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# Fabrication of core-shell CdO/ZnS nanocomposites: Transition metal ions

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**ABSTRACT**

Transition metal ions doped CdO/ZnS nanocomposites have been synthesized using a simple wet chemical method. The prepared samples are characterized by powder XRD, SEM, Optical, EPR, PL, VSM and FT-IR techniques. From XRD the prepared nanocomposites are comprised for cubic phase of both CdO and ZnS in a close contact with each other. SEM images show nanoclusters. Optical absorption and EPR spectra of TM ions doped nanocomposites exhibited the characteristic absorption bands and resonance signals of TM ions. Distorted octahedral site symmetry is observed for all TM ions doped CdO/ZnS nanocomposites. Tetragonal and rhombical distortion in octahedral site is observed for $VO^{2+}$ and $Cu^{2+}$ ions doped CdO/ZnS nanocomposites. The PL spectra of all the dopants exhibit various emission bands correspond to UV and visible regions. The corresponding CIE coordinates are also calculated. Magnetometric measurements show all TM ions doped CdO/ZnS nanocomposites exhibits ferromagnetism at room temperature. FT-IR spectra exhibited the fundamental modes of vibrations of CdO, ZnS and other functional groups.

**KEY WORDS:** Nanocomposites, core-shell, transition metal ions, wet chemical method, XRD and PL.

## 1. INTRODUCTION

Size dependent optical and electrical properties of semiconducting nanomaterials have attracted researchers in the field of nanotechnology. Among the numerous new-style materials, the creation of nanocomposites has fascinated considerable attention both in industry and academia, because they often exhibit remarkable improvement in materials properties when compared with conventional micro and macro-composites. Especially, CdO/ZnS nanocomposites are important II–VI compound semiconductors with direct band gap energy of 2.3 and 3.7 eV at 300 K respectively (Ghoshal 2007; Ramasamy 2012).

The n-type CdO has smaller band gap energy, simple cubic rock salt structure and is a member of transparent conducting oxide having various applications in solar cells, photodiodes, IR detectors, transparent electrodes, photo catalyst for wastewater treatment, etc. (Champness 1985; Kondo 1971; Ocampo 1993; Gulce, 2013). Surface modification is the most superior and exciting method to specially made these materials for technological and biological applications (Prinsa, 2011; Bruchez, 1998). The II–VI group of semiconducting material ZnS is discovered in ancient times. The cubic phased ZnS with larger bandgap energy has thermal stability below 1000°C and transformed to wurtzite structure above 1000°C. ZnS is a low toxic, chemically more stable at RT. ZnS has immense interest among other semiconductors because of its potential applications, such as pharmaceutical, biomedical devices, optical coating, photoconductors, optical sensors, phosphors, window material, dielectric filter, the field emission display and also in LEDs (Champness, 1985; Dimitrova, 2000; Sambasivam, 2009; Ziabari, 2013; Kim, 2014; Xiaosheng Fang, 2010; Pathak, 2013). Recently Kim (2014) noticed that ZnS on the surface of CdSe/CdS semiconductors increases the electron recombination resistance and life time of the electron.

Doped semiconductor nanocomposites are particularly attractive for their excellent surface- enhanced photonic crystals, catalysis, nano-electronic devices, biochemical sensors etc. Especially semiconductors doped with TM ions such as $VO^{2+}$, $Cr^{3+}$, $Fe^{3+}$ and $Cu^{2+}$ find extensive applications in nanophotonics and spintronics reported by Babu (2014). Joyce Stella (2015) synthesized CdO/ZnS nanocomposites, and 3d TM ions namely $VO^{2+}$, $Cr^{3+}$, $Fe^{3+}$, $Cu^{2+}$ doped CdO/ZnS nanocomposites and they are characterized by various structural, spectral, luminescence and magnetic techniques.

