Review on Synthesis of Cd Doped ZnO Nanoparticles

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Abstract – To improve the applications of ZnO, metal ion doping is found to be the most effective approach which induces structural modifications. Doping changes the optical, magnetic and electrical properties of nanoparticles due to this the nanoparticles are doped with metals like Fe, Cd, Mn, Ni, Al, etc. But here we mainly analyse the Cd doped ZnO nanoparticles.

Preparation of doped materials such as the Cd doped ZnO are important for creating a new combinations to form a substance of modified optical properties. Electrical conduction has been found to increase for higher concentration of Cd in ZnO which can be useful in the various optoelectric devices such as Solar cells, LEDs, Light absorption and emission, Photodiodes, Laser diodes.

Keywords: ZnO, Cd, Dopping

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INTRODUCTION

Nanotechnology (NT) is operating in various fields of science. Nanoparticles are particles between 1 and 100 nanometres (nm) in size. Nanoparticles can be fashioned with a wide range of metals and semiconductor core materials that impart useful properties such as fluorescence and magnetic behaviour. There are various types of nanoparticles e.g., metal nanoparticles, metal oxide nanoparticles, and polymer nanoparticles. Among all these, metal oxide nanoparticles stand out as one of the most versatile materials, due to their diverse properties and functionalities. Among different metal oxide nanoparticles, zinc oxide (ZnO) nanoparticles have their own importance due to their vast area of applications, e.g., gas sensor, chemical sensor, bio-sensor, storage, optical and electrical devices, solar cells, and drug-delivery. Zinc oxide has several constructive properties, including good transparency, high electron mobility, wide band gap (3.37eV), and strong room-temperature luminescence. Advantages associated with a large band gap include higher breakdown voltage (75 V), ability to sustain large electric fields, lower electronic noise, and high-temperature and high-power operation.

Cd doping of ZnO nanoparticles can be synthesized by various methods such as

- Hydrothermal method
- Microwave method
- Polyol method
- Sol-gel method
- Sonochemical method
- Co-precipitation method, etc.

The rapid development of nanotechnology and nanomaterials has led to a need for nanoparticle surface modification for a variety of applications. The surface can be tailored to specific physical, optical, electronic, chemical, and biomedical properties by coating a thin film of material on the surface of the nanoparticles. Thus the encapsulation of nanoparticle is done according to the requirement. Conventional nanoparticle coating methods include dry and wet approaches. Dry methods include: (a) physical vapor deposition, (b) plasma treatment, (c) chemical vapour deposition, and (d) pyrolysis of polymeric or non-polymeric organic materials for in situ precipitation of nanoparticles within a matrix. Wet methods for coating nanoparticles include: (a) sol–gel processes and (b) emulsification and solvent evaporation techniques.

However one of the most important use of Cd doped ZnO is as a catalyst for degradation of the organic pollutants. Environmental pollution and industrialization on a global scale have drawn attention to the vital need for developing new hygienically friendly purification technologies. Photocatalysis, using nanostructures of metal oxide semiconductors like zinc oxide (ZnO) and Cd doped ZnO can be an attractive way of water purification as it is capable of removing chemical as well as biological contaminants. Photocatalysis applications in the agriculture and microbiology are gaining wide spread acceptance and also it can be implemented in purification of drinking water.

This paper is a comparative study of different method to synthesis cadmium doped zinc oxide nanoparticles and its characteristic properties.

Co-precipitation Method

Jeyakumari et al, (2017) synthesized Zinc Oxide (ZnO) and Cd doped Zinc Oxide by Co-precipitation method. The preparation method used is very economic one, using Zinc acetate, ethanol and NaOH. A 0.2 M of zinc acetate ($ZnC_4H_6O_4$) was dissolved in 20 ml of absolute ethanol and stirred at room temperature for 30 min. Then 36 mg of NaOH was dissolved in 20 ml of ethanol. The NaOH solution was added to the zinc acetate solution in drop wise in constant stirring. The pH value of the solution was measured to be 12. The solution was continuously stirred for 2 hours at room temperature. The solution became turbid form which indicated the ZnO nanoparticles were formed. The solution was filtered and precipitates were collected and washed with distilled water and absolute ethanol and acetone for several times. The final product was annealed at 200°C for 1 hour.

