

Spectroscopic studies on PVA capped ZnSe nanoparticles

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ZnSe nanoparticles are prepared by using chemical method in the presence of an optically transparent and semicrystalline polyvinyl alcohol (PVA) polymer matrix. The as-synthesized sample was characterized by using X-ray diffraction (XRD), Transmission electron microscope, UV-Vis absorption, photoluminescence spectroscopy and FT-IR spectroscopic techniques. The average crystallite size was found to be 6 nm from the XRD pattern. Optical absorption spectrum exhibited the bands which were corresponds to pure ZnSe. Photoluminescence spectrum exhibits the emission band at 431 nm with the excitation of 350 nm. FT-IR spectrum confirmed that PVA played the role of capping agent and coexisted in the lattice.

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1. Introduction

Semiconductor nanoparticles are currently being extensively studied due to their unique size dependent properties. It has been demonstrated by several groups that nanocrystalline II-VI semiconductors show enhanced luminescence, increased oscillator strength and shorter response time. The II-VI types of semiconductor nanoparticles represent ideal systems for dimension-dependent properties and have been extensively studied for their optoelectronic, photochemical and non-linear optical applications [1]. There is currently a great interest in II-VI semiconductor nanoparticles, particularly organically capped soluble particles or embedded in polymeric matrices for their ready to use application in devices [2-6]. Among these, zinc selenide (ZnSe) material belongs to II-VI semiconductor with a direct bandgap of 2.7 eV at room temperature. Zinc selenide is a wide bandgap semiconductor, which is advantageous for optoelectronics optical properties, particularly for light-emitting diodes and lasers working both in visible and infra-red regions of the spectrum.

There has been great interest to control the size of nanoparticles using surface capping agents. Polymers are able to achieve surface passivation, prevent particles from agglomeration which are in favour of controlling the particles size and size distribution effectively. The use of polymers is a prominent method for the synthesis of semiconductor nanoparticles. The reason is that the polymer matrices provide good processability and solubility. Polyvinyl alcohol (PVA) is a hydrophilic biodegradable, biocompatible, non-toxic, non-carcinogenic polymer. It is used in various pharmaceutical, medical, cosmetic, food and agricultural products [7]. PVA is an optically transparent polymer which is characterized by good chemical resistance and film forming ability [8].

Begum et al. reported their results in the previous papers on ZnSe nanoparticles [9-11].

In the present we have discussed the optical properties of ZnSe nanoparticles prepared by chemical method using PVA as capping agent. For the prepared sample the spectral characterizations like XRD, optical, PL and FT-IR studies are carried out.

2. Materials and methods

2.1. Materials

Zinc chloride ($\text{ZnCl}_2 \cdot 5\text{H}_2\text{O}$), Sodium Hydrogen Selenide (NaHSe), Polyvinyl alcohol (PVA) were used as starting materials and used without further purification. All the chemicals were of analytical grade and are used as received. Double distilled water was used as a solvent in the experiment.

2.2. Method

All steps of the synthesis were carried out at room temperature. At first, 0.054g of Zinc chloride (ZnCl_2) was added to 2.2g PVA and volume of the solution is completed to 50 mL by double distilled water. The complete solution was left for 24 hours at room temperature to swell. The solution was warmed up to 60 °C and stirred for 4 hours until viscous transparent solution is obtained. One milliliter (mL) of Sodium Hydrogen Selenide (NaHSe) (50 mM) was dropped into the solution with gentle stirring [12] to get transparent solution. The prepared solution was casted on flat glass plate dishes. After the solvent evaporation PVA capped ZnSe nanoparticles were obtained. The prepared film was

washed with de-ionized water to remove other insoluble salts before measurements.

2.3. Characterization

Using PANalytical X'Pert PRO X-ray diffractometer with CuK_α radiation (1.5406 \AA) source, X-ray diffraction pattern of the sample is recorded. The optical absorption spectrum is recorded using JASCO V-670 Spectrophotometer in the range from 400-800 nm. Photoluminescence spectrum is recorded on Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450W) and pulsed (35W) lamps as excitation sources. Bruker FT-IR spectrophotometer is used for recording the FT-IR spectrum in the region from $500\text{-}4000 \text{ cm}^{-1}$.

