



OPTICAL, STRUCTURAL AND MORPHOLOGICAL CHARACTERIZATION OF CADMIUM ION DOPED WO₃ NANOPARTICLES

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ABSTRACT

Tungsten trioxide (WO₃) has been demonstrated to possess visible light photoactivity and presents a means of overcoming the UV-light dependence of photocatalysts, such as titanium dioxide. In this study, Cadmium ion doped WO₃ nanoparticles were successfully prepared by chemical Co-precipitation method. Cadmium chloride and sodium tungstate solutions were used as precursors. The crystalline structure and optical properties of Cd ion doped WO₃ nanoparticles were characterized by UV, XRD, FESEM, EDAX and PL spectroscopic techniques. The morphological studies of the Cd ion doped WO₃ nanoparticles revealed crystal like morphology. The energy dispersive analysis confirmed the presence of Cd ion in the doped WO₃ lattice. From UV-Visible spectra of WO₃, Cd ion doped WO₃ nanoparticles exhibited absorption at 310 nm and 320 nm. The XRD spectrum showed diffraction peaks corresponding to the crystal planes of crystalline tungsten oxide. Using Debye scherrer formula, the size of the undoped and Cd ion doped tungsten oxide nanoparticles were also calculated. The optical properties of the prepared nanoparticles were studied by PL spectroscopy.

Keywords: Nanoparticles, UV, FESEM, EDAX, PL.

1. INTRODUCTION

Nanosized materials such as ZnO, ZnS, CdO and CdS are being used for a number of applications such as transistor, light emitting diodes (LED) and nanolaser [1-6]. Semiconductor nanoparticles doped with transition metal ions have attracted wide attention due to their excellent luminescent properties and the unique optical properties. Semiconducting optoelectronic materials play functional role in variety of applications due to their extraordinary optical, electrical and magnetic properties. The physical behavior of semiconductor nanoparticles strictly depends on their size, structure and morphology [2]. WO₃ exhibits enhanced photo absorption in visible-light irradiation because of its smaller band compared with that of titania (band gap, 3.0 eV to 3.2 eV) [7, 8]. Thus, WO₃ can be used in indoor pollutant treatment. WO₃ can degrade volatile organic compound gases by using domestic light sources where ultraviolet light is limited. In outdoor applications, WO₃ can use sunlight for the treatment of harmful pollutants in industrial wastewater and shows potential for hydrogen production. However, pure WO₃ has lower light energy conversion efficiency

compared with TiO₂ because the reduction potential is relatively low [9].

Cadmium (Cd) is a naturally occurring metal situated in the Periodic Table of the Elements between zinc (Zn) and mercury (Hg), with chemical behavior similar to Zn. It generally exists as a divalent cation, complexed with other elements (*e.g.*, CdCl₂). Cd exists in the earth's crust at about 0.1 part per million, usually being found as an impurity in Zn or lead (Pb) deposits, and therefore being produced primarily as a byproduct of Zn or Pb smelting. Commercially, Cd is used in television screens, lasers, batteries, paint pigments, cosmetics, and in galvanizing steel, as a barrier in nuclear fission, and was used with zinc to weld seals in lead water pipes prior to the 1960s. Approximately 600 metric tons are produced annually in the United States, and about 150 metric tons are imported [10]. The synthesis was carried out by chemical Co-Precipitation method. Tungsten oxide (WO₃) is a potential semiconductor material with an excellent optical property was carried out by UV-visible spectroscopy. Scanning electron microscopy (SEM) with energy dispersion spectroscopy analysis was carried out

to study the surface morphological features of the synthesized sample. The phase of the synthesized sample with crystallites size was measured from X-ray diffraction (XRD) analysis. In this work, optical properties of the prepared nanoparticles are studied by PL spectroscopy.

2. MATERIAL AND METHODS

2.1. Material

Sodium Tungstate, Concentrated Hydrochloric Acid, Cadmium chloride and deionized water were used to synthesize WO_3 nanoparticles and cadmium ion doped WO_3 nanoparticles.

2.2. Synthesis of Undoped WO_3 nanoparticles

WO_3 nanoparticles were synthesized at room temperature by chemical Co-precipitation method. WO_3 nanoparticles were synthesized by using sodium tungstate as the precursor material. All the reagents used were of analytical grade and used without further purification. The entire process was carried out in deionised water for its inherent advantages of being simple and environment friendly. In a typical preparation, solution of 0.1M sodium tungstate was prepared in 100ml of deionised water and then aqueous solution of (100ml, 1M) hydrochloric acid was added drop wise to this solution making a final volume of 200ml. This mixture was stirred well for 1h and refluxed at a temperature of about 80 °C which resulted in the formation of green coloured WO_3 nanoparticles. The precipitate was separated from the reaction mixture, washed several times with deionised water to remove the impurities. The precipitate was dried at room temperature.

