nanoparticles are investigated regarding doping [8]. The intensity behind doping is to modify the properties of nanoparticles. Further, to improve the applications to photodegradation of dye stuff solution, doping of transition metal ions such as Ni, Co and Mn on ZnO were carried out by the research groups [9]. A number of research studies have reported on Co doped ZnO nanomaterials [10]. Talaatet al., synthesized Cobalt doped ZnO nanocrystals with an average crystal size of 5 - 11 nm by using Sol gel method. H. J. Sugahara in his studies reported an increase in photo luminescence properties by Co doping. Room temperature ferromagnetism of Co doped ZnO nonmaterial's was

*Corresponding author: kalpana@svce.ac.in

reported by Shalendra Kumar in his studies. From theoretical and experimental point of view doping of the transition metal ions with ZnO nanomaterials still continue to be an emerging topic [11]. In this work we report an investigation on structural and optical properties of ZnO particles doped with Cobalt ions and used for degradation of dye solution [12]. The advantages of using co-precipitation method than other methods are: low synthesis temperature, novel materials, and low capital costs [13]. The effect of cobalt doping on structural and optical properties of ZnO was analyzed using X-ray diffraction (XRD) (Rigaku D max-C) with Cu Ka radiation (1.5406 Å)., Scanning electron microscopy (SEM) (SEM with EDXA, Sirion) and UV analysis(JASCO V-570) [14].The results of photocatalytic decolourisation was analysed by measuring the absorbance of the centrifugate of Methylene Blue dye sample using UV–Visible spectrophotometer at 668 nm. The degradation efficiency has been calculated. [4].

2.Experimental Procedure

2.1 Synthesis of Pure and Co Doped ZnO nanoparticles

Pure ZnO nanoparticles were prepared using 0.6 M of Zinc sulphatehepta hydrate and sodium hydrogen carbonate solution (Sol A) by chemical precipitation method. To get homogeneous solution solutions were stirred individually using magnetic stirrer. Sodium hydrogen carbonate solution was added drop wise into the Zinc sulphatehepta hydrate solution under magnetic stirring for 30minutes. The precipitate formed was centrifuged and filtered. The ZnO precipitate was annealed at 450ºC for one hour. To prepare Cobalt doped ZnO, was prepared by addition of Cobalt Nitrate hexahydrate to Sol A. All the pure and Co doped ZnO samples were annealed at 450ºC for one hour. The structural and optical analysis of the prepared pure and Cobalt doped ZnO nanoparticles have been carried out using X-ray diffraction method (XRD), scanning electron microscope (SEM) and UV spectroscopy.

2.2. Characterisation of Co Doped ZnO nanoparticles

The prepared Pure and 0.05M, 0.075M and 0.01M Cobalt doped ZnO nanoparticles annealed at 450 ºC were characterized by X-ray diffraction (Rigaku D max-C) with Cu Kα radiation (1.5406 A). Morphology and composition of the synthesized samples were investigated using scanning electron microscope (SEM with EDXA, Sirion). The optical absorption spectra of ZnO nanoparticles were recorded using a UV-VIS spectrophotometer (JASCO V-570).

3. Results and Discussion

Figure 1.shows the XRD analysis of Co doped ZnO hexagonal wurtzite without the change in the structure, signifying that cobalt ions incorporated to the Zn^{2+} sites in the crystal structure**.** The XRD results show that the cobalt ions successfully substituted on zinc sites without change in the crystal structure of ZnO. The doping of cobalt ions increases crystal lattice. The crystal size in $Zn_{1-x}Co_xO$ nanoparticles is noticed to be increasing with increasing values of x, which shows that cobalt ions doped in a wurtzite structure of ZnO. The important principal peaks like 100,002,101 were indentified and get sharpened due to the addition of cobalt ions onto ZnO lattice structure.

