Chapter 6

Studies on CdS nanoparticles prepared in DNA and BSA based biotemplates

Abstract

This chapter discusses band gap tunability of CdS nanoparticles in biotemplates deoxyribonucleic acid (DNA) and bovine serum albumin (BSA). DNA is more efficient in controlling the size of the nanoparticles compared to BSA. Since nanoparticles are capped with biomaterials, they are very useful for biolabeling. The photo luminescence spectrum of CdS nanoparticles in DNA template shows sharp emission peak at 490 nm with shoulders at 430 nm and 530 nm while that of CdS in BSA template has emission peak at 530 nm with shoulders at 477 nm and 410 nm. We also studied excitation wavelength dependence on fluorescence emission of CdS nanoparticles stabilized with DNA and BSA. The excitation wavelength dependent shift of PL peak is found to be between 40 and 50 nm for a change in excitation wavelength from 260 to 420 nm.

The results of this chapter are communicated to Journal of Applied physics
6.1. INTRODUCTION

Synthesis of semiconductor nanoparticles having a controlled size distribution has attracted significant interest in research because of their luminescent properties, quantum size effects and other important physical and chemical properties. The broad area of applications include solar energy conversion, optoelectronic devices, molecular and cellular imaging and trace detection. A major feature of semiconductor nano particles is the quantum confinement effect, which leads to spatial enclosure of the electronic charge carriers within the nanocrystal. The spectral properties of these semiconductor nanocrystals can be controlled effectively by tuning the size, composition, surface properties and crystal structure of the nanocrystals. Because of this effect we can tune the light emission from these media throughout the ultraviolet, visible, near-infrared, and mid-infrared spectral ranges. For instance, the band gap emission is tunable over wide wavelengths by adjusting an appropriate size of the particle. The particles prepared from such application viewpoint will be useful as a fluorescent agent for optical and biotechnological applications. In comparison with organic dyes and fluorescent proteins, semiconductor quantum dots represent a new class of fluorescent labels with unique advantages and applications. For example, the fluorescence emission spectra of quantum dots can be continuously tuned by changing the particle size, and a single wavelength can be used for simultaneous excitation of all different sized quantum dots [1-10].

CdS is one of the most important II–VI semiconductor compound having excellent optical properties. It is a direct band gap material of energy band gap 2.42 eV at 300 K. Considerable amount of effort has been devoted to the synthesis and study of optical property of CdS related nanoparticles and quantum dots. Biological applications of CdS quantum dots has increased dramatically because of its unique spectral properties, which enable simultaneous multiplex labelling and detection [11, 12]. Most importantly, highly monodispersed CdS
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nanocrystals can be synthesized via size restricting growth modes. Adding surface capping organic materials to the solution is one of the ways to achieve growth restriction. This simple preparation method has opened the way towards tunable light emitting devices and low voltage display devices. One of the highly cited methods for making CdS or CdSe quantum dots is organometallic precursor [13]. Lee and Chang have reported an efficient and non-corrosive polysulphide electrolyte for CdS quantum dot sensitized solar cell application. The efficiency of the CdS-sensitized solar cell was 1.15% [14]. Bulk CdS shows an absorption onset of 2.42 eV and absorbs radiation in the visible region. Semiconductor nanoparticles are known to exhibit unique size dependent optical properties, which make them attractive from the viewpoint of integrated photonic devices. There is significant change in the properties when the dimensions of the nanocrystallites become comparable or less than the Bohr radius of the excitons corresponding to the widening of the energy gap as size decreases. In CdS, quantum size effect is observed for crystallite dimensions below 5 nm which is approximately the Bohr exciton diameter in CdS [15]. Because of the quantum confinement effect, semiconductor nanocrystals exhibit size dependent, molecular like discrete electronic and optical transitions. Nanocrystalline CdS has been prepared by different workers using various techniques such as pulsed laser deposition, chemical bath deposition, spray pyrolysis, successive ionic layer adsorption and reaction, screen printing and sol–gel spin coating method [16-20]. Chemical method is a simple and really cost efeective method.

Among biological molecules deoxyribo nucleic acid (DNA) and bovine serum albumin (BSA) have been used extensively as a biotemplate to grow inorganic quantum confined structure and to organize non biological building blocks into extended hybrid materials because of their physicochemical stability and unique structure [21-24]. The integration of nanotechnology with biology
and medicine is expected to produce major advances in molecular biology, and bioengineering. The development of functional nanoparticles that are covalently linked to biological molecules such as peptides, proteins, and nucleic acids are the recent advances in biotechnology. For example nickel has been successfully synthesized by using DNA network templates [22]. Using biomolecule as a template to synthesis inorganic nano particles is an effective method to fabricate functional materials with well defined structure and controllable dimensions. We adopted the preparation technique reported by Yong Yao et.al. [23] to synthesize CdS nano particles in both DNA and BSA templates. The size and assembly of nano particles can be controlled by changing the amount of biological molecules in medium. In the present chapter we compare the band gap tunability and photoluminescence properties of CdS nano particles in two biological template, DNA and BSA.