2.3. Synthesis Of Cadmium Ion Doped WO_3 Nanoparticles

Cadmium ion doped WO_3 nanoparticle was prepared at room temperature by chemical Co-precipitation method. To a 100ml of 0.1M solution of sodium tungstate, hydrochloric acid solution (100 ml of 1M) was added in drops. The resulting solution was stirred for 30 minutes. It resulted in a yellow coloured solution. Then $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ in (100ml in 0.1M) deionised water was added to the above solution. The resulting solution was stirred for about 30 min and this solution was refluxed for 3 h at a temperature of about 80 °C which resulted in the formation of Cd ion doped WO_3 nanoparticles. The precipitate so obtained was filtered and the filtrate was washed several times with distilled water to remove the

impurities. The precipitate was dried at room temperature [11].

2.4. Characterization

Computer controlled JASCO V-530 was used to study UV-VIS spectral behavior. Photoluminescence (PL) spectra of the samples were recorded on a spectrofluorometer (JASCO, FP8300). XRD measurements were made by Panalytical X'Pert Powder X'Celerator Diffractometer, measurement range: 10 to 80 degree in 2θ and particle size was calculated using Scherrer's equation. The EDAX and FESEM measurements were carried by JEOL JSM-6700F field emission scanning electron microscope.

3. RESULTS AND DISCUSSION

3.1. Optical Study

In order to study the optical property and band gap energy of the undoped WO_3 and Cd ion doped WO_3 samples were characterized by UV-Vis transmission spectral analysis. UV-Vis transmission spectra of WO_3 and Cd ion doped WO_3 samples were shown in Fig.1 & Fig. 2, respectively. The UV spectrum of WO_3 nanoparticles shows a sharp peak at 310nm [12]. The absorbance value is found to be 1.4 for the corresponding peak. By using this peak value band gap is calculated. The calculated band gap value for WO_3 nanoparticles is 4.2 eV.

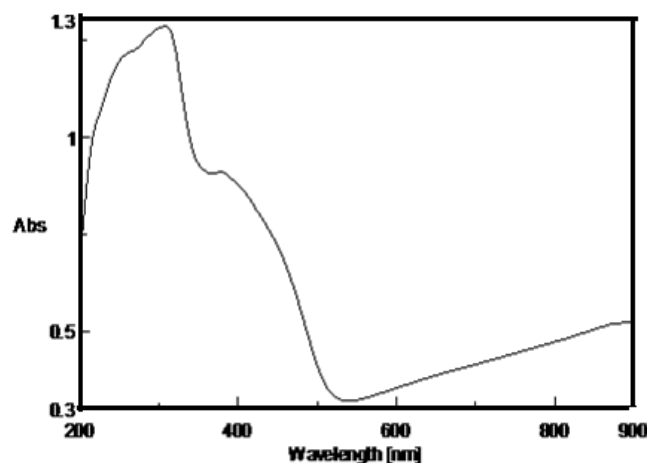


Fig. 1: UV-VIS absorption Spectrum of undoped WO_3 nanoparticles

The spectrum of Cd ion doped WO_3 nanoparticles exhibited a sharp peak at 320nm [12]. The absorbance value is found to be 1.3 for the corresponding peak. By

using this peak value band gap is calculated. The calculated band gap value for Cd ion doped WO_3 nanoparticles is 4.0 eV. The origin of the main strong peak is attributed to the electronic transition of the tungsten ion. Optical absorption study reveals the existence of several transitions at energies below band gap in WO_3 [13,14]. The observed decrease in band gap energy can be attributed to the formation of the WO_3 between valance band to conduction band due to Cd ion doping [10].