## 2. EXPERIMENTAL

**Synthesis procedure:** CdO/ZnS core/shell nanocomposites were synthesized by a two-step wet chemical method. At first CdO nanopowder was prepared, then ZnS nanoparticles deposited on the surface of CdO nanopowders. In the first step, about 2.2 g of cadmium acetate dehydrate was dissolved in 200 ml of deionised water and stirred for 10 min at room temperature. About 1.5 g of tri-sodium citrate in 10 ml water and 4.2 ml of 25% ammonia solution were added to it. Then 20 ml of 2 M NaOH solution was added drop wise at room temperature with vigorous stirring. The temperature was then raised to 85°C and kept for 8 h. The contents were centrifuged at 10,000 rpm about 30 min, several times washed with water and ethanol to eliminate impurities and dried at 80°C for 1 h then grinded. After that, for better yield of CdO nanopowder temperature rises to 120°C and kept for 2 h in hot air oven. A powder with brown colour was obtained which confirmed the formation of CdO. In the second step, ZnS nanoparticles were deposited on the surface of CdO. For this 250 mg of CdO nanopowder was dispersed in 100 ml of water and allowed

to stir for 10 min. 1 mM of zinc acetate and 10 mM of thioacetamide were then added and the contents were stirred for 1 h at 60°C. The precipitates were centrifuged, washed with water, ethanol and dried at 70°C. The yield of CdO/ZnS core/ shell nanocomposite was obtained. For the synthesis of transition metal ions doped CdO/ZnS nanocomposites, 0.01 mol% of transition metal oxides were added to the above mixture in the similar procedure. Finally undoped and transition metal ions doped CdO/ZnS nanocomposites were obtained. The synthesized nanocomposites were characterized by using different characterization techniques.

**Characterizations:** Powder X-ray diffraction pattern recorded on PANalytical Xpert Pro-diffractometer with CuKα radiation (1.5406Å). Elemental compositions of the prepared samples were examined through energy dispersive spectroscopy (EDS) by using Oxford Inca Penta FETx3EDS instrument attached to Carl Zeiss EVOMA15 scanning electron microscopy. Transmission electron microscopy (TEM) experiments were performed using a HITACHI made H-7650 instrument with an accelerating voltage of 100 kV. The as prepared powder sample was dispersed in ethanol or water and a drop of the homogeneous dispersion was then loaded onto a carbon coated copper grid and allowed to dry prior to analysis. Optical absorption spectrum was recorded from JASCOV-670 Spectrophotometer in the region of 200–1400 nm wavelength at room temperature. EPR spectrum was taken on JES-FA series X-band EPR spectrometer having 100 kHz field modulations. Photoluminescence (PL) spectrum was obtained from Horiba Jobin-Yvon Fluorolog-3 Spectrofluorimeter with Xe continuous (450 W) and pulsed (35W) lamps as excitation sources. The magnetic properties were investigated using vibrating sample magnetometer (Lakeshore 7404). Fourier Transformed InfraRed (FT-IR) spectrum was recorded using KBr pallets on Thermo Nicolet 6700 spectrometer in the range of 4000-400 $cm^{-1}$.

## 3. RESULTS AND DISCUSSION

**XRD Analysis:** The powder X-ray diffraction describes that these synthesized materials exhibit two different phases of material with cubic crystal structure of both CdO and ZnS. The crystallographic data shows good agreement with standard diffraction data of JCPDS file No. 05-0640 and 05-0566 for CdO and ZnS respectively. The average crystallite size is calculated using Debye-Scherrer's formula $D = k\lambda/\beta\cos\theta$ and lattice cell parameters are evaluated from the XRD data. The cell volume and lattice cell parameters are reported in Table 1. The existence of transition metal ions may cause the slight variations in the cubic lattice cell parameter (a) and volume of the host lattice for both CdO and ZnS. The crystallite size and micro strain of as synthesized materials are given in Table.2.

