TEA-CAPPED CdSe NANOPARTICLE: “GREEN” SYNTHESIS, CHARACTERISATION AND OPTICAL PROPERTIES

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TEA capped CdSe nanoparticles were synthesized by a simple and “green” route at room temperature using Cd(CH₃COO)₂ as Cd-precursor and Na₂SeSO₃ as source of Se²⁻ ion. NH₃ was used as pH stabilizer. The structural characterization of the nanoparticles was done by X-ray diffractometer (XRD). The analysis of XRD spectra of the as-prepared CdSe nanoparticles showed cubic structure with highest intense reflection peak along (111) having lattice parameter, \( a = 6.073 \, \text{Å} \) which is in good agreement with JCPDS file no. 19-0191 (\( a = 6.077 \, \text{Å} \)). The average crystallite sizes of the CdSe nanoparticles were found to be 10.42 nm and 6.36 nm when the concentrations of [Cd(CH₃COO)₂] were 0.2 M and 0.5 M respectively. The optical absorption spectra of the nanoparticles showed an increase in band gap energy of 1.82eV and 1.88eV when the concentration of [Cd(CH₃COO)₂] were 0.2 M and 0.5 M respectively as compared with the bulk value of CdSe (1.74eV). The PL study showed emission peaks assigned to shallow and deep trap states emissions. The particle sizes were also determined by using simplified Brus equation.

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Keywords: CdSe nanoparticles; TEA-capping; Energy band gap

1. Introduction

Group II-IV compound semiconductor quantum dots have many applications in the field of photo catalysis, microelectronics and electrochemical devices due to their optical and electrical properties. Among all the semiconductor nanoparticles, metal selenides nanoparticles attracted much attention of many researchers due to their interesting properties and used as optical filters, optical recording materials and biomedical labeling. Because of high photosensitivity, CdSe nanoparticles have been used in photoconductive devices and moreover it became one of the most attractive selenide among all the metal selenides [1,2]. In recent years, the synthesis of CdSe nanoparticles by using different methods has been reported by many workers [3-15]. All the mentioned processes require very stringent experimental conditions and highly toxic reagents. So, many researchers have attempted to find more convenient, easy, economical and environmentally friendly methods for the preparation of CdSe nanoparticles. Interestingly, chemically grown synthesis of nanoparticles is the most convenient and cheapest method. Nanoparticles formed in solution are less stable and always tend to aggregate. In order to avoid aggregation, suitable capping agents are used to passivate the nanoparticles [16-25]. Most of the passivating agents used are toxic and will pollute the environment. In this paper we report a simple and environmental friendly synthesis of CdSe nanoparticles using highly water-soluble triethanolamine (TEA) as capping agent in aqueous medium at room temperature. The effect of concentration of cadmium precursor on the size of nanoparticle and their optical properties are presented.

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2. Experimental

2.1 Materials

Analytical grade cadmium acetate \([\text{Cd(CH}_3\text{COO)}_2]\), Selenium powder (Se) and sodium sulfite crystals (\(\text{Na}_2\text{SO}_3\)) were used as precursors for the synthesis of CdSe nanoparticles. Triethanolamine (TEA) \([\text{N(CH}_2\text{CH}_2\text{OH)}_3]\) was purchased from S.d fine-chem Ltd. India and used as capping agent whereas ammonia solution was used as pH stabilizer.

2.2 Synthesis of TEA capped CdSe nanoparticles

0.25 M sodium selenosulfate (\(\text{Na}_2\text{SeSO}_3\)) solution was prepared by refluxing 4 g of Se powder with 20 g of sodium sulfite (\(\text{Na}_2\text{SO}_3\)) in a three-necked round bottom flask containing 100 ml of deionised water at 70°C in \(\text{N}_2\) atmosphere for 5 hrs. and filtered. The filtrate is used as stock solution of Se source. Aqueous solution of cadmium acetate \([\text{Cd(CH}_3\text{COO)}_2]\) was used as Cd precursor whereas triethanolamine \([\text{N(CH}_2\text{CH}_2\text{OH)}_3]\) was used as capping agent. Triethanolamine (TEA) capped CdSe nanoparticles were synthesized by mixing measured volumes of precursor \(\text{Na}_2\text{SeSO}_3\) and various concentrations of \(\text{Cd(CH}_3\text{COO)}_2\) solution in presence of 5 ml of TEA. Required amount of \(\text{NH}_3\) solution was added to the reaction mixtures in order to maintain pH value of 11. The orange red nanoparticle formed was collected after 24 hrs. and washed several times with deionised water and dried at room temperature. Then, the samples were annealed at 500°C and were used for characterization.

