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Research Article

SPECTROSCOPIC PROPERTIES OF Fe^{3+} DOPED PVA CAPPED CdSe NANOPOLYMER

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ABSTRACT

In the present study, Fe^{3+} doped PVA capped CdSe nanopolymer has been synthesized by wet chemical method. Different spectroscopic techniques were used to understand the influence of Fe^{3+} ions on the structural, optical and luminescent properties of the nanopolymer. XRD pattern reveals the zinc blended cubic structure of CdSe and the average crystallite sizes is found to be 6 nm. The optical absorption spectrum exhibited the characteristic bands. Crystal field and Racah parameters were evaluated as Dq = 970, B = 950 and C = 3800 cm^{-1}. EPR spectrum exhibited two resonance signals at g = 2.02 and 4.31. Optical and EPR studies reveal the distorted octahedral site symmetry and moderately covalent bonding between the Fe^{3+} ions with the host lattice. PL spectrum shows the blue emission. FT-IR spectrum exhibited the characteristic bands of PVA in CdSe polymer and other functional groups.

INTRODUCTION

Development of nano-materials based photo electrochemical devices could potentially lead to inexpensive energy sources with enhanced power-conversion efficiency [1]. CdSe is one of the most important II-VI semiconductor material with a tunable bandgap of 1.74 eV, which has interesting optical, electrical and optoelectronic properties via quantum confinement in nanocrystals [2, 3] there by being a promising candidate for the potential applications in various fields such as optoelectronics, biosensors, laser diode, solar cells, biomedical labelling and so forth [4]. Moreover, CdSe has earned pronounced attention for its device grade properties like excellent optical conductivity, such as non-linear optical properties, luminescent properties and quantum size effect. Therefore, CdSe is suitable for many practical applications including catalysis [5], photovoltaic devices [6] in photo-electrochemical solar cells [7], light-emitting diodes [8], and electro-luminescent devices [9]. Different methods have been used for the preparation of CdSe such as wet chemical [10], microwave [11], sonochemical [12] sol-gel [13], solvothermal [14], cathodic-electro deposition [15] chemical bath deposition method [16], thermal evaporation technique [17], electrochemical deposition [18] and also hydrothermal treatment [19]. The work in order to synthesize better quality and high yield nanostructured materials of CdSe is still on-going.

A series of morphologies such as nanodots [17], nanorods [20], nanowires and branched structures [16] of CdSe have been synthesized by these methods. Dai *et al*. [21] have reported the synthesis of CdSe nanowires by thermal evaporation and the excellent optical waveguide property of the CdSe nanowires. Sharma *et al*. [22] have reported that CdSe nanorods grown within polyvinyl alcohol (PVA) show green emission properties and good photo stability. Zhao *et al*. [23] have found that CdSe nano-tetrapods with different arm lengths have significant influence on FE performance. Li *et al*. [24] have reported that the excellent FE properties are related to the unique morphology of CdSe. Therefore, the morphology and size of CdSe have significant influence on their optical properties and FE performance.

Doping with specific ions is a normal way of obtaining new physical properties or improving properties of a given undoped matrix. The effect of specific impurity on electrical conductivity depends on the substitution site so that the trivalent ion like Fe^{3+} behaves as an acceptor when substitution occurs at the site or as a donor when it substitutes for the site. The analysis of optical absorption spectra of iron is more complicated than the other transition metal ions. The optical absorption spectra can often be assigned to electronic transitions between well-defined electronic energy levels in transition metal ions. These transitions are characteristic of

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cation, its valance state and nature of its environment. EPR spectroscopy enables to identify the oxidation and spin states of the metal as well as its bonding site and symmetry. Thus, optical absorption study is complementary to EPR technique. Therefore, site symmetry and the dynamic behaviour of metal ion in the host lattice can be investigated using EPR and optical absorption studies. The considerable attention has also been devoted to the possibility of tailoring the optical and electrical properties of CdSe by using donor impurity. A large number of interesting studies are available on the environment of iron ions in various inorganic materials [25-27]. These ions exist in different coordinations in host matrices with respect to their valence states [28]. It is expected that Fe^{3+} influences the luminescence of the materials to a large extent. The present study describes the synthesis and characterization of Fe^{3+} doped PVA capped CdSe nanopolymer prepared by wet chemical route. Further, as prepared nanopolymer was characterized by different spectroscopic techniques such as XRD, optical absorption, EPR, PL and FT-IR spectroscopy.

Experimental Details

Materials

Cadmium Chloride ($CdCl_2.2H_2O$), Poly Vinyl Alcohol (PVA), Sodium Hydrogen Selenide (NaHSe) and Iron Chloride ($FeCl_3$) were used as starting materials without further purification. All the chemicals used were of analytical grade. Double distilled water was used as a solvent in the experiment.

