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Investigation On Spectroscopic Properties Of Co^{2+} Doped CdSe Nanopolymer.

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ABSTARCT

Co^{2+} doped CdSenanopolymer was prepared by using poly vinyl alcohol (PVA). The prepared samples were characterized by X-ray diffraction, optical absorption, Photoluminescence, EPR and FT-IR studies. XRD pattern reveals the cubic zinc blende crystalline phase of CdSe and the average size is in the order of nano range. Optical absorption spectrum exhibited characteristic features of Co^{2+} in distorted octahedral symmetry. EPR spectrum exhibited two resonance signals at $g = 4.29$ and 2.01 . Photoluminescence spectrum exhibited four characteristic bands centred at 420, 448, 479 and 525 nm and corresponding CIE chromaticity coordinates are calculated. FT-IR spectrum exhibits the fundamental mode vibrations of PVA in CdSe.

Keywords: Nanopolymers, CdSe-PVA, EPR, PL and FT-IR

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INTRODUCTION

The development of nano-structured polymer-semiconductor hybrid materials has evolved into an important research area of nano-science and nanotechnology [1-3]. These nanocomposites combine advantageous properties of polymers with size-tunable optical, electronic, catalytic, and other properties of semiconductor nanoparticles. Generally, the role of the polymers is to encapsulate the nanoparticles and enable better exploitation of their characteristic properties. However, polymers cannot solely be regarded as good host materials, as they can also be used to modify the surface and/or to control the growth of nanoparticles. Surface modification could be of great importance for possible use of semiconductor nanoparticles in biomedical applications and diagnostics [4]. Semiconductor nanocrystals with physical dimensions smaller than the exciton Bohr radius exhibit novel electronic, optical, chemical, magnetic and mechanical properties, which cannot be obtained from their bulk counter parts [5-6]. Among the various semiconductors, colloidal II–VI group metal chalcogenides such as CdS, CdSe and CdTe have been studied intensively on their quantum confinement effects including size-dependent photoemission properties, due to the latest development in synthesis leading to high quality ensembles with narrow size distribution. However, CdSe have been extensively studied as a model system aiming at various applications, partly because their emitting color can be easily controlled in the visible range by changing their sizes. Spectroscopic properties of these CdSe semiconductors are well tuned with the incorporation of transition metal ions. In general, impurity occupation and coordination geometry can be investigated by means of optical absorption and electron paramagnetic resonance (EPR) studies.

Cobalt is a chemical element with symbol Co and atomic number 27. The electron configuration of cobalt is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$. The electron configuration of a neutral cobalt atom is written as $[\text{Ar}] 4s^2 3d^7$. The most common oxidation states are +2, +3. The compounds in which cobalt exhibits the +2 oxidation state (Co^{2+} , the ion being stable in water) are called cobaltous, while those in which cobalt exhibits the +3 oxidation state (Co^{3+}) are termed cobaltic. Both Co^{2+} and Co^{3+} form numerous coordination compounds, or complexes. The coordination number of the complexes is generally six. In octahedral coordination, the ionic radius of Co^{2+} (0.72 Å) is smaller than that of Cd^{2+} (0.92 Å). The presence of Co^{2+} in various hosts activates luminescence emission in the UV and visible region and the spectral properties are strongly affected by the surrounding environment like symmetry, covalence, coordination and crystal-field strength. This aim of the paper to describes the synthesis and spectroscopic characterizations of Co^{2+} doped CdSenanopolymer by using XRD, optical absorption, EPR, PL and FT-IR spectroscopy.

EXPERIMENTAL PROCEDURE

Materials

AR grade chemicals of Cadmium Chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$), Poly Vinyl Alcohol (PVA), Sodium Hydrogen Selenide (NaHSe) and Cobalt Chloride (CoCl_2) are used as starting materials without further purification. Double distilled water is used as a solvent in the experiment.

Synthesis of Co^{2+} doped PVA capped CdSenanopolymer

Cadmium Chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$), 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 °C and stirred magnetically until viscous transparent solution is obtained. One millilitre of NaHSe (50mM) was added to the solution to obtain red transparent solution and then 0.01 mol% CoCl_2 solutions was added to above solution with continuous stirring. The solution is casted on flat glass plate dishes. After the solvent evaporation, a thin film containing Co^{2+} doped PVA capped CdSenanopolymer was obtained. The film was washed several times with deionised water to remove other insoluble salts before measurements. The synthesized polymers were further used for the characterizations.