The Diffraction analysis provides detailed information on the structural properties like peak intensity, peak position and full width half maximum (FWHM) data. XRD pattern of Pure ZnO nanoparticles consist of diffraction peaks for 2θ = 31.90˚, 34.55˚, 36.39˚, 47.57˚, 56.56˚ and 68.85˚ respectively. XRD pattern of Co doped ZnO Nanoparticles consists of diffraction peaks for 2θ = 18.42˚, 19.16˚, 23.75˚, 23.73˚, 24.06˚, 25.20˚, 27.11˚, 28.71˚, 29.54˚, 32.53˚, 33.04˚, 33.95˚, 34.63˚, 38.45˚, 41.31˚, 41.94˚, 43.74˚, 47.75˚, 48.48˚, 49.79˚, 58.34˚, 68.02˚ and 69.46˚ respectively. The peaks clearly indexed the formation of Hexagonal wurtzite structure from JCPDS powder diffraction card file (PDF#80-0075) [15].

For each sample, all observed diffraction peaks were indexed to a ZnO wurtzite structure and no other impurity phase was found, which indicates that Co ions successfully occupy the

lattice site rather than interstitial ones. Average crystallite sizes were obtained by using Scherer's equation. All high intensity peaks the XRD pattern were used to calculate the average crystallite size. Lattice parameters which was obtained for all the prepared Co doped ZnO nanoparticles are in good agreement with literature. The peak shift in the XRD pattern for Co doped ZnO nanoparticles are indiscernible is may be owing to the same range of ionic radius of Co^{2+} (0.58 Å) and Zn^{2+} (0.60 Å) ions in the tetrahedral coordination. Our results were good agreement with JCPDS file 36-1451.

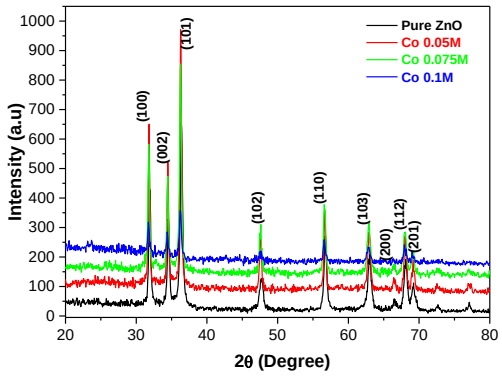

Fig. 1. XRD pattern of pure and cobalt doped (0.05,0.075,0.1M) ZnO

This was also noticed that when the dopant cobalt concentration decreases the sharpness and peak height also increases than pure ZnO. Thus, our results indicate the replacement of Zn ions by Co ions in ZnO matrix with 2+ valence state.

SEM is highly useful tool for scientists to analyse useful and important information about microscopic processes with macroscopic implications. The figures 2. (a, b, c) represent SEM images of Cobalt doped ZnO nanoparticles obtained at different

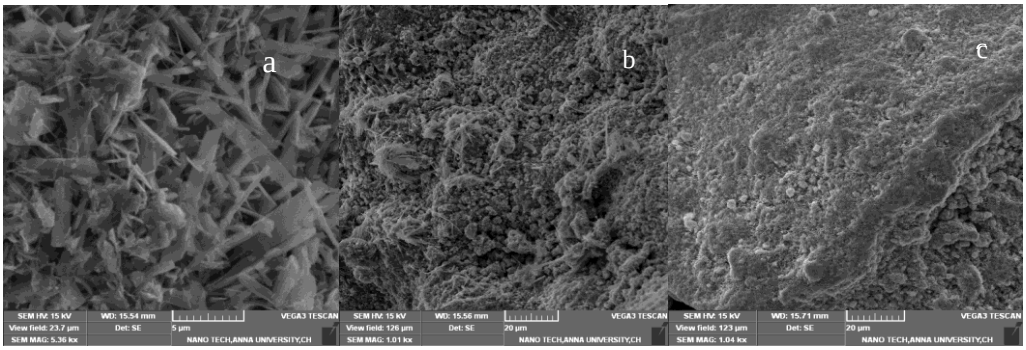

Fig. 2. SEM images (a, b, c) of Cobalt doped ZnO nanoparticles

magnifications. From the SEM images, it is clearly identified that the nanostrips at lower concentration of cobalt dopant and changes into cauliflower like ZnO observed on the surface of the doped ZnO nanoparticles. The morphological observation of SEM results indicates particles with less aggregation can be obtained from this method [16].