3. Results and discussion

3.1. X- ray diffraction studies

XRD pattern of PVA capped ZnSe nanoparticles are shown in Fig.1. The diffraction pattern indicates a diffraction band around $2\theta = 19.6^\circ$ ($19^\circ < 2\theta < 20^\circ$) for PVA, depicting its semi crystalline nature. The important feature of semicrystalline PVA is that the presence of crystalline and amorphous regions and its physical properties, which are resulting from the crystal-amorphous interfacial effects. The peak around 19.6° may be due to the presence of strong intra-molecular hydrogen bonding in individual monomer unit of PVA and inter-molecular hydrogen bonding between its different monomer units [13]. The other diffraction angle at $2\theta = 25.9^\circ$ corresponds to ZnSe. The average crystallite size was calculated from the full width at half maximum intensity of the XRD peaks using Debye - Scherrer's formula [14]

$$D = (K \lambda / \beta \cos\theta)$$

where D is the mean crystallite size, K is a grain shape dependent constant (0.9), λ is the wavelength of the incident beam, θ is the diffraction angle and β is the full width half maximum intensity of the diffraction peak. From the XRD studies the calculated value of average crystallite size was found to be 6 nm.

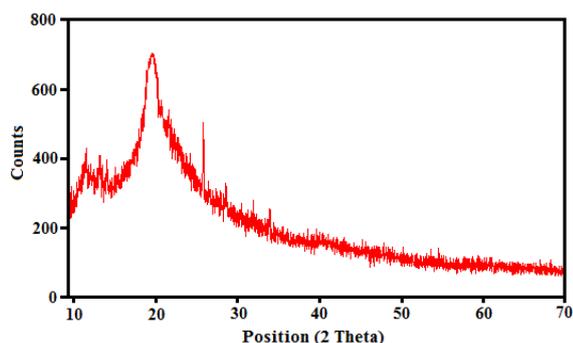


Fig. 1. XRD pattern of PVA capped ZnSe nanoparticles

3.2. Transmission electron microscope

TEM measurements were performed to confirm the nanocrystalline nature of the prepared sample. The TEM images of PVA capped ZnSe nanoparticles are depicted in Fig. 2. The TEM image is look like a netted like structure and the crystallite size of the prepared sample is around 7 nm [15].

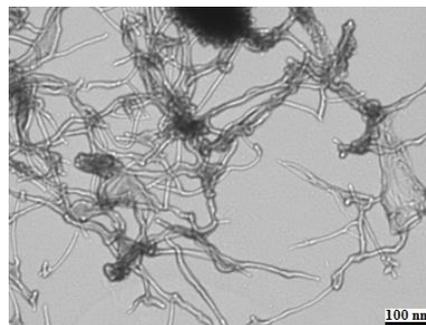


Fig. 2. TEM image of PVA capped ZnSe nanoparticles

3.3. Optical absorption studies

The UV-visible absorption spectroscopy is a usual technique to examine the optical properties of nano sized particles and hence nano thin films. Fig. 3 shows optical absorption spectrum of PVA capped ZnSe nanoparticles. The absorption band at 295 nm related to pure PVA and it is assigned to the electronic transition of $\Pi \rightarrow \Pi^*$, which came from unsaturated bonds and the sharp absorption edge around 263 nm indicates the semicrystalline nature of PVA matrix as a result of irradiation [16].

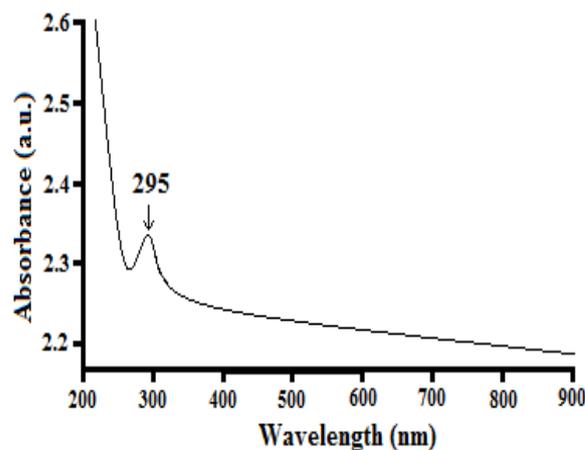


Fig. 3. Optical absorption spectrum of PVA capped ZnSe nanoparticles

Photoluminescence (PL) measurement is a sensitive non-destructive technique to investigate the intrinsic and extrinsic defects in a semiconductor. It provides abundant information on the energy states of impurities and defects, even at very low densities, which is helpful for

understanding structural defects in semiconductors [17]. A semiconductor is characterized by the electronic band structure in which the highest occupied molecular orbital is called the HOMO or valence band (VB) and the lowest unoccupied molecular orbital is called the LUMO or conduction band (CB). In the present case, the required value of energy between HOMO and LUMO orbitals is around 3.6 eV. PL spectrum is recorded with an excitation wavelength of 350 nm and is shown in Fig. 4. PL spectrum consists of luminescent peak at 431 nm which corresponds to blue region. The PL spectrum centered near 431 nm which is attributed to the recombination of excitons resulting in blue emission from the recombination of photon-generated holes with charge states [18].