Characterizations

PANalyticalX`Pert Pro-diffractometer is used for X-ray diffraction pattern of the sample. 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 IRAffinity-1S Spectrophotometer in the region from 650 - 4000 cm^{-1} .

RESULTS AND DISCUSSION

X-ray Diffraction Studies

X-ray diffraction pattern of Co^{2+} doped PVA capped CdSenanopolymer is shown in Fig. 1. An intense peak is observed at a scattering angle around 19.5° which corresponds to PVA [7]. The crystalline nature of PVA resulting from the strong intermolecular interaction between PVA is through intermolecular hydrogen bonding. The other diffraction peaks of Co^{2+} doped CdSenanopolymer are observed at $2\theta = 41.39^\circ, 49.86^\circ$ 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 and micro-strain of Co^{2+} doped CdSenanopolymer is calculated by using Scherrer's formulae, $D = 0.9 \lambda / \beta \cos\theta$ and $\epsilon = \beta \cos\theta / 4$, Where λ is the wavelength of X-ray Cu $K\alpha$ radiation (1.5406 Å), β is the full width at half maximum (FWHM) and θ is the diffraction angle. Based on the FWHM, the average crystallite size and Micro-strain are estimated to be 6 nm and 5.875×10^{-3} respectively.

Optical Absorption Studies

It is a powerful technique to explore the optical properties of semiconducting nanoparticles. Optical absorption spectrum of Co^{2+} doped PVA capped CdSenanopolymer is shown in Fig. 2. The spectrum exhibited six characteristic absorption bands of Co^{2+} ions in octahedral site symmetry.

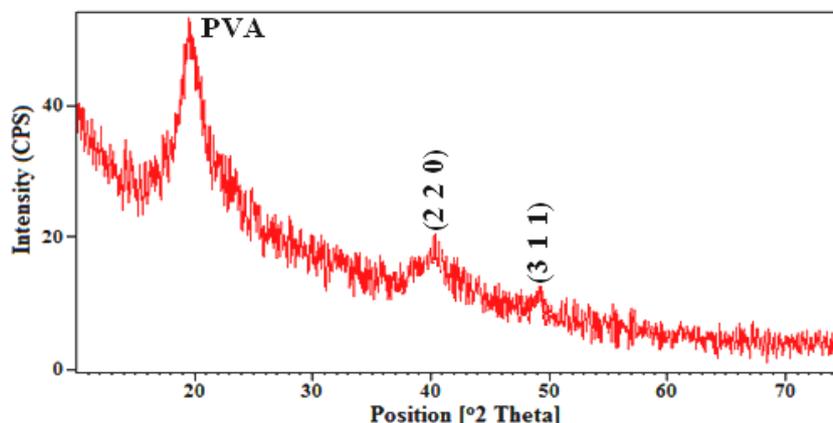


Fig 1: X-ray diffraction pattern of Co^{2+} doped PVA capped CdSenanopolymer.

Generally Co^{2+} in d^7 configuration gives rise to the free ion terms of 4F , 4P , 2G and several doublet terms, in which 4F splits into $^4T_{1g}(F)$, $^4T_{2g}(F)$ and $^4A_{2g}(F)$ whereas 4P splits into $^4T_{1g}(P)$. The doublet term 2G splits into $^2A_{1g}(G)$, $^2E_g(G)$, $^2T_{1g}(G)$ and $^2T_{2g}(G)$. Among these, the term $^4T_{1g}(F)$ being ground state for all crystal fields. Based on the T-S diagrams the absorption bands at 1198, 660, 550, 449, 415 and 370 nm are assigned as follows $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow ^2T_{2g}(H)$, $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ (ν_2), $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$, $^4T_{1g}(F) \rightarrow ^2A_{1g}(G)$ and $^4T_{1g}(F) \rightarrow ^2T_{1g}(G)$ respectively.