Fig.3, indicated the UV-Visible absorption spectrum of ZnO with different concentrations of cobalt. Absorption edges were observed at 364, 319,319 and 388 nm for pure ZnO, 0.05, 0.075 and 0.1M Cobalt doped ZnO nanoparticles, respectively. The position of the absorption peak is identified to shift towards the lower wavelength region with increasing Co dopant concentration in ZnO up to 0.075M of Co dopant, which indicate a blue shift in the energy band gap with Co doping when the samples were annealed at 450^{o}C. The similar type of blue shift of the absorption edges was obtained in the Co doped ZnO samples (0 to 7 %) from 361 to 340 nm [17].

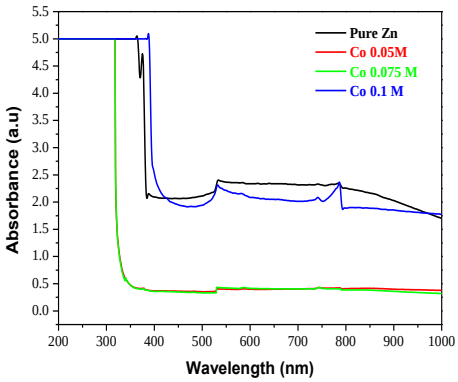

Fig. 3.UV-Visible absorption spectrum of ZnO with different concentrations of cobalt

The photocatalytic degradation of Methylene Blue (MB) dye by using Cobalt doped ZnO (0.05, 0.075 & 0.1M) nanoparticles (a,b and c) at various pH levels (pH= 2,4 and 6) was carried out. Degradation percentage of MB dye sample was carried out using pre fixed amount of cobalt (Co) doped ZnO (0.05, 0.075 & 0.1M) nanoparticles (a, b and c) at various pH levels (pH= 2,4 and 6) using wooden photoreactor in presence of UV light source.

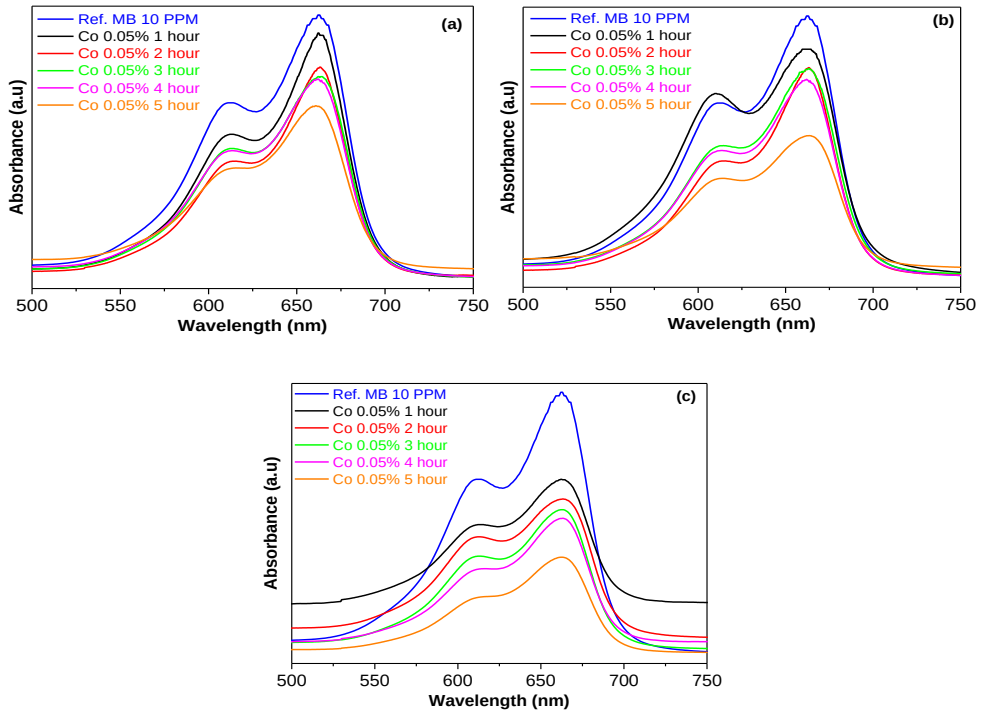

Fig. 4.The time dependent UV-Vis absorption spectra (a, b & c) for different pH = 2,4 & 6 MB degradation of Co-ZnO 0.05%

