5. Properties of CdS Nanoparticles prepared by Electro-explosion of Wires

Abstract

In this chapter we investigate the properties of CdS nanoparticles prepared by electro-explosion of wire. Structural and optical characterization of the CdS nanoparticles is carried out using techniques similar to those employed to study ZnS nanoparticles in chapter 4. Here we study the evolution of structural, electronic and optical properties of CdS nanoparticles strongly interacting with surrounding water molecules. An attempt has been made to explain the structural transformation of CdS nanoparticles on the basis of the change occurring in their crystallinity, band structure and local chemical environment.
5.1 Introduction

Alike ZnS, cadmium sulphide (CdS) is another technologically important group II-VI wide band gap direct semiconductor. In the previous chapter we have studied ZnS nanoparticles synthesized by the exploding wire method. In this chapter we carry out the same experimental exercise to study the various properties of CdS nanoparticles prepared by this new method. The characterization of CdS nanoparticles prepared by exploding wire method is important as we believe that a wide variety of semiconductors (especially zinc and cadmium chalcogenides) can be synthesized employing the potential of the novel technique of electro-explosion of wire (EEW). From a number of chalcogenides we have chosen CdS because of its close structural resemblance to ZnS.

In the subsequent sections we provide evidence for the formation of CdS nanoparticles employing the novel and facile approach of EEW. Pure CdS particles in the size range 2.3nm-13.4nm are obtained as free standing particles in the form of colloidal suspension.

The resulting CdS particles show broadening of the characteristic X-ray powder diffraction (XRD) lines. Atomic force microscopic (AFM) measurements partly exhibit the particle sizes but show aggregation. Fourier transform infrared (FTIR) spectroscopy allows us to identify the various vibrational modes present in the material. X-ray photoelectron spectroscopy (XPS) confirms the presence of cadmium and sulphur at the surface of the prepared film. Optical properties of these particles were studied by employing UV-Visible absorption and photoluminescence (PL) spectroscopy. Increased band gap of the CdS nanoparticles is indicated in their UV-Visible spectra. Various channels of radiative emission and hence few aspects of the band structure of CdS nanoparticles and its temporal evolution are revealed by PL spectroscopy.

5.2 Experimental Details

Our method of synthesizing pure CdS nanoparticles is to employ the EEW technique [1-3]. The details of this synthesis method have already been provided in chapter 2. The methodology of preparing CdS nanoparticles is same as that of ZnS nanoparticles and the formation of both types of nanoparticles is primarily driven by the same reaction
mechanism. The only change in case of CdS nanoparticles is that a wire and a plate of cadmium metal are used for electro-explosion. However, for the sake of completeness, the preparation procedure is briefly explained as follows:

High purity (99.999%) cadmium wires, 1 mm in diameter, are exploded against a Cd plate (held at 12-24V with respect to the wire) achieving current densities of the order of $10^8$ amp.m$^{-2}$. These explosions are carried out in a reactor vessel containing sodium sulphide solution. Aqueous solution of Na$_2$S generates the S$^{-2}$ ions. As the free end of the Cd wire is contacted with the plate, the accompanying explosion fragments the cross-sectional region of the Cd wire to atomic dimensions. Cd$^{+2}$ ions created by the explosion react with the S$^{-2}$ ions present in the chamber and therefore, produce CdS nanoparticles.

Following several explosions, CdS nanoparticles are obtained as a greenish-black coloured colloidal suspension. In order to make powder samples, this suspension is centrifuged at 5000 RPM for 45 minutes. Centrifugation segregates the CdS nanoparticles from liquid. After discarding the liquid part, the remaining CdS nanoparticles are extracted with acetone. A thin powder film of the nanoparticles is prepared by layered deposition of the colloidal suspension of the nanoparticles on a glass substrate.

A number of colloidal and then subsequently powder samples of CdS nanoparticles were prepared by varying the synthesis conditions, e.g., amount of Cd metal exploded, voltage applied for explosion and concentration of Na$_2$S solution etc.

In short, synthesis and sample preparation for characterization of CdS nanoparticles is carried out in the same fashion as what has been done in the case of nanocrystalline ZnS.

In the subsequent section we present the results of various characterization performed employing the AFM, XRD, FTIR, XPS, UV-Visible and PL techniques to study the structural and optical properties of CdS nanoparticles.

