



Investigation On Synthesis Of Mn^{2+} Ion Doped Poly Vinyl Alcohol Capped Cdse And Its Characterization Using Various Techniques.

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Abstract:

Nanostructured semiconductors, particularly CdSe, exhibit unique properties due to quantum confinement, making them ideal for applications in biomedical tagging, LEDs, lasers, and near-infrared communication devices. This study focuses on the synthesis and characterization of Mn^{2+} ion doped Poly Vinyl Alcohol (PVA) capped CdSe nanostructures using a wet chemical route. Materials used include Cadmium Chloride ($CdCl_2 \cdot 2H_2O$), Sodium Hydrogen Selenide (NaHSe), Manganese Chloride ($MnCl_2$), and PVA. Cadmium Chloride and Sodium Hydrogen Selenide supply Cd^{2+} and Se^{2-} ions, while PVA prevents nanoparticle agglomeration. Manganese Chloride introduces Mn^{2+} ions to modify the nanostructures' properties.

The synthesis involved dissolving Cadmium Chloride in PVA solution, followed by heating and stirring. Sodium Hydrogen Selenide was added to form CdSe nanostructures, then Manganese Chloride was introduced for Mn^{2+} doping. The mixture was cast onto glass plates to form thin films, which were washed to remove residual salts. Characterization using X-ray diffraction (XRD) revealed the crystalline nature of the CdSe nanostructures, with peaks corresponding to the (220) and (311) planes and an estimated crystallite size of 5 nm. PVA presence was indicated by a peak at $2\theta = 19^\circ$. Electron Spin Resonance (ESR) spectroscopy showed an unresolved hyperfine structure at $g = 2.01$, indicating Mn^{2+} ions in octahedral site symmetry, with a hyperfine splitting parameter ($A = 94.93 \text{ cm}^{-1}$). The positive g-value shift suggested covalent bonding between Mn^{2+} ions and ligands. Mn^{2+} ion doping significantly altered the absorption and emission properties of CdSe, enhancing its suitability for

optoelectronic and biomedical applications. The covalent bonding is expected to improve stability and performance in devices such as infrared detectors and lasers.

In conclusion, Mn^{2+} doped PVA capped CdSe nanostructures exhibit promising electronic and optical properties. Detailed characterization underscores their potential in advanced technological applications, with future research aimed at exploring other dopants and optimizing synthesis.

Keywords: Confinement, Nanoparticle, Characterization, Diffraction Spectroscopy

1. Introduction

Nanostructured semiconductors smaller than the exciton Bohr radius display unique electronic, optical, chemical, magnetic, and mechanical properties compared to their bulk forms. Colloidal II–VI metal chalcogenides like CdS, CdSe, and CdTe have been extensively researched for their quantum confinement and size-dependent photoemission properties. Advances in synthesis have produced high-quality materials with narrow size distributions. The photoluminescence (PL) spectra of these materials can be adjusted by modifying their size and composition. These chalcogenides surpass organic dyes with high PL intensity, narrow bandwidth, and significant photo stability, making them ideal for biomedical tagging, LEDs, lasers, and near-infrared communication devices. CdSe, in particular, is valued for its size-dependent optoelectronic properties, making it suitable for nanoscale electronics, laser technology, and biological fluorescent labeling. Its bandgap (1.74 eV) and tunable morphology enhance its application in photovoltaic and optoelectronic devices.

Controlled doping or combining semiconductors to form junction structures improves charge separation and photo electrochemical performance. Introducing transition metal (TM) ions like Mn, Fe, Co, Ni, and Cu into CdSe nanostructures creates new electronic properties through interactions with the host semiconductor's valence electrons. This doping can induce disorder, resulting in unique crystalline, magnetic, and chemical characteristics, suitable for infrared detectors, lasers, and other optical devices.

Transition Metal (TM) ion doping modifies energy levels and influences photocatalytic and spectroscopic properties, which depend on the position and coordination of the doped ions. Manganese, with its interesting optical properties, acts as a paramagnetic ion and luminescence activator in inorganic phosphors. This present research work investigates Mn^{2+} -doped Poly Vinyl Alcohol (PVA) capped CdSe nanostructures, synthesized via a wet chemical route and characterized using techniques such as X-ray diffraction (XRD), electron spin resonance (ESR) and photoluminescence (PL). Mn^{2+} ions significantly affect the host material's absorption and emission properties.

