

Comparative Study of Crystallite Size from XRD and TEM Results for Pure and V₂O₅ Doped CdO-FePO₄ Composite Nanopowders

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CdO-FePO₄ composite nanopowders (CNPs) with V₂O₅ ions as dopants are prepared by a sol-gel technique. The as-synthesized CNPs are characterized by peak profile analysis of powder X-ray diffraction (XRD) and Transmission electron microscopy (TEM). The powder XRD analysis reveals that the prepared products are crystalline with the cubic phase of CdO. The Debye-Scherrer's method and Williamson-Hall (W-H) plot analysis are worn to find out the separate contributions of the size of the crystal lattice and microstrain on the peak broadening of prepared CNPs. The other relevant physical parameters like microstrain and dislocation density values are determined for all the XRD peaks related to the cubic phase of CdO between 10 and 80 degrees of 2-theta values. The morphological analysis and determination of mean crystallite size are done from TEM images. The estimated crystallite size values obtained from the XRD (W-H plot and Debye-Scherrer's method) and TEM analysis revealed that the results are highly inter-correlated. The EDX spectra confirm the presence of elements Cd, Fe, P, V, and O in the prepared sample. FT-IR study exhibited functional groups related to phosphates and oxides.

Keywords: CdO-FePO₄ CNPs, V₂O₅, XRD, TEM, W-H method

INTRODUCTION

Among the rapidly emerging developments in nanoscience & technology during the recent years, phosphate-based nanomaterials are acting as the best host materials owing to their good thermal, chemical, mechanical stability, self-activation, and low phonon energy [1]. Amongst the diverse phosphates, FePO₄ has very poor or low electrical conductivity due to its wide bandgap of about 4 eV [2]. The strong covalent bond between the P⁵⁺ ions and oxygen to form the (PO₄)³⁻ group allows for good stabilization [3], greatly inhibiting high-rate applications in the fields of wastewater purification, high proton conductivity, corrosion protection, catalysis, as a positive electrode, etc. [4-6]. Accordingly, CdO is an n-type oxide

semiconductor having a direct bandgap energy value of 2.5 eV. The combination of varying amounts of two or more elements forms a binary/ternary single-phase inter-metallic solid with tuned parameters and can be used in diverse technological applications such as digital, magnetic drug delivery carriers, sensors, and storage devices [7]. Further, it is also been recognized that transition metal-doped FePO₄ might be worn as a good precursor for the preparation of LiFePO₄ for excellent electrochemical performances [8]. Some studies reported that the transition metals viz., Mg, Mn, Zn, and Al doping of FePO₄ [9] enhanced its properties. Besides, there were many research efforts to design hybrid nanostructures of FePO₄ by coating conductive materials like metals, metal oxides, and polymers via different synthetic routes or by substitution of supporting matrices to improve the FePO₄ conductivity [10].

On the other hand, the substitution of ferrites in

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cadmium forms n-type semiconductors, and the raise of cadmium content results in a gradual decrease of the Seebeck coefficient. Also, Cd-Fe-based complex oxides are highly sensitive to ethanol gas over hydrogen, carbon monoxide, and isobutene [11]. T. Aswani *et al.* [12] synthesized Fe³⁺ doped CdO nanopowders and studied their spectral characterization. Hu Zhou *et al.* [5] synthesized Graphene oxide-FePO₄ nanocomposite and characterized its photocatalytic properties. N. Kerkouri *et al.* [13] studied FTIR, Raman, EPR, and optical absorption spectra of V₂O₅ doped cadmium phosphate glasses. P. Nagaraju *et al.* [14] studied Vanadium doped FePO₄ catalysts for the methyl pyrazine ammoxidation. Ian D. Johnson *et al.* [15] synthesized Vanadium doped LiFePO₄/C nanocomposite high-rate cathodes for Li-ion batteries. K.S. Lohar *et al.* [16] synthesized Vanadium substituted Nickel Cadmium Ferrite by sol-gel method and studied their structural and magnetic properties. Recently some work has been done on spectroscopic studies of Mn²⁺ doped CdO-Zn₃(PO₄)₂ nanocomposite synthesized by chemical precipitation method [17]. Despite the considerable studies available on Cd-Fe-based nanocomposite systems, as such, there are no studies on CdO-FePO₄ CNP. Thus the present research is aimed to couple CdO and FePO₄ to attain a novel CdO-FePO₄ CNP for its possible use in diverse potential applications like photo-catalyst, cathode material in rechargeable batteries. Further, among the all group-B transition metals V₂O₅ is chosen as a dopant since VO²⁺ is a stable molecular state compared to all the vanadium oxide family and also plays crucial role in phosphate metabolism [18]. After wide literature evaluation sol-gel method is adopted for the synthesis of CdO-FePO₄ CNPs with V₂O₅ ions as dopants because this method requires low temperature, low cost, and easy compositional control to produce narrow size distribution and excellent crystalline structure [19].