**Table.1.Lattice cell parameters of CdO/ZnS and transition metal ions doped CdO/ZnS nanocomposites**

| | CdO | | ZnS | |
|---|---|---|---|---|
| **Nanocomposites** | **a (nm)** | **V x $10^{-3}$ ($nm^3$)** | **a (nm)** | **V x $10^{-3}$ ($nm^3$)** |
| CdO/ZnS | 0.4691 | 103.23 | 0.5374 | 155.16 |
| CdO/ZnS: $VO^{2+}$ | 04722 | 105.28 | 0.5379 | 155.62 |
| CdO/ZnS: $Cr^{3+}$ | 0.4723 | 105.34 | 0.5381 | 155.81 |
| CdO/ZnS: $Fe^{3+}$ | 0.4733 | 105.99 | 0.5373 | 155.12 |
| CdO/ZnS: $Cu^{2+}$ | 0.4689 | 103.68 | 0.5379 | 155.63 |

**Table.2.The crystallite size and micro strain of CdO/ZnS and transition metal ions doped CdO/ZnS nanocomposites**

| **Nanocomposites** | **Size** | **Strain** |
|---|---|---|
| CdO/ZnS | 22.5 | 4.6 |
| CdO/ZnS: $VO^{2+}$ | 19 | 6.5 |
| CdO/ZnS: $Cr^{3+}$ | 33.65 | 14.9 |
| CdO/ZnS: $Fe^{3+}$ | 35 | 3.5 |
| CdO/ZnS: $Cu^{2+}$ | 16 | 2.15 |

Crystallite size of all the composites is in the order of nanometer range and in between the assortment of 15-35 nm. Trivalent transition metal ions possess more crystallite size and divalent transition metal ions possess less crystallite size when compared to host material. The micro strain value is more in the case of $Cr^{3+}$ ions. Fig.1, shows the variation of crystallite size and the strain values with respect to the transition metal ions.

**Morphological studies:** The SEM images of prepared composite material are recorded at different magnifications. SEM images of CdO/ZnS nanocomposite are in irregular shaped morphology with agglomerated particles. This agglomeration is more often in case of nanopowders may be mainly due to high surface to volume ratio of nanoparticles results the clustering of small particles. Incorporation of dopant ions changes the irregular shaped structures to sphere like structures. Also from TEM images the same and clear surface structure morphology is observed. EDS study confirms the presence of Cd, O, Zn and S along with the respective transition metal ions. Hence purity of the materials is projected from the EDS spectrum by observing no other impure elements.

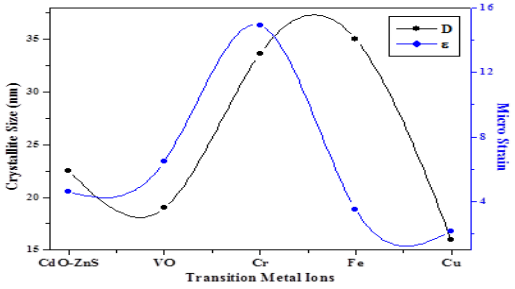


**Figure.1. Variation of crystallite size and the strain values with respect to the transition metal ions.**

**Optical and EPR studies:** The characteristic absorption bands and resonance signals are not observed from the optical absorption and EPR spectra of CdO/ZnS nanocomposite. While in case of transition metal ions doped CdO/ZnS nanocomposites, optical absorption and EPR spectra of has been exhibited the characteristic absorption bands and resonance signals of corresponding transition metal ions. The site symmetry of doped transition metal ions ascribed as octahedral. The $VO^{2+}$ ions are entered into the frame-work as tetragonally compressed octahedral site symmetry. The crystal field parameter (Dq) and tetragonal field parameters (Ds and Dt) are evaluated from the optical absorption spectrum for $VO^{2+}$ ions. From the absorption bands, crystal field (Dq) and Racah parameters (B, C) are evaluated for trivalent transition metal ions by using their respective cubic field energy matrices. For $Cr^{3+}$ and $Fe^{3+}$ ions the site symmetry is distorted octahedral in the host lattice. Whereas in the case of $Cu^{2+}$ doped CdO/ZnS nanocomposite, the site symmetry is rhombically distorted octahedral. From EPR spectral data, the evaluated bonding parameter suggested that there exists a covalent bonding nature between the doped $Cu^{2+}$ and its ligands. Table 3 summarizes the evaluated crystal field, tetragonal field and Racah parameters for transition metal ions doped CdO/ZnS nanocomposites.