The tests done on the final product samples revealed its properties. Fourier-transform infrared spectroscopy (FT-IR) spectra were used to confirm the presence of Cd dopant which was shown in the results by shift in the low frequency region. The nature of the sample was also tested by XRD which showed the sample possessing crystalline nature and having sizes of 21nm and 18nm for pure and Cd doped ZnO respectively. Scanning electron microscopy was used to analyze the surface of the sample formed. The photo luminescence analysis spectrums of these samples were also recorded. It showed blue shift at 366 nm. The energy gap value for pure and Cd doped ZnO were also determined. Anti-bacterial activity of Cd doped ZnO was also studied. The optical transmittance of Cd doped ZnO used in optoelectronic application like display devices and LEDs. Low cost production is the main advantage for any product to compete in the market and ZnO nanostructure being their solution provides much potential to become the choice for cheap devices In addition, devices with ZnO nanorods exhibit better performance due to a better interfacial contact, having fewer defects and improved light extraction. The optical energy gap of the pure and Cd doped ZnO nanomaterials (Eg=3.1eV, Eg=3.2eV) were confirmed by UV-spectra and photoluminescence spectra. Theyare also used for fabrication photovoltaic devices.

Suman et al, (2017) studied the properties of Cd doped ZnO prepared by simple co-precipitation method. The method includes use of aqueous solution of 0.1 M of zinc acetate $(CH_3COO)_2Zn.H_2O$ and DI water which were mixed together. Then 3, 6 and 9 at % cadmium acetate was added in it. About 0.3M NaOH is dissolved in DI water in another beaker which is then mixed in the above solutions. The final solution was stirred for 1 h and white precipitate are formed which are then washed with DI water. At last, solution is dried in oven to form the oxide particles and to remove the impurity the process of annealing is done at 300°C for 3 h.

Various tests were done to test the properties of the sample thus prepared eg: - XRD, FTIR and RAMAN spectroscopy. Presence of the dopant (Cd) was detected with the help of FTIR by the changes in position, shapes and sizes of IR peaks. The XRD analysis revealed that the sample possess crystalline nature and the particles sizes decreases as Cd concentration increases. UV Spectroscopy displayed that band gap decreases continuously with increasing cadmium concentration and finally Raman spectroscopy results also concluded the Cd incorporation in the particles being successful.

Combustion Method

Jose et al, (2013) stated that Cadmium doped Zinc oxide nanopowder can be synthesized by simple and inexpensive combustion technique using zinc nitrate and glycine. It was found that combustion technique is capable of producing ultra-fine powders of metal oxide nanopowder in a shorter time and at a lower calcinations temperature with improved powder characteristics. In this process glycine acts as a fuel material and zinc nitrate served as a precursor and oxidiser to synthesize ZnO nanopowder. The dopant Cd is added to zinc nitrate with required molar ratio and glycine is also added along with it, in a molar ratio of 0.9:1(zinc nitrate + Cd:glycine) and stirred well for 80 minutes in 100ml double distilled water. The obtained solution is heated (150^{o}C) till combustion reaction occurs. The resultant Cd doped ZnO powder formed was collected and dried at 80^{o}C in oven and it was utilized for further characterization.

The various tests performed on the sample include XRD analysis that confirms the crystallinity of the sample with crystallite size of 50 nm for the various doping concentration of 1%, 3%, 5%. The UV spectroscopy shows that the absorbance of the sample in the visible region decreases with the increase in concentration of dopant.

Sol-Gel Method

Rajput and Purohit, (2016) investigated that Sol gel is effective methods because of low cost and reproducibility. Different compounds or chemical such as acetates, chlorides, nitrates of cadmium and zinc used in this method. Here Cd doped ZnO nanoparticles are produced at room temperature using zinc acetate dihydrate [Zn $(COOCH_3)_2{\cdot}2H_2O$] and cadmium acetate dehydrate [$Cd(COOCH_3)_2{\cdot}2H_2O$]. As a precursor 2-Methoxyethanol ($C_3H_8O_2$) is used and monoethanolamine (C_2H_7NO, MEA) as a solvent and stabilizer used in process.

Zhang et al, (2012) studied photoluminescence properties of Cd doped zinc oxide nanoparticles or QDs (quantum dots) which is prepared by sol-gel method. The effect of Cd concentration on the structural and luminescent properties of the nanoparticles, as well as the effect of the mass ratio of trioctylphosphine oxide (TOPO)/ octadecylamine (ODA), has been investigated. The ZnO and Cd-doped ZnO nanoparticles have hexagonal wurtzite structures and are 3 to 6 nm in diameter. When the Cd content was increased, the particle size was reduced; this effect was confirmed in the corresponding ultraviolet–visible spectra. Zinc acetate dihydrate (99.0%), cadmium acetate dehydrate (99.5%), lithium hydroxide (90.0%), Absolute ethanol (99.7%) and n-hexane (98.0%),) were used to synthesise Cd-doped ZnO nanoparticles. UV-visible absorption spectra of ZnO QDs with different concentrations of Cd has been studied. Blue shifts of the UV absorption peaks of the Cd-doped ZnO QDs were observed with increasing Cd concentration, which indicated a reduction of the QD size and a strengthening of the quantum confinement effect after doping. Through various measurements, including UV, PL, XRD and FT-IR, the surfaces of the QDs were found to play an important role in their optical properties.