The crystallite size and lattice strain are the two core properties of powder XRD peak width analysis. A size measure of coherently diffracting domains is called the crystallite size whereas a measure of the distribution of lattice constants occurring as of crystal imperfections (*viz.*, lattice dislocations, stacking faults, contact or sinter stresses, coherency stresses, and grain boundary triple junction) is termed as lattice strain [20]. Both of these

parameters affect the Bragg peak in diverse ways such as increasing the peak intensity & width and shifting in peak position (2θ). To determine the crystallite sizes and lattice strain, powder XRD remained a dominant method among the various techniques. There are various methods for quantitative analysis of XRD and determination of crystallite size and lattice strain *viz.*, Scherrer's equation, Warren-Averbach analysis, Williamson-Hall method, pseudo-Voigt function, and Rietveld refinement [21]. But still, Scherrer's equation is widely utilized when compared to W-H plot analysis for crystallite size and microstrain determination. TEM is also employed to observe the morphology and to measure the particle size of synthesized CNPs. In general, the crystallite size of the particles differs slightly from the particle size owing to the formation of poly-crystalline aggregates [22]. The present work is focused to report a comparative evaluation of the crystallite size from powder XRD procedures and the mean particle size of the CdO-FePO₄ CNPs with V₂O₅ ions as dopants obtained from direct TEM measurements.

Materials and Methods

In order to synthesize CdO-FePO₄ CNP by sol-gel route, high purity chemicals of Cadmium oxide (CdO) from Sigma-Aldrich Corp., Iron/Ferric Phosphate (FePO₄), Vanadium Pentoxide (V₂O₅) from Merck Chemicals are chosen as preliminary resources without further purification. At first requisite stoichiometric proportions of precursors are dissolved in equal volumes of the deionized water-ethanol mixture and the solution was magnetically stirred at 1200 r.p.m for about 8 h until a homogeneous yellowish-brown color solution is obtained. During this continuous stirring NaOH dissolved in de-ionized water (which serves as pH controller and precipitating agent) is added to the above solution to obtain a homogeneous solution. Then after in order to remove further impurities, the solution was cleansed a few times with deionized water and later the precipitates were collected by centrifuging the mixture at 10,000 r.p.m for 30 min. Finally, the precipitate was allowed for subsequent calcination at 200 °C for 2 h in an annealing chamber operating at ambient pressure. A similar procedure is carried out for the synthesis of CdO-FePO₄ CNPs with V₂O₅ ions as dopants while the V₂O₅ dopant ions in a chosen stoichiometry (0.3, 0.6, and 0.9 mol%) are

added to the primary undoped solution during the stirring process. The as-synthesized nanocomposite was further used to analyze different spectroscopic characterizations.

Characterization Techniques

The phase evaluation, the crystal size, and other physical parameters of the prepared CNPs are determined using Philips: PW1830 X-ray diffractometer instrument with 1.5406 Å wavelength-Cu-K α radiations in the range of 10°-80° (2 θ) at a scanning rate of 2°/min upon maintaining the respective current 30 mA and operating voltage 40 kV. The morphology and mean particle size of the prepared CNPs are investigated using TEM (Hitachi HT7700 microscope) operated at 100 kV. A universal method for TEM sample preparation worn here is that the sample grid is set by dispersing the sample into ethanol with the assistance of ultrasonication; the droplets of the suspensions are deposited onto a carbon-enhanced copper grid and dried under a lamp in air. FEI Quanta FEG 200-HR-SEM of magnification ranging from 12x to greater than 1,00,000x is used to acquire EDX. Perkin Elmer Spectrum1: FT-IR Spectrometer is used to record FT-IR spectra of prepared CNPs mixed with KBr in the scanning range 4000-450 cm⁻¹.

