

Structural and optical properties of polyvinyl pyrrolidone (PVP) capped cadmium sulphide (CdS) nanoparticles: Potential entity for optoelectronic device applications

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In the present work, we report the synthesis of polyvinyl pyrrolidone (PVP) capped cadmium sulphide (CdS) nanoparticles employing facile chemical precipitation technique in a methanolic medium at room temperature. The powder X-Ray Diffraction (PXRD) confirmed the hexagonal wurtzite structure. The functional groups were confirmed by the Fourier Transform Infrared Spectroscopy (FTIR). The alteration of band gap with size-quantization was investigated by UV reflectance spectroscopy. Luminescent behavior of the CdS nanoparticles was established through photoluminescence analysis. The emission spectrum was analyzed through Commission International de l'Eclairage (CIE) 1931 chromaticity diagram to explore the dominant emission from the CdS nanoparticles. Dynamic light scattering (DLS) analysis gives the hydrodynamic diameter of the CdS nanoparticles.

Keywords: Capping agent; Hexagonal wurtzite; Quantum confinement; Photoluminescence; Dynamic light scattering.

1. Introduction

Semiconductor nanocrystals are of great interest for both fundamental research and industrial development. This is due to their unique size-dependent optical and electronic properties and their exciting utilization in the fields of light-emitting diode, electrochemical cells, laser, hydrogen producing catalyst, biological label [1]. Semiconductor nanocrystals exhibit quantum confinement effects when their sizes are comparable with the diameter of the bulk exciton which leading to a splitting of the continuum of electronic energy levels into discrete states with an effective band gap blue shifted from that of the bulk [2]. In the past two decades, more and more attention has been paid to the II-VI compound semiconductors, such as, CdS, CdSe and CdTe for their unique optical property and potential application to photoelectronics, light switch and light emitting devices. Among these direct-band-gap semiconductors CdS is the most commonly used one owing to its good optical transmittance and wide band gap of 2.42 eV [3]. For the synthesis of semiconductor nanomaterials, a large number of synthetic methods, like solvo/hydrothermal, thermal evaporation, plasma method, solution based chemical methods and sonochemical methods have been employed. Co-precipitation method is the most popular technique that is used in industrial

applications because of the cheap raw materials, easy handling and large scale production [4]. In this scenario, CdS is an important semiconductor material, owing to its unique electronic, optical properties and thus its wide range of potential applications, such as in bio imaging, solar cells, photocatalysis and so on [5]. Within this vision, structural and optical properties of CdS nanoparticles were selected to be the topic of study of the present research work.

2. Experimental

2.1 Materials

Cadmium nitrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) {Merck}, polyvinyl pyrrolidone (PVP) {Himedia}, sodium sulphide (Na_2S) {Himedia}, methanol and ethanol.

2.2 Synthesis

CdS nanoparticles were prepared through facile chemical precipitation technique using non-aqueous medium. Typically, 0.1 M cadmium nitrate was dissolved in appropriate amount of methanol. Subsequently, 0.3 M polyvinyl pyrrolidone was slowly added to the above solution. In the mean time, 0.1 M sodium sulphide flakes were added to the appropriate amount of methanol. After, completion of dissolving of sodium sulphide flakes in methanol; then it was poured into the former solution and stirred vigorously for sufficient period to attain the complete reacted state. Finally, the yellow precipitate was obtained then it was centrifuged and washed many times with deionized water and ethanol until the impurities were removed. The resultant precipitate

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was left in a dark environment for complete dryness. At last, the dried powder was annealed at 200°C for about 2 hours.

2.3 Characterization

The Powder X-Ray Diffraction (PXRD) profile was analyzed using ISO DEBYEFLEX 2000 diffractometer employing Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation. The Shimadzu FT-IR instrument with a 1.0 cm^{-1} resolution was used to identify the functional groups present in the samples. The UV-vis-NIR reflectance spectrum was recorded in the wavelength range from 190 to 900 nm in the diffuse reflectance spectrum (DRS) mode using LABINDIA Model UV 3092 spectrophotometer. Photoluminescence (PL) response was carried out using Cary Eclipse Spectrophotometer with a 450W Xenon arc lamp as an excitation source. The secondary particle size was determined by dynamic light scattering (DLS) using Zetasizer Nano-ZS (Malvern,UK) under deionized water as dispersing agent.

3. Results and Discussion

3.1 Powder XRD Analysis

The Powder X-ray diffraction pattern of synthesized CdS sample after calcination at 200°C is shown in figure 1. The nanocrystalline hexagonal wurtzite structure of cadmium sulphide is confirmed by the presence of (002), (110) and (112) plane peaks appeared at 2θ angles of 26.19°, 43.62° and 51.34° respectively [Ref. ICDD Card no.41-1049]. The broadened characteristic diffraction peaks indicates that the smaller size of the CdS nanoparticles. The crystallite size was obtained using Scherrer's formula as follows [6],

$$D = 0.94 \lambda / \beta \cos(\theta) \quad (1)$$

where D is the particle diameter, 0.94 is the shape factor (in case of spherical particles), β is the full-width-at-half-maximum (FWHM) of the diffraction peak, λ is the wavelength (1.5406 \AA) of the X-ray radiation and θ is the angle of diffraction. The crystallite size of CdS nanoparticles was determined by Scherrer's relation and is found to be approximately 3.5 nm.