**Table.3.Variation in crystal field, tetragonal field and Racah parameters for transition metal ions doped CdO/ZnS nanocomposites**

| Nanocomposites | Crystal field, tetragonal field and Racah parameters ($cm^{-1}$) | | |
|---|---|---|---|
| CdO/ZnS: $VO^{2+}$ | Dq = 1465 | Ds = -2918 | Dt = 742 |
| CdO/ZnS: $Cr^{3+}$ | Dq = 1660 | B = 733 | C = 3026 |
| CdO/ZnS: $Fe^{3+}$ | Dq = 765 | B = 660 | C = 2800 |

**Photoluminescence studies:** The PL spectra of host and all the dopants exhibit various emission bands which correspond to different regions like UV, blue, green, orange and yellow regions. The excitation wavelengths of all the dopants are in UV region. Both near band edge emission and deep level emissions are observed from all PL spectra. The near band edge emission around 420 nm is due to the recombination of electrons and holes from conduction band to valency band. The strong deep level emission in yellow region is observed mainly indicates the high crystalline nature of the material with less deep level defects. While in case of the $Cu^{2+}$ ions this strong band is observed in green region indicates the deep trap energy levels of $Cu^{2+}$ ions plays the major role in luminescence study.

The CIE chromaticity coordinates are calculated from PL data of all nanocomposite materials plotted in chromaticity diagram as shown in Fig.2. CdO/ZnS nanocomposite emits the near white light. The chromaticity coordinates and CCT values of CdO/ZnS and transition metal ions doped CdO/ZnS nanocomposites is given in Table.4. From PL studies it was clear that the prepared nanocomposites are well suited for light emitting materials in lamps and displays. From this CIE 1931 chromaticity coordinates (x, y), correlated colour temperature (CCT) is calculated using McCamy equation for all prepared samples. CCT is an indication of colour appearance of light emitted by the sample. Under long-wavelength UV excitation, a set of fluorescence with colour temperatures varying from 2000 to 10,000 K can be applied to circadian lights.

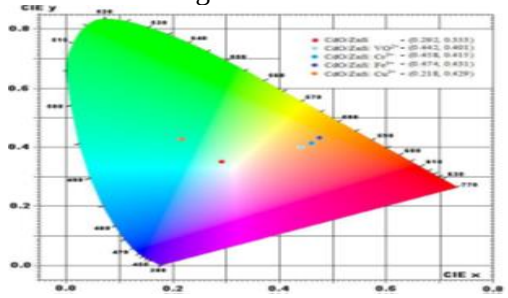


**Figure.2. Chromaticity diagram of CdO/ZnS and transition metal ions doped CdO/ZnS nanocomposites .**

**Table.4. Chromaticity coordinates and CCT values of CdO/ZnS and transition metal ions doped CdO/ZnS nanocomposites**

| Nanocomposites | CIE Coordinates | | CCT (K) |
|---|---|---|---|
| | x | y | |
| CdO/ZnS | 0.292 | 0.353 | 7367 |
| CdO/ZnS: $VO^{2+}$ | 0.442 | 0.401 | 2892 |
| CdO/ZnS: $Cr^{3+}$ | 0.458 | 0.415 | 2761 |
| CdO/ZnS: $Fe^{3+}$ | 0.474 | 0.431 | 2661 |
| CdO/ZnS: $Cu^{2+}$ | 0.218 | 0.429 | 9567 |

**Magnetic studies:** Magnetic studies of all samples are recorded at room temperature, from the M-H hysteresis loop it is confirmed that the samples exhibit room temperature ferromagnetism. The determined magnetism is mainly due to the intrinsic given by the absence of secondary phase elements in the composites. The values of saturation magnetization (Ms), coercive field (Hci) and retentivity (Mr) of all synthesized materials are given in Table.5. Among all the nanocomposites $Fe^{3+}$ doped CdO/ZnS nanocomposites possess more ferromagnetism at room temperature. Fig. 3 shows the variation in saturation magnetization with respect to transition metal ions.