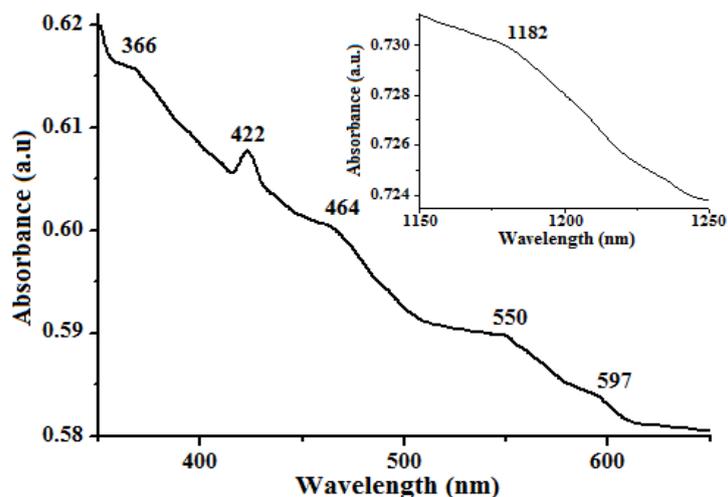


Fig 2: Optical absorption spectrum of Co²⁺ doped PVA capped CdSenanopolymer.

In O_h symmetry, theoretically the ratios of the energies of the transitions ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F): \nu_2$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F): \nu_1$ are almost invariable from 1.9 to 2.2 [8-9]. In the present study, from the band positions the ratio of ν_2 to ν_1 is found to be nearly 2.15 and this value indicated the characteristic nature of Co^{2+} ions in octahedral symmetry. The energy matrix for (d^7) configuration was solved for different sets of crystal field (Dq) and inter-electronic repulsion (B and C) parameters as $Dq = 970$ and $B = 950$, $C = 3800 \text{ cm}^{-1}$, these parameters gave a good fit with the observed band positions. The observed and calculated band head data of Co^{2+} doped CdSenanopolymer is presented in Table1.

Table 1: Band head data of Co²⁺ doped PVA capped CdSenanopolymer

Transition from ${}^4T_{1g}(F) \rightarrow$	Wavelength (nm)	Wavenumber (cm ⁻¹) observed	Wavenumber (cm ⁻¹) calculated
${}^2T_{1g}(G)$	366	27314	27322
${}^2A_{1g}(G)$	422	23690	23684
${}^4T_{1g}(P)$	464	21518	21545
${}^4A_{2g}(F)$	550	18176	18183
${}^2T_{2g}(H)$	597	16745	16773
${}^4T_{2g}(F)$	1182	8457	8484

Electron Paramagnetic Resonance (EPR) Studies

Generally the EPR spectrum of Co^{2+} is observed only at low temperatures because the spin lattice relaxation time is extremely short for octahedral coordination of Co^{2+} ions. At higher temperature, the spectrum becomes broader probably due to short relaxation time characteristic of the high spin state of Co^{2+} ions [10-11]. In exact octahedral symmetry, the d^7 configuration has an orbital triplet state the lowest of which is split by spin-orbit coupling to give a ground state Kramers' doublet with $g = 4.33$ [12]. The next excited states are only a few hundred wavenumbers higher in energy. Distortions which lower the symmetry mix these states. Therefore, the g values become anisotropic and are sensitive to variations in the crystal field [12]. In the present investigation, EPR spectrum of Co^{2+} doped CdSenanopolymer exhibit resonance signals at room temperature around $g = 4.29$ and $g = 2.01$ at 100 K as shown in Fig. 3. The value $g = 4.29$ line is attributed to Co^{2+} in octahedral symmetry and $g = 2.01$ line is due to a random distribution of distortions [13-14].

By correlating EPR and optical absorption spectral data, the covalency parameter (k_0) is evaluated by the following relation [15], $g = 3.33 + k_0 - 7.5 (\lambda/\Delta)$, Where g is the observed g -factor, λ is the spin-orbit coupling constant (-178 cm^{-1} for Co^{2+}) and Δ is the energy difference between ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$. Generally, the k_0 value lies between 0.5 and 1.0, the limits of pure covalent and pure ionic bonding respectively. The calculated k_0

value is 0.85 which indicates that the bonding between the Co^{2+} ions and the ligands is moderately covalent nature.