RESULTS AND DISCUSSION

Powder XRD Analysis

The powder XRD technique is employed for the phase investigation and purity of the as-synthesized products. The powder XRD patterns of the prepared CNPs are entirely consistent with the cubic phase of CdO with their reflection peaks at 33.02°, 38.38°, 55.34°, 65.93°, and 69.38° corresponding to the respective lattice planes (111), (200), (220), (311), (222) as indexed in Fig. 1 and are in accordance with the JCPDS 05-0640. The line broadening and sharp peaks signify that prepared samples are crystalline and are in nano-regime. No reflections of crystalline FePO₄ phases and dopant V₂O₅ phases can be detected since the scattering domains are so small that the large line width of the reflections makes it impractical to discern them from the background [23] or it could be thought due to lower atomic radius of V₂O₅ ~0.88 Å [24] and FePO₄ ~0.64 Å [25] when compared with CdO ~0.95 Å [26], they might have reacted with CdO and formed a stable

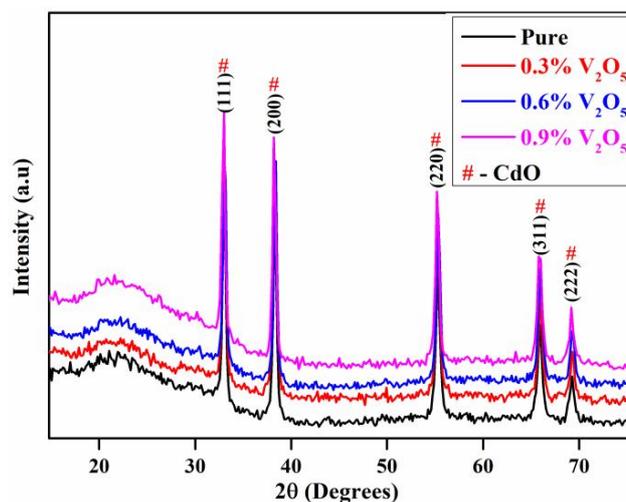


Fig. 1. XRD pattern of CdO-FePO₄ CNPs with V₂O₅ as dopant ions.

solid with no secondary phases and with CdO as the predominant phase. A similar sort of XRD pattern is evidenced in Nanostructured Pt-FePO₄ thin-film electrodes wherein the presence of amorphous FePO₄ and nanocrystalline Pt in the Pt-FePO₄ thin films was confirmed by XRD [27]. It is also found that the XRD pattern is free from other peaks corresponding to impurity phases. Moreover, an adequate shift in the peak position and increase in intensity is evidenced in V₂O₅ doped samples compared with pure samples indicating incorporation of VO²⁺ ions into CdO-FePO₄ CNP, thereby influencing the microstructure and local disorder of prepared CNP. Figure 2 represents the slight shift and variation in intensity in predominant peak position 2 θ ~ 33.02° corresponding to the respective lattice plane (111) of the XRD pattern of pure and V₂O₅ doped CdO-FePO₄ CNPs.

Crystallite Size and Strain

Crystallite sizes and strain induced in the lattice of synthesized CNPs are estimated in comparison with Debye-Scherrer's and W-H plot method as follows

The crystallite size (D) is calculated from the well-known Debye-Scherrer's formula [28]

$$D = \frac{0.89\lambda}{\beta \cos \theta}$$

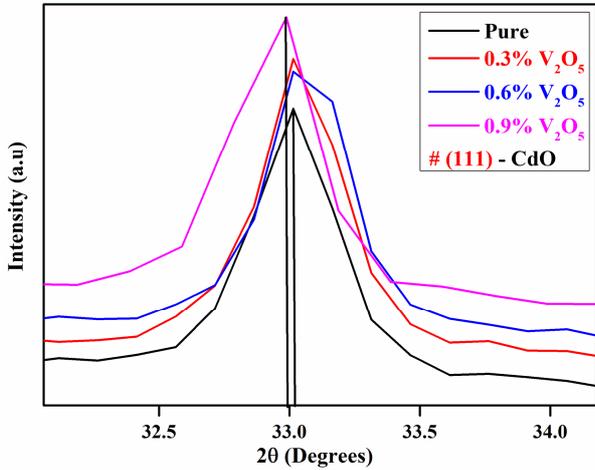


Fig. 2. Peak position shift and variation in the intensity of the predominant peak in the XRD pattern of CdO-FePO₄ CNPs with V₂O₅ as dopant ions

Here λ is the wavelength of monochromatic Cu-K α radiation (1.5406 Å), β denotes Full Width at Half Maxima

(FW-HM) of the broad and intense peaks, and θ is Bragg glancing angle related to (1 1 1) plane of XRD pattern.

