



Structural and linear optical properties of PbS/PVA/PVP nanocomposite film

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Abstract

PbS nanoparticles were synthesized by chemical precipitation using lead nitrate and sodium sulphide as precursors. By dispersing nanometre-sized PbS particles in a polymeric solution of PVA-PVP, the hybrid nanocomposite film was formed. The formation of a nanocomposite film with cubic phase of PbS was revealed by the X-ray diffraction and FTIR studies. When compared to bulk PbS, the optical absorption spectrum of PbS nanocomposite film revealed a strong quantum confinement effect.

Keywords: *Nanocomposite, thick film, lead sulphide, structural property and optical property.*

1. Introduction

Because of the good processability and solubility of organic polymers and the excellent optical, electronic, and magnetic properties of inorganic semiconductor nanoparticles, hybrid nanocomposite materials based on organic polymers and inorganic semiconductor nanoparticles have received much more attention in recent years [1, 2]. Because of its wide range of applications, poly vinyl alcohol (PVA) is the most intriguing organic polymer. It is a potential material with high dielectric strength, good charge storage capacity, and electrical and optical properties that are dopant-dependent. PVA has a carbon chain backbone with hydroxyl groups attached to methane carbons; these -OH groups can act as a source of hydrogen bonding, assisting in the formation of polymer complexes [3, 4]. The conductivity of pure PVA at room temperature is very low, but complexing it with poly vinyl pyrrolidone (PVP) increases it significantly. Pure PVA has a very low conductivity at room temperature, but complexing it with PVP and dopant increases its conductivity [5].

Because of its distinct properties, polyvinyl pyrrolidone (PVP) was chosen as the second polymer component for preparing a polymer blend with PEO. First, PVP is an amorphous polymer with higher ionic mobility than other semicrystalline polymers and low scattering loss, making it an ideal polymer for blend-based materials in optical applications [6]. Second, because PVP contains a carbonyl group (C=O) in its side chains, it forms a variety of complexes with various inorganic salts. It

interacts well with various ions and increases the number of free ions in the system. Another advantage of using PVP is that it can be thermally crosslinked, resulting in a blend material with exceptional thermal stability and mechanical strength [7, 8]. PVP is also highly soluble in polar solvents such as alcohol. As a result, both PVA and PVP play critical roles in enhancing nanoparticles' mechanical strength, long-term temperature stability, optical, electrical, excellent film forming properties, and surfactant materials.

Lead sulphide (PbS) is an important IV-VI semiconductor with a cubic crystal structure and a 0.41 eV direct energy band gap at 300 K. When compared to other semiconductors, PbS has a large exciton Bohr radius of 18 nm and a strong quantum confinement effect for relatively large sizes [9]. By forming nanoparticles, the band gap can be blue shifted from the near infrared (IR) to the visible region. It can exhibit excellent optical, electrical, and applications in nonlinear optical devices, electroluminescent devices, and optical devices such as IR detectors, Pb²⁺ ion-selective sensors, solar cells, light emitting diodes, and optical switches [10, 11]. Structure and optical properties of PbS/PVA/PVP nanocomposite film have been studied in this paper.

2. Experimental details

In a typical PbS nanoparticle synthesis experiment, lead nitrate and sodium sulphide were mixed in the distilled water with a molar ratio of 1:1. The magnetic stirrer was used to vigorously stirrer

the mixture solution. After 1 h, the entire solution had turned a dark brown colour. This is an indication of the formation of PbS. This reaction was carried out for up to 8 hours in order to form a homogeneous solution. The resulting solution was washed several times with distilled water to remove unwanted impurities before drying for 1 hour in a hot air oven at 80°C. To form a nanocomposite film, an appropriate amount of PVA and PVP (75/25) by weight to weight (wt%) were dissolved in distilled water while stirring the solution at 70°C to complete dissolution, and then an appropriate amount of PbS nanoparticles were added to the polymeric solution while stirring continuously and dispersed by ultrasonic agitation to ensure a homogeneous distribution of PbS nanoparticles. The solution was poured into a clean petri dish and left to evaporate at room temperature. The film was peeled from the petri dish after drying and stored in a vacuum desiccator until use. The structural properties of the nanocomposite film were investigated using X-ray diffraction (XRD) on a Rigaku Miniflex-II desktop x-ray diffractometer in the 10-60° range using CuK α radiation ($\lambda=1.5406$ Å). The Fourier transform infrared (FTIR) spectrum of a nanocomposite film was recorded at room temperature using a Bruker Tensor 27 FTIR spectrophotometer with a resolution of 2 cm⁻¹. The optical absorption properties were investigated using a PerkinElmer LAMBDA 35 UV-VIS-NIR spectrophotometer in the wavelength range of 200-1000 nm.

3. Results and discussion

The XRD pattern of a PbS/PVA/PVP nanocomposite film is shown in Fig. 1. The diffraction peaks at low diffraction angles below 25° indicate that PVA is semicrystalline [3-5].