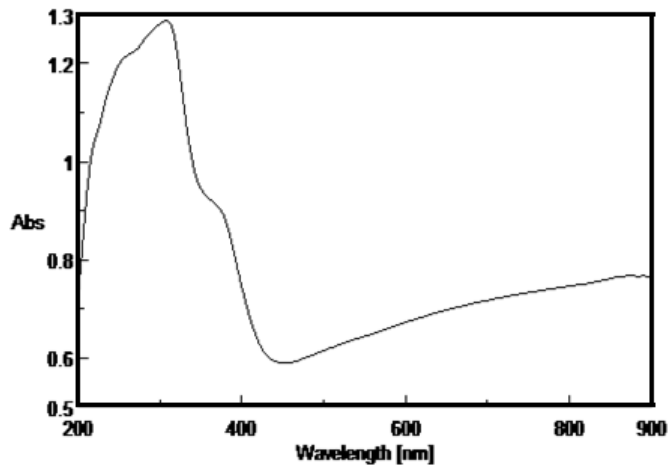


Fig. 2: UV-VIS absorption Spectrum of Cd ion doped WO_3 nanoparticles

3.2. Structural Characterization

Structural properties of the prepared metal oxide nanoparticles were studied by X-Ray Diffraction analysis. The crystallite size was calculated using the Debye-Scherrer formula

$$D = k\lambda / \beta \cos\theta$$

Where λ is the wavelength of radiation used (1.54060\AA for Cu K radiation), k is the Scherrer constant equal to 0.94, β is the full width at half maximum (FWHM) intensity of the diffraction peak for which the particle size is to be calculated, θ is the diffraction angle of the concerned diffraction peak and D is the crystalline size in nanometers (nm).

The XRD pattern of the undoped WO_3 nanoparticles is shown in the Fig.3. The sharp intense peaks obtained in all the samples at $2\theta \approx 16.68^\circ, 25.82^\circ, 33.57^\circ, 34.12^\circ, 35.12^\circ, 49.78^\circ, 56.32^\circ, 57.34^\circ$ and 58.55° are corresponding to the lattice planes (100), (101), (111), (111), (111), (112), (202), (220) and (220) respectively confirmed that the prepared samples are crystalline in nature with wurtzite hexagonal structure and are in agreement with the JCPDS data (01-075-1533)[15].

Average crystallite size of WO_3 nanoparticles are found to be 37.84nm, as calculated from Debye-Scherrer's equation.

Table 1: Crystallite Size of Nanoparticles

Samples	Size
Undoped WO_3 nanoparticles	37.84 nm
Cd ion doped WO_3 nanoparticles	18.94nm

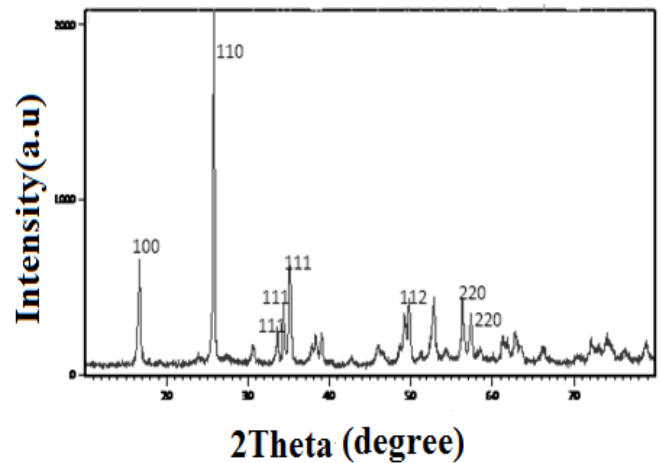


Fig.3: XRD pattern of Undoped WO_3 nanoparticles

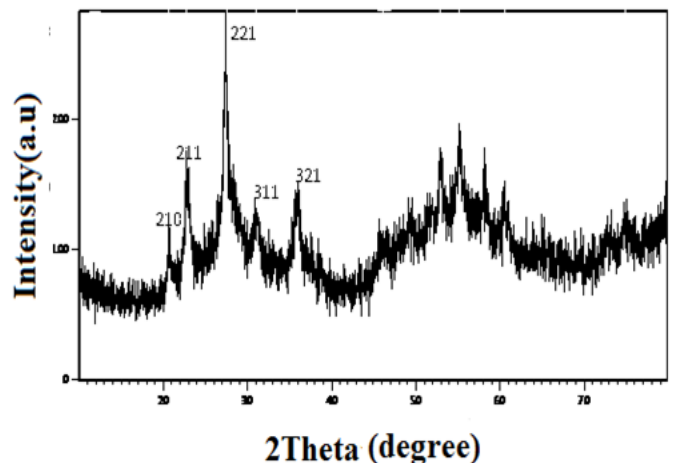


Fig. 4: XRD pattern of Cd ion doped WO_3 nanoparticles

The XRD pattern of Cd ion doped WO_3 nanoparticles are shown in Fig.4. The main diffraction angles are observed at 2θ values of $20.68^\circ, 22.71^\circ, 27.46^\circ, 31.07^\circ$ and 35.85° . The broad diffraction peaks suggest a well-amorphous nanomaterial and were identified to originate from (210), (211), (221), (311) and (321) planes [16]. The average amorphous size of the Cd ion doped WO_3

