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Controlled synthesis and optical properties of tunable CdSe quantum dots and effect of pH

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Cadmium selenide (CdSe) quantum dots (Q-dots) were prepared by using non-coordinating solvent octadecene instead of coordinating agent trioctylphosphine oxide (TOPO). Reaction processes were carried out at various temperatures of 240°, 260°, 280° and 300° C under nitrogen atmosphere. The prepared CdSe Q-dots which are highly stable show uniform size distribution and tunable optical absorption and photoluminescence (PL). The growth temperature significantly influenced the particle size; spectral behavior, energy band gap and PL intensity and the full width at half maxima (FWHM). Three different methods were employed to determine the particle size and the average particle size of the CdSe Q-dots is 3.2 - 4.3 nm, grown at different temperatures. In addition, stable and mono-dispersed water soluble CdSe Q-dots were prepared by the ligand exchange technique. Thus, the water soluble Q-dots, which are sensitive to the basic pH may be important for biological applications.

INTRODUCTION

The semiconductor nanocrystals (NCs), i.e., quantum dots (Q-dots) have attracted much attention due to their unique size dependent optical properties, i.e., absorption and photoluminescence (PL). Colloidal CdSe Q-dots can be tuned within the visible wavelength range of 475 - 670 nm and used for a wide range of possible applications including light-emitting diodes (LEDs), photovoltaic, single-electron transistors and fluorescent tags for biological imaging. The application of nanocrystals is based on their unique optical and electronic behavior. The semiconductor nanocrystals or Q-dots such as CdX and PbX (X = S, Se, and Te) and metal-chalcogenide based are used for light energy harvesting. In Q-dots semiconductors, excited electrons are injected into a large band gap semiconductor such as (ZnO or TiO₂) and holes are scavenged by a redox couple. One of the most exciting and challenging issues is to produce mono-dispersed CdSe Q-dots. There are various methods to grow CdSe Q-dots in which the most popular and efficient route is hot injection chemical method. Peng and Peng have introduced the reaction kinetic of CdSe nanocrystals by using relatively innocuous materials CdO and elemental Se, and considered as a green chemistry/synthesis. A high quality mono-dispersed CdSe Q-dots were prepared by hot injection method. In this route, organometallic precursor dimethyl cadmium (Cd(CH₃)₂) was used for initial nucleation. However, due to extremely high reaction rate of Cd(CH₃)₂, the growth process becomes uncontrolled due to which Cd(CH₃)₂ has been replaced by CdO. Thereafter, CdO approach has been considered more favorable for the synthesis of high quality Q-dots because of environmental and user friendly. These successful synthesis approaches, which include Cd(CH₃)₂ and CdO were carried out in coordinating solvent TOPO. It was considered that TOPO is an essential requirement for producing highly mono-disperse II–VI semiconductor nanocrystals, however, TOPO may generate unknown...
pollutants. Further, the TOPO could be replaced by a non-coordinating solvent octadecene (ODE) and produces mono-dispersed nanocrystals of CdSe. In addition to the non-coordinating solvent ODE, a supporting solvent trimethylpentyl phosphinic acid (TMPPA), hexadecyl amine (HDA) and tributyl phosphine (TBP) were also used to control the reaction condition. Thus, the replacement of TOPO makes the synthesis less expensive, safer and greener in comparison to the other solvents. Therefore, to make environmental friendly Q-dots less use of TOPO is desirable.

In this report, we prepared CdSe Q-dots in TOPO free environment at varying temperature of 240 - 300°C. The prepared CdSe Q-dots are homogeneous, stable and tunable in size (3.2- 4.3 nm) and shows significant quantum yield (QY). The QY of the water soluble Q-dots is higher at higher value of pH.

**MATERIAL AND METHODS**

**Materials**

All the chemicals including cadmium oxide (CdO), selenium (Se) powder (99.9%), trioctylphosphine (TOP, 90%), oleic acid (OA, 90%), mercapto propionic acid (MPA, 95%) and 1-octadecene (ODE, 90%) were purchased from Aldrich and used without further purification.

