Quantum Confinement and Trap-State Emission in Cds/Zns Nanoparticles Stabilized within A PVA Matrix

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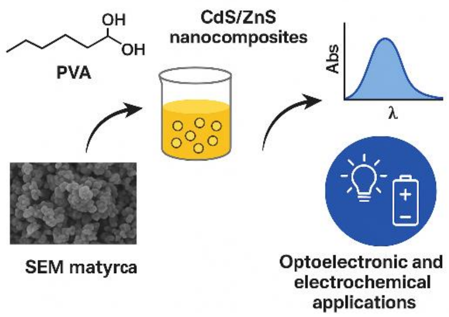
ABSTRACT

CdS/ZnS nanoparticles encapsulated within a polyvinyl alcohol (PVA) matrix were successfully synthesized via a simple solution-phase method and systematically investigated for their structural, optical, and morphological properties. UV–Vis absorption spectra exhibited a strong absorption band in the 200–220 nm region with a noticeable blue shift relative to bulk CdS and ZnS, confirming quantum confinement at the nanoscale. FT-IR analysis validated the presence of characteristic PVA functional groups along with distinct Cd–S and Zn–S stretching vibrations, confirming effective encapsulation of the nanoclusters within the polymer matrix. Photoluminescence spectra revealed broad visible-region emissions attributed to defect-related trap states, with Zn^{2+} incorporation influencing luminescence intensity. XRD analysis confirmed the nanocrystalline cubic zinc blende phase of CdS and ZnS, with crystallite sizes in the 10–20 nm range, while SEM micrographs showed agglomerated yet porous morphologies, offering enhanced surface area. The combined findings highlight the role of PVA in stabilizing CdS/ZnS nanoclusters, leading to nanocomposites with favorable structural and optical features. These results underscore the potential of CdS/ZnS/PVA nanocomposites for future applications in optoelectronic devices, photocatalysis, and electrochemical energy storage systems.

Graphical Abstract



Keywords: CdS/ZnS nanocomposites; Polyvinyl alcohol (PVA); Quantum confinement; Photoluminescence; Optical properties; Electrochemical applications

INTRODUCTION

Semiconductor nanomaterials, particularly cadmium sulfide (CdS) and zinc sulfide (ZnS), have attracted significant attention due to their tunable optical and electronic properties, which make them suitable for applications in optoelectronic devices, photocatalysis, sensors, and energy storage systems [1–3]. CdS, with a direct bandgap of ~2.4 eV, is well known for its strong visible light absorption, whereas ZnS, a wide bandgap semiconductor (~3.6 eV), offers high stability, non-toxicity, and effective surface passivation when combined with CdS [4,5]. The integration of CdS and ZnS into heterostructured systems not only enhances photophysical properties but also suppresses non-radiative recombination through efficient band alignment [6].

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Polyvinyl alcohol (PVA), a water-soluble, non-toxic, and biocompatible polymer, has been widely utilized as a stabilizing and encapsulating matrix for semiconductor nanoparticles due to its excellent film-forming ability, mechanical strength, and hydroxyl functional groups that facilitate nanoparticle dispersion. Encapsulation of CdS/ZnS nanostructures in PVA provides structural stability, prevents agglomeration, and allows tuning of surface states, thereby enhancing the optical and electrochemical performance of the composites [7-9].

Recent studies have demonstrated that CdS/ZnS nanocomposites exhibit superior luminescence, photocatalytic, and electrochemical characteristics compared to their individual counterparts, owing to synergistic effects and quantum confinement at the nanoscale [10–12]. Furthermore, PVA-based nanocomposites have been reported to offer improved ion diffusion pathways and high electroactive surface areas, which are advantageous for applications in supercapacitors and related energy devices [13,14].

In this study, undoped CdS/ZnS nanoparticles encapsulated within a PVA matrix were synthesized via a facile solution-phase method. The structural, optical, and morphological characteristics of the resulting nanocomposites were systematically investigated using UV–Vis, FT-IR, PL, XRD, and SEM techniques. The findings provide insights into the role of polymer encapsulation in modulating the properties of semiconductor nanoclusters for potential optoelectronic and energy-related applications.