Polyol Method

Samuel et al, (2013) prepared Cd doped ZnO nanoparticles by simple and inexpensive Polyol technique using zinc acetate, Cadmium acetate and ethylene glycol. In this method Zinc acetate, Cadmium acetate are used as starting materials. Ethylene glycol was used as a solvent and stabilizing ligand. First, an accurate weighed amount of Zinc acetate and cadmium acetate are added in 10 ml double distilled water and stirred well for 20 minutes. After that 20 ml of ethylene glycol was added to the solution. Solution was shaken and kept under stirring. A thermometer was used to measure the temperature. When the temperature was raised to 100^oC, around 2 gm. of urea was added and temperature was raised further to 120^oC and maintained at this temperature for 2 hours. The precipitate obtained after 2 h of reaction was cooled, centrifuged, washed twice with methanol, and twice with acetone. The precipitate was dried overnight under ambient conditions.

The obtained Cd-doped ZnO nanoparticles have a small and good absorption in the Ultraviolet and Vis regions. The powder XRD analysis confirms the crystalline nature of the synthesized sample with an average crystal size of 50 nm and average particle size of 246 nm for the doping concentration of 2%. The photoluminescence spectrum reveals the fact that the Cd dopant increases PL emission intensity. These results show a great possibility for the Cd-doped ZnO nanopowders to be used in applications like optoelectronic devices.

Hydrothermal Method

Karunakaran et al, (2012) Prepared Cd doped ZnO nanoparticles by Hydrothermal synthesis. Deionized distilled water and chemical like zinc nitrate, hexamine, ammonia used. To $Cd(NO_3)_2$ solution (0.18 mmole in 18 mL) aqueous ammonia (1:1) was added under stirring to reach a pH of 9. Continuing stirring for 30 min, $Zn(NO_3)_2$ (8 mmole in 20 mL) was added. This was followed by drop wise addition of hexamine (10 mmole in 25 mL). The contents were transferred to a Teflon lined stainless steel autoclave vessel (100 mL) and heated at 100 ^oC for 3 h in an air oven. After allowing cooling to room temperature the crystals were collected by filtration, dried and calcined at 500^o C for 2 h in a muffle furnace fitted with a PID temperature controller. The heating rate was 10 ^oC min^{-1}. The undoped ZnO nanocrystals were synthesized by adopting the same procedure but without $Cd(NO_3)_2$.

Peng et al, (2013) prepared by thermal decomposition method. 9.8 mmol of $Zn(NO_3)_2$ and 0.2 mmol of $Cd(NO_3)_2$ were firstly dissolved in 20 mL of absolute ethanol to form a homogeneous solution. Then, an equal volume of ethanol solution containing the stoichiometric amount of oxalic acid (10 mmol) was drop wise added into the above solution under magnetic stirring. Then the as obtained suspension was transferred into a Teflon-lined stainless steel autoclave, the system was sealed and heated at 130 ^oC for 10 h. The precipitate was collected and washed with deionized water and anhydrous ethanol several times, respectively, and dried in air at 60 ^oC for 4 h. Finally, the above dried product was calcined in air at 420 ^oC for 2 h to produce Cd-doped ZnO nanorods.

Sonochemical Method

Wang et al, (2012) investigate optical property of cadmium-doped zinc oxide nanoparticles. Cd-doped ZnO nanoparticles were synthesized by the sonochemical reaction. $Zn(CH_3COO)_2.2H_2O$ and $Cd(CH_3COO)_2.2H_2O$ were choose as the zinc precursor and cadmium source, respectively. The molar ratio of Cd and Zn was kept at about 1 : 20, 3 :

20, 2 : 5 and 4 : 5 for preparing 5%, 15%, 40% and 80% Cd-doped ZnO, respectively. In this paper, a sonochemical method has been used for the first time to synthesize $Cd_xZn_{1-x}O$ (x=0, 0.05, 0.15 and 0.40) nanoparticles. By XRD investigation, we have found that $Cd_xZn_{1-x}O$ nanoparticles can keep the wurtzite structure with increasing x up to 0.40, which indicates the stability of the $Cd_xZn_{1-x}O$ nanoparticles synthesized by the sonochemical method. In the wurtzite structure, the lattice parameters gradually increase with increasing x. The findings of the Raman investigation are consistent with the XRD results. We also observed Cd-doping induced red-shifts of the band gap and a near band-edge (NBE) emission band for $Cd_xZn_{1-x}O$ nanoparticles. The Cd-doping can modify the photoluminescence bands of CdxZn1_xO nanoparticles. Therefore, the sonochemical method is a useful tool for the synthesis of doped nanoparticles.