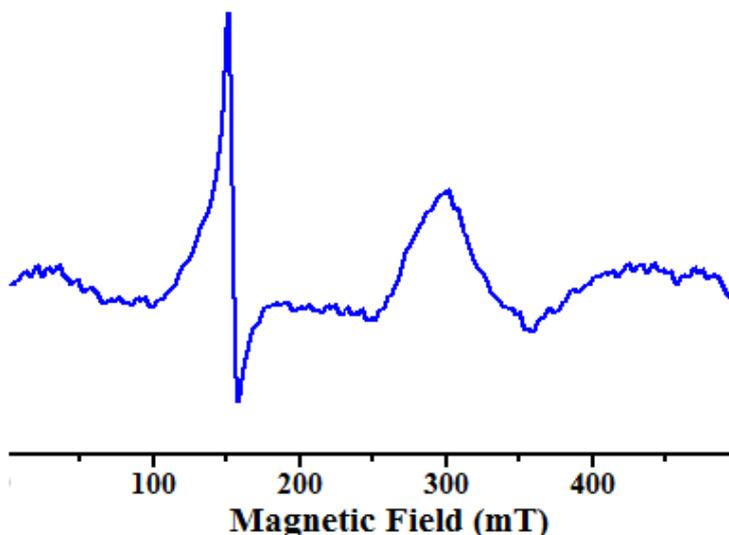


Fig 3: EPR spectrum of Co^{2+} doped PVA capped CdSenanopolymer.

Photoluminescence Studies

Photoluminescence (PL) spectrum of Co^{2+} doped PVA capped CdSenanopolymer exhibited various bands in visible region caused by the defects such as vacancies, local lattice mismatches or dangling bonds [16]. The incorporated Co^{2+} ions greatly influence the luminescence properties of the host material. As shown in Fig. 4, PL spectrum of Co^{2+} doped CdSenanopolymer exhibited four characteristic bands centred at 420, 448, 479 and 525 nm. The blue emission peaks at 420 and 448 nm are corresponding to the trap state emissions. The trap states acts as an electron hole acceptor and recombined radioactively. These trapped states thus form a series of metastable energy levels within the band gap result into a strong PL signal at room temperature. The strong peak at 479 nm is due to surface defects related to Cd vacancies or interstitials. The small peak at 525 nm may be attributed to crystalline defects induced during growth.

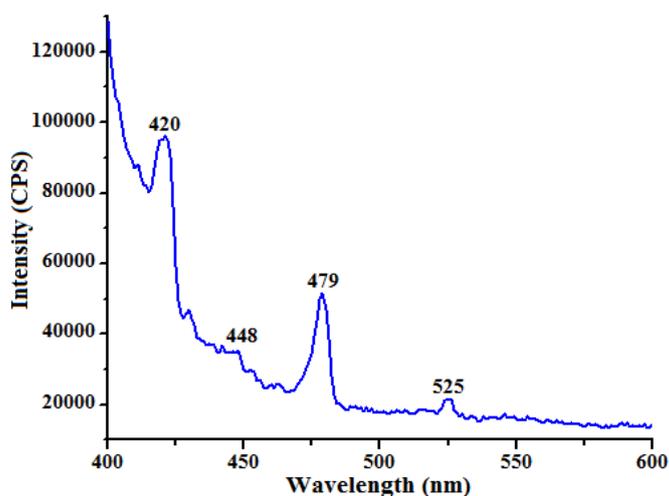


Fig 4: PL spectrum of Co^{2+} doped PVA capped CdSenanopolymer.