Synthesis of Fe^{3+} doped PVA capped CdSe nanopolymer

Cadmium Chloride ($CdCl_2$. $2H_2O$), 50 mM was added to 2.2 g PVA (13,000 g/mol) and the volume of solution was completed to 50 mL by bi-distilled water. The completed solution was left for 24 hours at room temperature to swell. Then the solution was warmed up to 60 ^{0}C and stirred magnetically until viscous transparent solution was obtained. One millilitre of NaHSe (50 mM) was added to the solution to obtain red transparent solution and then 0.01 mol% $FeCl_3$ solutions was added to above solution with continuous stirring. The solution was casted on flat glass plate dishes. After the solvent evaporation, a thin film containing Fe^{3+} doped PVA capped CdSe nanopolymer was obtained. The film was washed several times with deionized water to remove other insoluble salts before measurements. The synthesized nanopolymers were further used for the characterisations.

Characterizations

X-ray diffraction pattern of the sample was recorded using Shimadzu XRD 6100 X-ray diffractometer. The optical absorption spectrum is recorded using JASCO V-670 Spectrophotometer in the range from 200-1400 nm. Photoluminescence spectrum is recorded at room temperature on Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450W) and pulsed (35W) lamps as excitation sources. EPR spectrum is recorded at room temperature on JES-FA series EPR Spectrometer operating at X–band microwave frequency. FT-IR spectrum was recorded on Shimadzu IR Affinity-1S FT-IR Spectrophotometer in the region from 650-4000 cm^{-1}.

RESULTS AND DISCUSSION

X-ray Diffraction Studies

X-ray diffraction patterns of Fe^{3+} doped PVA capped CdSe nanopolymer is shown in Fig. 1. An intense peak observed at a scattering angle around 19.5^o which corresponds to PVA [29]. The crystalline nature of PVA results from the strong intermolecular interaction between PVA through intermolecular hydrogen bonding. The other diffraction peaks of Fe^{3+} doped CdSe nanopolymer observed at $2\theta \sim 41.79^o$, 50.21° corresponds to (2 2 0) and (3 1 1) planes of zinc blended cubic structure, which is well consistent with the standard JCPDS data, 65-2891. Average crystallite size of Fe^{3+} doped CdSe nanopolymer is evaluated using Scherrer's formula,

$$\mathbf{D = 0.9\, \lambda / \beta \, Cos\theta}$$

Where λ is the wavelength of X-ray CuKα radiation (1.5406 A^o), β is the full width at half maximum (FWHM) and θ is the diffraction angle. Based on the FWHM, the average crystallite size is estimated to be 6 nm. The micro-strain is also evaluated using the following relation and it is found to be 5.097×10^{-3}.

$$\mathbf{\varepsilon = \beta \, Cos\theta / 4}$$

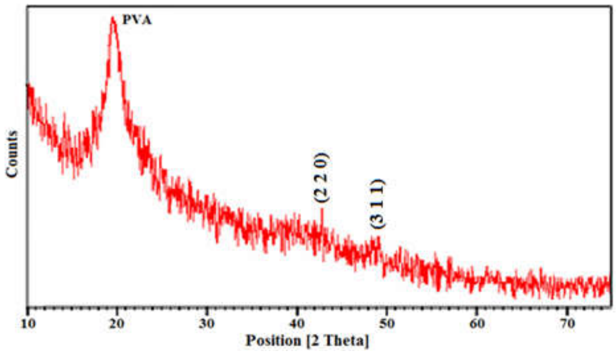

Fig 1 X-ray diffraction pattern of Fe^{3+} doped PVA capped CdSe nanopolymer

Optical Absorption Study

Fig. 2 predicts the optical absorption spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer at room temperature. The spectrum shows the characteristic bands of Fe^{3+} ions in octahedral site symmetry. The absorption spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer, the spectrum shows four bands corresponding to d^5 high spin Fe^{3+} cations. The bands at 599 (16690 cm^{-1}), 467 (21407 cm^{-1}), 414 (24148 cm^{-1}) and 347 nm (28810 cm^{-1}) were assigned to the transitions $^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$, $^4T_{2g}(G)$, $^4A_{1g}(G) + {}^4E_g(G)$ and $^4E_g(D)$ respectively. The assignment of these bands is given in Table 1. The values of crystal field (Dq) and Racah parameters (B and C) with the Tree's correction factor ($\alpha = 90$ cm^{-1}) for the Fe^{3+} cation are calculated as 875, 835 and 2810 cm^{-1} respectively. From the optical absorption spectrum it is concluded that the site symmetry for Fe^{3+} ion in frame work is identified as distorted octahedral.

