SYNTHESIS AND CHARACTERIZATION OF PVA CAPPED CdSe NANOPARTICLES FROM AN AMMONIA FREE BATH

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Abstract- Polymer capped cadmium selenide (CdSe) nanoparticles of average sizes within quantum dot (QD) regime have been synthesized by a simple chemical route without using any complexing agent. Polyvinyl alcohol (PVA) was used as a stabilizer as well as host matrix to prevent agglomeration of nanoparticles. The growth of the CdSe nanoparticles (NPs) was investigated with the help of UV-Vis spectroscopy during the progress of the reaction. The formation of CdSe nanoparticles were further confirmed by the photoluminescence (PL), X-Ray diffraction (XRD) and transmission electron microscopy (TEM). The XRD result reveals that as synthesized CdSe nanoparticles have a hexagonal phase. Further, TEM analysis shows that as synthesized CdSe NPs are spherical in shape and well dispersed within the PVA system.

Keywords - PVA, Nanocomposite, Band gap shift

I. INTRODUCTION
Synthesis of CdSe nanoparticles (NPs) with uniform size distribution and controlled dispersity is an important area of research in the field of optoelectronics and semiconductor devices due to their unique optical properties, bright photoluminescence and tuneable size [1, 2]. Various inorganic/organic capping agents have been used as a stabilizer for obtaining stable CdSe nanoparticles [2]. Among these, polymer capped CdSe NPs are found to be suitable because use of polymer is a prominent method for synthesizing semiconductor nanoparticles in thin film form as polymer matrices provides easy and controlled processability, in terms of growth and morphology. CdSe NPs with controlled size and dispersity in polymer matrix was reported by various workers [3-7]. Polyvinyl alcohol (PVA) polymers have especially been given a great deal of attention due to their excellent chemical resistance, physical properties and biodegradability. Moreover PVA is a good host matrix for the embedding of metal nanoparticles [7, 8]. PVA capped CdSe NPs with the size within their quantum dot regime have been applied in the fabrication of LEDs, TFTs, solar cells etc [9-10]. In most of the synthesis technique for CdSe NPs, the complexing agent ammonia plays a key role in the reaction mechanism [11-12]. However, due to volatility of ammonia, it is difficult to control the pH at a fixed value. The changes in the pH of the reaction medium may results into non-uniformity in their sizes and shapes.

Here in we have reported a simple technique for synthesis of CdSe NPs in which polyvinyl alcohol was used as a stabilizing agent. The growths of the CdSe nanoparticles were studied by UV-Vis absorption spectroscopy with aging of time. The sizes of the nanoparticles were determined from EMA method and TEM analysis.

2. EXPERIMENTAL:
2.1. MATERIALS AND CHARACTERIZATION TECHNIQUES:
All reagents such as sodium sulphite (Na2SO3), metallic selenium powder (Se), cadmium chloride (CdCl2.H2O) and polyvinyl alcohol (PVA, MW= 14,000 gm) were of analytical grade, purchased from Merk (India) Ltd and used directly as received without any further purification. Deionised water was used throughout the experiment.

For optical studies, absorption spectra were recorded with a Hitachi (U 3900) UV-Vis Spectrophotometer. Photoluminescence spectra were recorded with a Hitachi (F-2700) Fluorescence spectrophotometer. The crystallographic structure of the CdSe/PVA thin films were analysed with a Rigaku Ultima-IV X-ray diffractometer using CuKα radiations operated at 40 kV and 40 mA. The transmission electron microscopy (TEM) image was taken by a TECNAI – T 30 model instrument operated at an accelerating voltage of 300 kV.