5.3 Results & Discussions

The colour of colloidal suspension of CdS nanoparticles just after the explosion is greenish-black. Interestingly this greenish-black coloured suspension turns out to yellow after around a month. There is no further visible change in the colour of colloidal suspension of CdS nanoparticles after one month (i.e. after a yellow coloured solution is
obtained). The visual change in colour of colloidal CdS nanoparticles is shown in Fig. 5.1.

![Fig. 5.1: Snaps demonstrating the colour change of colloidal CdS nanoparticles. The colour of the suspension just after the explosion is greenish-black (a) which turns to yellowish-orange after one month (b).](image)

This rate of change of the colour of colloidal CdS nanoparticles is far slower than what has been observed in the case of colloidal suspension of ZnS nanoparticles. It has been discussed in the last chapter that a black coloured colloidal suspension of ZnS nanoparticles changes to rust-brown and then finally to white coloured stabilized form of ZnS nanoparticles. In the present case of CdS suspension there is no clearly seen intermediate/metastable stage between the greenish-black and yellow coloured forms. At most we can state that there is no intermediate/metastable stage in the case of CdS nanoparticles and even if there is any such stage, it could not be visibly observed.

There is another remarkable difference in the process of transformation of ZnS and CdS nanoparticles. We observed that colour of the powder samples of ZnS nanoparticles extracted from their colloidal suspensions at the three stages retain the colours of their parent solutions. But this is not the case with the CdS nanoparticles. With the drying up of colloidal CdS particles (extracted with acetone) the colour of powder film rapidly turns to yellow. Therefore, the final colour of powder films prepared by either the greenish-black (at initial stage) or yellow (at final stage) colloidal suspensions is same (i.e. yellow).
Fig. 5.2 shows the change in the colour of nanoparticles following powder film formation just after the explosion.

![Image of nanoparticle change](image)

Fig. 5.2: Change in the colour of CdS nanoparticles during the powder film formation. Greenish-black coloured film (a) turns to yellow (b) upon drying.

This rapid change in colour upon drying (i.e. removal of water) indicates that in the case of CdS nanoparticles, rate of change of colour has a greater dependence on the aqueous environment as compared to ZnS nanoparticles.

These indications of the transformation in CdS nanoparticles prepared by the exploding wire technique prompt us to characterize these samples by various techniques. Since the characterization of the powder samples in wet state was not possible in several experimental techniques employed in the present study, in this chapter we discuss the results pertaining to the dry powder (yellow-coloured) of CdS nanoparticles.

### 5.3.1 Atomic Force Microscopy

An AFM was employed in the contact mode to obtain real space topographic images of the powder film of CdS nanoparticles. AFM morphology not only illustrates the shape of nanoparticles but we can also directly measure the sizes of CdS nanoparticles. In Fig. 5.3 we show a typical topographic data obtained for a thin film of CdS nanoparticles. Here the topograph on the left is a two-dimensional (2-D) AFM image for 1μm² scan area of the film. In the line plot to the right, the height profile of two particles (selected by a line in AFM picture passing over these two particles) is also shown.
Fig. 5.3: A 2-D AFM image (left) for the CdS nanoparticles and the height profile (right) of the particles corresponding to a line drawn in the image.

Particles of irregular shapes were seen in the AFM images for all the CdS samples. The minimum size of the particles which can be distinctly observed is ~ 20nm. It is evident in the AFM image as well as in the plot for height profile that average size of most of the particles is ~ 40nm. Moreover, the AFM image shows the presence of larger particles and agglomerates. Therefore, the AFM image demonstrates a broad size distribution of CdS nanoparticles in the powder film.

5.3.2 X-Ray Diffraction

In Fig. 5.4, we show the reference 0-20 scan for cadmium metal used for explosion in the preparation of CdS nanoparticles. The intense peaks at 31.4143° (002), 34.2596° (100), 38.0033° (101), 47.4376° (102), 60.6156° (103), 61.9634° (110), 71.2479° (112) and 75.1414° (201) match closely the hexagonal crystal system of bulk cadmium (ICDD reference code: 05-0674) [4].

XRD pattern of powder CdS nanoparticles prepared employing the electro-explosion of Cd wire is shown in Fig. 5.5.
Fig. 5.4: XRD pattern for the cadmium metal used for explosion. Prominent peak positions are marked by arrows.