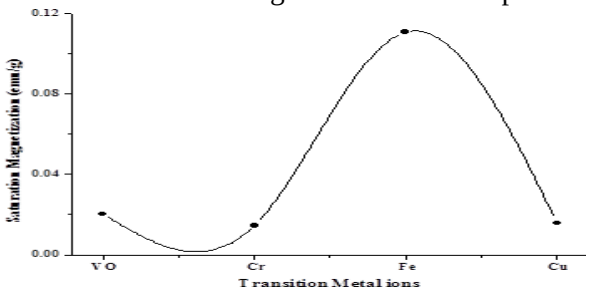


**Figure.3.Variation in saturation magnetization with respect to transition metal ions**

**Table.5. The values of saturation magnetization (Ms), coercive field (Hci) and retentivity (Mr) of CdO/ZnS and transition metal ions doped CdO/ZnS nanocomposites**

| Nanocomposites | Coercivity (Hci) (G) | Magnetization (Ms) (emu/g) | Retentivity (Mr) (emu/g) |
|---|---|---|---|
| CdO/ZnS: $VO^{2+}$ | 98.677 | 2.02E-02 | 1.61E-03 |
| CdO/ZnS: $Cr^{3+}$ | 97.944 | 1.46E-02 | 1.21E-03 |
| CdO/ZnS: $Fe^{3+}$ | 108.79 | 0.11062 | 1.17E-02 |
| CdO/ZnS: $Cu^{2+}$ | 98.345 | 1.58E-02 | 1.43E-03 |

**FT-IR study:** From the FT-IR studies, the fundamental vibrations of stretching and bending modes of CdO and Cd-OH are observed at around 450, 723 and 858 $cm^{-1}$ respectively. ZnS vibrational mode is found at 530 $cm^{-1}$. The other carbohydroxyl and carbonyl groups (C=O, O=C=O) were observed in their respective positions. The characteristic metallic bonding of strong CdO bands and week ZnS bands are observed from all transition metal ions doped FT-IR spectra, confirm the successful synthesis of composite material with fewer amounts of ZnS.

## 4. CONCLUSION

Undoped and transition metal ions doped CdO/ZnS nanocomposites are successfully synthesized by simple two step wet chemical method, several structural and luminescence studies have been done at room temperature. All the prepared nanocomposites are in cubic crystal phase of both CdO and ZnS with average crystallite size is in the order of nanoscale. From both SEM and TEM, composite particles are seemed to be bigger in size most probably due to the clustering of small particles on the grid. Optical, EPR studies confirm that the site symmetry of $Cr^{3+}$, $Fe^{3+}$ ions in octahedral site symmetry, where as in the case of $VO^{2+}$ and $Cu^{2+}$ ions the site symmetry is in distorted octahedral site. Photoluminescence studies identified that the prepared nanocomposite samples exhibit various colours as light emitting materials. The magnetic hysteresis curves represents the ferromagnetic nature exhibits for all transition metal ions doped in CdO/ZnS nanocomposites at RT. FT-IR spectrum clearly reveals the characteristic vibrational bands of CdO, ZnS compounds.

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**REFERENCES**

Babu B, Thirumala Rao G, Pushpa Manjari V, Ravindranadh K, Joyce Stella R, Ravikumar RVSSN, Sonochemical assisted synthesis and spectroscopic characterization of $Fe^{3+}$ doped ZnO diluted magnetic semiconductor, Journal of Materials Science: Materials in Electronics 25, 2014, 4179–4186.

Babu B, Manjari VP, Aswani T, Rao GT, Stella RJ and Ravikumar RVSSN, Structural, optical and magnetic properties of $Cr^{3+}$ doped ZnO nanopowder, Indian Journal of Physics, 88, 2014, 683–690.