6.2. SYNTHESIS

All chemicals and biopolymers used in this work were obtained from commercial sources (SRL, Merck). DNA and BSA capped CdS nanoparticles were synthesized according to published procedures [23]. The concentration of BSA and DNA were varied from 0.05 wt% to 0.2 wt%. Cadmium acetate at 50mM solution and DNA solutions were mixed completely. Thiourea solution was added to the prepared mixture and heated at 70 °C for 100 min. The yellow reaction product was filtered and dried in a desicater to obtain yellow coloured CdS nano particles. We used aqueous solution of BSA to prepare BSA coated CdS nanoparticles. Concentrations of the both stabilizers needed for effective capping of CdS particle was found to be in the same range.

6.3. CHARACTERIZATIONS

Optical absorption of the samples prepared with various concentrations of capping agent (DNA and BSA) were studied. The UV-visible absorption
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Spectroscopy has been used to monitor the optical absorption properties of quantum-sized nanoparticles. The absorption spectra of the nanoparticles of CdS in DNA template are shown in Fig. 6.1, where C1, C2, C3, C4 represent DNA concentration of 0.06, 0.128, 0.16, 0.2 wt% respectively. The spectra exhibit a well-defined absorption edge in the 400-500 region. Blue-shifted absorption edge indicating quantum size effect is clearly seen [25]. Fig. 6.2 shows the absorption spectra of CdS nanoparticles in BSA template. In this case exciton peak appeared around 470 nm which is blue shifted indicating quantum size effect, where C1, C2, C3, C4 represents BSA concentration of 0.06, 0.128, 0.16, 0.2 wt% respectively. Blue shift in the absorption edge increases with increase in stabilizer concentrations for both capping agents. Fig. 6.3 shows absorption spectra of CdS nanoparticles without using DNA and BSA. Here thiourea is used as a sulphur source and capping agent. In this case the absorption edge is found to be around 480 nm. In all cases the absorption band is found to be broad which indicates particle size distribution in samples.

Figure: 6.1. Absorption spectra of CdS nanoparticles at different concentration of DNA
Figure: 6.2. Absorption spectra of CdS nano particles at different concentration of BSA.

Figure: 6.3. Absorption spectra of CdS nano particles without adding biopolymers DNA and BSA
Optical properties of semiconductor nanocrystals depend on the electronic structure of valence and conduction bands. As indicated above one of the most interesting effects of low dimensional semiconductor quantum structures is the size dependent band gap. There are two cases, called the weak confinement and the strong confinement regime depending on the particle size is larger than or smaller than the radius of the electron-hole pair.

A simple model was initially adapted by Efros in 1982 to spherical clusters with infinite potential wells as boundary conditions [26]. These authors assumed an energy dispersion close to the valence band maximum (VBM) and the conduction band minimum (CBM) with effective masses of CBM electron and VBM hole. This model is called the “effective mass approximation” (EMA). A further development of the EMA model has been made by Brus [27, 3]. The latter has introduced the Coloumb interaction. The grain size of CdS nanoparticles can be determined using Brus equation

\[ E = E_g + \frac{h^2}{8R^2}\left[\frac{1}{m^*_e} + \frac{1}{m^*_h}\right] - 1.8e^2 / 4\pi\varepsilon_0\varepsilon_a R - 0.124e^4 / (\hbar / 2\pi) \]

\[ (4\pi\varepsilon_0\varepsilon_a)^2 \left[\frac{1}{m^*_e} + \frac{1}{m^*_h}\right]^{-1} \]

\[ \alpha = A(h\nu - E_g)^p \]

where \( E \) is the onset of absorption of the sample, \( E_g \) is the bulk band gap, \( R \) is the radius of the particle, and \( m^*_e, m^*_h \) are the reduced masses of the conduction band electron and valence band hole in units of the electron mass, \( \varepsilon_0 \) is the vacuum permittivity and \( \varepsilon_a \) is the high-frequency dielectric constant. In semiconductors, the relation connecting the absorption coefficient \( \alpha \), the incident photon energy \( h\nu \) and optical band gap \( E_g \) takes the form

where \( A \) is constant related to the effective masses associated with the bands and \( p=1/2 \) for a direct band gap material, 2 for an indirect band gap material and 3/2
for a forbidden direct energy gap. Since better linearity was obtained in the \((\alpha h \nu)^2\) vs \(h \nu\) plot, which is shown in Fig.6.4 (CdS in DNA template), the direct band gap values were determined by extrapolating the linear portion of these plots to the energy axis.