Fig. 5.5: X-ray diffractogram of powder CdS nanoparticles. Peaks due to CdS nanoparticles are marked by double-tailed arrows and single arrow indicates the most prominent peak due to bulk cadmium used for explosion.
This diffractogram (Fig. 5.5) shows broad peaks at 26.4226°, 43.6606°, 51.5807° and 72.6622°. These peaks are indexed to diffractions from (111), (220), (311) and (331) planes of CdS. The peak-positions match with the cubic structured CdS crystal (Reference code 10-0454 for Hawleyite) [5]. A less prominent but sharp peak at 38.1864° is also observed in the XRD pattern. Since this peak matches with the most prominent (101) plane of the bulk Cd used for explosion, we attribute this peak to the presence of a small quantity of Cd particles in the powder film. However, a comparatively reduced intensity of this peak indicates that Cd particles are in very minute amount in the sample.

Broad peaks are the signature of finite size of the crystal as the long range periodic structure is lacking in the case of nanoparticles. The average size of the nanoparticles has been determined from the broadening of the XRD lines, employing the Debye-Scherrer equation [6, 7] by recording the full width at half maxima (FWHM) of the peaks. The estimated size of the nanocrystallites is in a broad range 2.3nm -13.4nm. Since the Bohr excitonic diameter of CdS particles is 6nm, not all the CdS nanoparticles prepared by EEW method are quantum confined. The smallest particles seen in the AFM image (Fig. 5.3) are approximately close to the higher limit of size-range estimated by the Debye-Scherrer relation. In AFM we see many particles far larger than the maximum size of particles calculated by XRD line broadening. These larger particles/agglomerates observed in AFM are actually physically bonded smaller units of CdS nanocrystallites.

5.3.3 Fourier Transform Infrared Spectroscopy

FTIR spectrum of the CdS nanoparticles in KBr pressed pellets is shown in Fig. 5.6. This spectrum demonstrates the presence of many vibartional modes in the CdS nanoparticles embedded in a KBr matrix. We have assigned the various peak positions to their corresponding functional groups. In the following we discuss point-wise only those vibrational modes which are most relevant to this study.

(i) Strong interaction of water with the surface of CdS is reflected by a broad dip at ~3460cm⁻¹ due to O-H stretching and a sharp peak at 1633cm⁻¹ due to H-O-H bending mode of the adsorbed lattice water [8]. This would signify almost free water molecules, trapped in the lattice, in the process of initiating a composite interaction with the lattice. Moreover, lattice water also absorbs the low frequency region (300-600cm⁻¹) owing to
librational modes as the rotational motions of the water molecule are restricted in the crystal lattice because of H-bonding to neighbouring atoms [8]. Peaks at 468, 660 cm\(^{-1}\), may be due to such modes. The sample also has sulphates (1000-1050 cm\(^{-1}\)) compounded with water [8]. A peak observed at 1008 cm\(^{-1}\) is a signature of sulphate formation.

Figure 5.6: FTIR spectrum of CdS nanoparticles in the scan range 390-4000 cm\(^{-1}\). Inset shows the Zoomed portion of the curve in the 2204-2588 cm\(^{-1}\) range. The peak position of S-H vibration is marked by an arrow in the inset.

(ii) The most remarkable distinction that comes forth is a signature peak at 2361 cm\(^{-1}\) for the water-stabilized CdS samples (peak position is marked by an arrow in the inset to Fig. 5.6). This peak can be assigned to the presence of S-H groups according to published data for electronic grade ZnS by Hertl [9]. Lately, Zhang et al. [10] have also reported the S-H stretching band at \(\sim 2360\) cm\(^{-1}\). The shape of S-H vibration in our FTIR data is similar to what has been reported for S-H peak by Zhang et al [10].

The presence of this peak reveals that CdS nanoparticles are also stabilized by water and the peak for S-H vibration is the direct evidence of such an interaction.

(iii) Often a peak at 405 cm\(^{-1}\) is reported to be the vibration of Cd-S [11, 12, 13]. A weak peak around 407 cm\(^{-1}\) is the representative of Cd-S vibration in our samples. However a peak at 415 cm\(^{-1}\) is more readily seen. This 8 cm\(^{-1}\) blue shift can be inferred as a deviation
from the fundamental Cd-S vibration. This shift can be justified as in our sample most of the CdS particles are not pure as free particles and due to strong interaction with water most of them have transformed to water-stabilized CdS nanoparticles. In the Fig. 5.7 we show a pictorial representation of the water-induced stabilized structure of CdS nanoparticles.

