SPECTROSCOPIC STUDIES OF SOL-GEL SYNTHESIZED CdOFePO₄ COMPOSITE NANOPOWDER

SK. Khaja Muswareen and Sandhya Cole*

Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar,
Guntur - 522510, A.P., India.

*E-mail: sandhya.cole@gmail.com

ABSTRACT

CdOFePO₄ composite nanopowder (CNP) successfully prepared by the sol-gel method has been investigated by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray diffraction (EDS), Fourier transforms infrared (FT-IR) spectroscopy, Diffused reflectance spectroscopy (DRS). The XRD analysis confirmed the purity of the as-prepared CdOFePO₄ CNP and reveals the cubic crystal structure of CdO and amorphous structure of FePO₄ in the prepared sample. The lattice cell parameters are also evaluated for the cubic phase of CdO. The ϵ and δ values for the synthesized CdOFePO₄ CNP are also calculated from XRD data. The morphology of the CdOFePO₄ CNP is evidenced as combined spherical agglomerations and rods as analyzed with SEM image and the Cd, Fe, P and O stoichiometry is revealed through EDS analysis. FT-IR spectra explored the existence of functional groups like PO₄³⁻, chemical bonding and other fundamental modes of the host lattice. The application of the Kubelka-Munk function on obtained reflectance spectra resulted in the value of the optical bandgap energy of the prepared CNP for its probable usage as a semiconductor.

Keywords: Composite Nanopowder, XRD, SEM, FTIR, Diffused Reflectance Spectroscopy.

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INTRODUCTION

In recent times nanoparticles have attracted enormous interest due to their unique physical and chemical properties, which differ from those of either the single atoms or bulk materials.¹ Also, crystalline metal oxide nanomaterials are of a crucial point of research due to their part in diverse technological applications.² Among transition metal oxides, cadmium oxide (CdO) is focussed by researchers due to its applications in many areas of research such as in electro-optical and other applications, including gas sensors, photodiodes, phototransistors, solar cells, transparent electrodes.¹ Recently it has been revealed that phosphate materials can build novel stable complex oxide structures that allow safer design and performance of large scale storage batteries due to their lower cost, stability, safety, and low toxicity.³ Iron phosphate (FePO₄) is broadly used in many fields such as ferroelectrics, wastewater purification systems, steel and glass industries and in recent times been proposed as the cathode in rechargeable batteries and also a good catalyst for selective oxidation reactions.⁴ In particular, FePO₄ is used as a cathode and an anode or as the precursor for the phosphate-based anode in the field of rechargeable batteries.⁵ Some researchers have afforded doping of CdO with metals such as Ni, Al, Fe, etc via sol-gel calcinations, solid-state reaction methods and sol-gel spin coating.² However, there are few reports on CdO/phosphate-based materials prepared by chemical precipitation method but no former report exists on the synthesis of CdOFePO₄ CNP by the sol-gel method. The present study focuses on the synthesis of CdOFePO₄ CNP by sol-gel method and the spectroscopic investigations viz., powder XRD, SEM with EDS, FT-IR are done for the prepared CNP.

Various mechanical (or) chemical-based methods can be worn to synthesize nanomaterials such as acidification method, chemical co-precipitation method, hydrothermal method, and sol-gel etc., out of these, sol-gel is an economical, low temperature and research familiarized technique. This method offers good control of stoichiometry upon producing high purity ultrafine particles with enhanced compositional homogeneity within quite short processing time at low temperatures⁶.

EXPERIMENTAL

Materials and Methods

CdO, FePO_4 of 99% Analar Grade purity are used as precursors. The stoichiometric precursors viz., CdO and FePO_4 are then dissolved in 240 ml of ethanol-deionized water matrix and are let for continuous stirring for 8hrs at room temperature utilizing a magnetic-stirrer. During this process, an equivalent molar amount of NaOH is added to the over solution to obtain an aqueous solution. The solution thus turns to yellowish-brown which is indicative of the formation of CdOFePO_4 CNP. The precipitates got separated via centrifugation are annealed at 200°C to get CdOFePO_4 CNP. The schematic diagram of the sol-gel route employed in the present work is shown in Fig.-1.