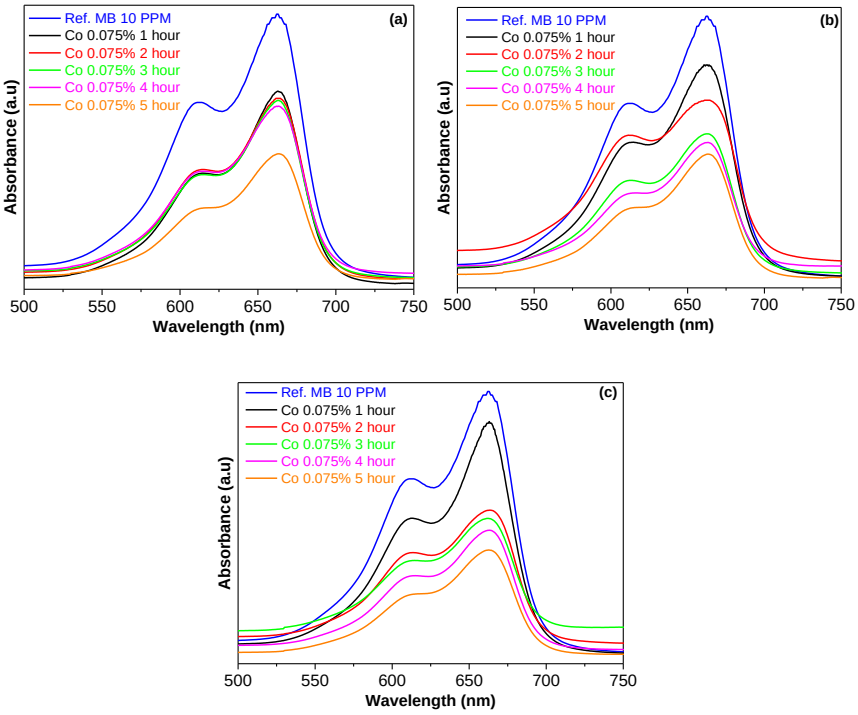

Fig. 5.The time dependent UV-Vis absorption spectra (a, b & c) for different pH = 2,4 & 6 MB degradation of Co-ZnO 0.075%

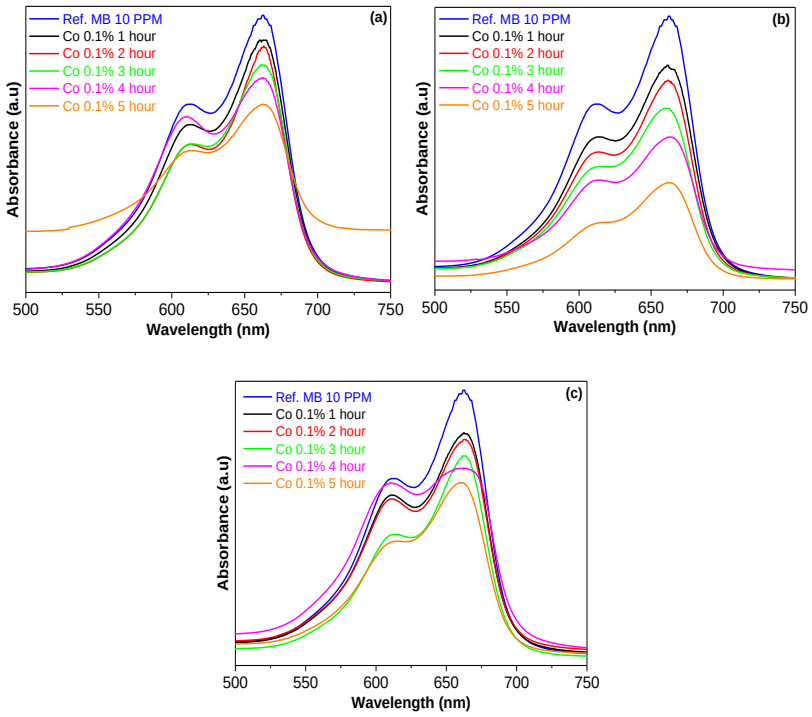

Fig. 6.The time dependent UV-Vis absorption spectra (a, b & c) for different pH = 2,4 & 6 MB degradation of Co-ZnO 0.1%