Fig. 5.7: An artistic impression of water-stabilized CdS nanoparticles. Figure shows the CdS molecule interacting with the H₂O. S-H interaction is illustrated by a dashed line.

(iv) Jin et al. [14] have attributed the weak peaks at 1558 and 1417 cm⁻¹ to a bit of unreacted Cd²⁺ in a micelle nucleus. Their result is in good agreement with the research of Urquhart et al. [15] in which they propose that the formation of CdS particle during reaction of carbonyl cadmium with H₂S could not be complete.

We also have peaks at 1417 and 1555 cm⁻¹ in the FTIR spectrum of CdS nanoparticles. In the light of above observations, the probable reason behind these peaks may be understood as the presence of unreacted Cd²⁺ ions (Cd⁺⁻Cd⁺) in our sample. This follows our description that the CdS nanoparticles are prepared due to the reaction of Cd²⁺ ions with S²⁻ ions. In order to produce a sufficient amount of CdS nanoparticles and therefore to achieve a sufficient amount of Cd²⁺ ions we iterate the spark/explosion process several times. It is likely that after few sparks all the S²⁻ ions get exhausted by reacting with the equiproportion amount of Cd²⁺ ions and then there is no S²⁻ ions available for further reaction and as a result the surplus Cd²⁺ ions remain unreacted. This assumption is endorsed by the presence of a peak at 38.1864° in the XRD of CdS nanoparticles (Fig. 5.5) which corresponds to the (101) plane of bulk cadmium (ICDD reference code: 05-0674) used for the production of nanoparticles (Fig. 5.4).
(v) Organic-modes:
A band at 1700 cm$^{-1}$ is associated with carbonyl stretch $\nu_a$ (C=O) stretching [16]. A peak observed at 1700 cm$^{-1}$ in our case could be due to such a mode. The asymmetric $\nu_a$ (CH$_2$) and symmetric $\nu_s$ (CH$_2$) methylene stretching modes have been reported to appear at 2919 and 2850 cm$^{-1}$ [15]. The weak peaks at 2918 and 2852 cm$^{-1}$ may be due to these modes. Most of these organic modes, especially carbonyl (C=O) stretch most probably arising due to minute residue of acetone as it is used during various cleaning and making a pellet to obtain the FTIR data of CdS nanoparticles.

5.3.4 X-Ray Photoelectron Spectroscopy

![XPS Spectrum](image)

**Fig. 5.8:** Broad scan (0-1300 eV) XPS spectrum of CdS nanoparticles. Sulphur (S 2p$_{3/2}$) and Cadmium (Cd 3d$_{5/2}$ & Cd 3d$_{3/2}$) photoelectron peaks are shown in the left and right insets respectively.

In Fig. 5.8, a broad scan survey spectrum in the range 0-1300 eV shows the presence of various photoemission and Auger emissions pertaining to the constituents of the CdS nanoparticles. In the left and right insets to Fig. 5.8 we show the core level spectra for sulphur (S 2p$_{3/2}$) and cadmium (Cd 3d$_{5/2}$ & Cd 3d$_{3/2}$) photoelectron peaks [17, 18]. The presence of core level photoelectron emissions from Cd 3d$_{5/2}$ (404.6 eV) & Cd 3d$_{3/2}$
(411.4eV) and S 2p3/2 (161.6eV) convinces us regarding the presence of CdS nanoparticles on the surface of the powder film.

In the broad scan (0-1300eV) the various peak positions are assigned in the following table 5.1 [17, 18].