Fig.-1: Schematic Diagram of sol-gel Method

Materials Characterization

The CdOFePO_4 CNP is examined by using various devices. Philips: PW 1830 X-ray diffractometer with Cu $K\alpha$ radiation wavelength ($1.5406 \text{ \AA}$) and 2 degrees/min scanning speed is used for recording the XRD pattern of CdOFePO_4 CNP in the scanning range of 10° - 80° (2θ). Scanning electron microscope: S-3400 model having 10 kV accelerating voltage is used to analyze the surface morphology of synthesized CNP and to attain EDS pattern for chemical composition analyses. The diverse vibrational modes of CdOFePO_4 CNP mixed with KBr are obtained from FT-IR spectra recorded with Spectrum1: Perkin Elmer FT-IR spectrometer in the wavenumber range 4000 - 400 cm^{-1} (viz., middle IR region). The diffused reflectance spectroscopy is carried out with UV/VIS/NIR Lambda 900 spectrophotometer in the 200 - 900 nm wavelength region and by applying the Kubelka-Munk function to the resultant spectra the optical energy band gap can be estimated. All characterizations are performed at room temperature.

RESULTS AND DISCUSSION

Powder XRD

Powder XRD pattern of CdOFePO_4 CNP prepared by the sol-gel route is shown in Fig.-2. The broadening of lines in the XRD pattern specifies the existence of the nanometre regime. The sharp diffraction peaks observed at 2θ values corresponding to the diffraction planes are in fine agreement with the cubic structure of CdO phase with standard JCPDS #05-0640. The peaks corresponding to FePO_4 are not detected since FePO_4 is possibly amorphous at the preferred annealing temperature i.e., 200°C and CdO is the predominant phase. The diffraction peaks corresponding to CdO along with their respective (h k l) lattice planes are given in Table-1. The evaluated values of cell parameters, Unit cell volume and Axes of symmetry of CdOFePO_4 CNP are tabulated in Table-2.

There are many methods to calculate the values of average crystallite size and lattice strain from the XRD data such as Scherrer method, W-H (Williamson-Hall) method, Reitveld refinement, etc. In the present work, the Scherrer method is employed which is most simple and commonly used.

Table-1: The Diffraction Peaks with their Respective (h k l) Lattice Plane Corresponding to CdO.

Peak No	Peak Position (2θ in Degrees)	Lattice Planes (h k l)
1	33.01	111
2	38.38	200
3	55.34	220
4	65.93	311
5	69.38	222

Fig.-2: XRD Pattern of CdOFePO₄ Composite NanopowderTable-2: Lattice Cell Parameters, Unit Cell Volume and Axes of Symmetry of CdOFePO₄ Composite Nanopowder.

CdO		
Lattice Cell Parameters (Å°)	Unit Cell Volume V (Å°) ³	Axes of Symmetry α=β=γ
a=b=c		
4.691	103.210	90°

The well-known Debye-Scherrer's formula to determine average crystallite size (t) of the prepared CNP is expressed as:^{8,9}

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

The Stokes-Wilson equation to calculate induced lattice strain is given by:¹⁰

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

Where, λ is the wavelength of X-Ray (1.5406 Å), β is full width at half maximum (FWHM) in radians of diffracted peak and θ is Bragg's diffraction angle.

The Williamson-Smallman relation¹¹ used to calculate dislocation density (δ) is certain by,

$$\delta = 1/D^2$$

Here, D is the average crystallite size.

The calculated values of t, ε and δ for CdOFePO₄ CNP along with the value of crystalline degree are given in Table-3. It is to be noted here that if the value of t increases ε viz., induced strain in the sample reduces.

SEM and EDS Study

The complete surface data of prepared nanocomposite comprising information regarding topographical, morphological and compositional data is offered with a high-resolution microscope i.e., SEM. The surface morphological image of prepared CdOFePO₄ CNP is shown in Fig.-3. This image reveals that the synthesized CNP show spherical like agglomerations with some rod-like structures. The variation between average crystallite size calculated from XRD data and observed grain size in SEM image might be due to the aggregation behavior of the nanocrystallites that form domains.¹²

Table-3: Average Crystallite Size, Strain, Dislocation Density and Crystalline Degree of CdOFePO₄ Composite Nanopowder.