**Synthesis of CdSe Q-dots**

Synthesis was carried out under nitrogen (N₂) environment following the procedure described earlier with some modifications and without considering the TOPO. In order to provide rigorously oxygen and water free environment for the synthesis, all the substances were dried and degassed before used. Initially, solutions of the Cd and Se precursors were prepared separately. To prepare Se precursor, 0.0205 gm Se powder, 0.12032 ml TOP and 2 ml octadecene (ODE) were mixed in the glass vial and put the mixer on the hot plate stir for around one hour. Similarly, for the Cd precursor, a mixer of 0.102 gm CdO, 1.23 ml oleic acid and 14 ml ODE were taken and then the mixture (CdO-OA-ODE) was transfer into three neck flask and stirred continuously with heating rotamantle at 180°C until the solution became colorless. For the growth of CdSe Q-dots, further temperature was increased up to 240°C or 260°C or 280°C or 300°C, when the solution attend the required temperature then 2 ml Se stock solution was injected into three neck flask (which contained Cd solution) at a constant stirring. After the injection of Se precursor the temperature was dropped about 10°C from the attended values. The color of the reaction solution changed immediately after the injection of the Se precursor, which indicated fast in nucleation and growth. After about 60 second of Se precursor injection, the heating mantle was removed then 20 ml methanol was added into the reaction mixture and finally centrifuged the obtained solution at 6500 rpm for 10 min. The process is repeated 2-3 times to obtained pure CdSe Q-dots, and then the obtained eluent was dispersed into toluene for further investigation. Similarly, the reaction process was repeated to obtain CdSe Q-dots at different growth temperatures of 260°C, 280°C and 300°C.

The method of preparation of CdSe Q-dots involved the injection of a cool solution of Se precursor into hot liquid (mixture of CdO - OA-ODE). The injection of Se precursor leads to the instantaneous formation of CdSe nuclei. With increasing growth temperature, the size of the resulting CdSe nanocrystals increases. The formation of new nuclei was prevented at each growth temperature by reducing the growth temperature about 10°C. Thus, it appears that below temperature of 300°C the nucleation process is under controlled and produced nearly mono-dispersed CdSe Q-dots.

**Synthesis of water soluble CdSe Q-dots**

In order to use the Q-dots for biological applications such as labeling and imaging, we need to prepare water soluble Q-dots because almost all the biological environments is aqueous.

However, the above prepared CdSe Q-dots are not water soluble because of the presence of ligands (OA/TOP). These hydrophobic ligands could be replaced by water soluble bi-functional
SCHEME 1. Water soluble CdSe Q-dots capped with bifunctional molecules mercaptopropionic acid (MPA).

molecules MPA, following the method of ligands exchange or phase transformation\(^{28}\) in which one end connected to Q-dots and the other end is hydrophilic and reactive (Scheme 1). In this process, oleic acid capped nanocrystals\(^{29}\) were dissolved in 2 mL of chloroform to obtained high concentration (the optical density of the CdSe solution is \(\sim 2\)) and added the same volume of a water solution containing MPA under vigorous stirring condition. The amount of MPA was adjusted to roughly 150% of the total Cd atoms. After 3 hrs, the NCs transferred into the water phase, but the solution was not optically clear at pH \(\sim 5\) to 8, possibly due to inter-particle hydrogen bonding of carboxyl functions of the ligands. To remove excess MPA from the supernatant solution, these particles were separated by centrifugation and decantation. At higher pH (\(> 8\)), successive redispersion of the particles into water yields a clear solution.

Methods

Steady-state optical measurements were performed in toluene and water (for water soluble Q-dots) at ambient temperature. Absorption spectra were recorded with the UV/VIS/NIR spectrometer, Lambda-750, Perkin-Elmer. Photoluminescence (PL) spectra were collected by Horiba Jobin Yvon Fluorolog-3 spectrofluorometer equipped with double-grating at excitation as well as at emission monochromators (1200 grooves/mm) and Hamamatsu R928P photomultiplier tube (PMT). The excitation source was a 450 Watt CW xenon lamp. An instrumental correction was applied on all PL spectra to correct for the wavelength dependent PMT response and variation in output intensity from the lamp and grating efficiencies.

