Influence of Growth Time in the Formation of CdTe Nanostructure

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ABSTRACT

Cadmium Telluride (CdTe) nanostructures are grown chemically using a simple cost effective method as chemical reduction route. Ethylenediamine (EDA) has been used as a capping agent while Sodium borohydride is used as a reducing agent. CdTe nanostructures are grown by varying growth time from 3 hours to 9 hours. The samples are all grown at room temperature. The grown nanostructures are characterized structurally by X-Ray diffraction (XRD) and transmission electron microscopy (TEM). The grown nanostructures are characterized optically by Optical Absorption, Photoluminescence (PL) study. Transmission electron microscopy picture indicates that nanostructure changes from nanoparticle to nanorods as growth time increases. An increase in band gap is observed compared to bulk CdTe in each growth condition. This shows quantum confinement. Also band gap decreases as the growth time increases indicating size dependence of band gap. An attempt is made to correlate the structural and optical properties.

Keywords: Synthesis of Nanomaterials, Nanostructures, Structural Properties, Optical Properties, Band gap.

1. INTRODUCTION

Semiconductor nanoparticles (NPs) have gained great attention during the past decade because of their potential application in many fields of optoelectronics devices such as Light Emitting Diodes (LED)\(^1\), solar cells\(^2\), biological labeling\(^3\), photo detectors, biosensors, etc\(^4,9\). Semiconductor nanoparticles, which exhibit properties different from bulk materials, are a new class of materials that hold considerable promise for numerous applications in the field of electronics and photonics. Nanoscale modification of the molecular design and morphology of such particles provides a powerful approach toward control of their electrical and optical
properties. The most important features of nanoparticles (NPs) are their high photochemical stability and their size dependent optical properties, which result from the quantum confinement effect of charge carriers. This means that the colour of the photoluminescence (PL) of NPs can be varied by their particle size. Among the colloidal nanocrystals, CdTe (generally Gr-II to Gr-VI) is studied because of the efficiency of its synthesis, the high quality of the resulting sample, the fact that the optical gap lies in the visible range, has a high optical absorption coefficient ($>10^4$ cm$^{-1}$) and small bulk direct band gap energy ($E_g$) of 1.58eV and large Bohr radius (10 nm in bulk). Also it is an important semiconducting material with unique electrical properties, which makes it a promising material in the field of photo-electronic devices and biological labeling devices. There are various methods of the preparation of CdTe nanoparticles as physical and chemical vapour deposition, hydrothermal growth, and laser ablation. Some of the above mentioned methods have some drawbacks. Used precursors are unstable, are an environmental hazard, and require very high temperatures. These methods are not cost effective also hence it is necessary to develop a simple method to synthesis CdTe nanostructures. Hence a simple chemical reduction route provides a better route for the fabrication of CdTe nanostructures. The grown sample is characterized structurally, optically by varying the growth time. CdTe nanoparticles are characterized by X-ray diffraction (XRD), Transmission electron microscopy (TEM), UV–VIS absorption spectra and Photoluminescence (PL) technique.

2. EXPERIMENTAL SECTION

2.1 Materials

Anhydrous Cadmium Chloride (CdCl$_2$), Tellurium Powder (Te), Sodium Borohydride (NaBH$_4$), Ethylenediamine (EN, NH$_2$CH$_2$CH$_2$NH$_2$) was purchased from Merck, India. All materials were used as starting materials without any purification.

2.2 Materials Preparation

Anhydrous CdCl$_2$ (molecular weight-201.32gm/mole) (603.96 mg), Tellurium (molecular weight-127.6gm/mole) (382.8 mg) powder and sodium borohydride (molecular weight-37.83gm/mole) (113.49 mg) have been taken to prepare different samples at the ratio 1:1:1. Ethylenediamine (EDA) has been used as a capping agent. Sodium borohydride has been taken to initiate the reaction at room temperature.

In order to prepare different samples, the amounts of CdCl$_2$, Te and NaBH$_4$ were taken in 1:1:1 ratio in EDA. The samples are grown for different durations (3 hours, 6 hours and 9 hours) at room temperature.

Briefly, the solution was freshly prepared by dissolving 603.96 mg of CdCl$_2$ (Cadmium Chloride) in 45 ml of ethylenediamine and 382.8 mg of Te powder was added into it and the magnetically stirring was continued at a particular speed. After 5 minutes, 113.49 mg NaBH$_4$ was added into this solution and the magnetic stirring is continued for 3 hours.
Similarly these processes were also conducted for 6 and 9 hours. The reaction was conducted at room temperature. The resulting mixture was washed by injecting into distilled water and filtered. The washed precipitates were collected in a clean petridish and finally dried in vacuum.

2.3 Materials Characterization

The X-ray diffraction (XRD) pattern on the samples were recorded by a X-ray diffractometer (miniflex II, desktop-X-ray diffractometer) using Cu-kα radiation of wavelength $\lambda = 1.54$ Å for 2θ ranging from $20^\circ$ to $70^\circ$.

As for TEM measurements, the as-prepared CdTe nanoparticles have been dispersed in Toluene by ultrasonicator. A small drop of dispersed CdTe nanoparticle has been taken on a thin carbon film supported on the copper grid and kept for some time for drying. The Transmission Electron Micro-graph of the as-prepared samples has been taken using a JEOL-JEM-2010 transmission electron microscope operating at 200 kV. Selected area electron diffraction (SAED) pattern of the said nanomaterials were also performed.