2.2. SYNTHESIS OF PVA CAPPED CdSe NPS:
Nanoparticles of CdSe dispersed in PVA matrix was prepared through a simple complexing agent free chemical method by reacting Cd2+ ion loaded PVA with sodium selenosulphite (Na2SeSO3). Cadmium chloride (CdCl2.2H2O) and sodium selenosulphite (Na2SeSO3) was chosen as the sources of Cd2+ ion and Se2- ion respectively. Polyvinyl alcohol was used as a stabilizer as well as host polymer matrix in the reaction medium. Sodium selenosulphite (Na2SeSO3) solution was prepared by dissolving 0.05 mol of Se powder into 100 ml of 1M sodium sulphite solution (Na2SO3) and refluxing the mixture at 70°C for 3 hours under constant stirring.
After refluxing, the final product was filtered with a Whatman 42 no. filter paper and was stored at (60°C) to prevent decomposition against its instability at room temperature.

In a typical reaction, a matrix solution was prepared by adding 1 ml of 0.6 M CdCl₂ solution into 20 ml of 5% (w/v) PVA solution and then stirred continuously for 20 minutes. 1 ml of freshly diluted sodium selenosulphite was added drop by drop into the matrix solution and the reaction mixture was stirred continuously for 15 minutes. Initially, the colour of the resultant mixture was transparent, but on stirring it gradually turns into light orange. The change of colour is an indication of the formation of the CdSe nanoparticles. The reaction mixture was left itself for further progress of the reaction and the gradual change of colour from light orange to dark red indicates the evolution of various sized CdSe nanoparticles in the PVA matrix. Further, it was observed that, after 24 hour of reaction time, there was no significant change in colour of the solution and this indicates the formation of stable sized CdSe nanoparticles.

3. RESULTS AND DISCUSSION:

3.1. OPTICAL STUDIES:

As UV-Vis absorption spectroscopy was used to study the growth kinetics of the formation of CdSe quantum dots (QDs) in PVA matrix. The absorption spectra of CdSe NPs evolved at various times are shown in Fig 1. From the spectra it is observed that the excitonic absorption peak shifts towards a higher wavelength, as the time progresses. This indicates agglomeration to larger CdSe nanoparticles on aging, even in the presence of PVA. It seems that PVA is not able to completely stop the aggregation process, although it reduces its rate to a certain extent. However, in the absence of PVA, aggregation takes place much faster, leading to almost instant formation of a CdSe precipitate. Further it is observed that until 3 hours (curve a-c) of the reaction time, growth is not significant and no prominent peak was observed. However, the growths have continued and after 5 hours (curve d) of the reaction time, an absorption peak at around 550 nm was observed which indicates the formation of CdSe NPs. A prominent peak at 580 nm was observed after 24 hours (curve f) of the reaction time. The reaction was allowed to continue for the next 48 hours and the absorption spectra of the sample so obtained (curve g) shows no significant changes in the absorption peak. Thus it can be stated that the CdSe-PVA system was found to be stable after 24 hours of reaction time and it may be assigned that PVA has assisted in restricting the final size of the particles to a certain upper limit.

3.2. PHOTOLUMINESCENCE MEASUREMENT:

The formation of the CdSe NPs was also confirmed by Photoluminescence spectroscopy as CdSe NPs exhibits light emitting behaviour at specific wavelengths [6]. Usually two emission bands are observed for semiconductor nanoparticles: an excitonic and a trapped emission. The excitonic emission is sharp and located near the absorption edge. The trap emission is broad and stokes-shifted [13]. In the present case, the PL spectrum of CdSe NPs excited at 400 nm shows an intense emission band at around 600 nm and a broad emission band at around 500 nm. For hexagonal CdSe, the near-band-edge (NBE) emission at room temperature is about 1.738 eV i.e., ~716 nm [10]. Therefore, the emission peak at 600 nm for the CdSe NPs may be attributed due to the near band edge (NBE) emission. The broad emission band at lower wavelength (500 nm) may be attributed due to the presence of deep level trapping site and electron hole recombination via trap state or imperfection site. Such lattice phenomena are observed in nanomaterials and these results confirm the nano-crystalline nature of the CdSe NPs [11].

