Optical Properties of CdTe Quantum Dots Synthesized at Different pH

Dilip Saikia
Department of Physics, Handique Girls’ College, Guwahati-781001, Assam.

ABSTRACT: In this piece of work a simple aqueous method is employed to synthesis CdTe quantum dots (QD). Cadmium chloride and Sodium Telluride are used as the source of cadmium and tellurium, further Mercaptosuccinic acid is used as a capping agent in the synthesis process. UV-vis absorption and photoluminescence (PL) spectra of the CdTe QD samples synthesized at different pH ranging from 4 to 11 are recorded. Effect of the pH on growth of QDs are studied and mentioned in this paper. Band gap of the samples are calculated and graph of bandgap vs refluxing time is plotted. Bandgap vs refluxing time curve clearly shows the size quantization effect.

Keywords: Absorption, aqueous method, bandgap, photoluminescence, quantum dots.

I. Introduction:

Properties of quantum dots has been investigated all around the world, by various research groups. Several routes for the synthesis of QDs has been developed, which uses either top down or bottom up approach [1]. Molecular beam epitaxy (MBE), e-beam lithography, ion implantation, X-ray lithography etc. are the some of the common top-down approaches. The chemical methods used for the synthesis of QDs via chemical reactions are the bottom-up process [2, 3, 4, 5]. Newer strategies to develop such quantum dots have been undertaken by many research groups worldwide. The bottom-up processes used for the synthesis of QDs is mainly divided into vapor-phase and wet-chemical process [1]. The wet-chemical process is based on the conventional precipitation method. In this process, a chemical reaction occurs between the various precursors which are taken, by careful control of various parameters such as the chemical composition, temperature, pH etc. During the process of the synthesis, nucleation and limited growth of the nanoparticles occurs. Again the nucleation occurring in the process may be heterogeneous, homogenous, or secondary nucleation [6]. Some of the wet-chemical methods for the synthesis of QDs are sol-gel method [7, 8, 9], hot-solution decomposition [10, 11, 12], microemulsion, ultrasonic or microwave irradiation method [13], competitive reaction chemistry and electrochemistry etc. Some of the commonly known vapor phase methods for the synthesis of QDs are self-assembly of nanostructured materials by the MBE process, aggregation of the gaseous monomers, sputtering [1].
Among the II-VI semiconductors, the Cadmium telluride (CdTe) systems have potential for a range of high color tunable emissions [14]. Zheng et al. used a simple aqueous method to synthesize CdTe/CdSe CS QDs. The synthesized QDs emits radiations of the spectral range of 510-640 nm having maximum QY value of about 40%. Synthesis of CdTe QDs using an aqueous method involves two steps: preparation of the Te precursor and followed by growth of the CdTe QDs with/without protection of inert gas. Al₂Te₃ and Te powder are generally used as the raw materials for the preparation of the Te precursor solutions. Inconvenience is caused by the limited availability of the source (Al₂Te₃) also Te is extremely sensitive towards to oxygen. However, the air-free synthesis process significantly influences the reproducibility of high-quality CdTe QDs [15].

QDs are gaining more interest now a days due to their promising applications in the field of laser, bio-imaging, LED and sensors. QDs can show tunable photo luminescent property by controlling the particle size. In particular, we are interested in the synthesis of CdTe QDs via a aqueous route, such QDs have smaller bandgap than the other II-VIQDs. Due to their smaller bandgap they can emit near-infrared light with high quantum efficiency. As the size of the QDs becomes smaller their bandgap becomes larger. Several methods have been reported by several group all around the globe to tune the bandgap of CdTe QDs. Amongst them 1) controlling the growth temperature and time, 2) injection of additional precursor solutions 3) and modification of the surface of the QDs by chemical methods [16]. In this paper, we present the method new bandgap engineering method of controlling the time of growth to tune the bandgap. We have also studied the effect of pH on the bandgap of the CdTe QDs and presented in the paper.

II. Objectives of the Study:

The main objective of the study is to synthesis CdTe QDs at different pH by a simple cost effective process and to investigate their optical and structural properties using advanced characterization techniques.