The induced strain is deliberate using the Stokes-Wilson equation [29]

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$

The graphical way of the W-H plot method [30] is used to calculate the mean crystallite size and microstrain of pure and V₂O₅ doped CdO-FePO₄ CNPs by taking the width of a peak as a function 2θ from the expression as follows

$$\beta \cos \theta = (0.89\lambda/D) + 4\varepsilon \sin \theta$$

A graph is plotted between $4 \sin \theta$ and $\beta \cos \theta$ along x and y-axes respectively. The corresponding slope and intercept of the line give the value of microstrain and crystal size. Figure 3 depicts the W-H plot of pure and V₂O₅ doped CdO-FePO₄ CNPs.

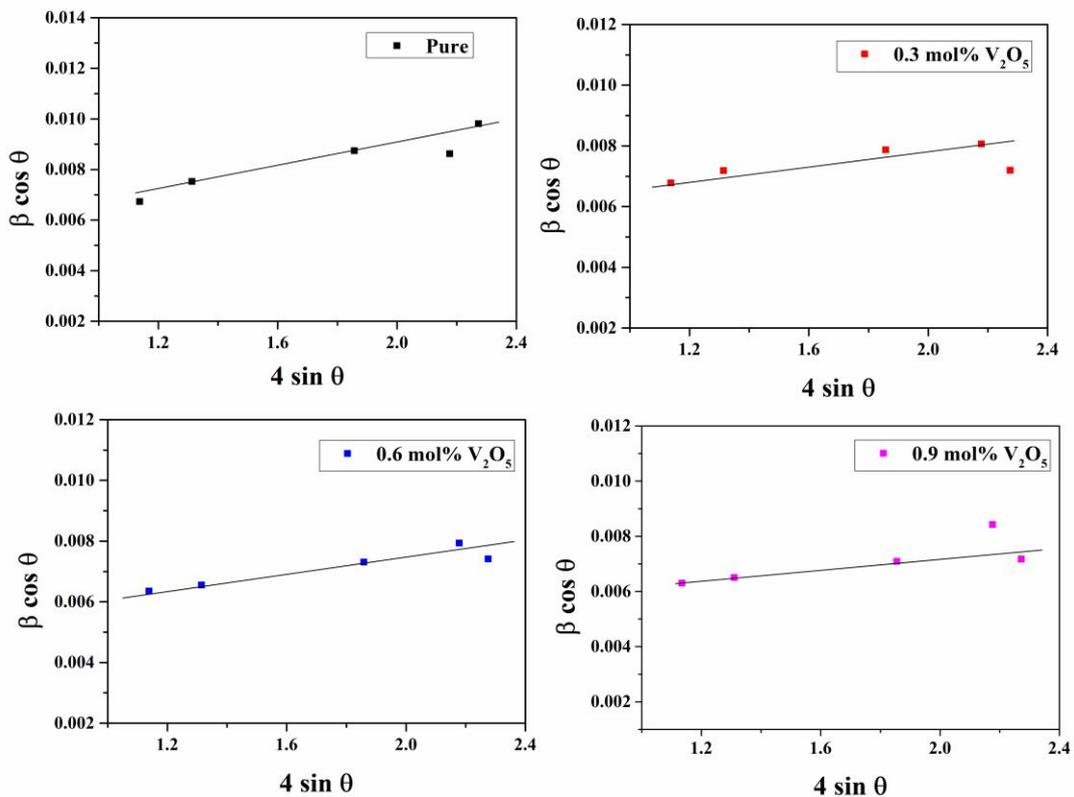


Fig. 3. Williamson-Hall plot of CdO-FePO₄ CNPs with V₂O₅ as dopant ions.