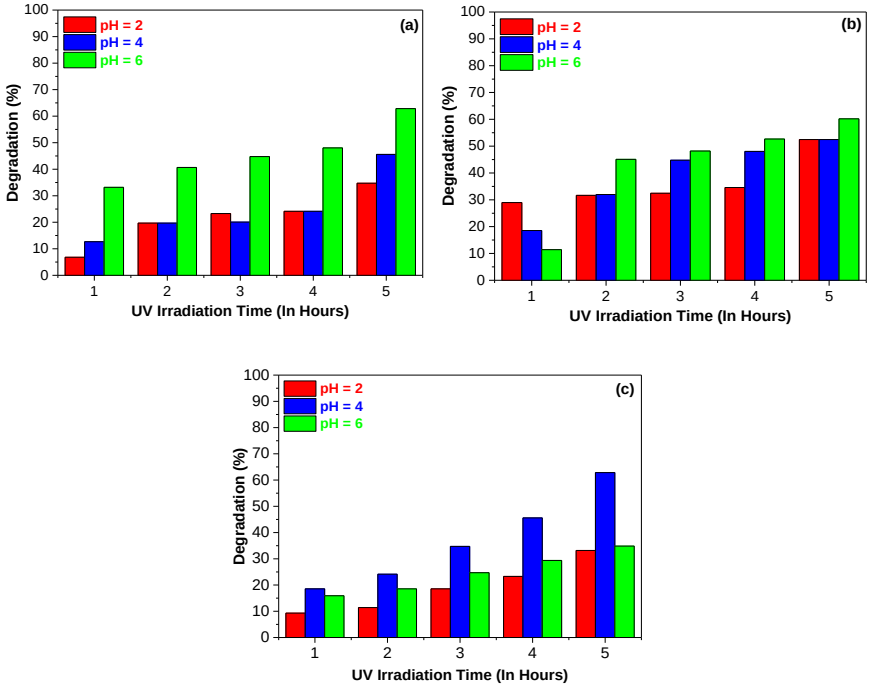

Fig. 7.MB degradation of (a, b & C) Co doped ZnO (0.05, 0.075 & 0.1M)) nanoparticles at various pH levels

The degradation of MB dye increase with increase of UV irradiation [18, 19]. In particular the effect of pH on degradation of dye sample with 100mg of 0.05 M Co doped ZnO photocatalyst is increase with increase of UV irradiation time. For one hour of UV contact time, the degradation varies from 6.5%, 28% and 10% for Co doped ZnO (0.05, 0.075 & 0.1M)) nanoparticles at pH =2 level respectively. Then the percentage removal increases gradually and show maximum of 52% at 5 hours for 0.05M Co doped ZnO photocatalyst. For pH = 4 also the same kind of results were obtained and the degradation was reaches 45%, 62% and 65% at 5 hours of UV irradiation time for Co doped ZnO (0.05, 0.075 & 0.1M)) nanoparticles at pH =4 respectively. The degradation pattern changed as 65%, 61% and 35% at 5 hours of UV irradiation time for Co doped ZnO (0.05, 0.075 & 0.1M)) nanoparticles at pH =6 respectively. The 0.05M, 0.075M Co doped ZnO exhibit maximum degradation at pH = 6 and 0.01M Co doped ZnO show good result at pH = 4 for 5 hours of UV light contact with MB dye solution.

5. Conclusions

Co doped ZnO nanoparticles were prepared by co precipitation method by different concentrations. All the prepared nanoparticles were annealed at 450º C. The particle size increases with increase of cobalt dopant concentration. The photocatalytic activity of the prepared Co doped ZnO nanoparticles shows that good photocatalytic activity in presence of UV light for the removal of methylene blue dye. The results reveal that decolourisation is good at lower pH values. The photo decolourisation increases in presence of UV into the dye solution. Co-doped ZnO nanocrystal shown good photocatalytic activity degradation.

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