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Peak assignment</th>
<th>Peak position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cadmium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd 3d5/2</td>
<td>404.4</td>
</tr>
<tr>
<td></td>
<td>Cd 3d3/2</td>
<td>410.9</td>
</tr>
<tr>
<td></td>
<td>Cd 3p1/2</td>
<td>651.0</td>
</tr>
<tr>
<td></td>
<td>Cd 3p3/2</td>
<td>618.6</td>
</tr>
<tr>
<td></td>
<td>Cd 4p3/2</td>
<td>68.8</td>
</tr>
<tr>
<td></td>
<td>Cd 4d</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>Cd M3N4S4N4S</td>
<td>1111.8</td>
</tr>
<tr>
<td></td>
<td>Cd M4N4S4N4S</td>
<td>1105.3</td>
</tr>
<tr>
<td>2.</td>
<td>Sulphur</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S 2p3/2</td>
<td>162.2</td>
</tr>
<tr>
<td></td>
<td>S 2s1/2</td>
<td>224.7</td>
</tr>
<tr>
<td>3.</td>
<td>Oxygen</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O 1s1/2</td>
<td>532.1</td>
</tr>
<tr>
<td>4.</td>
<td>Sodium</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Na 1s1/2</td>
<td>1070.7</td>
</tr>
<tr>
<td></td>
<td>Na KL23L23 (A)</td>
<td>497.5</td>
</tr>
<tr>
<td>5.</td>
<td>Carbon</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C 1s1/2</td>
<td>284.6</td>
</tr>
<tr>
<td></td>
<td>C KL23L23</td>
<td>1224.2</td>
</tr>
</tbody>
</table>

The peak at 10.8eV, which is assigned to the emission of Cd 4d, may have interference due to photoemission from S 3s1/2. The photoelectron peak due to oxygen may be due to any of the following three reasons:

(a) Absorption of atmospheric moisture

(b) Lattice water trapped in the sample, as indicated in FTIR results

(c) Due to the combined effects of both factors a & b

The photoemission and Auger peaks of carbon are due to the exposure of sample to the atmosphere while processing and experimentation.

**Quantitative analysis:**

In the last chapter we have used eqn. (4.21) to determine the relative concentrations of various constituents of ZnS nanoparticles. Following the same method we have also calculated the atomic concentrations of the constituents in the CdS nanoparticles.
A generalized expression for determination of the atom fraction ($C_x$) of any constituent (x) in a sample can be given as:

$$C_x = \frac{n_x}{\sum_i n_i} = \frac{I_x / S_x}{\sum_i I_i / S_i}$$

where, $S$ = Atomic sensitivity factor (A.S.F.)

$I$ = Intensity (number of photoelectrons/sec)

$n$ = Number of atoms of element/cm$^3$ of sample

The A.S.F. values used in this calculation were obtained from the available data. These values for Cd 3d$_{5/2}$, S 2p$_{3/2}$, O 1s and Na 1s are reported as 2.55, 0.35, 0.63 and 2.27 respectively [18].

The estimated values of atomic concentrations of the constituents in the stabilized CdS nanoparticles are presented in the following table.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Relative Concentrations</th>
<th>Compositional Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd 3d$_{5/2}$</td>
<td>S 2p$_{3/2}$</td>
</tr>
<tr>
<td></td>
<td>2.04</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Possible compounds present in the sample/Remarks:

CdS + Cd$_{1.04}$O$_{0.95}$Na$_{0.34}$

Therefore, there is no possibility of Na$_2$S. Only remaining option can be written as: CdS + (Cd$_{1.04}$+Na$_{0.34}$+O$_{0.95}$)

The results of the stoichiometric analysis confirm the formation of cadmium sulphide. Moreover, there is no amount of sulphur remaining, as all the sulphur gets associated with cadmium to form CdS. Hence in the stabilized stage there is no free sulphur or Na$_2$S. However, an additional amount of Cd is determined. Since in the XRD pattern (in Fig. 5.5) we do not observe the presence of any compound other than CdS, there is no possibility of CdO formation. CdO formation is further ruled out by the XPS core level spectra of O(1s) where a binding energy of ~532 eV is observed. So the only remaining possibility is the presence of free Cd particles. The presence of Cd particles was revealed in the XRD pattern (in Fig. 5.5) and further noticed in FTIR spectrum (Fig. 5.6) of CdS nanoparticles.

137
The presence of sodium may be in the form of residual NaOH etc. due to formation of some complex with water. The remaining amount of oxygen is most probably due to the presence of O in the form of trapped lattice water. This lattice water assists in water-induced stabilization of CdS nanoparticles.