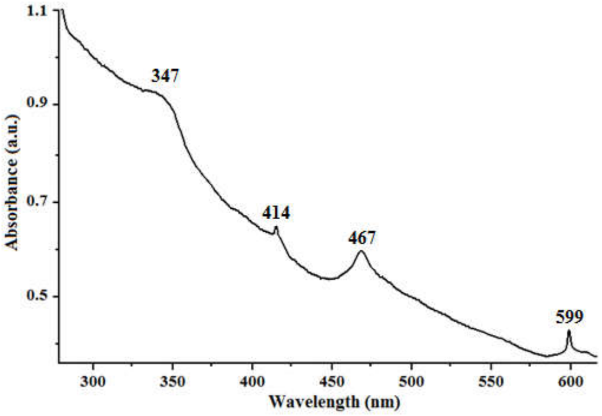

Fig. 2 Optical absorption spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer

Table 1 Band head data of Fe^{3+} doped PVA capped CdSe nanopolymers

Transition From	Band position		
$^6A_{1g}(S) \rightarrow$	Wavelength nm	Wave number (cm^{-1}) observed	calculated
$^4T_{1g}(G)$	599	16690	16704
$^4T_{2g}(G)$	467	21407	21412
$^4A_{1g}(G) + {}^4E_g(G)$	414	24148	24183
$^4E_g(D)$	347	28810	28817

Electron Paramagnetic Resonance (EPR) Study

Fig. 3 depicts the EPR spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer at room temperature. Fe^{3+} has five unpaired electrons in weak crystal fields, with a high-spin state ($^6S_{5/2}$). Since Fe^{3+} belongs to d^5 configuration with ^6S ground state in free ion and there is no spin-orbit interaction, g value is expected to lie very near to free ion value of 2.0023 [30]. In perfect T_d or O_h, i.e. cubic ligand fields, only one signal appears at g = 2.0 in the X-band frequency. However g value very much greater than 2.0 often occurs, in particular an isotropic at g = 4.2, due to the presence of certain symmetry elements. In the case of d^5 transition metal ions, it is known that axial distortion of octahedral symmetry gives rise to the three Kramer's doublets [31]. The resonance signal at g = 4.3 is often associated with low-symmetry rhombic sites of either tetrahedral or octahedral coordination. However, g = 2.0 resonance is associated with both axially; distorted sites and spin–spin interactions.

In the present study, the EPR spectrum exhibited a strong resonance signal at g = 2.02 corresponding to and another poorly resolved signal at g = 4.31. The g values for the observed resonances indicate the presence of Fe^{3+} ions and the observed phenomenon has been attributed to the high spin Fe^{3+}. The similar results observed in the previous literature [32]. From these results, the site symmetry of Fe^{3+} ions in the host lattice is identified as octahedral which also confirms the same from the optical absorption studies. The bonding between the doped metal ions and its ligands is covalent in nature.

Photoluminescence Studies

Photoluminescence spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer exhibited various bands in visible region under the excitation wavelength of 370 nm. Fig. 4 shows the PL spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer, the spectrum shows two emission bands at green (517 nm) and red (641 nm) regions. The shoulder peak at 517 nm is due to surface defects related to Cd vacancies or interstitials. The low intense red emission band at 641 nm is attributed to crystalline defects induced during growth.

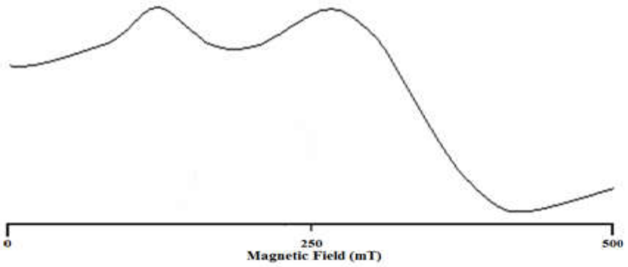

Fig 3 EPR spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer

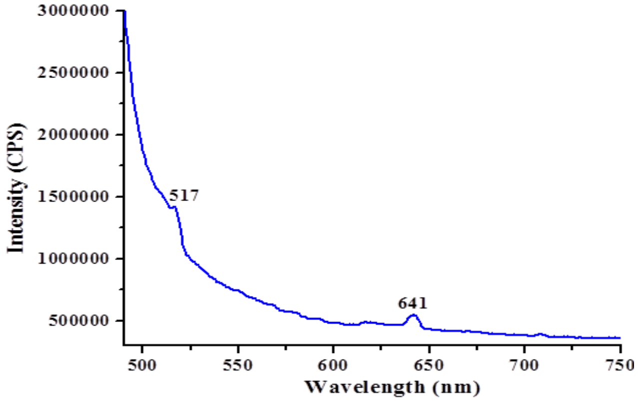

Fig 4 PL spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer

CIE chromaticity coordinates are evaluated using the PL data. The 1931 CIE chromaticity diagram of Fe^{3+} doped PVA capped CdSe nanopolymer is shown in Fig. 5. The CIE diagram shows blue emission for Fe^{3+} doped CdSe nanopolymer. The evaluated CIE coordinates of Fe^{3+}doped PVA capped CdSe nanopolymer are (x = 0.191, y = 0.201).