Experimental

Synthesis of CdS/ZnS/PVA Encapsulated Nanoparticles

CdS/ZnS/PVA nanoparticles were synthesized via a solution-phase method. A predetermined amount of cadmium (Cd) was dissolved in ethanol to prepare the Cd precursor solution. Separately, sodium sulfide (Na_2S) was dissolved in distilled water, and polyvinyl alcohol (PVA) was dissolved in ethanol to obtain the PVA solution. For the matrix preparation, the Cd precursor was added dropwise into the PVA solution under constant stirring at room temperature, yielding a transparent and homogeneous PVA–Cd^{2+} solution. Subsequently, the Na_2S solution was introduced dropwise under continuous stirring, leading to the formation of a yellow-colored suspension. The reaction mixture was stirred for an additional 1 h, after which a zinc nitrate solution (prepared in distilled water) was added to the system. The resulting precipitate was allowed to settle overnight, and the supernatant ethanol was decanted. The collected precipitate was dried in a vacuum oven at 60 °C for several hours, ground into a fine powder, and stored in airtight sample bottles for further analysis.

Characterization Techniques

Fourier Transform Infrared Spectroscopy (FT-IR):

The functional groups and bonding characteristics of the synthesized nanocomposites were examined using a BRUKER FT-IR spectrometer.

UV–Visible Spectroscopy (UV–Vis):

The optical absorption properties of the CdS/ZnS/PVA nanocomposites were measured on a Shimadzu UV-240 spectrophotometer in the wavelength range of 200–800 nm.

Cyclic Voltammetry (CV):

The electrochemical behavior of the nanocomposites was investigated using an Origalys SAS France (OGF01A) instrument. Measurements were performed within a potential window of 100–1000 mV at a scan rate of 30 mV s^{-1}.

X-Ray Diffraction (XRD):

The crystalline structure and phase composition were analyzed using a Rigaku D/max-2500 diffractometer equipped with Cu Kα radiation (λ = 1.542 Å), operating at 40 kV.

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Scanning Electron Microscopy (SEM):

The morphology and particle size of the nanoparticles were characterized by scanning electron microscopy (SEM) using a JEOL JSM-7500F instrument.

RESULTS AND DISCUSSION

UV–Visible Spectroscopy

The optical absorption spectrum of the undoped CdS/ZnS/PVA nanocomposites is shown in Figure X. A strong and sharp absorption peak was observed in the range of 200–220 nm, which can be attributed to the electronic transition from the valence band to the conduction band within the CdS/ZnS nanoclusters. The position of this absorption band reflects the combined effect of the wide bandgap of ZnS (~3.6 eV) and the smaller bandgap of CdS (~2.4 eV). At the nanoscale, band structure modifications occur, and the observed blue-shift relative to the bulk counterparts confirms the presence of strong quantum confinement.

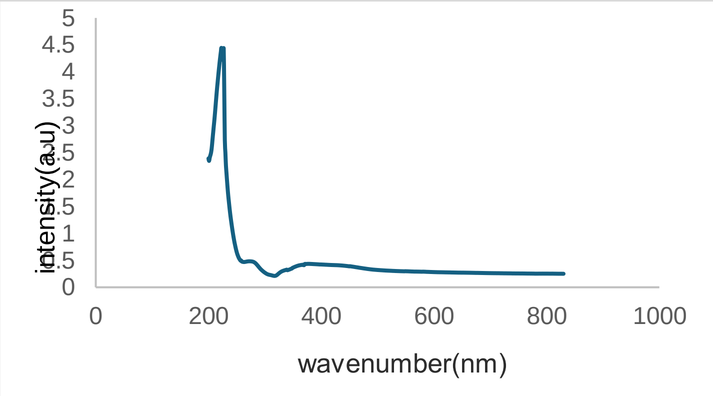

Fig.1 UV spectra of CdS/ZnS/PVA nanocomposites

A broad absorption tail extending beyond 300 nm was also observed, which can be ascribed to defect states, surface trap states, and interfacial states between CdS and ZnS. Such broadening may also arise due to particle aggregation or variation in particle size distribution. The overall spectral features clearly suggest that the nanoparticles are in the quantum-confined regime, supporting their nanoscale dimensions.

Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectrum of the CdS/ZnS/PVA nanocomposites was recorded in the range of 4000–400 cm^{-1} (Figure Y). A broad absorption band in the region 3410–3180 cm^{-1} was assigned to O–H stretching vibrations, confirming the presence of hydroxyl groups from the PVA matrix as well as contributions from adsorbed moisture. The bands observed at 2930–2850 cm^{-1} correspond to C–H stretching vibrations of methylene ($–CH_2–$) groups in PVA. A distinct band at 1650–1600 cm^{-1} was attributed to C=O stretching or H–O–H bending vibrations, suggesting the presence of bound water molecules and possible interactions between PVA and the nanoparticle surface.

Additional absorptions at 1460–1400 cm^{-1} and 1370–1320 cm^{-1} were assigned to C–H bending and O–H bending vibrations of PVA, respectively. Strong peaks in the region of 1140–1080 cm^{-1} were associated with C–O–C stretching and C–O stretching vibrations, further confirming the structural integrity of the PVA polymer matrix.