nanoparticles are found to be 18.94nm. The average crystallite size for undoped and Cd ion doped WO_3 nanoparticles was found to be 37.84 nm and 18.94nm respectively. It is clearly evident from these Table.1 shows that the crystallite size decreases when WO_3 is doped with Cd ion [17]. Values have very good agreement with the reported data, which indicates the formation of pure WO_3 nanoparticle. From the XRD pattern, the most intense peak was observed at $2\theta = 25.82^\circ$. Also no impurity peaks were observed [18].

3.3. Morphological Study

Surface morphologies of undoped WO_3 nanoparticles and Cd ion doped WO_3 doped nanoparticles are investigated by FESEM as shown in Fig.5. The morphology of Cd ion doped samples is different from undoped samples. The

surface morphologies of synthesized WO_3 nanoparticles (Fig.5a) exhibited square like structure [19]. For the undoped sample, only aggregates are formed whereas for the Cd ion doped WO_3 nanoparticles, the FESEM image shows that ice bar shaped nanoparticles (Fig.5b) which are well separated [20].

3.4. Energy dispersive X-ray analysis

The presence of elements in the synthesized nanoparticles were identified and confirmed through the EDAX analysis. The EDAX spectrum is shown in Fig.6, which exhibits the presence of two elements in WO_3 nanoparticles namely O and W [5]. The EDAX spectrum (Fig.7) of the Cd ion doped WO_3 nanoparticles revealed that doped sample contain W, Cd ,C and O as its constituent components.

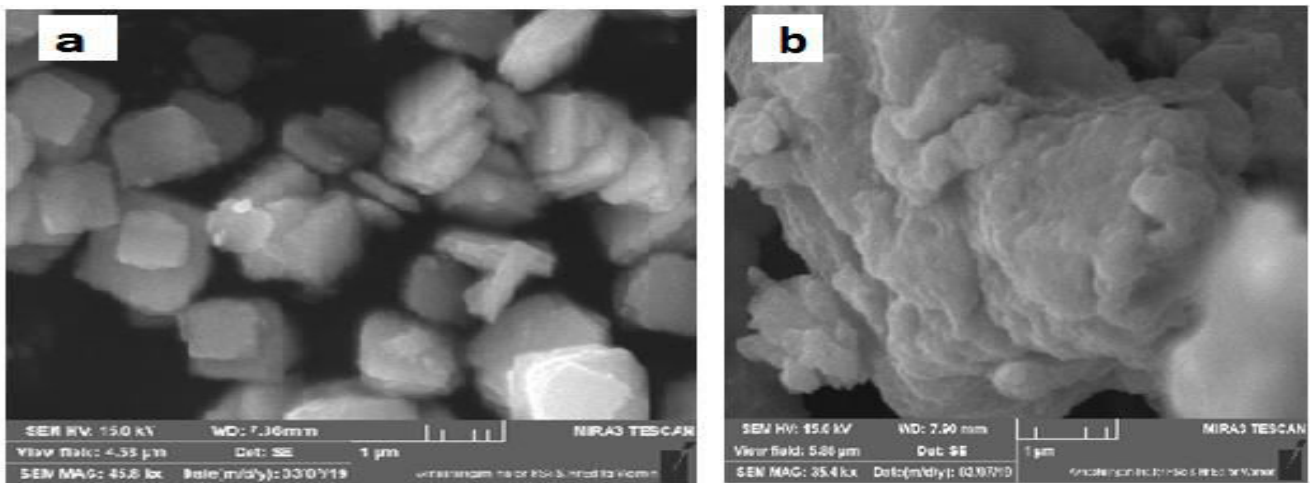


Fig. 5: FESEM images of a) undoped WO_3 nanoparticles b) Cd ion doped WO_3 nanoparticles