Excitation and emission slit width was selected to be 1.0 nm and same for all measurements, and the excitation wavelength was 450 nm. High resolution transmission electron microscopy (HRTEM) images where recorded by Tecnai G\(^{2}\) 20 electron microscope operated at accelerating voltage of 200 KV. For HRTEM images, CdSe samples were prepared on 300-mesh carbon coated Cu grids, a very small amount of Q-dots were dispersed in toluene (for a dilute solution) and then put onto carbon coated Cu grids and thereafter dried the samples. The energy-dispersive X-ray (EDX) spectra and X-ray diffraction (XRD) pattern were recorded by Hitachi-640 at accelerating voltage of 15 KV and BRUKER- D8, respectively.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of CdSe Q-dots coated over glass substrate grown at temperature of 240° C. The XRD patterns are broadened as compared to those of bulk materials, thus the peaks and the broadening indicating to the nanocrystalline nature of the CdSe Q-dots. The peaks obtained
FIG. 1. The XRD pattern of CdSe Q-dots grown at temperatures of 240° C. The peak identified with the standard JCPDS (ref. card no. 892944).

at (2θ) angles of (25.6), (42.7) and (50.0) are correspond to the reflection from (111), (220) and (311) crystal planes, respectively, as identified by standard JCPDS (card no. 652891) data. The XRD pattern clearly demonstrated to the hexagonal phase with wurtzite structure and also indicates the preferential growth of crystallites in a particular direction of (111) plane. Then the average crystall sizes (d) were calculated based on the width of the peak of (111) planes by using the Scherrer’s formula:

\[
d = 0.94 \frac{\lambda}{\beta \cos \theta},
\]  

where \( \lambda \), \( \beta \) and \( \theta \) are the X-ray wavelength, full width at half maxima (FWHM) and the Bragg’s angle of reflection, respectively. The average crystalline size calculated from the equation (1) is 4.2 nm.

Figure 2 shows HRTEM images and the corresponding statistical size distribution histograms of CdSe Q-dots grown at various temperatures of 240°, 260° and 300° C. The HRTEM images confirm that the prepared Q-dots are nearly spherical with uniformity in size and shape. The images show a change in the particle size, the particle size increases monotonically with increasing the growth temperature from 240° to 300° C, indicating that the reaction temperature has essential effects on CdSe Q-dots. The average particle size of the CdSe Q-dots is 3.2 - 4.3 nm grown at temperature of 240°- 300° C, respectively. The energy dispersive X-ray (EDX) spectra and percentage amount of each identified elements of CdSe Q-dots grown at various temperatures are given in Fig. S1 and Table I, respectively.

Figure 3 shows the steady-state absorption spectra of CdSe Q-dots dispersed in toluene grown at temperature of 240 - 300° C. The lowest energy absorption band shifted towards the longer wavelength, i.e., from 547 to 572 nm as the growth temperature increases from 240 to 300° C. The red shift in absorption maximum clearly indicates to the increase of the particle size. The energy band gap or optical energy band gap (\( E_g \)) of CdSe Q-dots grown at various temperatures was estimated from absorption spectra using Tauc’s relation, as given:

\[
a h \theta = A (h \theta - E_g)^n,
\]  

where \( a \) is the absorption coefficient, \( h \nu \) is the photon energy, \( A \) is a constant and \( n \) assumes the values 1/2, 2, 3/2 and 3 for allowed direct, indirect, forbidden direct and indirect transitions, respectively. For allowed direct transitions the relation can be given as:

\[
a h \theta = A (h \theta - E_g)^{1/2}
\]
FIG. 2. The HRTEM images (a-c) and the size histogram (a’-c’) of CdSe Q-dots grown at temperature of 240° (a, a’), 260° (b, b’) and 300° C (c, c’).