A small amount of the sample was dispersed in toluene for certain minutes by ultrasonification. Optical absorption measurements of the dispersed samples have been studied in the range of 280 nm–800 nm using a Shimadzu Pharmaspec 1700 UV–VIS Spectrophotometer. PL spectra of the dispersed samples are recorded using Perkin Elmer LS 55 Fluorescence Spectrophotometer.

3. RESULTS AND DISCUSSIONS

3.1 Structural Properties using XRD

The XRD of the synthesized samples for growth time 3 hours, 6 hours and 9 hours are shown in Fig 1. All the diffraction peaks come mainly from the cubic phase of CdTe. The peak at (200) is the highest intensity peak. The XRD pattern matches with JCPDS file No. 75 – 2083 25-27 and JCPDS file No. 80-0089.

3.2 Morphological study using TEM

Morphologies of the products synthesized at fixed reactional temperature for different times are shown in fig 2. The diameter of the nanoparticles is in the order of 8 nm to 12 nm. (approximately ) at 3 hours growth condition. With increase of growth time CdTe changes its shape from nanoparticles to nanorods. At 6 hour growth condition TEM clearly indicates the presence of nanorods with particles. But at 9 hour growth condition it completely changes to nanorods. Also each nanorod seems to be composed of a number of nanocrystals stacking along the rod growth condition25. The transformation from nanoparticles to nanorods may be due to the reaction rate and this is possibly due to the slow reaction rate as the growth time increases.
Fig 1: XRD pattern of as prepared CdTe nanostructure

Fig 2: (a) HRTEM image of CdTe grown for 3 hours, (b) HRTEM image of CdTe grown for 6 hours, (c) HRTEM image of CdTe grown for 9 hours, (d) SAED image of CdTe grown for 3 hours, (e) SAED image of CdTe grown for 6 hours, (f) SAED image of CdTe grown for 9 hours.

Fig 3: Schematic diagram of the growth of CdTe nanoparticles to nanorods with the growth time

Fig 3 shows the schematic diagram of the growth of CdTe nanoparticles to nanorods with the growth time variations. This is in agreement with the process called Ostwald Ripening. Selected area electron diffraction (SAED) pattern indicates that crystallinity is good for lower growth time. The nanoparticle size and nanorod diameter are shown in table-I.

### 3.3 Optical Properties of CdTe nanostructure

Optical properties of CdTe samples were determined through UV-VIS absorbance spectroscopy and photoluminescence studies. The CdTe nanomaterials were dispersed in Toluene using ultrasonication for 20 minutes for UV-VIS absorption measurements.

Fig-4: Plot of optical absorption spectra of as prepared CdTe nanostructure dispersed in Toluene
Fig – 4 shows the optical absorbance spectra of CdTe samples grown at different times. The band gap of the as-prepared nanoparticles is determined by using the Tauc’s relation $28$

$\alpha h\nu = C (h\nu - \Delta E_g)^{1/2}$ where $C$ is a constant, $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $E_g$ is the band gap of the material.

Fig 5: Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ to determine band gap in each case

Fig - 5 shows the plot of $(\alpha h\nu)^2$ vs. energy $(h\nu)$ and it is used to determine band gap. The linear part of the curve is extrapolated to energy $(h\nu)$ axis to determine band gap. The band gap is found to be 2.46 eV for 3 hours, $26-27$, 2.36 eV for 6 hours and 2.22 eV for 9 hours. S. K. Tripathi et al., obtained band gap of 2.50 eV for CdTe nanoparticles $29$. At each growth condition band gap is found to be greater than the bulk value and this indicates quantum confinement. Also with increase of growth time band gap decreases and comes closer to bulk value. This is due to the increase of nanorod diameter with increase of growth time.

3.4 Photoluminescence Properties of CdTe nanostructure

The photoluminescence (PL) experiment is employed to study the optical response of samples and the spectrum taken at room temperature is shown in Fig 6. The PL spectra were measured with excitation wavelength 360 nm of the CdTe sample products grown for 3 hours, 6 hours and 9 hours.
Fig. 6 shows PL spectra of the CdTe samples prepared at different times. PL peak shifts slightly towards higher wavelength with increase of time which is in agreement with the absorption result. At three hours growth condition, we observe PL peak is very sharp. This indicates that width of luminescence state is almost discrete. This is possible as the size (10nm) of the crystal is small in 3 hours growth condition. With increase of growth time width of the PL peak increases as the crystal shape is changed to nanorods and its diameter (13.5 nm-76 nm) is large. Also peak position indicates that luminescence occur in each case from the state close to the band gap.

<table>
<thead>
<tr>
<th>Name of Samples</th>
<th>Growth Time (Hours)</th>
<th>Shape of Nanostructure</th>
<th>Average Size of the Nanostructure (nm)</th>
<th>Band Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe -1</td>
<td>3</td>
<td>Spherical nanoparticles</td>
<td>Diameter-10</td>
<td>2.46</td>
</tr>
<tr>
<td>CdTe -2</td>
<td>6</td>
<td>Nanoparticles and Nanorod</td>
<td>Nanorods length- 26 , Diameter- 13.5</td>
<td>2.36</td>
</tr>
<tr>
<td>CdTe -3</td>
<td>9</td>
<td>Nanorods</td>
<td>Nanorods length- 300 , Diameter- 76</td>
<td>2.22</td>
</tr>
</tbody>
</table>

CONCLUSIONS

CdTe nanoparticles are formed at smaller growth time while nanorods are formed at higher growth time. It is clearly observed that the size and shape of CdTe nanomaterials generally depend on the growth time. Optical absorption study shows that with increase of growth time the band gap shifts towards lower energy value. This clearly indicates that at higher growth time the quantum confinement is less. The synthesis route is easily controllable and cost effective.

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REFERENCES