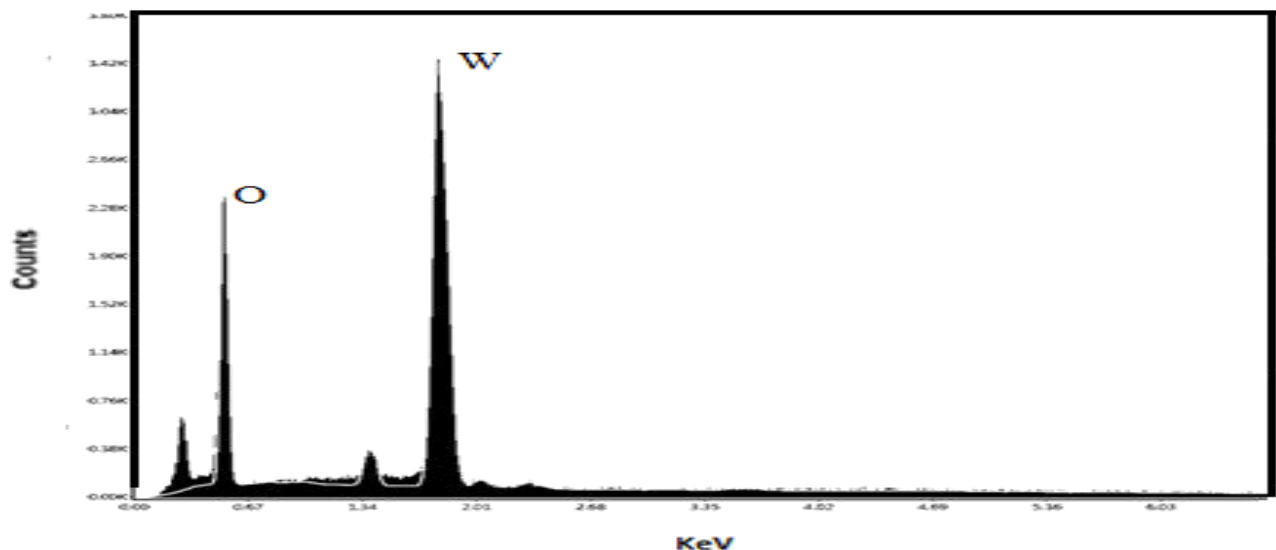


Fig. 6: EDAX spectrum of undoped WO_3 nanoparticles

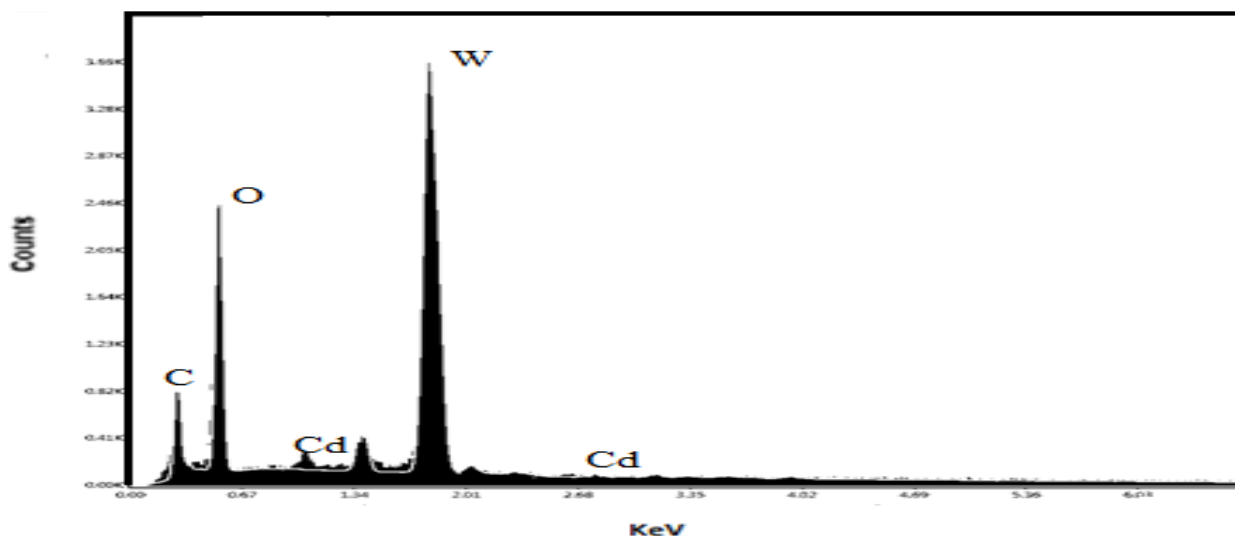


Fig. 7: EDAX spectrum of Cd ion doped WO_3 nanoparticles

3.5. Photoluminescence Study (PL)

Photoluminescence emission spectra of both undoped and Cd ion doped WO_3 nanoparticles are shown in Fig. 8 and Fig. 9.