![Graph](image)

**Figure: 6.4. The \((\alpha h \nu)^2\) vs \(h \nu\) plot of CdS nanoparticles in DNA template**

Value of the band gap obtained from the absorption spectra are given in table 6.1. On increasing the concentration of DNA, the optical band gap was found to increase from 2.58 to 2.92 eV. The reduction in the particle size gives a shift in the optical band gap of the sample since bandgap increases the particle size is reduced. Particles capped with BSA at concentration range 0.06 wt% to 0.2 wt% show band gap tunability from 2.58 eV to 2.73 eV. The wide tunability of band gap is obtained in the case of DNA capped nanoparticles compared to BSA capped.
Table: 6.1. Band gap of semiconductor nanoparticles in DNA and BSA template

<table>
<thead>
<tr>
<th>Wt% of BSA and DNA</th>
<th>Energy Band Gap of CdS nanoparticle in DNA (ev)</th>
<th>Energy Band Gap of CdS nanoparticle in BSA (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0(Fig. 6.3)</td>
<td>2.58 ± 0.01</td>
<td>2.58 ± 0.01</td>
</tr>
<tr>
<td>0.06(C1 in figure)</td>
<td>2.65 ± 0.02</td>
<td>2.64 ± 0.01</td>
</tr>
<tr>
<td>0.128(C2 in figure)</td>
<td>2.85 ± 0.01</td>
<td>2.67 ± 0.02</td>
</tr>
<tr>
<td>0.16(C3 in figure)</td>
<td>2.89 ± 0.03</td>
<td>2.70 ± 0.02</td>
</tr>
<tr>
<td>0.2(C4 in figure)</td>
<td>2.92 ± 0.02</td>
<td>2.73 ± 0.03</td>
</tr>
</tbody>
</table>

X-ray diffraction studies were carried out for DNA and BSA capped CdS samples and a typical pattern for sample C2 is presented in Figs. 6.5 and 6.6. The XRD pattern exhibits prominent, broad peak at value 27°. The average grain size of the sample is determined using Scherrer’s equation [28].

\[ D = \frac{0.89 \lambda}{\beta \cos \theta} \]  

...(6.3)

where D is the average diameter of the nano particles, \( \lambda \) is the wavelength of the CuK\( \alpha \) line (1.54 Å), \( \beta \) is the full width half maximum of the diffraction peak in radian and \( \theta \) is the diffraction angle. The average nano particle diameter calculated from Brus equation and Scherrer formula is shown in table 6.2.
Table: 6.2. Particle size of nanoparticles in DNA and BSA template obtained from X-ray diffraction and optical absorption studies

<table>
<thead>
<tr>
<th>Wt % of DNA and BSA</th>
<th>Particle size of CdS in DNA template (nm)</th>
<th>Particle size of CdS in BSA template (nm)</th>
<th>Particle size of CdS in DNA template from XRD (nm)</th>
<th>Particle size of CdS in BSA template from XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.71 ± 0.01</td>
<td>4.71 ± 0.01</td>
<td>4.69</td>
<td>4.71</td>
</tr>
<tr>
<td>0.06</td>
<td>4.19 ± 0.03</td>
<td>4.23 ± 0.03</td>
<td>4.09</td>
<td>4.11</td>
</tr>
<tr>
<td>0.128</td>
<td>3.14 ± 0.02</td>
<td>4.02 ± 0.04</td>
<td>3.28</td>
<td>3.30</td>
</tr>
<tr>
<td>0.16</td>
<td>3.03 ± 0.04</td>
<td>3.99 ± 0.05</td>
<td>3.13</td>
<td>3.98</td>
</tr>
<tr>
<td>0.2</td>
<td>2.92 ± 0.03</td>
<td>3.68 ± 0.04</td>
<td>2.86</td>
<td>3.58</td>
</tr>
</tbody>
</table>

Figure: 6.5. XRD pattern of CdS nanoparticles in DNA(C3) matrix

As the particle size obtained from X-ray diffraction and optical absorption studies is smaller than Bohr radius of CdS, the strong confinement
effect can be assumed to be present in the CdS nanoparticles.