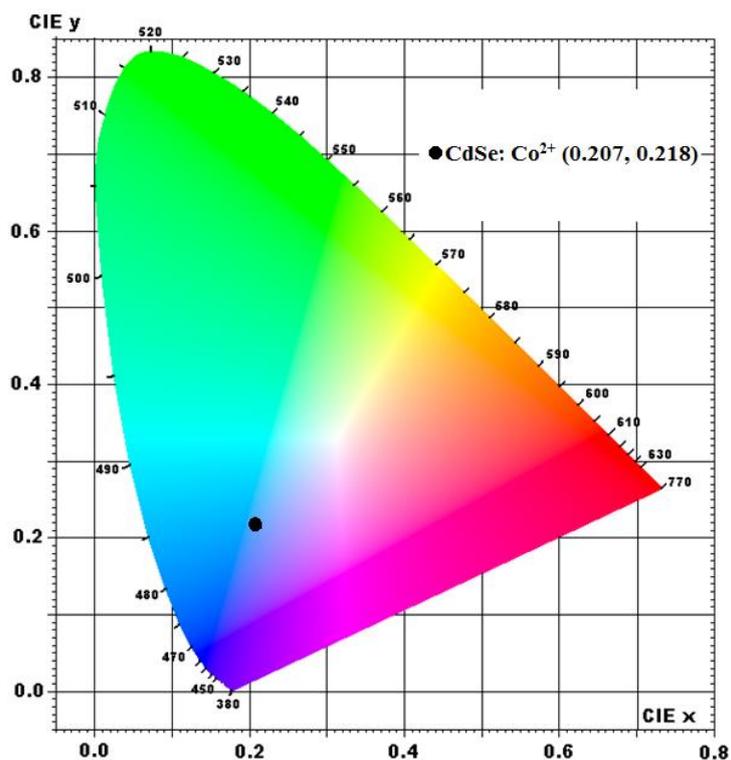


Fig 5: CIE chromaticity diagram of Co²⁺ doped PVA capped CdSenanopolymer.

CIE chromaticity coordinates are evaluated using the PL data, which reveals colour vision of the prepared samples. Fig. 5 depicts the 1931 CIE chromaticity diagram of Co²⁺ doped CdSenanopolymer. The CIE coordinates of Co²⁺ doped CdSenanopolymer are evaluated as (x = 0.207, y = 0.218) which represents the blue emission.

FT-IR Studies

Fig. 6 depicts the FT-IR spectrum of Co²⁺ doped PVA capped CdSenanopolymer. The spectrum exhibits various molecular vibrations of PVA in CdSe. The bands observed at around 3276 cm⁻¹ are attributed to O-H stretching vibrations, indicates the presence of hydroxyl groups [17-18]. Asymmetrical and symmetrical stretching vibrations of -CH₂- occur at 2923 and 2850 cm⁻¹ respectively [19]. The bands at 2308 and 1586 cm⁻¹ are due to the C=O stretching modes arising from the absorption of atmospheric CO₂ on the surface of the polymer [20]. The bands at 1731 and 1648 cm⁻¹ are attributed to C=O, C=C stretching modes respectively [19]. The absorption band occurring at 1421 cm⁻¹ is due to bending vibrations of CH₂ groups respectively. The bands at 1248 cm⁻¹ corresponds to C-O stretching of acetyl groups present on the PVA backbone. The bands at 1089 cm⁻¹ are assigned to ν (C-O) stretching vibration [21]. The bands observed at 1016 cm⁻¹ is assigned to C-O stretching and O-H bending vibrations. A band observed at 944 cm⁻¹ is assigned to C-C stretching vibration [22]. The band at 828 cm⁻¹ corresponds to stretching vibration of C-C group.

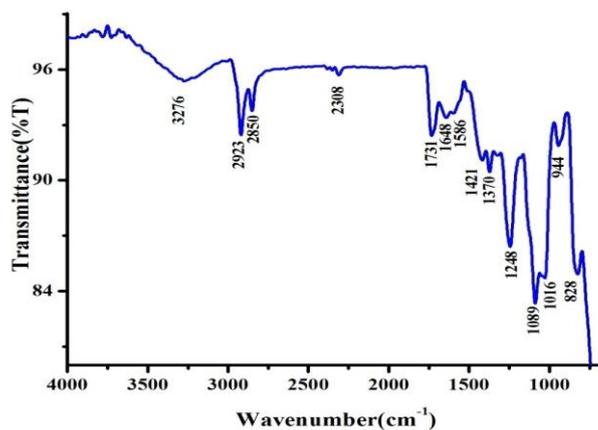


Fig 6: FT-IR spectrum of Co^{2+} doped PVA capped CdSe nanopolymer.

CONCLUSION

In summary, Co^{2+} doped PVA capped CdSe nanopolymer was synthesized by using wet chemical route. The influence of doped Co^{2+} ions on structural and optical properties of PVA capped CdSe nanopolymer was investigated. XRD pattern reveals the zinc blended cubic structure of CdSe and polycrystalline nature. The average crystallite sizes of Co^{2+} doped CdSe nanopolymer was found to be 6 nm. Optical absorption spectrum exhibited characteristic bands for Co^{2+} in octahedral site symmetry. Crystal field and Racah parameters were evaluated as $Dq = 970$, $B = 950$ and $C = 3800 \text{ cm}^{-1}$. EPR spectrum exhibited two resonance signals at $g = 4.29$ and 2.01 . By correlating optical and EPR studies, the coordination geometry and bonding nature of Co^{2+} 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 polymer and other functional groups.

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