Position (2θ)	FWHM (β)	Crystallite size (t) (nm)	Lattice Strain [(ε)×10 ⁻⁴]	Dislocation Density (δ) (lines/m ²)	Crystalline Degree
33.02	0.4019	20.39	59.13	2.40×10 ¹⁵	31.27

Fig.-3: SEM Image of CdOFePO₄ Composite Nanopowder

The specific composition of CdOFePO₄ CNP is firm from the EDS study that reveals the existence of elementary components viz., Cd, Fe, P and O. The corresponding EDS pattern of SEM image of CdOFePO₄ nanocomposite is shown in Fig.-4. The inset of Fig.-4 thereby presents the obtained stoichiometric values of elements Cd, Fe, P, and O in the form of a table. It is noticed that these values concur with the values of starting stoichiometry.

Fig.-4: EDS Pattern of CdOFePO₄ Composite Nanopowder

FT-IR

FT-IR spectra of CdOFePO₄ nanocomposite recorded in the middle infrared (IR) region of 4000 to 400 cm⁻¹ at room temperature is given away in Fig.-5, which confirms the synchronization environments of CdO and FePO₄ groups. In the IR spectral region of 700–400 cm⁻¹, the transmittance bands eminent at around 467 cm⁻¹ (weak peak) and 628 cm⁻¹ (strong peak) are considered to contribute to the characteristic metallic bonding of CdO¹³. The strong band noted at 1058 cm⁻¹ could be owing to anti-symmetric stretching of PO₄³⁻ group⁶. The peak at 1431 cm⁻¹ is ascribed to the C-H related impurities viz., bending vibrational mode of CH₂ molecules¹⁴ that may be originated from starting materials. The broad peak in the higher region at around 3424 cm⁻¹ and a small peak at 1631 cm⁻¹ could have resulted due to superposition of stretching vibrations of water molecules that are adsorbed and the vibrational modes of hydroxyl groups i.e., bending and stretching vibrational modes of hydroxyl groups¹⁵⁻¹⁸. Thus, the local environmental structures of CdOFePO₄ CNP are familiar with IR spectra. Various detected peak positions in IR spectra of CdOFePO₄ CNP and their subsequent characteristic assignments are given in Table-4.

Fig.-5: FT-IR Spectra of CdOFePO₄ Composite NanopowderTable-4: Peak Positions and Corresponding Assignments in Spectrum of CdOFePO₄ Composite Nanopowder

Wave number (cm ⁻¹)	Assignment
3424	-OH stretching
1631	-OH bending
1431	-CH ₂ bending
1062	Anti-symmetric stretching of PO ₄ group
634	Symmetric P-O stretching
470	Metallic bonding of CdO

Optical Studies

Since the accurate assessment of optical bandgap energies of semiconductor CNPs is difficult via UV-Vis absorption spectroscopy. Therefore, to obtain the optical energy bandgap value of CdOFePO₄ CNP, UV-Vis spectroscopy in the reflectance mode i.e., diffused reflectance spectroscopy is employed in the present investigation using the Kubelka-Munk equation:¹⁹⁻²³

$$F(R) = \frac{(1 - R)^2}{2R}$$

Upon rewriting the above equation with the equation relating band gap (E_g):

$$(\alpha h\nu) = F(R)h\nu = A(h\nu - E_g)^n$$

Here, $F(R)$ is a K-M function, $h\nu$ is photon energy incident on a sample, A is transition probability depended constant, $n = 1/2$ or 2 corresponds to respective direct or indirect allowed transitions, thus giving direct and indirect band gaps). Therefore a plot amongst $(F(R)h\nu)^2$ versus energy ($h\nu$) determines the energy bandgap of synthesized CNP upon extrapolating a straight line to $(F(R)h\nu)^2 = 0$. The spectra determining the optical energy bandgap of the prepared CNP is shown in Fig.-6. The optical energy bandgap value as observed from Fig.-6 is 1.96eV indicating that the synthesized CNP act as a semiconductor.

Fig.-6: Optical Energy Band Gap Spectra of CdOFePO₄ Composite Nanopowder

CONCLUSION

CdOFePO₄ nanocomposite is prepared by the sol-gel route. XRD analysis reveals that the prepared CNP is in nanoscale. EDS spectral analysis confirms that the observed weight percentages of Cd, Fe, P and O agreed well with their initial amounts. From IR spectra, the existence of phosphate (PO₄³⁻) groups and Cd-O bands demonstrate the formation of CdOFePO₄ CNP. The 1.97eV optical energy bandgap obtained from UV-Vis diffused reflectance analysis results indicates that the CdOFePO₄ CNP act as a semiconductor.

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