The dislocation density values are evaluated using the equation $\delta = 1/D^2$. The determined values of crystallite sizes, induced microstrain, and relevant dislocation density parameters employing Debye-Scherrer's and W-H methods are tabulated in Table 1. From these obtained values, it has been practical that the crystallite size and lattice strain varied systematically with doping concentrations of V_2O_5 *i.e.*, the crystallite size value increased slightly when compared with a pure sample upon increasing V_2O_5 concentration. The dislocation density depends on the value of crystallite size. Furthermore, the cause of strain is consistent with lattice irregularity. Thus, the higher the value of microstrain, the lesser the crystallite size. This behaviour may be attributed to the shift in 2θ peak position & intensity, and increment/decrement in the Bragg peak width, caused by the tensile or compressive stress on the lattice derived from the incorporation of VO^{2+} ions into CdO-FePO₄ CNP [31,32].

TEM and EDX Analysis

The accuracy in the microstructure of the synthesized samples can be determined by a vital technique, TEM. TEM images of pure and V_2O_5 doped CdO-FePO₄ CNPs are illustrated in Fig. 4.

A keen view of the images demonstrates that the samples are exhibiting an assembly of spherical and rod structures of different diameters and sizes with little surface agglomerations. The agglomeration could be arisen due to the mutual interaction between the particles, electrostatic forces, and Vander walls forces [33]. The rod structures might be due to the CdO phase. Similar CdO nanorods have

been reported by Sumeet Kumar *et al.*, [34] synthesized by a co-precipitation method. The spherical structures could be due to the FePO₄ phase. Similar FePO₄ spherical structures have been reported by Jeannine Baumgartner *et al.*, [35]. It is reported that the particle shape usually contributes about 10% to the total lattice variation [36]. Here in this study, only a slight change in morphology of increase in rods is observed with an increase in doping concentration. Further, it is also reported that control of shape in transition metal nanostructures can be easily done with the help of stabilizing reagent which prevents the agglomeration of the nanostructures and uncontrolled growth [33].

The elemental chemical compositions of pure and V_2O_5 doped CdO-FePO₄ CNPs are analyzed by using EDX analysis and the corresponding recorded spectra are shown in Fig. 5. The EDX pattern confirms the existence of Cd, Fe, P, O in pure and Cd, Fe, P, O, V elements in V_2O_5 doped CdO-FePO₄ CNPs. It is apparent from the figure that no more peaks related to impurities or contaminants are noticed, which confirms the purity of the synthesized CNPs. The acquired compositions of elements Cd, Fe, P, O, and V that are certain in the table in the inset of Fig. 5 are in good concurrence with the experimental stoichiometric calculations. After the compositional analysis, it is noticed that the content of "V" is found to increase by varying V_2O_5 doping concentration (0.3, 0.6, 0.9 mol%), signifying the replacement of Vanadium ions with other ions of the host lattice, without much disturbing the host lattice structure.

The mean particle sizes of the prepared CNPs are determined from TEM images by counting 50 particles in each sample to minimize errors and plotting histogram plots

Table 1. Average Crystallite Size, Lattice Strain, and Dislocation Density of CdO-FePO₄ CNPs with V_2O_5 as Dopant Ions from Debye-Scherrer's and W-H Plot Calculations

Sample code	Crystallite size (nm)		Lattice strain ($\epsilon \times 10^{-4}$)		Dislocation density (δ) $\times 10^{15}$ lines/m ²	
	Scherrer's	W-H plot	Scherrer's	W-H plot	Scherrer's	W-H plot
V ₀	20.39	21.01	59.13	66.05	2.40	2.26
V ₁	20.46	21.11	59.17	65.71	2.38	2.24
V ₂	21.92	22.78	55.58	60.90	2.08	1.92
V ₃	22.01	22.96	55.50	60.42	2.06	1.89