5.3.5 UV-Visible and Photoluminescence Spectroscopy

Till now we have discussed the results from the powdered CdS nanoparticles at the stabilized stage when the yellow coloured film is completely dry. The reason behind probing the nanoparticles only at this stage was that the CdS after preparation directly forms the stabilized phase after drying. Thus variation in AFM, XRD, FTIR and XPS characteristics of the CdS nanoparticles could not be investigated, as dried powders are prerequisite for these techniques. After attaining the stabilized stage, the results of these investigations were not different for the CdS nanoparticles. Therefore, we have presented only single graph/spectrum for each characterization.

However, the yellow coloured ZnS nanoparticles showed variation with time when investigated with UV-Visible and PL spectroscopy. Now we proceed to understand the change in the band structure and hence change in the optical properties of the CdS nanoparticles at various stages as defined below. The three stages have been chosen as follows:

(a) Stage 1: just after the explosion
(b) Stage 2: after retaining in water for 7 days
(c) Stage 3: after retaining in water for 20 days

There is no remarkable change in the UV-Visible absorption and PL emission spectra of CdS nanoparticles after 20 days. As mentioned before, all samples are visibly yellow in colour.

In the Fig. 5.9 we show the normalized UV-Visible absorption spectra of the CdS nanoparticles at three stages in the wavelength range 200-800nm. The bulk band gap for the cubic CdS is 2.42eV at 300K (i.e. room temperature), which correspond to the wavelength 515nm [19, 10]. In all the spectra a, b and c recorded we observe an absorption edge developing at approximately 470nm. We can further determine the exact
position of maxima by differentiating the spectrum. The peak position thus ascertained is 465nm (i.e. 2.67eV).

Fig. 5.9: UV-Visible absorption spectra of CdS nanoparticles for (a) just after the explosion (circles), (b) after 7 days (squares) and (c) after 20 days (triangles). While the single arrow shows the band edge absorption the double-tailed arrow demonstrates the evolution of a peak at approx. 700nm.

This blue shift of peak by 0.17eV from the bulk band gap indicates the enhanced band gap of CdS nanoparticles. Presence of this peak in the spectra a, b and c confirms the formation of CdS nanoparticles just after the explosion and their presence afterwards. Usually a distinct excitonic peak is anticipated for quantum mechanically confined CdS nanoparticles at room temperature. However we do not get any such peak, possibly due to broad size distribution of the particles as clearly revealed by AFM and XRD, and therefore not all of the CdS nanoparticles present in the sample are quantum confined particles.

Interestingly we observe that there is no peak around 700nm in the CdS nanoparticles just after the explosion but an edge starts developing in the sample after 7 days and then this peak gets prominent in the spectrum for CdS nanoparticles after 20 days. Emergence of this new peak indicates the change in the band structure of CdS
nanoparticles in an aqueous environment. The emergence of this peak coincides with the lack of uniform small sized particles. A peak at 650-700nm has indeed been seen in the literature for CdS in presence of capping agents containing aniline. We propose this peak to be a complex formation of CdS with the water present during the process of obtaining these particles. Unlike ZnS where such a complex is weak and subsequently breaks down yielding ZnS nanoparticles, large CdS complexes tend to stabilize here.

The presence of larger CdS complexes also explains the onset of UV absorption at around 500nm, rather than a lower value of ~400nm as reported by some workers.

In order to analyze the change in the band structure we characterize the CdS nanoparticles employing PL spectroscopy at stages b (after 7 days) and c (after 20 days). In the Fig. 5.10 we show the normalized PL emission data for the CdS nanoparticles after 7 days and after 20 days.

![Normalized PL emission spectrum of CdS nanoparticles (i) after 7 days (lower) and (ii) after 20 days (upper). Inverted triangle and double-tailed arrows show the green and red emission respectively while the shift in the emission peak in the IR region.](image)

The most prominent emission in both the spectra is observed at 700.3nm. The energy equivalent to this peak position is 1.76eV. While an emission peak at 873.2nm is
observed for the CdS nanoparticles after 7 days. This peak in the IR region gets blue shifted by 0.053eV to appear at 841.8nm for the CdS nanoparticles after 20 days.

Blue-shift in the peak position for the luminescence of CdS nanoparticles is often reported to be due to dissimilar chemical environment [12, 20, 21]. The blue shift of the peak position in our case indicates the change in the chemical environment of CdS nanoparticles under the influence of water. The temporal evolution of band structure is most evident in the form of a new peak appearing at 551.8nm (2.24eV) for the CdS nanoparticles after 20 days. The structural alteration of CdS nanoparticles is leading to the variation in the band structure of CdS nanoparticles with time.