The plots between $(a\nu)$ vs $(\nu)$ obtained at different temperature are given in Fig. 4. The straight line nature of the plots over a wide range of photon energy indicates the direct type of transitions. The $E_g$ of Q-dots is determined by extrapolation of the linear regions on the energy axis. The estimated values of $E_g$ for CdSe Q-dots grown at temperatures of 240°, 260°, 280° and 300° C come out to be 2.81, 2.78, 2.74 and 2.60 eV, respectively, these values are significantly larger than the bulk...


<table>
<thead>
<tr>
<th>Samples</th>
<th>Elements</th>
<th>Weight %</th>
<th>Atom %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe at 240° C</td>
<td>Cd</td>
<td>66.32</td>
<td>58.04</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>33.68</td>
<td>41.96</td>
</tr>
<tr>
<td>CdSe at 300° C</td>
<td>Cd</td>
<td>72.36</td>
<td>65.20</td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>27.64</td>
<td>34.80</td>
</tr>
</tbody>
</table>

CdSe ($E_{\text{bulk}} = 1.74$ eV),\(^{31}\) and are indicating to the band gap between highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) of CdSe Q-dots.

Further, the particles size has also been estimated from the optical spectra using the effective mass approximation.\(^{35}\) The strong confinement regime and confinement energy of the first excited electronic state (lowest energy absorption band) can be approximated by the Brus equation:

$$E_g = E_{\text{g}}^{\text{bulk}} + \frac{\hbar^2 \pi^2}{2 R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - \frac{1.8 e^2}{4 \pi \varepsilon_o R},$$

where $E_g$ is the optical transition energy of CdSe Q-dots, $E_{\text{g}}^{\text{bulk}}$ is the energy gap of the bulk CdSe and $m_e^*$ and $m_h^*$ are the effective mass of conduction band electron and valence band holes of CdSe, respectively. The value of $m_e^*$ is 0.13 $m_0$ and $m_h^*$ is 0.45$m_0$.\(^{33,34}\) and $m_0$ is the electron rest mass ($9.1 \times 10^{-31}$ kg). The estimated size of CdSe Q-dots grown at temperatures of 240°, 260°, 280° and 300° C comes out to be 3.2, 3.4, 3.6 and 4.0 nm, respectively. The size of the Q-dots estimated by the simplifed Brus relation (4) is approximately the same as estimated using HRTEM.

Figure 5 shows PL spectra of the CdSe Q-dots grown at temperatures of 240°, 260°, 280° and 300° C. The excitation wavelength was 450 nm. The PL spectra show an apparent red shift, i.e., the PL band maximum shifted from 565 to 580 nm as the growth temperature increases from 240°-300° C. However, the FWHM of the PL decreases monotonically with increasing the growth temperatures. As an example, the FWHM is 33.7, 33.3, 31.5 and 29.9 nm at 240°, 260°, 280° and 300° C, respectively. At 300° C, the FWHM is very small (< 30 nm) indicating that the size distribution of the resulting Q-dots is nearly homogeneous/narrow, which are comparable with one of the best results obtained using TOPO.\(^{35}\) The PL QY of CdSe Q-dots ($\Phi_s$) has been estimated
FIG. 4. Tauc’s plots for CdSe Q-dots obtained between $(\alpha h \nu)^2$ and $(h \nu)$.

FIG. 5. The photoluminescence (PL) spectra of CdSe Q-dots dispersed in toluene grown at various temperature of 240° - 300° C.
using the relation;

$$\Phi_S = \Phi_R \frac{I_S}{I_R} \left( \frac{1 - 10^{-A_R}}{1 - 10^{-A_S}} \right) \left( \frac{n^2_S}{n^2_R} \right)$$

where $\Phi_R$ is the absolute QY of reference rhodamine 6G (0.95), $I_R$ and $I_S$ are the integrated fluorescence intensity of the reference (rhodamine 6G) and sample (Q-dots), respectively $A_R$ and $A_S$ are the respective absorbance and $n_R$ and $n_S$ are the refractive index of solvents (toluene for Q-dots and methanol for the rhodamine 6G). The estimated QY for CdSe Q-dots is $0.16 \pm 0.01$ at temperature of $240^\circ\text{C}$.