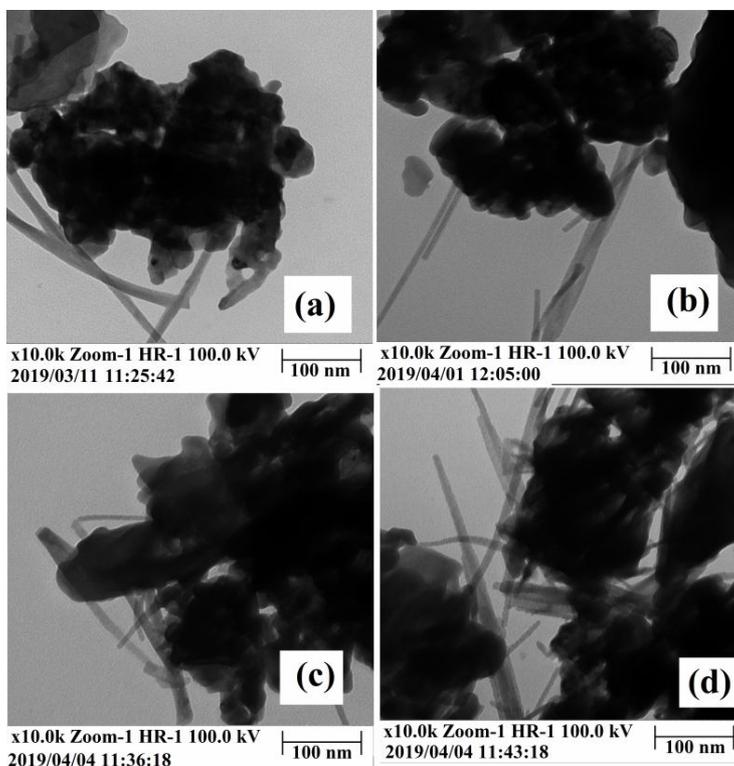


Fig. 4. TEM images of CdO-FePO₄ CNPs with V₂O₅ as dopant ions (a) pure; (b) 0.3 mol% V₂O₅; (c) 0.6 mol% V₂O₅; (d) 0.9 mol% V₂O₅ doped CdO-FePO₄ CNPs.

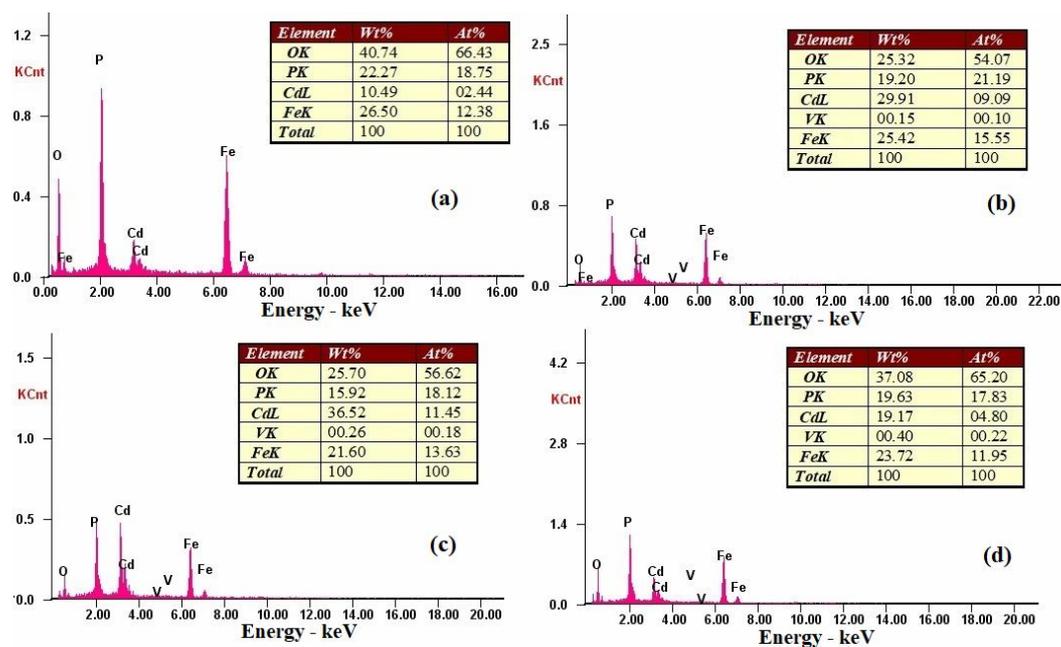


Fig. 5. EDX pattern of CdO-FePO₄ CNPs with V₂O₅ as dopant ions (a) pure; (b) 0.3 mol% V₂O₅; (c) 0.6 mol% V₂O₅; (d) 0.9 mol% V₂O₅ doped CdO-FePO₄ CNPs.

(Fig. 6) representing the estimated particle size distributions related to the measured diameters and measured widths of respective spheres and rods for all CdO-FePO₄ CNPs. The log normal distribution fit represented as a solid line in these figures corresponds to the value of the mean particle size of all CdOFePO₄ CNPs.