3. Results and discussion

3.1. Reaction mechanism

The mechanism of the chemical reaction is:

\[
\begin{align*}
\text{Step 1} & \\
\text{Cd(CH}_3\text{COO)}_2 & \rightarrow \text{Cd}^{2+} + 2\text{CH}_3\text{COO}^- \\
\text{Step 2} & \\
\text{Se} + \text{Na}_2\text{SO}_3 & \xrightarrow{\text{N}_2, 70°C} \text{Na}_2\text{SeSO}_3 \\
\text{Step 3} & \\
\text{Na}_2\text{SeSO}_3 + 2\text{OH}^- & \xrightarrow{\text{NH}_3 \text{ solution}} \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{Se}^{2-} \\
\text{Step 4} & \\
\text{Cd}^{2+} + \text{Se}^{2-} & \xrightarrow{\text{TEA}} \text{TEA capped CdSe}
\end{align*}
\]

Triethanolamine (TEA) which is a water soluble amino alcohol is frequently used as surface stabilizing agent [26]. Amino group of TEA molecules interact with the Cd atom and thus prevent the agglomeration of CdSe. Fig. 1 showed the schematic representation of TEA capped
CdSe nanoparticle. Thermogravimetric (TG) analysis of the samples was carried out by using PerkinElmer, STA 6000. Fig. 2 showed the TG curve of TEA capped CdSe nanoparticle. Weight loss below 100°C was due to the desorption of water from the precursor. Whereas, weight loss between 100°C and 350°C was caused by the decomposition of the residual organic compound. At temperature above 350°C no further weight loss was observed, which indicates the complete removal of the organic residues and formation of pure crystalline CdSe. So, the minimum annealing temperature for organic free precursor was chosen above 350°C.

![Fig. 1. Schematic representation of the TEA capped CdSe nanoparticles.](image)

3.2. X-Ray diffraction

X-ray diffractograms of the synthesized nanoparticles were measured by using PANanalytical powder diffractometer (X'Pert PRO). Fig. 3a and Fig. 3b showed the XRD pattern of the as-prepared TEA capped CdSe nanoparticles, synthesized at 0.5 M and 0.2 M concentrations of Cd(CH₃COO)₂ respectively. In Fig. 3b the observed diffraction peaks at 2θ = 25.5°, 42.0°, 49.4° were assigned to (111), (220) and (311) planes respectively with highest intense reflection peak along (111) plane of cubic nanocrystalline CdSe and its average lattice constant \( a \) is calculated by using the following formula

\[
a = \frac{d(h^2 + k^2 + l^2)^{\frac{1}{2}}}{2}
\]
and is equal to 6.073 Å which in good agreement with the literature value of \( a = 6.077 \text{ Å} \) (JCPDS File No. 19-0191). Interplanar distance spacing \( d \) of lattice plane, \( h, k, l \) is calculated by using the formula

\[
d = \frac{\lambda}{2\sin\theta}
\]

where, \( \lambda = 1.5406 \text{ nm} \) and \( \theta \) is Bragg diffraction angle. Structural parameters of TEA capped CdSe nanoparticle calculated from the XRD spectra is shown in Table 1. The crystallite size, \( D \) was calculated from XRD line broadening data using Scherrer formula

\[
D = \frac{k\lambda}{\beta \cos\theta}
\]

where, \( \lambda \) is the wavelength of the X-ray radiation used and is equal to 0.15406 nm, \( \beta \) is full width at half maxima (FWHM) of the diffraction peak (in radian), \( \theta \) is Bragg diffraction angle and \( k \) is a constant and is equal to 0.9. The crystallite sizes calculated from Fig. 3a and Fig.3b were found to be 6.36 nm and 10.42 nm respectively. The broader nature of peaks in Fig. 3a showed that crystallite size is smaller when the initial concentration of Cd(CH₃COO)₂ is higher and it is in agreement with the trend shown by the optical studies.

![Fig.3. XRD pattern of TEA capped CdSe nanoparticle.](image)

<table>
<thead>
<tr>
<th>[Cd(CH₃COO)₂] (M)</th>
<th>Standard JCPDS ( d ) value (Å)</th>
<th>Calculated ( d ) value (Å)</th>
<th>Plane ((hkl))</th>
<th>20°</th>
<th>Calculated ( a ) (Å)</th>
<th>Average ( a ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2M</td>
<td>3.5100</td>
<td>3.48827</td>
<td>(111)</td>
<td>25.354</td>
<td>25.5150</td>
<td>6.0418</td>
</tr>
<tr>
<td></td>
<td>2.1490</td>
<td>2.14516</td>
<td>(220)</td>
<td>42.0883</td>
<td>42.0883</td>
<td>6.0674</td>
</tr>
<tr>
<td></td>
<td>1.8330</td>
<td>1.84207</td>
<td>(311)</td>
<td>49.698</td>
<td>49.4383</td>
<td>6.1094</td>
</tr>
</tbody>
</table>

| 0.5M              | 3.5100          | 3.52187         | (111)    | 25.354  | 25.2676         | 6.0728          |
|                   | 2.1490          | 2.13801         | (220)    | 42.2342 | 42.2342         | 6.1000          |
|                   | 1.8330          | 1.81700         | (311)    | 50.1669 | 50.1669         | 6.0579          |
3.3. UV-vis absorption spectrum