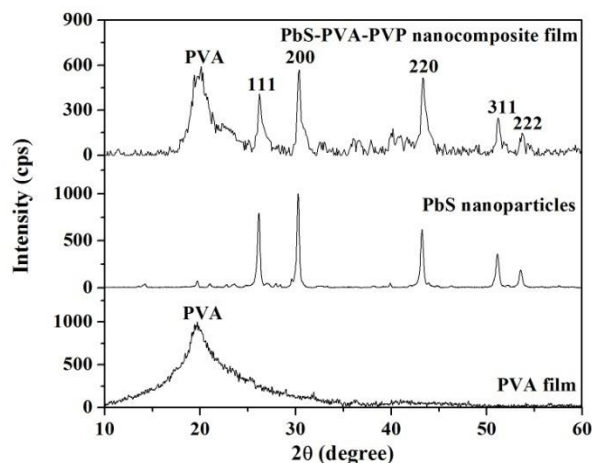


Fig. 1. XRD pattern of PVA film, PbS nanoparticles and PbS-PVA-PVP nanocomposite film

PVP did not have a single peak. It alludes to the amorphous nature of PVP. The peaks in 2θ values of 26°, 30.4°, 43.2°, 51.3° and 53.5° are assigned to the diffraction lines produced by the crystalline planes (111), (200), (220), (311), and (222) of the fcc cubic phase rock salt structure of PbS. The lattice constant was calculated to be approximately $a = 5.929$ Å, which is close to the standard data (JCPDS Card File No. 5-592). Using the Debye-Scherrer equation as given below [12],

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where D is the nanocrystallite size, K is Scherrer constant, λ is the wavelength of the light and β is the full width at half maximum. The average crystallite size of PbS in composite film was calculated to be 6.4 nm.

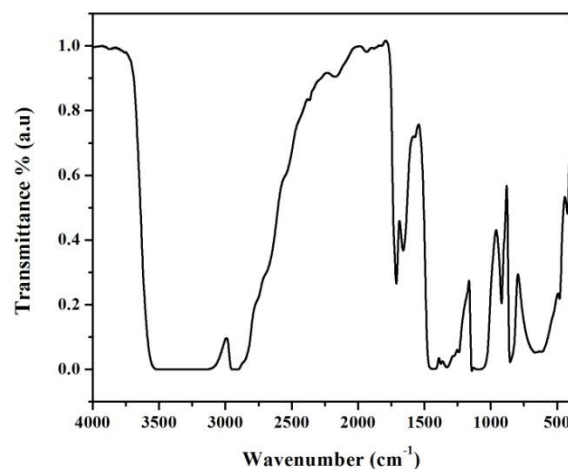


Fig. 2. FTIR spectrum of PbS-PVA-PVP nanocomposite film

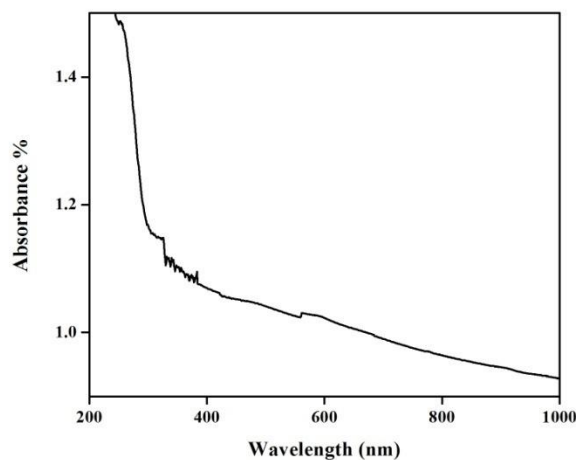


Fig. 3. Optical absorption spectrum of PbS-PVA-PVP nanocomposite film

Fig. 2 depicts the FTIR spectra of PbS/PVA/PVP film. Peaks in the spectrum are assigned to O-H stretching, C-H stretching, C=O stretching, bending of CH₂, CH₂ rocking, CH₂ stretching, and O-H wagging of PVA at 3315, 2949, 1712, 1426, 1142, 918, 854, and 665 cm⁻¹ [3-5]. The observed PVA peaks in the PbS/PVA/PVP film shifted towards higher wave numbers, indicating that the incorporation of PVP causes a reasonable shift in some PVA peaks along with PbS nanoparticles. This interaction between the nanoparticles and the polymeric matrix are very strong and has previously been observed with PbS nanoparticles in various polymer matrix [9, 10, 11].

Fig. 3 depicts the optical absorption spectrum of a PbS/PVA/PVP. The figure shows that the spectrum has a shoulder-like band (between 248 and 301 nm) with weak absorption. Despite the weak absorption, the absorption onset of the product obtained by us exhibits a large blue-shift when compared to bulk PbS (3020 nm), which is attributed to the strong quantum confinement effect. To estimate the corresponding band gap for an allowed direct transition, Brus equation has been used as given below:

$$E_g = E_b + \frac{h^2}{8R^2} \left[\frac{1}{m_e^*} + \frac{1}{m_h^*} \right] - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_r R^2} \quad (2)$$

where E_g is the band gap of nanoparticles, E_b is the band gap of bulk material, h is the Planck's constant, R is the radius of nanoparticles, m_e^* is the effective mass of electron, m_h^* is the effective mass of hole, ϵ_0 is the permittivity of vacuum and ϵ_r is relative permittivity [12]. The E_g value is estimated to be 3.8 eV.

4. Conclusion

Using a simple chemical method, PbS nanoparticles dispersed PVA/PVP nanocomposite film has been successfully synthesised. XRD confirmed the cubic structure of PbS nanocrystallite in PVA/PVP film and the size of PbS nanocrystallite is estimated to be 6.4 nm using Debye-Scherrer equation. FTIR spectrum of film proved the formation of PbS nanoparticles dispersed in PVA/PVP nanocomposite film. A strong blue shift has been observed on the optical absorption spectrum of PbS/PVA/PVP nanocomposite film, with the comparison of bulk PbS, representing the presence of the quantum confinement effect.

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