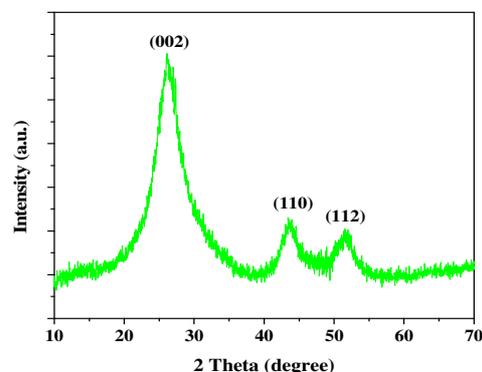


Figure 1. Powder XRD spectrum of PVP capped CdS nanoparticles

3.2 FTIR analysis

The Fourier transform infrared (FTIR) spectrum of PVP capped CdS nanoparticle is shown in figure 2. The band centered at 3437 cm^{-1} is attributed to O-H stretching mode of H₂O molecule. The peaks around 1276 cm^{-1} and 1651 cm^{-1} may corresponds to C-N stretching vibration and C=O stretching vibration of PVP [7]. The peaks centered at 1380 cm^{-1} and 2919 cm^{-1} were ascribed to the C-H bonding due to the presence of PVP. This may be due to the formation of coordinate bond between the nitrogen atom of the PVP and the Cd²⁺ ions as in the reported results [8]. The peaks emerged at 721 and 674 cm^{-1} have been assigned to CdS stretching bands [9]. These observations confirm the interaction of PVP molecule with the CdS nanoparticles.

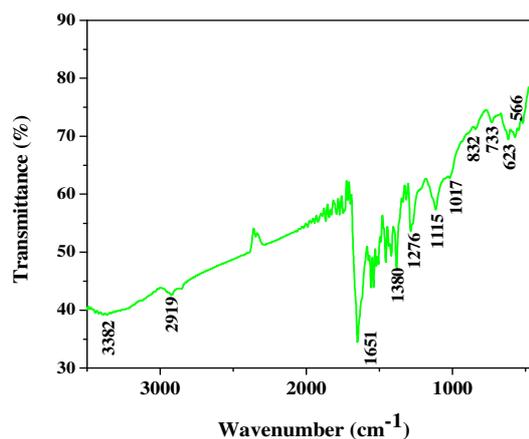


Figure 2 FTIR spectrum of PVP capped CdS nanoparticles

3.3 UV-vis-NIR reflectance analysis

UV-vis-NIR reflectance spectrum of PVP capped CdS nanoparticle is shown in figure 3. The absorption edge for the synthesized CdS nanoparticles is found at 477 nm corresponds to a band gap of 2.59 eV, which is blue shifted from the bulk band gap of CdS (2.42 eV, 515 nm) [10]. It is clearly seen from the spectrum that the absorption edge shifts towards lower wavelength leads to blue shift in the absorption edge of the synthesized CdS nanoparticles. In contrast to the bulk CdS, nanoparticle shows conventional blue shift in the absorption edge which indicates that the synthesized material is in the nanoscale regime.

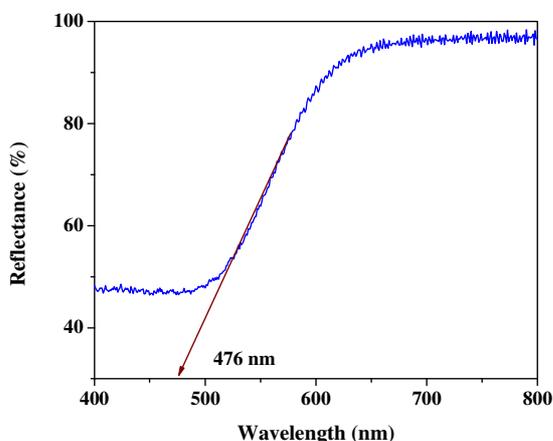


Figure 3. UV-vis-NIR reflectance spectrum of PVP capped CdS nanoparticles

3.4 Photoluminescence analysis

Photoluminescence spectrum of PVP capped CdS nanoparticle is shown in figure 4. It clearly shows the broad peak at 485 nm is attributed to radiative electron-hole recombination occurs near the band edge. The peak centered at 528 nm corresponds to green emission due to excitation from S interstitial [I_s^-] to the conduction band. Another peak centered at 544 nm gives out the yellow emission due to interstitial cadmium [I_{cd}^+] sites [11]. The origin of the defect levels may be coupled with cadmium and sulfur vacancies [3]. In order to investigate the emission color of the CdS nanoparticles, emission spectrum was characterized using CIE 1931 chromaticity diagram. Hence, in our present work, the color chromaticity coordinates (x, y) of CdS nanoparticles were calculated from the emission spectrum by using the commission international De

l'Eclairage (CIE) system. The standard x and y coordinates ($x=0.33, y=0.33$) corresponding to the location of the white light emission is always sited at the center of the CIE 1931 chromaticity diagram [12]. The CIE chromaticity diagram for CdS nanoparticles upon excitation at 400 nm is shown in figure 5. The CIE coordinates (x, y) are found to be (0.2285, 0.2329) which lies within the blue region. Therefore, it may be concluded that the synthesized CdS nanoparticles can serve as a blue color producing material for visible light device applications and light emitting diodes.

