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# Cadmium dopant induced morphology and optical changes in ZnO nanostructure

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## ABSTRACT

Cd-doped ZnO hollow / disc-like nanostructure have been synthesized using a simple solution method. The corresponding morphology, structure, and chemical composition were investigated using scanning electron microscope, transmission electron microscope, X-ray diffraction and EDX. The XRD patterns, SEM and TEM micrographs of Cd-doped ZnO revealed the formation of hollow / disc-like nanostructure of different sizes (100- 900 nm), indicating that a little Cd<sup>2+</sup> is substituted into the ZnO host structure of the Zn<sup>2+</sup> site. Transmission Electron Microscopy image also shows that each hollow nanostructure is made up of nanoparticles with average sizes 3-6 nm. The band gap of host material can be tuned from 3.63 to 3.51 eV with increase of Cd doping levels from 0 to 10 %. © 2011 Trade Science Inc. - INDIA

### **INTRODUCTION**

Zinc oxide (ZnO) nanocrystals have attracted a great deal of attention from researchers for both their fundamental size dependent optoelectronic properties and their wide range of applications<sup>[1-6]</sup>. ZnO is a versatile material that has achieved applications in photo-catalysts, solar cells, chemical sensors, piezoelectric transducers, transparent electrodes, electroluminescent devices and ultraviolet laser diodes<sup>[7,8]</sup>. ZnO has a wide band-gap of 3.37 eV and rather large exciton binding energy, which makes the exciton state stable even at room temperature.

Magnetic, electrical, optical, and catalytic properties of ZnO are mostly size and surface dependent. Attempts<sup>[9-11]</sup> have been made to improve these proper-

## KEYWORDS

ZnO; Nanostructure; Morphology; Doping.

ties and enhance the industrial applications of ZnO nanoparticles. Doping of ZnO with Ib and IIb transition elements is relatively less common<sup>[12]</sup> compared to IIIb elements such as Al. Doping of ZnO with metal and transition metals might shift the optical absorption of ZnO to the visible region, i. e. to longer wavelength. Doping of ZnO films with cobalt (Co)<sup>[13]</sup> has reported to significantly decrease the band gap of cobalt-doped ZnO films resultantly causes hyperchromic shift in its optical absorption. It has been reported to significant decrease the band gap of ZnO to 2.75 eV. It was reported that Mg dopant increased the band gap of ZnO nanocrystal while it was decreased by Cd dopant<sup>[14]</sup>. Therefore, very few reports in Cd-doped ZnO have been published so far. Recently, Cd-doped ZnO

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nanotubes have been reported<sup>[15]</sup>. Very recently, we synthesized the Mg-doped ZnO nanoparticles by simple solution method<sup>[4]</sup>. It was found that the doping of ZnO with Mg increased the band gap of ZnO.

Self-assembly of nanocrystals provides an elegant bottom-up method for the preparation of extended, highly ordered nanostructures with potentially useful properties<sup>[16,17]</sup>. Hierarchical self-assembly methods generally employ template mediated directional ordering of monolayer functionalized nanoparticles into 1D-, 2D- or 3D- structures under the influence of supramolecular interactions<sup>[18]</sup>. However, recent observations of aggregation based nanoparticle self-assembly in artificial systems<sup>[19]</sup>, and natural bio-mineralization processes<sup>[20]</sup> revealed an alternate coarsening mechanism wherein defect-less, extended, artificial solids are formed by the mesoscale crystallization of colloidal nanoparticles. Spherical structures such as mesoscale and hollow spheres have been reported for transition metal doped ZnO<sup>[21-24]</sup>. Hollow spheres offer possibilities in material design for applications in catalysis, nanoelectronics, nano-optics, drug delivery systems, and as building blocks for lightweight structural materials<sup>[25]</sup>.

Here the synthesis and characterization of Cd-doped ZnO hollow/disc-like nanostructure are reported by using Non-basic simple method with particle size ~3 to ~6 nm, without the assistance of base, template and surfactant. In this letter, the changes in the structural, morphologies and optical properties of ZnO nanoparticles and Cddoped ZnO nanostructures are also discussed.