2. Method used:

Materials for the synthesis include Cadmium Chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$), Poly Vinyl Alcohol (PVA), Sodium Hydrogen Selenide (NaHSe), and Manganese Chloride (MnCl_2), all of which are used without further purification to ensure consistent results. These chemicals are of analytical grade, guaranteeing their suitability and high purity for laboratory research and experiments.

- i) Cadmium Chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$) acts as the cadmium source, providing Cd^{2+} ions essential for forming the cadmium selenide (CdSe) nanostructures. This compound ensures that cadmium ions are readily available in the reaction mixture, facilitating the formation of the desired nanostructures.
- ii) Poly Vinyl Alcohol (PVA) serves as a stabilizing agent and capping material. It not only prevents the agglomeration of nanoparticles but also enhances their dispersion in the solution. This ensures uniform size distribution and stability of the synthesized nanostructures.
- iii) Sodium Hydrogen Selenide (NaHSe) is the selenium source in the reaction, supplying Se^{2-} ions necessary for forming CdSe . It ensures a controlled release of selenium ions, promoting the formation of high-quality nanostructures.
- iv) Manganese Chloride (MnCl_2) is incorporated to introduce manganese ions (Mn^{2+}) into the CdSe nanostructures, enabling the doping process. Introduction of Mn^{2+} is crucial for modifying the electronic and optical properties of the CdSe nanostructures, as manganese acts as a paramagnetic ion and luminescence activator.
- v) Double distilled water is used as the solvent, providing a pure medium for the reactions. The use of double distilled water minimizes impurities that could affect the reaction and ensures the consistency and reproducibility of the experimental results.

3. Synthesis of Mn^{2+} ion doped Poly Vinyl Alcohol (PVA) capped CdSe nanostructure

To synthesize Mn^{2+} ion doped Poly Vinyl Alcohol (PVA) capped CdSe nano structure, 50 mm of Cadmium Chloride ($\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$) was added to 2.2 g of Polyvinyl Alcohol (PVA) with a molecular weight of 13,000 g/mol. The mixture was diluted to a final volume of 50 mL using bi-distilled water, ensuring a high purity solvent environment. This solution was allowed to remain as such for 24 hours at room temperature to facilitate the swelling of PVA, a crucial step for achieving uniform dispersion of cadmium ions within the polymer matrix.

After the swelling period, the solution was heated to 70°C and subjected to magnetic stirring. This process continued until a viscous, transparent solution was obtained, indicating that the PVA had fully dissolved and formed a homogeneous mixture with the cadmium chloride. Next, 1 mL of 50 mM Sodium Hydrogen Selenide (NaHSe) was introduced to the solution. The addition of NaHSe , which provides selenium ions (Se^{2-} ion), resulted in the formation of a red, transparent solution, signifying the formation of cadmium selenide (CdSe)

nanostructures within the PVA matrix. Subsequently, a 0.01 M% solution of Manganese Chloride was added to the mixture under continuous stirring. The incorporation of Mn^{2+} ion is essential for doping the CdSe nanostructures, thereby modifying their electronic and optical properties due to the paramagnetic and luminescent nature of manganese ions.

The resultant solution was then cast onto flat glass plate dishes to form thin films. These films were left to dry, allowing the solvent to evaporate and leaving behind a thin film of Mn^{2+} ion doped PVA capped CdSe nanostructure. To ensure purity, the film was washed multiple times with deionized water to remove any residual, insoluble salts.

4. Characterization of the sample CdSe nanostructure prepared

4.1 X Ray diffraction Technique

4.1.1 Introduction

X-ray diffraction (XRD) is a powerful analytical technique used to determine the crystallographic structure, chemical composition, and physical properties of materials. When a focused beam of X-rays strikes a crystalline sample, the atoms within the crystal lattice cause the X-rays to diffract in specific directions. By measuring the angles and intensities of these diffracted beams, a diffraction pattern is generated, which can be analyzed to reveal detailed information about the atomic arrangement within the crystal. It is particularly valuable for identifying unknown crystalline substances, characterizing the phases present in a sample, determining lattice parameters, and studying the purity and structural integrity of materials. The technique is non-destructive and can be applied to a wide range of materials, including metals, ceramics, polymers, and nanostructures. Its high precision and reliability make XRD an essential tool in materials science, chemistry, physics, and related fields for advancing the understanding of material properties and behaviors.