The summary of the above literature is given in Table 1.

Table 1. Summary of literature

Sr. NO.	Title of Page	Name of Author and Year	Conclusion	Remark
1.	Structural, Optical and Antibacterial Activity of Pure and Cadmium Doped Zinc Oxide Nano Particles.	A.Pricilla Jeyakumari, P.Siva, P.Pachamuthu, M.Revathi (2017)	The powder X-Ray diffraction pattern of synthesized pure and Cd doped ZnO confirmed that the materials are nanomaterials of particles size 18 nm and 21 nm respectively. The functional groups present in the pure and Cd doped ZnO nano materials have confirmed by FT-IR spectral analysis. The surface morphology of the samples was determined by scanning electron microscopy (SEM). The optical transmittance lie in the visible region is the advantage of ZnO used in optoelectronic application like display devices and LEDs.	Low cost production is the main advantage of this method. In addition, devices with ZnO nanorods exhibit better performance due to a better interfacial contact, having fewer defects and improved light extraction.
2.	Synthesis and Characterization of Cadmium Doped ZnO Nanoparticles, Book-Recent Trends in Materials and Devices,	Suman, Sonia, Vinod Kumar, Sacheen Kumar and Dinesh Kumar (2017).	The XRD analysis revealed that crystalline size decreases from 14 to 3 nm and band gap tuned from 3.26 to 3.17 eV as Cd concentration increases. In UV Spectroscopy we evaluated that band gap decreases continuously with increasing cadmium concentration.	There is a clear changes in the positions, sizes and shapes of nanoparticle when Cd is incorporated with ZnO host.
3.	Preparation and Characterization of Cd Doped ZnO Nanoparticle by Combustion Method, International Journal of Science and Research (IJSR)	L. Arun Jose, L. Allwin Joseph, S. Arun Mathew, J. Mary Linet, S. Jerome Das (2013).	The powder XRD analysis confirms the crystallinity of the synthesized sample with crystallite size of 50 nm for the various doping concentration of 1%, 3%, 5%. The absorbance near UV region decreases with increase in dopant concentration. It is evident that from the photoluminescence spectrum, the PL intensity increases with increase in Cd dopant.	In photoluminescence spectrum, the PL intensity increases with increase in Cd dopant.
4.	A study of photoluminescence properties and performance improvement of Cd-doped ZnO quantum dots prepared by the sol–gel method	Jun Zhang, Su-Qing Zhao, Kun Zhang, Jian-Qing Zhou and Yan-Fei Cai (2012).	The ZnO and Cd-doped ZnO QDs have hexagonal wurtzite structures and are 3 to 6 nm in diameter. When the Cd content was increased, the QD particle	Synthetic method is effective for the preparation of doped QDs with high-fluorescence quantum efficiency.

			size was reduced; this effect was confirmed in the Corresponding uv spectra. Fourier transform infrared and X-ray diffraction techniques proved that the polymer successfully coated the surfaces of the QDs.	
5.	Photocatalytic and bactericidal activities of hydrothermally synthesized nanocrystalline Cd-doped ZnO , Superlattices and Microstructures	C.Karunakaran, A.Vijayabalan, G.Manikandan (2012).	Cd-doping by hydrothermal method decreases the grain size and destroys the microstructure. Although doping does not modify the band gap, it suppresses the deep level emission, decreases the charge-transfer resistance and increases the capacitance.	Cd-doping enhances the photocatalytic and bactericidal activities.
6.	Optical investigation on cadmium-doped zinc oxide nanoparticles synthesized by using a sonochemical method	Yue Wang, Yuetao Yang, Xingan Zhang, Xiaojun Liu and Arao Nakamura (2012).	X-ray diffraction (XRD) and Raman scattering spectroscopy indicate that the wurtzite structure can be kept in $Cd_xZn_{1-x}O$ nanoparticles up to x = 0.40. UV-Visible and photoluminescence spectroscopy indicate that, both the band gap and the NBE emission band for Cd doped ZnO nanoparticles show red-shift with an increase in Cd-doping.	Cd-doping can modify the photoluminescence bands of $Cd_xZn_{1-x}O$ nanoparticles. Therefore, the sono-chemical method is a useful tool for the synthesis of doped nanoparticles.

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