#### **EXPERIMENTAL**

The method of synthesis was the same as used elsewhere<sup>[4,26]</sup>. Zinc acetate dihydrate,  $Zn(Ac)_2.2H_2O$  (99.9 %, Sigma Co.), cadmium acetate tetrahydrate (Cd(Ac)\_2.4H\_2O) (99.9 % Sigma Co.) and methanol (99.9 % Sigma Co.) were used as received, without further purification. In a typical experiment, 0.01 mol. of  $Zn(Ac)_2.2H_2O$  and the respective amount of Cd(Ac)\_2.4H\_2O were dissolved in 50 ml of methanol under vigorous stirring at room temperature and then ultrasonicating for 10 min. A clear transparent solution was obtained. The solution was heated at 65 °C under reflux for 12 h. The precipitates were carefully collected and washed with absolute ethanol several times to re-

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The UV-vis absorption spectra of ethanolic nanoparticle solutions were recorded with Hewlett Packard8453 spectrometer. Scanning electron microscopy (SEM) was performed with a Philips X130 ESEMFEG with energy dispersive x-ray (EDX) spectroscopy. The transmission electron microscopy (TEM) analysis was done with a Tecnai F300 transmission electron microscope. Crystal structure identification and crystal size analysis were performed with an XDS 2000 X-ray diffractometer, (Scintac Inc.,USA) with CuKα radiation source and scan rate of 2°/min.

#### **RESULT AND DISCUSSION**

Figure 1 shows the XRD patterns of Cd-doped ZnO as prepared samples. The XRD analysis shows that all samples exhibited the single crystal of hexagonal wurtzite structure in correspondence with JCPDS database of card number 36-1451, without the appearance of any secondary phase, suggesting that Cd incorporated to the Zn<sup>+2</sup> sites in the crystal. The pattern can be indexed for diffractions from the (1 0 0), (0 0)2), (101), (102), (110), (103) and (112) planes of wurtzite crystals with lattice constants a = 0.324 and c = 0.523 nm, which correspond to ZnO. The most intense peak (101) is at 37.5°, shows a slightly shifting towards high angle sides on Cd2+ doping in comparison to that pure ZnO. The lattice expansion indicates that the substitution of smaller Zn<sup>+2</sup>ion (with ionic radius 0.60 Å) by the larger Cd2+ ion (with ionic radius 0.74 Å) takes place on the equivalent crystallographic position Zn+2 in hexagonal wurtzite structure. The percentage of Cd in the doped ZnO samples (TABLE 1) obtained by EDX analysis shows that the amount of Cd incorporated into ZnO matrix is much smaller than the actual amount of dopants added during the synthesis because a little Cd doping did not change the crystal structure of ZnO, which is a stable phase (the wurtzite phase). The increase in peak intensity over Cd dopants as is shown in Figure 1 could be attributed to the increase in the particle size of ZnO, which is in a good agreement with previous reported result<sup>[15]</sup>. The particle sizes estimated from the FWHM of (101) diffraction peak using the Scherrer

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formula<sup>[4]</sup>. The particle size is increased from 3 to 7 nm for Cd doping level from 0 to 10 % indicating that the Cd dopant (larger ionic radius is well integrated into the lattice by taking place of Zn (smaller ionic radius).

The morphology of the products was analyzed with scanning electron microscopy (SEM) and bright field transmission electron microscopy morphology (TEM). Figure



Figure 1 : XRD patterns of Cd-doped ZnO nanostructure (A) pure ZnO, (B) 3%, (C) 5%, (D) 7% and (E) 10% of Cd.

TABLE 1 : EDX analysis of Cd-doped ZnO samples

Element	undoped	3 at.%	5 at.%	7 at.%	10 at.%
Cd (%)	0	0.49	0.55	1.12	1.17
Zn (%)	99.80	99.51	99.45	98.88	98.83

2, SEM images show the morphology change of products with increasing Cd dopant level . In Figure 2a spherical nanoparticles were obtained for pure ZnO nanoparticles. Figure 2(b-e) presents the obtained ZnO nanostructure containing Cd dopant percentages (b) 3%, (c) 5%, (d) 7% and (e) 10%. The SEM images show the formation of hollow sphere / disk-like nanostructure. Their structures were porous with vacancies at their centers. Moreover, this figure shows the growth of hollow sphere / disclike nanostructure on Cd doping of ZnO.