4.1.2 Result and Discussion:

The phase identification, structural analysis, and crystallite size evaluation of the prepared sample of Mn^{2+} ion doped Poly Vinyl Alcohol capped CdSe nanostructures were conducted using powder X-ray diffraction (XRD).

The X-ray diffraction pattern of the Mn^{2+} ion doped PVA capped CdSe nanostructure is shown in Fig. 1 given below.

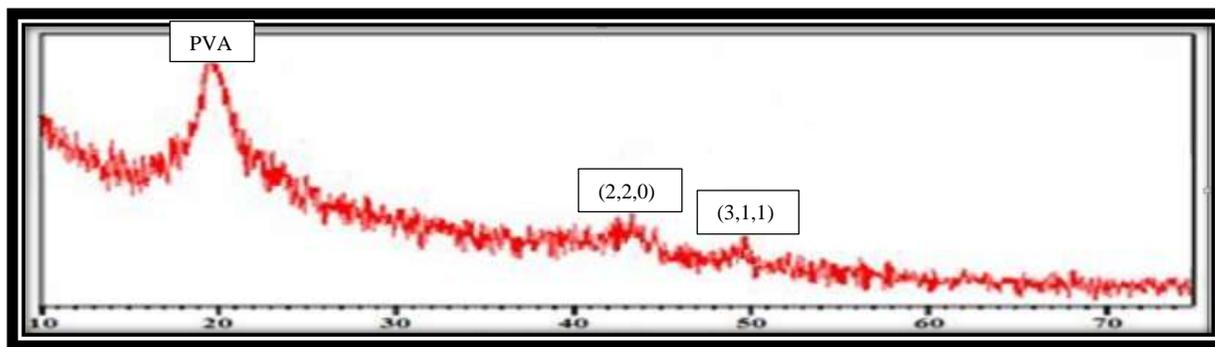


Fig. 1 X-Ray Diffraction Pattern obtained for sample CdSe prepared

An intense peak at a diffraction angle around $2\theta = 19^\circ$ corresponds to PVA, indicating its crystalline nature due to strong intermolecular hydrogen bonding. Additional diffraction peaks observed at $2\theta = 42.25^\circ$ and 48.75° correspond to the (220) and (311) planes of the prepared CdSe nanostructure sample, and it is also consistent with the results obtained from equation:

$$D = (0.90 \lambda) / (\alpha \cdot \cos \theta)$$

where, λ is the wavelength of X-ray (CuK α) radiation (1.5406 Å),

α is the full width at half maximum (FWHM), and

θ is the diffraction angle.

The estimated average crystallite size is 5 nm.

4.2 Electron Spin Resonance (ESR) Technique

4.2.1 Introduction

It is also known as Electron Paramagnetic Resonance (EPR) and is a powerful spectroscopic technique used to study materials with unpaired electrons. It is particularly effective in characterizing paramagnetic substances, including transition metal ions, free radicals, and defects in solids. By applying a magnetic field and microwave radiation, it detects the transitions between electron spin states, providing detailed information about the local magnetic environment and electronic structure of the sample.

In research, it is invaluable for investigating the electronic properties, structural dynamics, and interactions of paramagnetic species. It can elucidate the nature of chemical bonding, identify the presence and behavior of radicals, and measure distances between spin-labeled sites in biomolecules. This technique's sensitivity to subtle changes in the magnetic environment makes it essential for studying complex systems in chemistry, physics, materials science, and biology. Its ability to provide unique insights into the electronic and structural properties of materials underpins its widespread application in cutting-edge research.