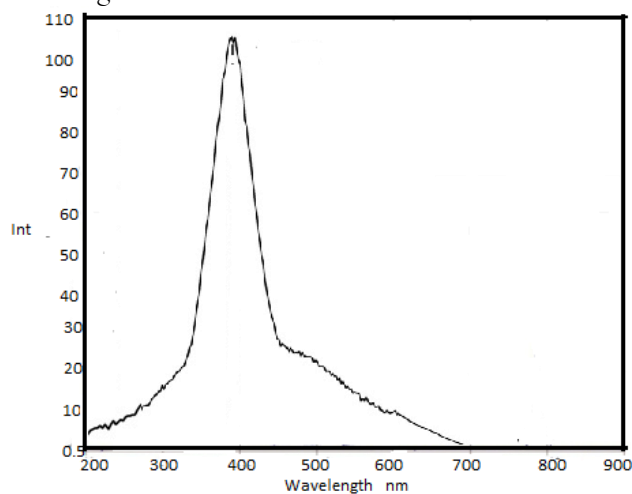


Fig. 8: Photoluminescence spectra of undoped WO_3 nanoparticles

This is measured by the range between 200nm to 900 nm. The wavelength of excitation chosen for the samples is 380 nm. It is interesting to note from that although the excitation spectra of undoped WO_3 and Cadmium doped WO_3 nanoparticles appear similar, an appreciable change in luminescence intensity is observed in the doped samples compared to the undoped samples. For doped samples there is increase in excitation intensity. This might be due to the interaction between Cadmium ion and WO_3 lattice. This provides an obvious evidence for the entry of Cadmium ion in the WO_3 lattice [20]. This emission is due to the different luminescent centers

namely defect energy levels arising because of tungsten interstitials and oxygen vacancies. The PL intensity of the Cd-doped sample was significantly higher than that of undoped WO_3 . This is due to recombination of photo-excited electrons and holes and then a lower PL intensity (undoped sample) might indicate a lower recombination rate of those electrons and holes under light irradiation [21].

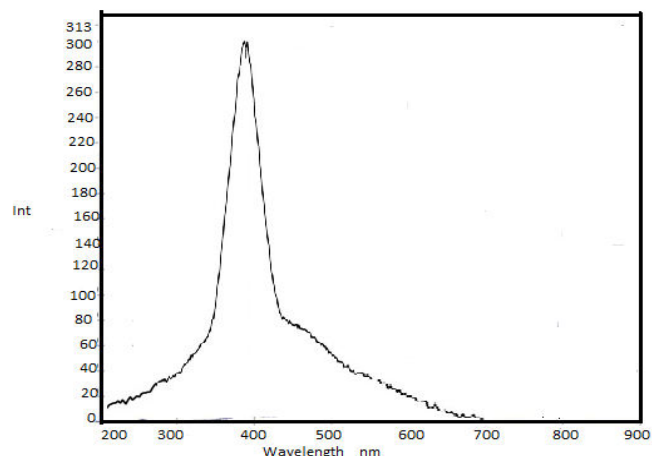


Fig. 9: Photoluminescence spectra of Cd ion doped WO_3 nanoparticles

4. CONCLUSION

Nano WO_3 and Cd ion doped WO_3 nanoparticles were synthesized using chemical co-precipitation method. The characterization of prepared samples were done by UV Spectroscopy, XRD, FESEM with EDAX analysis and photoluminescence studies. UV-Visible spectra of WO_3 and Cd ion doped WO_3 nanoparticles exhibited

absorption bands at 310 nm and 320nm respectively. From XRD analysis the crystallite size of WO₃ nanoparticles and Cd ion doped WO₃ nanoparticles were found to be 37.84nm and 18.94 nm respectively. Surface morphological features with particle size, shape and elemental composition were confirmed by FESEM and EDAX analysis. PL spectra revealed the change of luminescence intensity in the Cd ion doped sample compared to the WO₃ sample with almost a linear increase in excitation intensity. This provides an obvious evidence for the entry of Cadmium ion in the WO₃ lattice. Cd is used in television screens, lasers, batteries, paint pigments and cosmetics.

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