UV-vis spectra of the as prepared samples were studied by using Perkin Elmer Lambda 35 UV-vis spectrophotometer. Fig. 4 showed the UV-vis spectra of TEA capped CdSe nanoparticle synthesized with 0.2 M and 0.5 M Cd(CH₃COO)₂ solution with fixed concentration of Na₂SeSO₃ (0.25 M) at room temperature in aqueous medium. In the spectra, the absorption edges of the CdSe nanoparticles were blue shifted from the bulk (716 nm) which is due to the quantum confinement. The excitonic peak is shifted towards the lower wavelength which is indicative of small decrease in the size of the CdSe nanoparticles. Similar observations were also observed by the other workers [27]. From the UV-vis spectra, the band gap energies of 1.82eV and 1.88eV for 0.2 M and 0.5 M Cd(CH₃COO)₂ solutions respectively were observed. The increased in band gap energies as compared with bulk value of CdSe (1.74eV) is due to quantum confinement effect. The nanoparticle sizes were calculated by using simplified Brus equation (Equation 1).

\[
E_g = E_g(0) + \frac{\hbar^2}{8d^2} \left[ \frac{1}{m_e^*} + \frac{1}{m_h^*} \right]
\]

(1)

where, \(E_g\) is band gap of the nanoparticle, \(E_g(0)\) is the bulk band gap, \(m_e^*\) is effective mass of the electron, \(m_h^*\) is effective mass of hole, \(d\) is size of the nanoparticle in nm and \(\hbar\) is Planck constant. \(m_e^*\) and \(m_h^*\) for CdSe nanoparticle are 0.13\(m_0\) and 0.45\(m_0\) respectively, where \(m_0\) is mass of an electron. \(E_g(0)\) for CdSe is 1.74 eV. Hence, the size of nanoparticle is given by Equation 2.

\[
E_g = 1.7 + \frac{3.7}{d^2}
\]

(2)

The calculated sizes of the nanoparticle using the above equation 2 were found to be 5.14 nm and 6.80 nm when the concentrations of Cd(CH₃COO)₂ were 0.5 M and 0.2 M respectively. This is because, when the concentration of Cd²⁺ is varied and Se²⁻ is constant, there will be greater number of nucleation sites for the growth of CdSe nanoparticles and hence smaller will be size of the nanoparticles formed. Thus, from the knowledge of precursor concentrations, desire sizes of CdSe nanoparticles can be prepared.

![Fig. 4. UV-vis absorption spectra of TEA capped CdSe nanoparticles.](image-url)
3.4. PL spectrum

Photoluminescence spectra of TEA capped CdSe nanoparticles at room temperature taken with help of Perkin Elmer LS55 Florescence Spectrophotometer were illustrated in Fig. 5. A strong emission peak at 480 nm and another weak at 520 nm were observed in Fig. 5(a) when the concentration of Cd(CH₃COO)₂ is 0.5 M, whereas a strong peak at 487 nm and a weak peak at 600 nm were observed for 0.2 M and it is illustrated in Fig. 5(b). In both cases, the excitation wavelength was 395 nm. The two unequal peaks observed in both cases were due to shallow trap and deep trap states respectively [28]. Blue shifting observed in both cases and more shifting in case of 0.5 M than 0.2 M were due to quantum confinement effects.

![Fig. 5. PL spectrum of TEA capped CdSe nanoparticle.](image)

3.5. SEM analysis

Fig. 6 illustrated the SEM image of TEA capped CdSe nanoparticles taken with help of QUANTA 250 electron microscope. It is evident from the figure that the prepared product formed spherical shape nanoparticles with slight agglomeration. This agglomeration may be due to the aggregation of individual nanoparticles during the annealing of the samples.

![Fig. 6 SEM image of TEA capped CdSe nanoparticle.](image)
3.6. EDX analysis

The compositions of the prepared nanoparticle were determined by EDAX. Fig.7 shown EDX spectrum of the as prepared nanoparticle. It is clearly seen from the figure that the nanoparticle contains non other than Cd and Se in the stoicheometric ratio of 1:1.

![EDX pattern of TEA capped CdSe nanoparticle.](image)

4. Conclusions

TEA capped CdSe nanoparticles were prepared through easy, economical and environment friendly chemical route at room temperature. The as prepared nanoparticles were cubic in structure with lattice parameters fairly in agreement with JCPDS values. Nanoparticle size decreases with increasing Cd precursor concentration. It is found that the particle size of the nanoparticle is tunable by varying precursor concentrations.

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References