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Violet Color Emitting Cd doped ZnO Nanoparticles for UV Sensor Applications

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Abstract:

The cadmium (Cd) doped zinc oxide (ZnO) nanoparticles were prepared under room temperature by changing the doping concentration using simple chemical method. The obtained nanoparticles structural, morphological, optical properties were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet visible spectroscopy (UV) and photoluminescence spectroscopy (PL) techniques. A cubic crystal structure was observed from the XRD analysis and their calculated crystallite sizes were approximately ±15 nm. A blue-shifted optical absorption nature was observed from UV spectrum and their calculated bandgap energy value was approximately 3.6 eV. An enhanced emission nature was observed from the PL emission spectrum

Key Words — ZnO Nanoparticles, Simple Chemical Method, Cadmium doping and Optical properties.

I. INTRODUCTION

Generally, the thermodynamics and kinetic reaction properties differ from those in bulk material when the material size reduces towards nanometer scale. The size effect on the thermodynamics and kinetics of reactions are shown via decreasing the activation energy for the diffusion of atoms or ions makes the reaction easier in nano-scale materials. The temperature, pressure and other experimental parameters of reaction would be reduced by decreasing the size of the materials. For example, the ion-exchange reaction is easily achieved in nanomaterials and difficult for bulk materials [1-3]. Generally ZnO is the multifunctional semiconductor material important for morphologically controlled synthesis. The undoped ZnO emits UV and visible luminescence, whereas ZnO doped with transition metals exhibits both visible luminescence and ferromagnetism at or above room temperature [4-7]. According to the previous literature, the physical origin and occurrence of ZnO doped with were subjected to an active research. In addition, transition metal ions doped ZnO such as Co, Cd, Mn, Ni, Mg and Fe is a promising candidate for a room temperature photoluminescence [8-11]. In this case, the transition etal doping makes promising potential applications.

Therefore, in the present study, we aimed to synthesis Cd doped ZnO NPs by simple chemical precipitate method and analyzed their structural and optical properties.

II. EXPERIMENTAL TECHNIQUES

A. Chemicals

All chemicals used were standard analytical grade (AR) and not further treated. Zinc acetate ($Zn(CH_3COO)_2$), sodium hydroxide (NaOH) are the precursors with the solvent of double distilled water (DDW). The detailed samples preparation is described as follows.

B. Synthesis of Nanoparticles

The synthesis of ZnO nanoparticles, the freshly prepared 0.5 mole of $Zn(CH_3COO)_2$ solution was prepared using DDW and then stirred well using magnetic stirrer. Then the NaOH solution was slowly added dropwise into the zinc acetate solution till the pH becomes 10. The mixture was stirred vigorously and then the white color solution was obtained. Further, the solution was used to ultrasonic treated for stabilization of particles. Finally, the solution was stored without any disturb, then the particles sedimentation was obtained. The sedimentation was washed several times to removing unreacted compounds. After centrifuging, the particles are separated from the solution and then dried. Further the sample was oxidized through the annealing treatment using muffle furnace. Finally, a white color ZnO powder was obtained.

To synthesis of Cd doped ZnO nanoparticles, the above mentioned same procedure was followed and the only difference was presence of $CdCl_2$ solution before NaOH solution was added.

III. CHARACTERIZATION TECHNIQUES

The crystalline nature of the synthesized nanoparticles was analysed by using X-ray diffractometer (XRD, Shimadzu-6000). The formation of nanoparticles size and surface morphology of the nanoparticles were studied by scanning electron microscope (SEM, JOEL JSM-6390). The functional group present in the ZnO nanoparticles were recorded using FTIR spectrophotometer (FTIR, Brucker-Tensor 27). The absorption of the nanoparticles was measured using spectrophotometer (UV-VIS, Jasco V530). The emission spectra of the nanoparticles were measured using spectrofluorometer (Horiba Jobin, Flouromax-4).

IV . RESULTS AND DISCUSSION

A. Structural analysis – XRD

Figure 1 shows the XRD patterns of (a) 5%, (b) 10%, (c) 15% and (d) 20% of Cd doped ZnO nanoparticles. From the XRD pattern, the hexagonal crystal structure was observed which are in close agreement with the standard values (JCPDS card: 36-1451). In the case of Cd doped ZnO NPs, there was no major phase changes were observed due to the dopant effect [12] and however a small peak variations were observed in their intensity. The Debye-Sherrer's formula was used to estimate the crystalline sizes or average particles size or grain size (D) and the Bragg's relation was used to calculate inter planar distances (d).

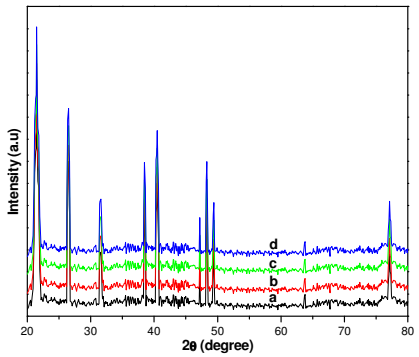

Figure 1. XRD patterns of (a) 5%, (b) 10%, (c) 15% and (d) 20% of ZnO:Cd nanoparticles.