Bruchez M, Moronne M, Gin P, Weiss S, Alivisatos AP, Semiconductor Nanocrystals as Fluorescent Biological Labels, Science, 281, 1998, 2013-2016.

Champness CH, Ghoneim K, Chen JK, An improved conventional Se–CdO photovoltaic cell, Canadian Journal of Physics, 63, 1985, 767-771.

Dimitrova V, Tate J, Synthesis and characterization of some ZnS-based thin film phosphors for electroluminescent device applications, Thin Solid Films, 365, 2000, 134-138.

Durgadas CV, Sreenivasan K, Sharma CP, Bright blue emitting CuSe/ZnS/silica core/shell/shell quantum dots and their biocompatibility, Biomaterials, 33, 2012, 6420-6429.

Ghoshal T, Soumitra K, Chaudhuri S, Synthesis of nano and micro crystals of $Cd(OH)_2$ and CdO in the shape of hexagonal sheets and rods, Applied Surface Science, 253, 2007, 7578–7584.

Gulce H, Eskizeybek V, Haspulat B, Sarı F, Gulce A, Avci A, Preparation of a New Polyaniline/CdO Nanocomposite and Investigation of Its Photocatalytic Activity: Comparative Study under UV Light and Natural Sunlight Irradiation, Industrial Engineering Chemistry Research, 52, 2013, 10924-10934.

Joyce Stella R, Thirumala Rao G, Pushpa Manjari V, Babu B, Rama Krishna Ch, Ravikumar RVSSN, Structural and optical properties of CdO/ZnS core/shell nanocomposites, Journal of Alloys and Compounds, 628, 2015, 39–45.

Joyce Stella R, Thirumala Rao G, Babu B, Pushpa Manjari V, Venkata Reddy Ch, Shim Jaesool, Ravikumar RVSSN, A facile synthesis and spectral characterization of $Cu^{2+}$ doped CdO/ZnS nanocomposite, Journal of Magnetism and Magnetic Materials, 384, 2015, 6–12.

Kim K, Park JE, Park ES, Park YC, Kim J, Im C, Lee M, ZnS- Passivated CdSe/CdS Co-sensitized Mesoporous $Zn_2SnO_4$ Based Solar Cells, Electrochimica Acta, 121, 2014, 223-232.

Kondo R, Okhimura H, Sakai Y, Electrical Properties of Semiconductor Photodiodes with Semi-transparent Films, Japanese Journal of Applied Physics, 10, 1971, 1547-1554.

Ocampo IM, Ferandez AM, Sabastian PJ, Transparent conducting CdO films formed by chemical bath deposition, Semiconductor Science and Technology, 8, 1993, 750-751.

Pathak CS, Mandal MK and Agarwala V, Synthesis and characterization of zinc sulphide nanoparticles prepared by mechanochemical route, Super Lattices and Microstructures, 58, 2013, 135-143.

Prinsa V, Avinash C.P, Capped semiconductor nanocrystals for device applications, Optics Communications, 284, 2011, 881-884.

Ramasamy V, Praba K, Murugadoss G, Synthesis and study of optical properties of transition metals doped ZnS nanoparticles, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 96, 2012, 963-971.

Sambasivam S, Reddy BK, Divya A, Madhusudhana Rao N, Jayasankar CK, Sreedhar B, Optical and ESR studies on Fe doped ZnS nanocrystals, Physics Letters A, 373, 2009, 1465-1468.

Xiaosheng Fang, Tianyou Zhai, Ujjal K. Gautam, Liang Li, Limin Wu, Yoshio Bando and Dmitri Golberg., 2010, ZnS Nanostructures: From Synthesis to Applications, Progress in Materials Science, 56, 175-287.

Ziabari AA, Ghodsi FE, Effects of the Cd:Zn:S molar ratio and heat treatment on the optical and photoluminescence properties of nanocrystalline CdZnS thin films, Materials Science in Semiconductor Processing, 16, 2013, 1629-1636.