In the synthesis route, oleic acid is used as capping agent, which always forms a shell on the surface of CdSe. The activity of the oleic acid increases with increasing growth temperature. The high growth temperature leads to the faster association/dissociation dynamics of the oleic acid on the surface. When oleic acid detaches from the surface of the particles, the smaller particles tends to becomes larger to reduce the surface energy. Therefore, at the higher reaction temperature, a larger particles size and higher growth rate is obtained. It was suggested that at higher temperature, the smaller particles diminished while the larger ones grew due to the Oswald ripening, and the size distribution became more uniform, as a result the PL spectrum became narrow as compared to the obtained at lower growth temperature. The Stoke’s shift (difference of lowest energy absorption and PL maximum) is reduced from 20 to 8 nm as the growth temperature increases from 240° to 300° C, which takes into account the coulomb interaction and the effects of dielectric mismatch.

**Steady-state absorption and photoluminescence of water soluble Q-dots**

Figures 6 and 7 show the optical absorption and PL spectra of water soluble CdSe Q-dots measured at different pH with at constant concentration. The size and PL maximum of initial CdSe Q-dots used for the preparation of water soluble Q-dots is about 3.5 nm and 553 nm, respectively. The lowest absorption band (HOMO-LUMO band gap) of CdSe Q-dots at different pH is the nearly same, i.e., lies at the same wavelength region. Similar trend is observed for the PL spectra, no significant spectral shift is obtained at different pH. However, the PL intensity changes with varying pH, especially from 8.5 to 11.5, and the PL intensity is highest at pH 11.5, though the PL does not follow exactly the Gaussian shape, which may be due to the presence of the ligands. At lower and higher pH, the PL spectrum does not show considerable change. The QY increases with increasing the pH of water (from 8.5 -11.5), as shown in Table II. At basic pH, the affinity of CdSe Q-dots is

![FIG. 6. The absorption spectra of CdSe Q-dots (original size = 3.5 nm) dissolved in water at different pH of 8.5 – 11.5.](image-url)
FIG. 7. The photoluminescence spectra of CdSe Q-dots dissolved in water at different pH of 8.5 – 11.5.

TABLE II. Quantum yield of water soluble CdSe Q-dots at different pH.

<table>
<thead>
<tr>
<th>Sample/pH</th>
<th>Quantum yield</th>
</tr>
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<tbody>
<tr>
<td>CdSe (pH) 8.5</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td>CdSe (pH) 9.5</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>CdSe (pH) 10.6</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>CdSe (pH) 11.5</td>
<td>0.10 ± 0.01</td>
</tr>
</tbody>
</table>

...more favorable due to deprotonation of the thioalkyl acid group, which becomes negatively charged and endeavors the coordination between the ligands and the semiconductor surface giving rise to an improvement in nanoparticles dispersibility and QY.\textsuperscript{38}

CONCLUSIONS

CdSe Q-dots have been prepared by hot injection colloidal method in TOPO free environment. The prepared CdSe Q-dots have a hexagonal phase with wurtzite structure. With increasing temperature of the reaction system, i.e., the growth temperature from 240° to 300° C: (i) the average particle size of CdSe Q-dots increased from 3.2 to 4.3 nm, (ii) the absorption maximum shifted towards longer wavelength region and hence the $E_g$ decreases from 2.8 to 2.6 eV, (iii) the Stoke’s shift reduced from 18 to 8 nm and (iv) the FWHM of the PL spectra decreased. In addition, stable water soluble CdSe Q-dots were prepared following ligand exchange process, which shows higher QY at higher pH. Thus, the study also reflects that the prepared water soluble CdSe Q-dots, which are sensitive to the basic pH may be suitable for biological applications.

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30 See supplementary material at http://dx.doi.org/10.1063/1.4930586 for Fig. S1.