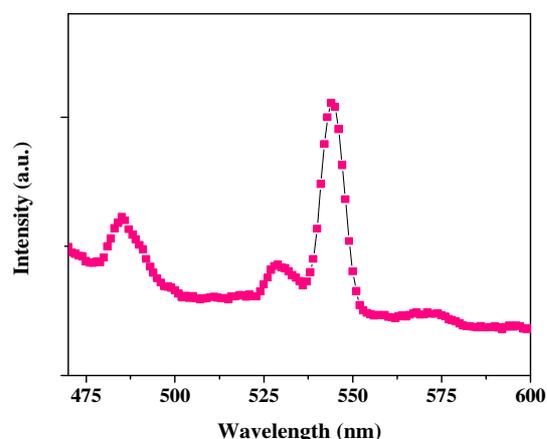


Figure 4. Photoluminescence spectrum of PVP capped CdS nanoparticles

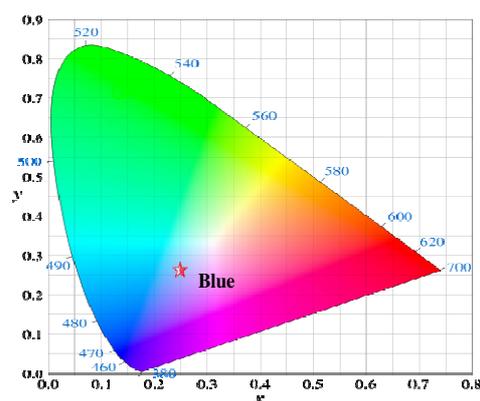


Figure 5. CIE color chromaticity diagram of PVP capped CdS nanoparticles

3.5 Dynamic light scattering analysis

Dynamic light scattering (DLS) is a commonly used particle sizing method that can be carried out directly in aqueous solution. DLS has been applied to a number of systems, including both organic and inorganic nanoparticles and for species ranging in size from nanometers to microns. However, because the diameters measured by DLS are hydrodynamic, the results can be affected by the attributes of the system other than the primary nanoparticle size, such as the aggregation state [13]. DLS spectrum PVP capped CdS nanoparticle is shown in figure 6. The secondary particle size of the CdS nanoparticles is found to be 532 nm which is very much large compared to that of TEM value. A great discrepancy in the particle size between TEM and DLS was observed. It is because aggregates of nanoparticles will diffuse more slowly in solution than individual nanoparticles. Thus the aggregates effectively behave as larger particles. In addition, the DLS measurement gives the mean hydrodynamic diameter of the CdS core surrounded by the organic and solvation layers, and the hydrodynamic diameter

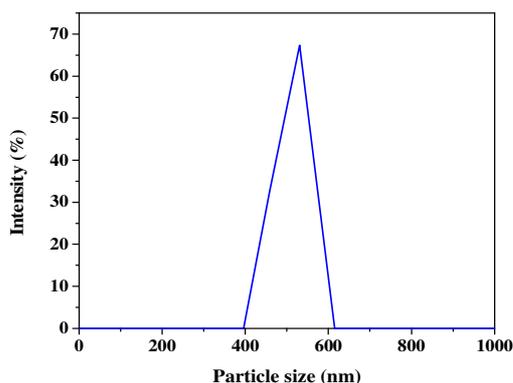


Figure 6 DLS distribution of particle size of PVP capped CdS nanoparticles

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is influenced by the viscosity and concentration of the solution [13, 14]. On the other hand, TEM gives the diameter of the core only. The single DLS peak for the synthesized sample shows the quality of CdS nanoparticles and they are mono-dispersed in nature. In short, the DLS results were well supported with the earlier reports.

4. Conclusions

In conclusion, PVP capped CdS nanoparticles were successfully synthesized by facile chemical precipitation technique. Powder XRD result reveals that CdS nanoparticles exhibit hexagonal wurtzite structure and crystallite size was found to be approximately 3.5 nm by using Scherrer's equation. FTIR analysis confirms the formation of CdS along with PVP through the existence of its functional groups. UV-vis-NIR reflectance spectrum proves the blue shift nature of the synthesized CdS nanoparticles and the band gap is found to be 2.59 eV. Excitonic and defect related emissions were analyzed through photoluminescence spectroscopy. CIE color chromaticity coordinates proves the dominant blue emission and establishes the suitability of CdS nanoparticles to blue light based device applications. Based on these valuable discussions, this work may open up some useful suggestions to fabricate optoelectronic devices.

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