![XRD pattern of CdS nanoparticles in BSA(C3) matrix](image)

**Figure: 6.6. XRD pattern of CdS nanoparticles in BSA(C3) matrix**

### 6.4. PHOTOLUMINESCENCE STUDIES

Figure 6.7 shows the photoluminescence (PL) spectra of CdS nanoparticles in DNA template at different concentrations of DNA at excitation wavelength 260 nm. The PL spectrum shows sharp emission peak at 490 nm with shoulders at 430 nm and 530 nm. Luminescence spectra is very broad. As concentration of the DNA increases, PL peak is shifted to blue region indicating quantum confinement effect. PL behaviour of semiconductor nanoparticles gives information on the energies and dynamics of photogenerated charge carriers as well as on the nature of the emitting states. PL occurs when an electron, undergoes radiative recombination either at valence band (band edge luminescence) or at traps/surface states within the forbidden gap [28-30]. Here
emission at 490 nm is the band edge emission due to recombination of the exciton in the mostly delocalized states in nanoparticles and it determines crystalline nature of nanoparticles. Prepared samples shows strong PL which indicates that the surface states remain very shallow, as it is reported that quantum yields of band edge will decrease exponentially with increasing depth of surface state energy levels. PL spectrum at 535 nm is usually attributed to trap state emission arising from surface defect sites. In CdS, defects consist of cadmium vacancies, sulphur vacancies, interstitial sulphur and cadmium atoms adsorbed on the surface. Side lobes in the higher energy side of PL spectra is due to the recombination of charge carriers in deep traps of surface localized states [28, 31-33]. Fig. 6.8 shows the photoluminescence spectra of CdS nanoparticles in BSA template at different concentration of DNA at excitation wavelength 260 nm. The PL spectrum shows sharp emission peak at 530 nm with shoulders at 477 nm and 410 nm. The emission band present at 530 nm is known as green emission band of CdS. Emission at 477 nm comes from band edge emission.

CdS nanoparticles with PL peaks at 509, 535, 569 and 585 nm correspond to particle size of 1.6, 2.2, 3.1 and 3.4 nm respectively as reported in literature [28]. In both case, (CdS in DNA and BSA templates) PL spectra consist of many emission peaks indicating particle size distribution in samples. In this case an appropriate excitation energy can excite several nanocrystals simultaneously producing a PL spectrum which contains more than one peak. The present sample may not be strictly mono dispersed and the structure on the high energy side of the green emission may be attributed to selectively excited photoluminescence.
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Figure: 6.7. PL spectrum of DNA capped CdS nanoparticles (where C1,C2,C3,C4 represent DNA concentrations 0.06, 0.128, 0.16, 0.2 wt% respectively)

Figure: 6.8. PL spectrum of BSA capped CdS nanoparticles (where C1,C2,C3,C4 represent BSA concentrations 0.06, 0.128, 0.16, 0.2 wt% respectively)
Figs. 6.9 and 6.10 show the excitation wavelength dependence of CdS nanoparticle in DNA and BSA templates respectively. In both cases when excitation wavelength changes from 260 nm to 420 nm peak fluorescence shifts towards red side. The shift in the fluorescence maximum is approximately 50 nm in the case of CdS in DNA matrix. A 40 nm shift in fluorescence peak is observed when excitation wavelength changes from 260 nm to 420 nm for CdS in BSA template. The emission maxima is different for both case. Excitation wavelength dependence may be due to the broad particle size distribution in the samples. Different particles may get excited for different excitation wavelength. The emission maxima is different for nanoparticles prepared in DNA and BSA templates. The absorption and emission band positions are dependent on the interaction between the capping agent and nanoparticles.

Figure: 6.9. Normalized fluorescence spectra of DNA capped CdS nanoparticles as a function of excitation wavelength.
6.5. CONCLUSIONS

The band gap tunability of CdS nanoparticles in biotemplates deoxyribonucleic acid (DNA) and bovine serum albumin (BSA) is studied. The band gap of these semiconductor nanoparticles can be controlled effectively by changing the concentration of biopolymers DNA and BSA. DNA is more efficient in controlling the size of the nanoparticles compared to BSA. Since nanoparticles are capped with biomaterials, they are found to be useful for biolabeling. The PL spectrum of CdS nanoparticles in DNA template shows sharp emission peak at 490 nm with shoulders at 430 nm and 530 nm. The PL spectra of CdS in BSA template shows sharp emission peak at 530 nm with shoulders at 477 nm and 410 nm. The emission band present at 530 nm is known as green emission band of CdS. Emission at 477 nm and 490 nm come from band edge emission. Studies on excitation wavelength dependence of PL spectra shows, shift of peak emission towards red side when excitation wavelength...
changes from 260 nm to 420 nm. The fluorescence emission spectra of nanoparticles can be continuously tuned by changing the concentration of BSA or DNA and excitation wavelength. The particles prepared from such viewpoint should be useful as a fluorescence agent for optical and biotechnological applications

REFERENCES