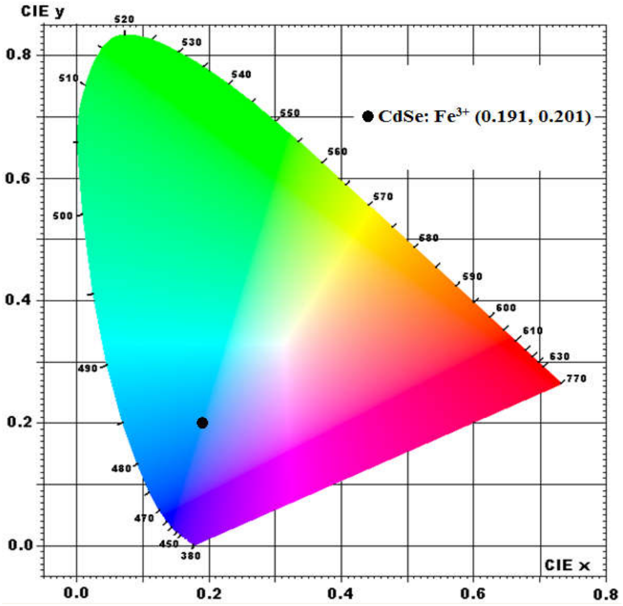

Fig 5 CIE chromaticity diagram of Fe^{3+} doped PVA capped CdSe nanopolymer

FT-IR Studies

FT-IR spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer is shown in Fig. 6. The spectrum exhibits various molecular vibrational bands corresponding to PVA, CdSe and other functional groups. The band observed at 3308 cm^{-1} is attributed to ν (OH) stretching vibrations, indicates the presence of hydroxyl groups [33, 34]. Asymmetrical and symmetrical stretching vibrations of $–CH_2–$ occur at 2920 and 2855 cm ^{1} respectively [35]. The band at 2320 cm^{-1} is due to the C=O stretching mode arising from the absorption of atmospheric CO_2 on the surface of the polymer [36]. The bands at 1726 and 1651 cm^{-1} are attributed to C=O, C=C stretching modes respectively [35]. The absorption band occurring at 1426 cm^{-1} is due to bending vibrations of CH_2 groups respectively. The bands at 1245 cm^{-1} corresponds to C-O stretching of acetyl groups present on the PVA backbone. The bands at 1082 cm^{-1} are assigned to ν (C–O) stretching vibration [37]. The bands observed at 1027 cm^{-1} is assigned to C-O stretching and O-H bending vibrations. A band observed at 941 cm^{-1} is assigned to C–C stretching vibration [38]. The band at 838 cm^{-1} corresponds to stretching vibration of C-C group.

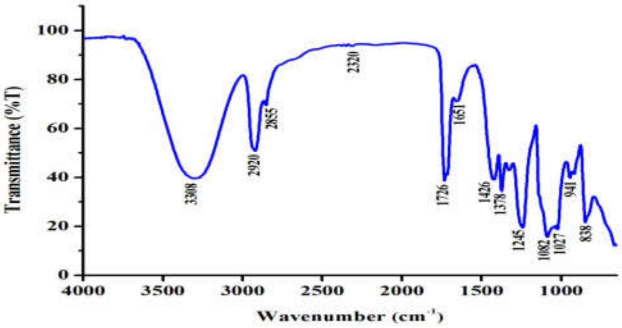

Fig 6 FT-IR spectrum of Fe^{3+} doped PVA capped CdSe nanopolymer

CONCLUSIONS

In summary, wet chemical method is used for the synthesis of Fe^{3+} doped PVA capped CdSe nanopolymer. The nanopolymer was further characterized by different spectroscopic techniques for the better understanding of the influence of Fe^{3+} ions on the structural, optical and luminescent properties of the nanopolymer. XRD pattern reveals the zinc blended cubic structure of CdSe and the average crystallite sizes is found to be 6 nm. The characteristic bands were observed in the optical absorption spectrum. Crystal field and Racah parameters were evaluated as Dq = 970, B = 950 and C = 3800 cm^{-1}. EPR spectrum exhibited two resonance signals at g = 2.02 and 4.31. By correlating optical and EPR studies, the coordination geometry and bonding nature of doped Fe^{3+} ions with the host lattice are distorted octahedral and moderately covalent respectively. PL spectrum and the corresponding CIE chromaticity diagram shows blue emission for the prepared sample. FT-IR spectrum exhibited the characteristic bands of PVA in CdSe nanopolymer and other functional groups.

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