4.2.2 Results and Discussion:

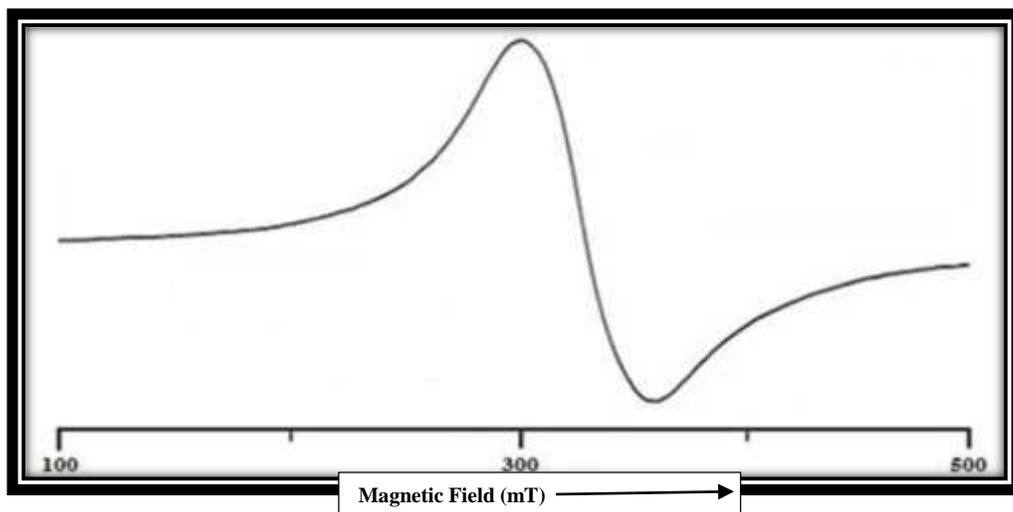


Fig. 2 ESR Pattern for prepared sample of CdSe

The room temp. ESR spectrum of Mn^{2+} ion doped PVA capped CdSe nanostructure is illustrated in above Fig. 2

Key Observations:

- i) The obtained ESR spectrum exhibits an unresolved hyperfine structure at $g = 2.01$.
- ii) This feature is characteristic of the octahedral site symmetry of Mn^{2+} ions within the framework.
- iii) The hyperfine splitting parameter is $A = 94.93 \text{ cm}^{-1}$

Hyperfine Structure Origin:

- i) The hyperfine structure arises from the interaction between the Mn^{2+} ion electron cloud and the Mn nucleus, which has a spin of $I = 5/2$.
- ii) This interaction indicates the presence of paramagnetic Mn^{2+} ion in the sample.

Bonding Nature:

- i) The g -value of the hyperfine splitting indicates the bonding nature between Mn^{2+} ions and ligands.
- ii) A negative shift from the free electron g -value (2.0022) suggests ionic bonding.
- iii) Conversely, a positive shift indicates covalent bonding. In this present study, the g -value shows a positive shift, indicating covalent bonding between Mn^{2+} ions and their ligands.

5. Conclusion:

This research explored the synthesis and characterization of Mn²⁺-doped Poly Vinyl Alcohol (PVA) capped CdSe nanostructures, focusing on their electronic and optical properties. The synthesis involved a wet chemical route using Cadmium Chloride, Sodium Hydrogen Selenide, Manganese Chloride, and PVA, ensuring high purity and uniform size distribution of the nanostructures. The resultant materials were characterized using X-ray diffraction (XRD) and Electron Spin Resonance (ESR) techniques. XRD analysis confirmed the crystalline nature of the synthesized CdSe nanostructures, with diffraction peaks corresponding to the (220) and (311) planes. The presence of PVA was also evident, indicated by a prominent peak at $2\theta = 19^\circ$. The average crystallite size was estimated to be 5 nm, demonstrating the successful formation of nanostructures within the desired size range.

ESR spectroscopy provided insights into the electronic environment of the Mn²⁺ ions in the CdSe matrix. The ESR spectrum exhibited an unresolved hyperfine structure at $g = 2.01$, characteristic of Mn²⁺ ions in an octahedral site symmetry. The hyperfine splitting parameter ($A = 94.93 \text{ cm}^{-1}$) further confirmed the paramagnetic nature of Mn²⁺ ions in the sample. The g -value shift suggested covalent bonding between Mn²⁺ ions and their ligands. The introduction of Mn²⁺ ions significantly altered the host material's absorption and emission properties, enhancing its potential applications in optoelectronics and biomedicine. The covalent bonding indicated by ESR analysis points to a stable incorporation of Mn²⁺ within the CdSe structure, which could lead to improved performance in infrared detectors, lasers, and other optical devices.

In conclusion, Mn²⁺ doped PVA capped CdSe nanostructures exhibit promising properties for various advanced applications. The successful synthesis and detailed characterization underscore the potential of these materials in enhancing the performance of devices that require precise control over electronic and optical properties. Future work could focus on exploring other transition metal dopants and further refining the synthesis process to tailor the properties of these nanostructures for specific applications.

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