The as-obtained values of particle size of CdOFePO₄ CNPs from TEM images are deliberate in Table 2. From the complete TEM analysis, it is been practical that the morphology gets modified with more rods-like structures, and also the trend of increase in particle size as evidenced from XRD for higher concentrations of V₂O₅ is followed in TEM analysis.

The crystallite sizes of CdOFePO₄ CNPs with V₂O₅ as dopant ions as obtained from XRD analysis methods and TEM are given in Table 3. From the obtained results, it was noticed that the calculated size of crystallite by employing

Table 2. Average Particle Size Obtained from TEM Images of CdO-FePO₄ CNPs with V₂O₅ as Dopant Ion

Sample code	Average particle size (nm)
V ₀	23.49
V ₁	21.86
V ₂	25.79
V ₃	28.12

all these techniques is increased with increasing doping concentration. The crystallite size calculated by employing Debye-Scherrer's formula and W-H plot method is well fitted for the prepared CNPs when compared to the crystallite size estimated from TEM studies.

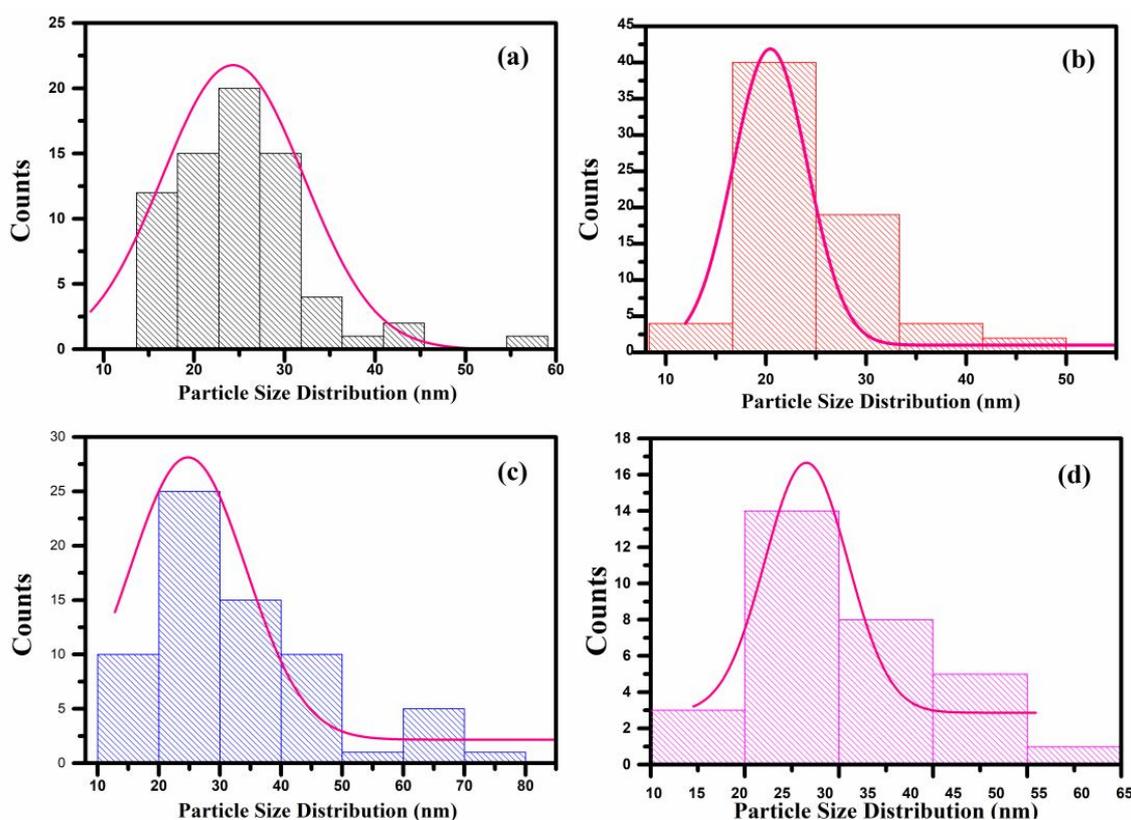


Fig. 6. Particle size distribution (nm) in CdO-FePO₄ CNPs with V₂O₅ as dopant ions (a) pure; (b) 0.3 mol% V₂O₅; (c) 0.6 mol% V₂O₅; (d) 0.9 mol% V₂O₅ doped CdO-FePO₄ CNPs.