Importantly, distinct bands appearing in the 690–600 cm^{-1} region were assigned to Cd–S and Zn–S stretching vibrations, which validate the successful formation of CdS/ZnS nanoclusters within the PVA framework. The absence of extraneous bands from undesired phases suggests a clean synthesis process. Overall, the FT-IR spectra confirm the effective encapsulation of CdS/ZnS nanoparticles within the PVA matrix, facilitated by hydrogen bonding and electrostatic interactions.

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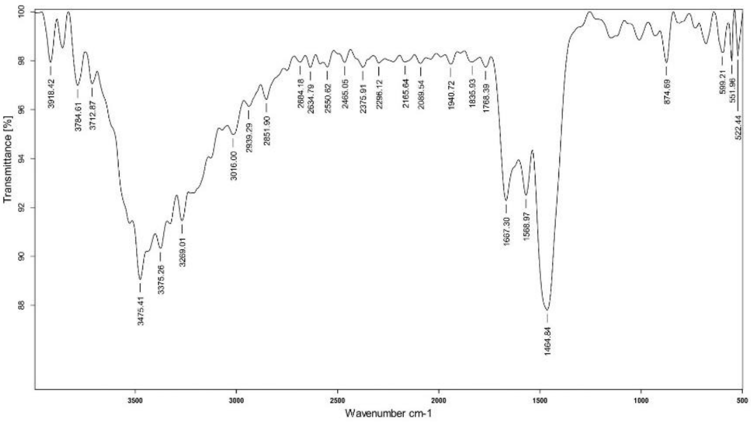

Fig.2 FT-IR Spectra of CdS/ZnS/PVA nanocomposites

Photoluminescence (PL) Spectral Studies

The room-temperature photoluminescence (PL) spectra of the synthesized nanoparticles, recorded at different excitation wavelengths, are shown in Figures 4.41 and 4.42. The spectra exhibit a broad emission band extending across the visible region, which is characteristic of nanoscale CdS-based systems.

The observed broadening in the PL spectra can be attributed to trap-state emissions arising from surface defect states .Upon photoexcitation, electrons are promoted from the valence band to the conduction band of CdS and subsequently become trapped at defect sites. The recombination of these trapped carriers with holes gives rise to defect-related emissions. The incorporation of Zn^{2+} ions further modifies the surface trap states, leading to an enhancement and slight shift of the luminescence band

CdS sample exhibited strong emission peaks at approximately 343 nm and 450 nm in the visible region. While the peak positions were nearly identical for all samples, notable variations in relative intensity were observed, suggesting that dopant incorporation and surface passivation influence the recombination dynamics.

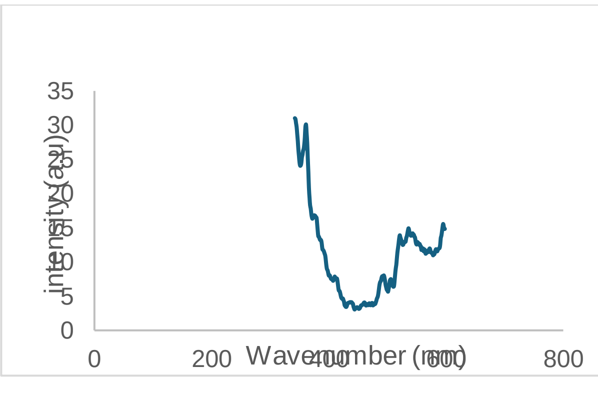

Fig.3 Photoluminus spectra of CdS/ZnS/PVA nanocomposites

X-Ray Diffraction (XRD) Analysis

The XRD pattern of the CdS/ZnS/PVA nanocomposites is presented in Figure Z. The diffraction profile exhibits several broad peaks, characteristic of nanocrystalline materials with reduced long-range order. The broadening of the peaks can be attributed to the small crystallite size and the amorphous contribution from the PVA matrix.

Distinct diffraction maxima observed at 2θ values around **26°, 28°, and 47°** can be indexed to the (111), (220), and (311) planes of the cubic zinc blende structure of CdS (JCPDS No. 10-0454) and ZnS (JCPDS No. 05-0566). The overlapping nature of CdS and ZnS reflections is expected due to their similar lattice parameters, further supporting the successful co-existence of both phases in the nanocomposite.

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The average crystallite size of the nanoparticles was estimated using the Debye–Scherrer equation The calculated crystallite size was found to be in the range of **10–20 nm**, indicating the formation of nanosized crystallites.

The absence of additional impurity peaks confirms the phase purity of the synthesized material. The broad background contribution is attributed to the semi-crystalline nature of the PVA polymer matrix, which encapsulates and stabilizes the CdS/ZnS nanoparticles.