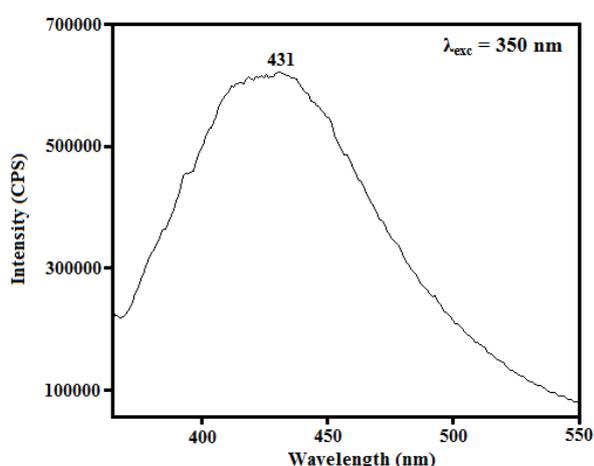


Fig. 4. Photoluminescence spectrum of PVA capped ZnSe nanoparticles

3.4. FT-IR studies

Fig. 5 represents the FT-IR spectrum of PVA capped ZnSe in the wavenumber range 500-4000 cm^{-1} . The bands observed at 3894, 3845, 3742, 3678, 3615 and 3280 cm^{-1} are attributed to ν (OH) stretching frequency, indicates the presence of hydroxyl groups [19, 20]. An intense strong band observed at 2920 cm^{-1} is due to ν_s (CH_2) stretching vibration [21]. The bands at 2362 and 1534 cm^{-1} are due to the C=O stretching mode arising from the absorption of atmospheric CO_2 on the surface of the nanoparticles [22]. Absorption peaks at 1711 and 1649 cm^{-1} are attributed to C=O, C=C stretching mode [23]. A band observed at 1424 cm^{-1} which is assigned to the symmetric bending mode of the δ (CH_2) group. A band assigned at 1372 cm^{-1} corresponds to the wagging mode of $\nu_w(\text{CH}_2)$. A band at 1330 cm^{-1} is assigned to the in - plane vibrations for the CH and OH modes. A strong absorption band observed at 1242 cm^{-1} is assigned to the wagging $\nu_w(\text{CH})$ group. In addition, C–O and C–C stretching vibration peaks appear at 1083 and 943 cm^{-1} respectively [24]. A band observed at 1024 cm^{-1} is assigned to C-O stretching and O-H bending vibrations. The band at 838 cm^{-1} corresponds to stretching vibration of C - C group. A band observed at 605 cm^{-1} is assigned to the wagging

mode of ν_w (OH) groups. A band observed at 538 cm^{-1} is assigned to the bending mode of δ (CO) group respectively [25].

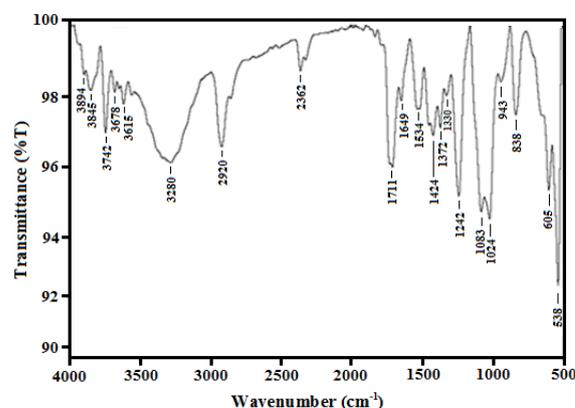


Fig. 5. FT-IR spectrum of PVA capped ZnSe nanoparticles

4. Conclusions

PVA capped ZnSe nanoparticles were prepared successfully by chemical reaction method. From the X-ray diffraction study, the evaluated average crystallite size of PVA capped ZnSe nanoparticles is 6 nm. The absorption band at 295 nm related to pure PVA and it is assigned to the electronic transition of $\Pi \rightarrow \Pi^*$. PL spectrum consists of luminescent peak at 431 nm which corresponds to blue region. The PL spectrum centered near 431 nm which is attributed to the recombination of excitons resulting in blue emission from the recombination of photon-generated holes with charge states. FT-IR spectrum shows the formation of vibrational bands at different regions.

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