*Model for PL emission in CdS nanoparticles:*

In this section we elucidate the photophysics behind CdS nanoparticles prepared by the exploding wire method. We have attempted to understand the change in the band structure on the basis of various radiative emissions occurring in the nanoparticles.

In CdS, the valence band consists largely of s and p orbitals from sulphur while the conduction band is mainly due to s-orbitals of cadmium [22]. Sulphur vacancies (Vₐ) in CdS are the localized sites just below the conduction band (CB) and interstitial sulphur (Iₐ) are above the valence band (VB). The position and role of interstitial sulphur and sulphur vacancies has already been discussed in detail in section 4.3.6 of chapter 4.

A considerable effort in the literature has been dedicated to study the luminescence of CdS nanoparticles or nanorods [23]. In a report as early as 1959 Vuylsteke et al. have explained the fundamental aspects of the luminescence of CdS crystals on the basis of sulphur vacancy mechanism in pure CdS [24]. They attributed the green emission at 524nm (2.38eV) to direct recombination whereas the red emission at 718nm (1.72eV), described in terms of a phenomenological model, was attributed to the presence of sulphur vacancies [24]. In few reports, the peak at 552nm has been assigned to the green photoluminescence in CdS nanoparticles [23, 25]. In our case, the peak at 551.83nm is close to the green emission peak at 552nm as reported by Liu et al. [25]. Similar to the shift in the position of green emission, the red emission in our CdS nanoparticles is also shifted by 18nm from the reported data and observed at 700.3nm (1.76eV) [24].
In the light of the report by Vuylsteke et al. the mechanism of green and red emission can be understood as follows [24]:

The 700.3nm radiation emitted in the trapping process is the observed red luminescence. Under sufficiently intense excitation it is assumed that an equilibrium is established in which each vacancy site contains only one electron, since the energy of the single remaining electron will be quite low and a site with one electron missing will repel additional holes. For incident intensities, beyond the value required to establish this condition, electrons and holes begin to recombine directly giving rise to the observed green emission at 551.8nm. In other words, the emission peak at 551.8nm is originating from a surface trap, which involves the recombination of electrons trapped inside a sulphur vacancy with a hole in the valence band of CdS nanoparticles. On the basis of this explanation we show the various optical processes (absorption and emission) in the following schematic diagram.

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Fig. 5.11: Schematic energy transfer diagram for the PL emission of CdS nanoparticles after 7 days (left) and after 20 days (right). Upwards arrows (↑) show the absorption and downward arrows (↓) show the emission process.Interstitial sulphur (Is) and sulphur vacancy (Vs) levels are also shown. All the values of transition energies are given in the units of nanometers (nm).
Based on the UV-Visible and PL spectroscopy we infer that new/modified channels of absorption and emission appear due to change in the band structure of CdS nanoparticles as seen in the Fig. 5.11. The broad distribution noticed in both the PL spectra is the effect of broad energy distribution for emission in CdS nanoparticles. The broad distribution of emission energy in our sample arises due to the broad size distribution of CdS nanoparticles as per our discussion of the AFM and XRD results.

Moreover, the change in the band structure is yet another evidence of water driven transformation of CdS nanoparticles. Correlating with ZnS, we can state that a structural transformation could be behind this as well. However, with the presently available tools at our disposal, such minute changes in the structure could not be ascertained.

5.4 Conclusions

The colloidal and then subsequently powder CdS nanoparticles were prepared employing exploding wire technique. Similar to the ZnS nanoparticles, CdS nanoparticles also show the transformation of structure with the evolution of time. These particles are sensitive to water as the enhanced surface states of CdS nanoparticles strongly interact with the polar water molecule. The principal cause of the stabilization of CdS nanoparticles is the S-H vibration which has been earlier noticed in the ZnS case too. Although the rate of transformation is different in ZnS and CdS nanocrystallites, both attain a water-induced stabilized form at which they achieve their minimum free energy configuration. Similar to ZnS the phase transition of CdS nanoparticles is also irreversible. The rapid change in the colour of CdS nanoparticles in the absence of water shows the tremendous water-sensing capability of these particles.
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