III. Methodology:

The chemical and reagents used are Cadmium chloride (Merck, 98%), Mercaptosuccinic acid (LobaChemie, 99%), L-Cysteine (LobaChemie, 96%), Sodium Telluride (LobaChemie, 98%), Sodium Borohydride (Merck, 95%), Sodium Hydroxide (LobaChemie 98%), Citric acid (Fischer Scientific, 99.5%) and Borax powder (Fischer Scientific, 98%). Milli-Q water was used as solvent in entire experiment.

In the synthesis process of CdTe QDs, 20 ml of 3mM CdCl₂, 20 ml of 0.75mM Na₂TeO₃ and 20 ml of 9mM MSA solutions were mixed to a buffer solution containing 10 ml 15mM Borax and 10 ml of 15mM Citric acid. The reaction mixture is mixed in a 250 ml round bottom three neck flask by stirring for about 5-10 min. After completely mixing the solutions pH of the solution is balanced to desired value. Immediately after balancing the pH, 40 mg of NaBH₄ is
added to the reaction mixture. Suddenly the colorless solution mixture turns light yellow in color indicating the initiation of QD nucleation. Sodium Borohydride is one of the common reducing agents used for the reduction of the ions from their salts. Hydrazine is also used for the same purpose in the synthesis of the nanoparticles, but there are some distinct advantages of using Sodium Borohydride as reducing agent. Among them are the (i) low equivalent weight of Sodium Borohydride and so 1 mol of NaBH₄ can supply eight electrons, (ii) high reducing power, (iii) it is capable of reducing metal salt in aqueous or non-aqueous media.

Characterization

The absorption spectra were recorded using a Shimadzu 1800 ultraviolet (UV)–visible light spectrophotometer and photoluminescence (PL) spectra were recorded using a Cary Eclipse spectrophotometer. TEM characterization were done using a JEOL JEM 2100 TEM operated at 200 kV. Field emission scanning electron microscopy (FESEM) with energy-dispersive X-ray (EDX) characterization were performed by a SIGMA–VP (ZEISS) scanning electron microscope (SEM).

IV. Result and Discussion:
MSA capped CdTe QDs have been synthesized at different pH values for different refluxing time and their corresponding UV-vis absorption spectra and PL spectra have been recorded. The recorded UV-vis absorption spectra of the MSA capped CdTe QDs at different pH values for different refluxing times are given in fig 1. The pH value affects the QD formation reaction mechanism. Hence the absorption properties of the particles are different for samples having same refluxing time with different pH values.
Figure 1: UV-vis absorption spectra of the MSA capped CdTe QDs synthesized at different pH values with different refluxing time.
Figure 2: PL spectra of the MSA capped CdTe QDs synthesized at different pH values with different refluxing time.

The UV-vis absorption spectra analysis is very important technique for the preliminary investigation of a QD sample because this tool gives the information about the band gap energy of the sample. The emission property of a QD sample depends on the bandgap energy. Analysis of the UV-vis absorbance spectra yields the information of band gap of the particles; the bandgap of different QD samples mentioned in the table 1 is calculated using the Tauc’s method. PL spectra of the MSA capped CdTe QDs at different pH values for different refluxing times are given in fig 2. The PL spectra of different samples also show a similar type of variation as obtained in the absorption spectra. The samples are excited at a wavelength of about 400 nm. The excitation wavelength should be less than its absorption wavelength, and otherwise, the charge carriers cannot cross the forbidden band of the sample and will not result in the emission spectra. The PL spectra of the samples shifted towards higher wavelength with the refluxing time. This result supports the results obtained from the absorption spectra analysis.

<table>
<thead>
<tr>
<th>Reflux Time (hr)</th>
<th>Band Gap (eV) pH 4</th>
<th>Band Gap (eV) pH 5</th>
<th>Band Gap (eV) pH 6</th>
<th>Band Gap (eV) pH 7</th>
<th>Band Gap (eV) pH 8</th>
<th>Band Gap (eV) pH 9</th>
<th>Band Gap (eV) pH 10</th>
<th>Band Gap (eV) pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.11</td>
<td>2.2</td>
<td>2.04</td>
<td>2.2</td>
<td>2.13</td>
<td>2.11</td>
<td>2.24</td>
<td>2.23</td>
</tr>
<tr>
<td>2</td>
<td>2.07</td>
<td>2.08</td>
<td>2.04</td>
<td>2.1</td>
<td>2.08</td>
<td>2.04</td>
<td>2.16</td>
<td>2.17</td>
</tr>
<tr>
<td>3</td>
<td>2.02</td>
<td>2.01</td>
<td>2.01</td>
<td>2.01</td>
<td>2.05</td>
<td>2</td>
<td>2.13</td>
<td>2.09</td>
</tr>
</tbody>
</table>
Table 1: Table of the band gap of CdTe QDs synthesized at different pH for different reflux time.