Debye-Scherer's formula was used to calculate the crystalline size (D),

$$D = \frac{K\lambda}{\beta \cos\theta}$$

Bragg's relation was used to calculate the inter planar spacing (d),

$$d_{hkl} = \frac{n\lambda}{2\sin\theta}$$

The calculated crystalline sizes and their corresponding d-spacing values are given the in **Table 1.**

Table 1. XRD parameters calculated at (1 1 1) plane of ZnO:Cd nanoparticles

Doping ratios	2θ (deg)	Crystalline sizes (nm)	d spacing (Å)
5 M	21.79	13.6	3.075
10 M	21.80	13.8	3.073
15 M	21.80	13.4	3.073
20 M	21.81	13.2	4.071

B. SEM-Surface Morphology analysis:

Figure 2 shows the SEM images of (a) 5%, (b) 10%, (c) 15% and (d) 20% of Cd doped ZnO nanoparticles. A clear surface morphology was not observed, due to the formation of very small sized particles. However, the surface looks like the growing stage of ball or spherical structure. Therefore, to know the clear observation of surface morphology TEM measurement is required.

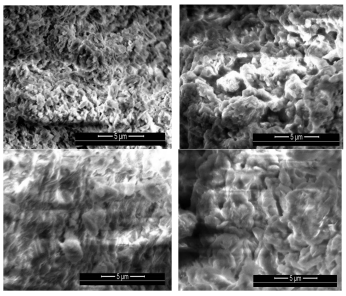

Figure 2. SEM images of (a) 5%, (b) 10%, (c) 15% and (d) 20% of ZnO:Cd nanoparticles.

C. FTIR-Chemical bonding analysis:

Figure 3 shows the FTIR spectrum of (a) 5%, (b) 10%, (c) 15% and (d) 20% of Cd doped ZnO nanoparticles. The as prepared nanoparticle FT-IR spectrum shows the Zn-O-Cd vibration of bands around 620 Cm^{-1} and 1120 Cm^{-1}. Therefore, the vibration of bands confirmed from the Zn-O stretching mode.

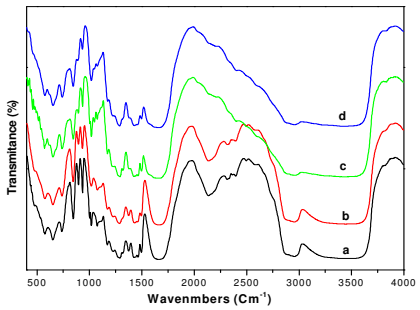

Figure 3. FTIR spectrum of (a) 5%, (b) 10%, (c) 15% and (d) 20% of ZnO:Cd nanoparticles.

D. UV-Optical analysis:

Figure 4 shows the UV absorption of (a) 5%, (b) 10%, (c) 15% and (d) 20% of Cd doped ZnO nanoparticles. The absorption band was obtained at approximately 311 nm which was blue-shifted absorption behaviours when compared with the bulk ZnO spectrum, because of quantum confinement effect. When increasing the dopant concentration, the absorption bands were slightly takes red-shift which was due to the effect of dopant. Therefore, it confirms the Cd^{2+} ions substitutional or interstitial effect on the ZnO crystal lattice [13].

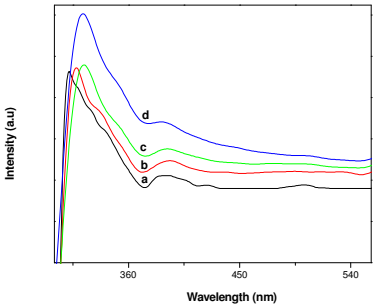

Figure 4. UV spectrum of (a) 5%, (b) 10%, (c) 15% and (d) 20% of ZnO:Cd nanoparticles.

The bandgap energy value was calculated using the relation of

$$E_{bg} = hc/\lambda$$

The calculated bandgap energy values were increased with decreasing their particles size when compared with bulk material. The optical absorption and

their corresponding bandgap energy values are given in **Table 2.**

Table 2. UV bandgap energy values of Cd doped ZnO nanoparticles

Doping ratios	Absorption wavelength (nm)	Bandgap energy (eV)
5 M	311	3.98
10 M	318	3.90
15 M	323	3.84
20 M	324	3.83

E. PL-Emission analysis:

Figure 5 shows the PL emission spectrum of (a) 5%, (b) 10%, (c) 15% and (d) 20% of Cd doped ZnO nanoparticles. Normally, the undoped ZnO nanoparticles has shown two emission natures which was at violet region and green region [14]. In the Cd doped ZnO NPs, a strong violet-blue emission nature were observed and it was entirely different emission nature when compared with undoped ZnO NPs. The green emission nature was completely absent due to Cd ions doping effect and Cd ions acting as emission quencher. Therefore, the emission nature assigned between the energy levels transition of Cd ions and conduction band which enhances the blue emission nature. Because of the Cd ions were entering into the ZnO crystal lattice which maybe substitution or interstitial effect and their results are confirmed with the previous reports [18-23].

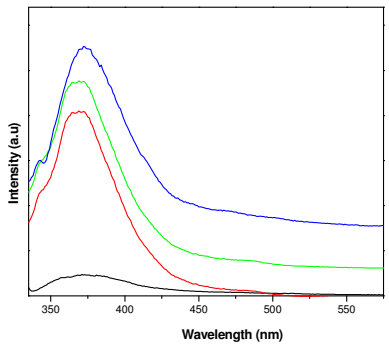

Figure 5. PL emission of (a) 5%, (b) 10%, (c) 15% and (d) 20% of ZnO:Cd nanoparticles.

V. Conclusion:

The cadmium (Cd) doped zinc oxide (ZnO) nanoparticles were successfully prepared through simple chemical method by changing the doping concentration. The obtained nanoparticles structural, morphological, optical properties were characterized. A cubic crystal structure was observed from the XRD analysis and their calculated crystallite sizes were approximately ±15 nm. A spherical shaped surface morphology nature was observed from the SEM analysis. A blue-shifted optical absorption nature was observed from UV spectrum and their calculated bandgap energy value was approximately 3.6 eV. An enhanced emission nature was observed from the PL emission spectrum.

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