Table 3. The Calculated Values of Crystallite Sizes Using XRD Methods and TEM Analysis

Sample code	Crystallite size (nm)		Particle size from TEM analysis (nm)
	Scherrer's method	W-H plot	
V ₀	20.39	21.01	23.49
V ₁	20.46	21.11	21.86
V ₂	21.92	22.78	25.79
V ₃	22.01	22.96	28.12

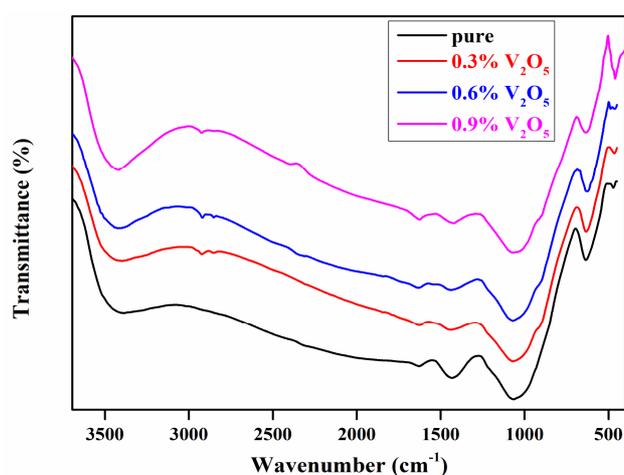
Table 4. FT-IR Vibrational Band Assignments of Pure and V₂O₅ Doped CdOFePO₄ CNPs

Pure	Wavenumber (cm ⁻¹)			Assignment
	0.3% V ₂ O ₅	0.6% V ₂ O ₅	0.9% V ₂ O ₅	
3427	3428	3426	3416	-OH stretching
-	2922	2922	2920	-CH stretching
1631	1629	1624	1624	-OH bending
1431	1437	1437	1423	-CH ₂ bending
1062	1062	1069	1057	Anti-symmetric stretching of PO ₄ ³⁻
-	885	887	886	Stretching mode of V-O-V
634	633	631	637	Symmetric P-O stretching
470	467	464	460	Metallic bonding of CdO

FT-IR Analysis

The functional groups and chemical bonding in pure and V₂O₅ doped CdO-FePO₄ CNPs are determined from FT-IR spectra shown in Fig. 7. The FT-IR spectrum exhibits a broad band at 3427 cm⁻¹ and a small band at 1630 cm⁻¹ due to stretching and bending vibrations of the O-H group linked chemically with CdO [37,38]. The OH/H₂O functional group present in the system may be due to atmospheric water vapors. The transmittance peak at 2920 cm⁻¹ can be linked to C-H anti-symmetric vibration [39]. The bands observed at 1062 cm⁻¹ and 634 cm⁻¹ can be attributed to asymmetric stretching of PO₄³⁻ ions and symmetric stretching of the P-O-P bridge [38,40]. The small bump observed at 885 cm⁻¹ in IR spectra of V₂O₅ doped CdOFePO₄ CNPs corresponds to the stretching mode of V-O-V [41]. A peak at 470cm⁻¹ refers to the formation of Cd-O bonds [39]. The slight shift of most of the bands towards smaller wavenumber due to the incorporation of dopant is evidence of the physical interactions between CdO/FePO₄/V₂O₅ nanostructures. Table 4 gives a short-list

for tentative assignments of recognized band positions in FT-IR spectra of pure and V₂O₅ doped CdOFePO₄ CNPs.

**Fig. 7.** FT-IR spectra of CdO-FePO₄ CNPs with V₂O₅ as dopant ions.

CONCLUSIONS

CdO-FePO₄ CNPs with V₂O₅ as dopant ions are synthesized by a novel sol-gel route and are characterized by powder XRD and TEM. Powder XRD revealed that prepared samples belong to the cubic phase of CdO with crystalline nature in nano-dimension. The line broadening in diffraction peaks of CdOFePO₄ CNPs caused due to the lattice strain and small crystallite size are analyzed using Scherrer's formula, a graphical way of W-H analysis. The TEM image of prepared CNPs exhibited spherical and rod-like agglomerated structures with average particle sizes that are in good agreement with the results of Scherrer's and W-H methods. Apart from TEM imaging, XRD analysis still holds a dominant position in particle-size determination. FT-IR analysis confirms the presence of fundamental modes of host lattice and dopant ions.

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