![Figure 1](image-url) (A) UV-Vis absorption spectra of PVA capped CdSe nanoparticles with different reaction times: a) 0h, b) 1h, c) 3h, d) 5h, e) 7h, f) 24h and g) 48h; (B) Band gap calculation for curve (c-g) & (C) Band gap calculation for curve (a & b).
The size of the CdSe nanoparticles calculated from FWHM of different reflection planes are tabulated in Table 2 and it shows an average size of ~10 nm in diameter.

### Table 1. Band gap, shift in band gap and particle sizes calculated from absorption spectra

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reaction time (hr)</th>
<th>Band gap from UV-Vis (eV)</th>
<th>Shift in band gap (eV)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0</td>
<td>3.2</td>
<td>1.46</td>
<td>2.02</td>
</tr>
<tr>
<td>b</td>
<td>1</td>
<td>2.85</td>
<td>1.11</td>
<td>2.59</td>
</tr>
<tr>
<td>c</td>
<td>3</td>
<td>2.8</td>
<td>1.06</td>
<td>2.65</td>
</tr>
<tr>
<td>d</td>
<td>5</td>
<td>2.34</td>
<td>0.6</td>
<td>3.53</td>
</tr>
<tr>
<td>e</td>
<td>7</td>
<td>2.18</td>
<td>0.44</td>
<td>4.12</td>
</tr>
<tr>
<td>f</td>
<td>24</td>
<td>2.08</td>
<td>0.34</td>
<td>4.72</td>
</tr>
<tr>
<td>g</td>
<td>48</td>
<td>2.06</td>
<td>0.32</td>
<td>4.83</td>
</tr>
</tbody>
</table>

### Table 2. Determination of Average particle size

<table>
<thead>
<tr>
<th>Sample</th>
<th>$2\theta$ (degree)</th>
<th>(hkl)</th>
<th>Grain Size D (nm)</th>
<th>Average D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>31.1</td>
<td>101</td>
<td>7</td>
<td>9.99</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>102</td>
<td>10.93</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40.5</td>
<td>110</td>
<td>13.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>45.36</td>
<td>103</td>
<td>8.45</td>
<td></td>
</tr>
</tbody>
</table>

#### 3.4. TEM ANALYSIS:

The TEM micrograph of the as synthesized CdSe NPs obtained for 24 hours of reaction time is shown in figure 4(A). The TEM micrograph shows that the particles are distinguishable and well resolved from each other in PVA matrix and thereby giving no room for significant agglomeration of the CdSe nanoparticles. This is in consistent with the result obtained from the UV-Vis spectroscopy. Most of the particles were similar in size and have irregular rounded shapes. The analysis of particle size distribution is done with the help of histogram and is presented in fig. 4(B). The size histogram of CdSe nanoparticles is constructed by counting the total numbers of particles spread on the region of TEM grid as shown in Fig.4(A). Out of 32 numbers of total calculated particles, highest population is obtained in the 5 nm size range. From this analysis it is found that as synthesized CdSe
nuclei exhibit an average size of about 5 nm in diameter.

4. CONCLUSION:
Hexagonal phase CdSe nanoparticles with an average size of ~5 nm in diameter have been synthesized in PVA matrix by a simple ammonia free route. The average size of the CdSe nanoparticles obtained from XRD and EMA method was found to be in close proximity to the sizes determined from TEM analysis. The evolution of the CdSe nanoparticles during the progress of the reaction were investigated with the help of the UV-Vis absorption spectroscopy and it shows that PVA has supported in restricting the final size of the particles and thereby preventing aggregation of nanoparticles.

ACKNOWLEDGMENTS:
The Authors acknowledge the financial support from Department of Electronics and Information Technology (DeitY), R & D Electronics group, Government of India, New Delhi under a major research project to Sibsagar College, Joysagar, Assam, India.

REFERENCES