The TEM micrograph of Figure 3 demonstrates a large scale overview images of the obtained the spheres samples. The formation of spheres with largely uniform structure confirmed that the synthesis process effectively generated spherical products with well-confined structure. The sizes of the spheres in Figure 3 were measured by TEM. The measured sizes were increased from 100 to 900 nm by Cd doping level from 3 % to 10 %. Figure 4 (a-e) shows the HRTEM micrographs and histograms of Cd-doped



Figure 2 : SEM micrographs of Cd-doped ZnO nanostructure (a) pure ZnO (b) 3 %, (c) 5 %, (d) 7 % and (e) 10 % of Cd.



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ZnO nanoparticles (a) pure ZnO (b) 3% (c) 5% (d) 7% and (e) 10% of Cd. The TEM micrographs show the most individual nanoparticles are of sizes 3-6 nm, which is consistent with the result calculated from XRD data.

Obviously, based on the experimental results mentioned above, the role of incorporation of Cd on microspheres formation could be explained as following. The important point is that the growth rate of pure ZnO was very fast in which ZnO separated from the colloidal solution after aging time of 1 hr. On the contrary, a very slow growth rate were greatly controlled by Cd dopant level in the reaction mixture. It was found that the required aging time for complete separation of Cd-doped ZnO from the colloidal solution was longer at higher Cd dopant level. As the dopant level increased from 3% to 10%, the aging time increased from 3 to 7 days. It can be now speculated that the growth rate is assumed to be governed by Cd dopant level which may in turn increase the aging time of reaction product before separation. Furthermore, the SEM micrographs of samples (Figure 2) clearly reveals that the microspheres of Cd-doped ZnO are made up of numerous nanosized nanoparticles.

The fine nanoparticles are reasonably self-aggregated spontaneously into spherical structure when the product mixture was aged for a period of more than three days.

The optical properties of the Cd- doped ZnO nanostructures were studied by UV-Vis absorption spectroscopy. Figure 5 shows the room temperature optical absorption spectra of undoped ZnO and Cddoped ZnO nanoparticles. The UV-Vis absorption spectrum shows the characteristic band of ZnO. A clear shift in the absorption band is seen in ZnO nanoparticles doped with Cd ion. As the Cd doping level is increased from 0 to 10%, the absorption band shifts from 341 to 355 nm, indicating a decrease in the band gap from 3.63 to 3.51 eV. Higher doping levels result in more pronounced shifts of the band gap of Cd-doped ZnO nanoparticles. It is reasonable to expect the band gap,  $E_{a}$ , to decrease with increasing of Cd dopant, since the band gap of CdO (bulk band gap = 2.3 eV) is lower than that of ZnO (bulk band gap = 3.3 eV). Furthermore, a number of previous experimental and theoretical investigations have proposed size effects have little influence on the band of ZnO nanoparticles<sup>[27,28]</sup>

 $(\mathbf{b})$ 



<u>султ</u> (d) (d) (d) (d)

Figure 3(a-d): TEM micrograph of Cd-doped ZnO nanostructure for (a) 3 %, (b) 5 %, (c) 7 % and (d) 10 % of Cd.

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Figure 4 : TEM micrographs and histograms of Cd-doped ZnO nanostructure (a) pure ZnO (b) 3 %, (c) 5 %, (d) 7 % and (e) 10 % of Cd.

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Figure 5 : UV-vis. spectra of Cd-doped ZnO nanostructure at room temperature.

#### CONCLUSION

In this work ZnO spherical nanoparticles and Cddoped ZnO nanostructure have been produced through a non-basic solution process. The obtained results highlight a facile, template-free and non-basic process for the formation of uniform spheres. The growth rate of spherical structure into larger scale could be controlled by adjusting the aging time of the reaction product. The XRD patterns, SEM and TEM micrographs of Cddoped ZnO revealed the formation of hollow spheres/ disc-like with different sizes of (100- 900 nm), Cd doping shifts the absorption band to red (341-355 nm) with Cd doping levels from 0 to 10 %.

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