<table>
<thead>
<tr>
<th>Time (hr)</th>
<th>pH 4</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 9</th>
<th>pH 10</th>
<th>pH 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.97</td>
<td>1.96</td>
<td>1.96</td>
<td>1.96</td>
<td>2.02</td>
<td>1.96</td>
<td>2.1</td>
<td>2.04</td>
</tr>
<tr>
<td>2</td>
<td>1.94</td>
<td>1.93</td>
<td>1.93</td>
<td>1.93</td>
<td>1.99</td>
<td>1.93</td>
<td>2.08</td>
<td>1.98</td>
</tr>
<tr>
<td>3</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
<td>1.9</td>
<td>1.97</td>
<td>1.9</td>
<td>2.06</td>
<td>1.94</td>
</tr>
</tbody>
</table>

Figure 3: Graph of band gap vs refluxing time of MSA capped CdTe QDs synthesized at different pH.

Optical band gap of QDs is estimated from the UV-vis absorption spectra by using Taucs’ method. In this method, a graph of $hν$ and $(αhν)^2$ is plotted, and the point where tangent drawn in the linear part of the graph intersects gives the optical band gap of the material. From the graph, we have seen the band gap of the different samples decreases with the increase in the refluxing time (fig. 3). There is not much difference in the PL and UV-vis absorption spectra of MSA capped CdTe QDs for different pH values. This indicates that the effect of pH on the growth of CdTe QDs can be neglected. The PL spectra are broadened along the longer wavelength. This may be due to the presence of defect states in the surface of QD samples. But, such broadening is absent for the higher values of pH (neutral and basic pH). The UV-vis absorption spectra for higher value of pH are homogeneous. This is absent in the case of the
samples synthesized at lower pH. So we have considered the samples synthesized at the higher pH as better ones compared to the samples synthesized at lower pH.

Figure 4: (a) TEM image (at 20 nm scale bars), (b) SAED pattern of CdTe QD synthesized at pH 9.

Figure 5: (a) FESEM image (at 200 nm scale bars) and (b) EDX spectra of CdTe QD synthesized at pH 9.

TEM and SEM image of the best CdTe QDs samples is shown in the fig 4 and fig 5. The TEM images of the CdTe QDs are found to be more or less spherical shaped, in fig 4 selected area electron diffraction (SAED) pattern of CS QD system shows diffraction rings with spots which can be attributed to the formation of crystal structures. FESEM image of CdTe QDs deposited on a glass substrate by the drop casting method is given in Figure 5(a). Energy-dispersive X-ray spectra (EDX) analysis is a powerful tool for elemental analysis to detect chemical purity and stoichiometry. EDX spectra of the samples is given in Figure 5 (b).
Strong peaks in Figure 5(b) confirm the presence of elements Cd and Te for the CdTe QDs. The atomic percentages of elements for CdTe QDs were found to be about 48.06, 30.47 and 21.47% for Cd, Te and S respectively.

VI. Conclusion:

CdTe QDs is synthesized using a simple aqueous method. MSA is used as a capping agent in the synthesis process, the synthesis is carried out at different pH; ranging from pH 4 to pH 11. The PL and UV-vis absorption spectra of MSA capped CdTe QDs synthesized at different pH values are almost similar. This result shows that the effect of pH on the growth of CdTe QDs can be neglected. However, the PL spectra are broadened along the longer wavelength. This may be due to the presence of defect states in the surface of QD samples. But, such broadening is absent for the higher values of pH (neutral and basic pH). The UV-vis absorption spectra for higher value of pH are homogeneous. This is absent in the case of the samples synthesized at lower pH. So we have considered the samples synthesized at the higher pH as better ones compared to the samples synthesized at lower pH.

Acknowledgements

Author is thankful to the Central Instrumentation Facility (CIF) facilities at IASST, NEHU.

References: