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Optical analysis of PVA/CdS nanostructure

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The optical properties of polyvinyl alcohol (PVA) matrix embedded with cadmium sulfide (CdS) nanostructures were investigated to understand their potential applications in optoelectronic devices. CdS nanoparticles were synthesized and uniformly dispersed within the PVA matrix using a solution-casting method. The structural and morphological characterization confirmed the formation of well-dispersed CdS nanostructures within the polymer matrix. UV-vis spectroscopy analysis revealed a significant blue shift in the absorption edge due to the quantum confinement effect of CdS nanoparticles. Photoluminescence (PL) studies indicated enhanced emission properties, suggesting strong interaction between the polymer and the semiconductor nanoparticles. The optical band gap was found to increase with decreasing nanoparticle size, demonstrating the tunability of optical properties through nanostructure formation. These results suggest that PVA/CdS nanostructures hold promise for applications in photonic and optoelectronic devices, including light-emitting diodes and photodetectors.

Keywords: CdS; Nanocomposites; Optical.

1. INTRODUCTION

Nanostructured materials have attracted significant attention due to their unique optical, electrical, and mechanical properties compared to their bulk counterparts. Among these materials, cadmium sulfide (CdS) is a widely studied semiconductor with a direct band gap of approximately 2.42 eV at room temperature, making it a promising candidate for optoelectronic applications such as solar cells, light-emitting diodes, and photodetectors. However, to enhance its stability, processability, and performance, CdS nanoparticles are often embedded in polymer matrices [1-10].

Polyvinyl alcohol (PVA) is a versatile polymer that has been widely used as a host matrix for nanocomposites due to its excellent film-forming ability, transparency, and mechanical strength. The incorporation of CdS nanostructures into the PVA matrix not only improves their dispersion but also allows for better control over their optical properties. The quantum confinement effect in CdS nanoparticles leads to a shift in the optical band gap, making these nanocomposites tuneable for various applications [11-15].

In this study, we analyse the optical properties of PVA/CdS nanostructures using UV-vis absorption spectroscopy and photoluminescence (PL) spectroscopy. The influence of CdS nanoparticle size and concentration on the optical band gap and emission characteristics is investigated to assess their potential for optoelectronic applications. The results provide insight into the interaction between PVA and CdS nanoparticles, as well as the tunability of their optical properties through nanostructure engineering [16-20].

2. EXPERIMENTAL

Cadmium chloride ($CdCl_2$) with a molecular weight of 183.32 and a specification assay of 95%, along with sodium sulfide (Na_2S) with a molecular weight of 78.04, were obtained from S.D. Fine-Chem. Ltd. Polyvinyl alcohol (PVA) (C_6H_7N), having a molecular weight of 6000 and a minimum assay of 99.5%, was sourced from Mallinckrodt. All chemicals were of analytical grade and were used without further purification.

To prepare the polymer solution, 9.0 g of PVA was dissolved in 300 mL of deionized water under continuous stirring for 2 hours. The solution was then heated to 100°C and allowed to cool to room temperature while stirring to maintain homogeneity. PVA/CdS nanocomposite films were synthesized by mixing 40 mL of PVA solution with 4 mL of $CdCl_2$ (0.01M) and 4 mL of Na_2S (0.01M), followed by stirring for 5 minutes to ensure uniform dispersion. The resulting solution was cast onto glass plates (Petri dishes with a 10 cm diameter) to form films of the desired thickness. These films were dried at room temperature (30°C) to prevent gelation. Both pure PVA films and PVA films embedded with CdS nanoparticles were successfully prepared. By adjusting the reaction ratios of $CdCl_2$ and Na_2S, different sizes of CdS nanoparticles within the PVA matrix were achieved.

The morphology and particle size distribution of the nanocomposite films were analysed using a JEOL JEM 2010 Transmission Electron Microscope (TEM) operating at an accelerating voltage of 200 kV. The samples were prepared by dispersing the films in distilled water using an ultrasonic water bath, followed by centrifugation to separate larger particles. A drop of the supernatant was then placed onto a carbon grid and left to dry. The crystalline structure of the samples was examined using a Philips (PW 13900) X-ray Diffractometer (XRD) with CuKα radiation ($\lambda = 1.54$ Å). Additionally, Fourier Transform Infrared (FTIR) spectroscopy (Jasco 6100) was used to study the vibrational spectra of the synthesized samples. The UV–visible spectra were recorded in the wavelength range of 1000–200 nm using a Jasco 570 UV–VIS–NIR spectrophotometer.

The dielectric constant (ε') of the nanocomposite films was measured using an RLC bridge (HIOKI model 3530, Japan) with an accuracy of less than 3%. It was calculated using the equation:

$$\varepsilon(f,T) = C(f,T)\, d/\varepsilon_0 A \tag{1}$$

where AA represents the film area, dd is the separation between parallel electrodes, C(f,T)C(f,T) is the capacitance, and ε0\varepsilon_0 is the permittivity of free space (8.85×10^{-12} F/m).
The AC electrical conductivity (σ\sigma) was determined using the equation:

$$\sigma\,(f,T) = d/R\,(f,T)\,A \tag{2}$$

where R(f,T)R(f,T) denotes the resistance at a specific frequency and temperature.

3. RESULTS AND DISCUSSION

The formation and distribution of CdS nanoparticles in the PVA matrix were examined using Transmission Electron Microscopy (TEM) and X-ray Diffraction (XRD). TEM images revealed a uniform dispersion of CdS nanoparticles within the PVA matrix, with particle sizes ranging from a few nanometers to tens of nanometers, depending on the precursor concentration. The nanoparticles exhibited a nearly spherical shape, indicating controlled growth during synthesis. The size distribution analysis confirmed that altering the $CdCl_2$ and Na_2S ratios affected the nanoparticle size [21,22].

XRD analysis confirmed the crystalline nature of the CdS nanoparticles embedded in the PVA matrix. The diffractograms exhibited peaks corresponding to the hexagonal wurtzite phase of CdS, with broadening of peaks suggesting nanoscale crystallite sizes. The presence of PVA was indicated by a broad amorphous peak around 20°, demonstrating the polymer's role in stabilizing the nanoparticles.

The optical characteristics of PVA/CdS nanocomposite films were analysed using UV–vis spectroscopy over the wavelength range of 200–1000 nm. The absorption spectra exhibited a noticeable blue shift in the absorption edge compared to bulk CdS, indicating the presence of the quantum confinement effect. The absorption peak of CdS nanoparticles was observed around 450 nm and shifted toward shorter wavelengths as the nanoparticle size decreased. The optical band gap (EgE_g) was determined using Tauc's relation, showing an increase with decreasing nanoparticle size, ranging from 2.5 eV to 3.2 eV. This demonstrates the ability to tune the band gap through nanostructuring.

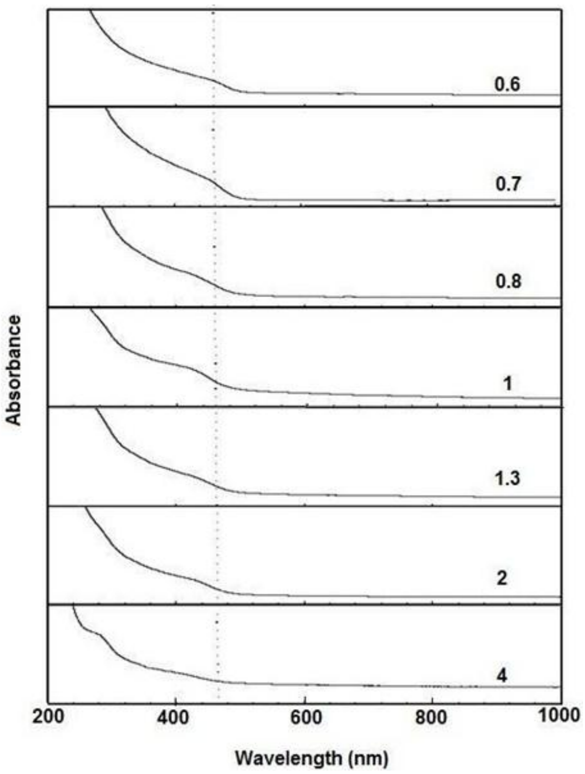

Figure 1 UV-Visible spectra of PVA/CdS.

Photoluminescence spectra of the PVA/CdS nanocomposite films exhibited strong emission peaks in the visible region. A prominent peak appeared around 520–550 nm, attributed to excitonic recombination in CdS nanoparticles. Additional peaks in the lower energy region were observed due to defect states, indicating the presence of surface states and structural imperfections. The intensity of emission varied with nanoparticle concentration, suggesting that the optical properties could be tailored by adjusting synthesis conditions (Figure 2) [23,24].

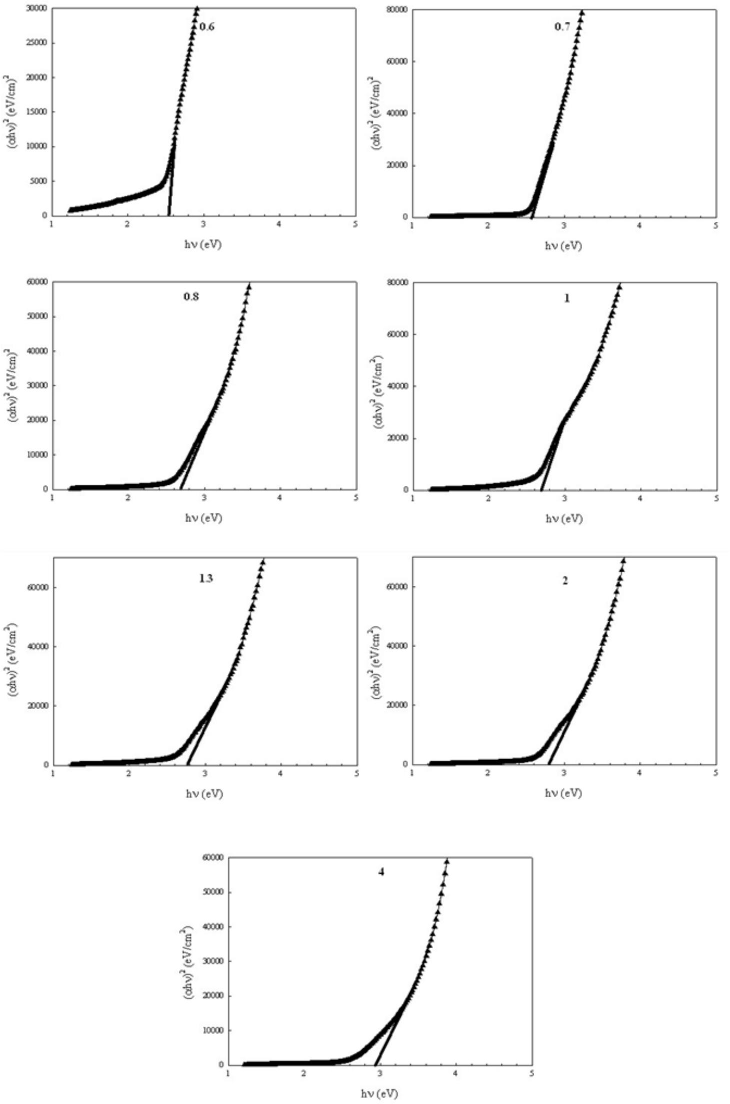

Figure 2 Relation between $(\alpha h\nu)^2$ vs $h\nu$ for different particle sizes of CdS.

Fourier Transform Infrared (FTIR) spectroscopy was employed to analyse the interaction between PVA and CdS nanoparticles. The distinct vibrational bands of PVA, such as O–H stretching at 3300 cm^{-1} and C–O stretching at 1100 cm^{-1}, were detected in both pure PVA and PVA/CdS nanocomposite films. The subtle shifts in these bands upon CdS incorporation indicated interactions between CdS nanoparticles and the functional groups of PVA, contributing to enhanced nanoparticle stabilization.

Table 1 The optical parameters of PVA/CdS nanocomposites.

		λ (nm)	Energy gap (eV)
PVA	$CdCl_2$:Na_2S		
PVA/C	0.6	450	2.56
PVA/C	0.7	448	2.61
PVA/C	0.8	436	2.7
PVA/C	1	431	2.75
PVA/C	1.3	423	2.8
PVA/C	2	417	2.85
PVA/C	4	410	2.94

The dielectric constant (ε′) of PVA/CdS nanocomposites was measured as a function of frequency and temperature. As expected for polymer nanocomposites, the dielectric constant decreased with increasing frequency due to the reduced dipole polarization at higher frequencies. The incorporation of CdS nanoparticles led to an increase in the dielectric constant compared to pure PVA, which can be attributed to interfacial polarization effects.

The conductivity increased with frequency, indicating a hopping conduction mechanism. Temperature-dependent studies showed an enhancement in conductivity with rising temperature, suggesting thermally activated charge transport in the nanocomposite films.

4. CONCLUSIONS

The optical analysis of PVA/CdS nanostructures demonstrated significant tunability in optical properties due to the quantum confinement effect. The structural and morphological investigations confirmed the formation of well-dispersed CdS nanoparticles within the PVA matrix. Optical absorption and photoluminescence studies revealed size-dependent band gap modulation and enhanced emission properties, making these nanocomposites promising for optoelectronic applications. The dielectric and electrical studies further confirmed the influence of CdS nanoparticles on charge transport and polarization behavior. These results suggest that PVA/CdS nanostructures hold potential for use in light-emitting devices, sensors, and energy storage applications.

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