Overall, the XRD analysis validates the successful synthesis of CdS/ZnS nanoclusters within the PVA framework, with crystallite sizes confined to the nanometer scale.

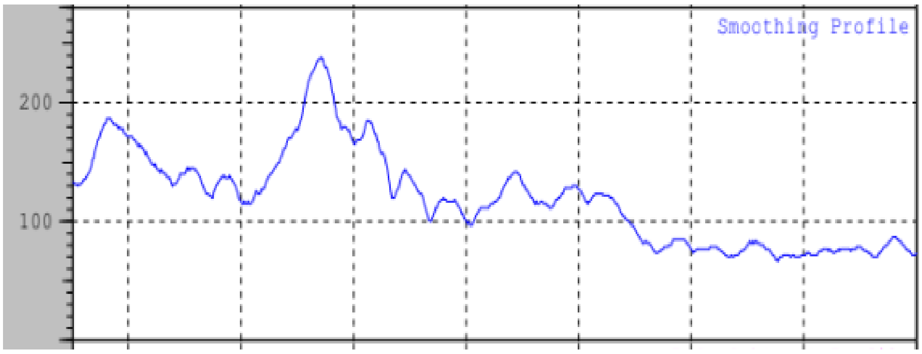

Fig.4. XRD of CdS/ZnS/PVA nanocomposites

Scanning Electron Microscopy (SEM) Analysis

SEM micrographs of CdS/ZnS/PVA nanocomposites (Figure .5) reveal agglomerated, irregularly shaped nanoparticles embedded in the PVA matrix. The particles form secondary clusters due to high surface energy and interparticle interactions, while rough surfaces with interconnected grains indicate partial coalescence of crystallites. The estimated submicron particle size agrees with the 10–20 nm crystallite size from XRD. Larger agglomerates arise from surface energy minimization, whereas the PVA matrix restricts excessive growth. The porous, rough morphology enhances ion diffusion and electroactive surface area, making the composites suitable for electrochemical and optoelectronic applications.

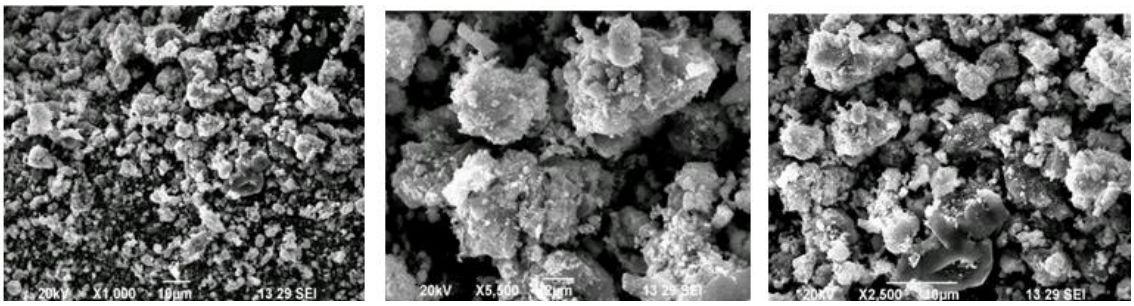

Fig.5 SEM Micrograph of CdS/ZnS/PVA nanocomposites

CONCLUSION

CdS/ZnS/PVA nanocomposites were successfully synthesized through a simple solution-phase method and systematically characterized by spectroscopic, structural, and morphological techniques. UV–Vis absorption studies revealed a strong absorption band in the 200–220 nm region, accompanied by a blue-shift relative to bulk CdS and ZnS, confirming the quantum confinement effect at the nanoscale. FT-IR spectra demonstrated the retention of PVA functional groups along with distinct Cd–S and Zn–S stretching vibrations, validating the successful encapsulation of CdS/ZnS nanoclusters within the polymer matrix.

Photoluminescence analysis showed broad visible-region emissions arising from trap-state recombination, with Zn^{2+} incorporation influencing both intensity and surface trap modification. XRD results confirmed the nanocrystalline cubic zinc blende phase of CdS and ZnS, with an average crystallite size of 10–20 nm, while the

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broad background contribution reflected the semi-crystalline nature of PVA. SEM micrographs revealed agglomerated but porous morphologies, with nanosized crystallites aggregated into larger secondary structures, offering enhanced surface area beneficial for electrochemical and optoelectronic applications.

Overall, the study demonstrates that the PVA matrix effectively stabilizes CdS/ZnS nanoclusters, yielding nanocomposites with favorable optical, structural, and morphological properties. These findings highlight the potential of CdS/ZnS/PVA nanomaterials for future applications in optoelectronic devices and electrochemical energy storage systems.

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