

Identification of (CdSe)₃₂ structure in microemulsion-based synthesis

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Abstract—We investigated the optical and physical properties of different ratio of (i) non-ionic sucrose ester S1670 surfactant, (ii) 1-heptanol and (iii) deionized water using polarizing optical microscope. Three stable phases have been identified; they are (i) lamellar phase lyotropic liquid crystal, (ii) microemulsion and (iii) emulsion. CdSe quantum dots (QDs) were successfully synthesized using microemulsion system consisting 40/50/10 weight % of surfactant, oil and water respectively. The extracted QDs were characterized using XRD, UV-Visible and photoluminescence spectroscopies, and transmission electron microscopy (TEM). A thermodynamically stable chemical structure of (CdSe)₃₂ has been identified using first principle density functional theory (DFT) and emitting states of the structure was calculated.

Keywords—CdSe quantum dots, density functional theory, photoluminescence

I. INTRODUCTION

Architecture of nanomaterial as building blocks is an important point of view in device fabrications. Parameters inclusive of size, shape and distribution are in focus grid of researchers in order to obtain meaningful and significant results. Two parameters, i.e., size and size distribution have been studied in our previous work. We have shown the importance of narrow size distribution of quantum dot (QD) as light absorber in solar cell that favoured unwanted self-injection of electron from small to big cluster of QD; which lower the efficiency of a solar cell. The search for the most electronically stable size of QD is done by calculation of thermodynamically stable structure at B3LYP/lan12dz level of DFT[1]. Microemulsions are isotropic and thermodynamically stable; homogenize mixture of two immiscible liquids (i.e. water and oil) by incorporation of appropriate type and amount of surfactant [2]. The microemulsion and emulsion terms are based on the size range of water droplet i.e., nanometer and micrometer respectively. At high concentration of surfactant regions, double layer of surfactant molecules formed and arranged into bilayer structure. The self-assembled bilayer consists of hydrophilic part of surfactant as outer layer while the non-polar lipophilic part as the inner layer. This layered structure is known as lamellar phase liquid crystal which is highly anisotropic and exhibit birefringency. Based on type of surfactant, oil phase and ratio of mixture, other type of lyotropic liquid crystal is observable, i.e., hexagonal and

cubic phases. The microemulsion and lyotropic liquid crystal offer thermodynamically stable medium for QD synthesis. Both phases i.e., microemulsion and lyotropic liquid crystal have been intensely utilized as template for nanomaterial synthesis [3-7]. However, the chemical structure of the yielded QDs has never been determined.

II. MATERIALS AND METHOD

A. Materials

Non-ionic food grade surfactant sucrose ester S1670 (HLB number 16) was purchased from Mitsubishi Kagaku Food, 1-heptanol (as oil phase) was supplied by Merck and deionized water (Purelab Prima Elga, 18.2 MΩ electrical resistivity) was used throughout sample preparations. All samples were prepared by mixing directly in glass vials by weight percentage (wt %) of each component and kept in water bath at 37 °C overnight to reach equilibrium state. Vortex mixer was used in order to homogenize all the components.

B. Phase determination

Phase determination was done based on optical property using light polarizing Nikon e-clipse 2000 optical microscope with Nikon D5000 camera and heating stage attachments. Lamellar phase lyotropic liquid crystals showed birefringency; easily observed compared to the isotropic emulsion phases that showed continuous black image upon polarization of light. At this point, the microemulsion and emulsion phases were distinguished based on their physical appearance. Microemulsion appeared in a form of clear and thick solution; whereas emulsion appeared in a form of turbid and thick solution. The size of droplets in emulsion is measureable under the microscope without polarization of light. The type of microemulsions later on determined using simple conductivity test. Water in oil (W/O) type of microemulsions have conductivity lower than 1 μS/cm; whereas the oil in water (O/W) microemulsions have higher than the specified value [8].

C. Reaction procedure

For CdSe nano-structure synthesis, ~0.25 M Sodium Selenosulphate as Se precursor was prepared by an overnight

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reflux process of 5 g Se powder (ACS Across) and 15 g Sodium Sulfite anhydrous (Fluka) in 200 ml deionized water at 98 °C with constant stirring. The solution then cooled down to room temperature and filtered away the undissolved Se. 0.0053 M $\text{Cd}(\text{NO}_3)_2$ (Merck) was used as Cd precursor. 40/50/10 microemulsion system was prepared. Each composition of surfactant/oil/water was prepared by using two different precursor solution, i.e., 0.25 M sodium selenosulphate and 0.053 M $\text{Cd}(\text{NO}_3)_2$. All systems were left to equilibrate overnight at 37 °C. Two microemulsion systems with the same weight ratio of surfactant/oil/water and different precursor were mixed under slow stirring process at 37 °C. The clear yellow microemulsion system turned to clear red after few minutes of reaction. The system then centrifuged at 12 000 rpm for 15 minutes to precipitate the yielded CdSe. The precipitates then suspended in ethanol, sonicate for 15 minutes and centrifuged for 7 minutes. This step was repeated two times by using deionized water in order to remove excess surfactant and byproducts. The precipitates were then dried at 70 °C for 12 hours. Absorption and emission spectra of CdSe were recorded using Shimadzu UV-2600 spectrophotometer and Edinburgh photoluminescence spectrometer respectively.

III. RESULTS AND DISCUSSIONS

A. Construction of Ternary Phase Diagram

63 samples of different weight ratio of surfactant, oil and water were prepared and characterized. Complete ternary diagram inclusive of all determined phases is depicted in Fig. 1. Three stable phases, i.e., (i) lamellar phase liquid crystal, (ii) microemulsion and (iii) emulsion exist in mixtures with surfactant weight ratio >10 wt %. S1670 molecules self-assembled at water-oil interface and in bulk water. The structure of assembly changes with the weight ratio of component. Along the line of 0 wt % of S1670; without surfactant adsorption at water-oil interface, interfacial tension is high enough to make them separated. Few of these immiscible phase samples formed homogen mixture upon vigorous shaking. However, phase separation occurred within few seconds; thus categorized as unstable phase. The region is represented by triangles in the phase diagram.

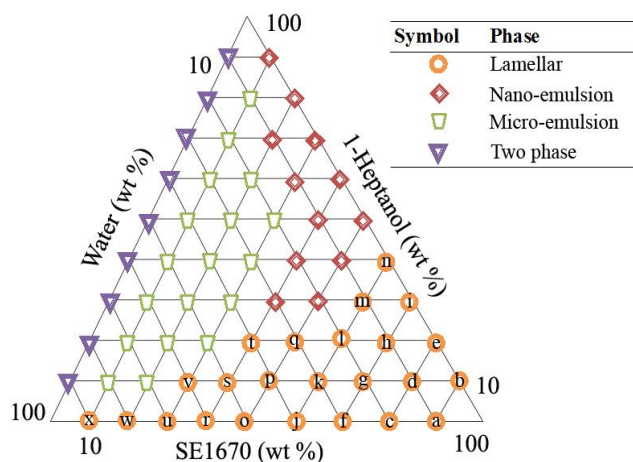


Fig. 1. Ternary phase diagram of S1670/1-heptanol/water system

B. Determination of Lyotropic Lamellar Liquid Crystal

Surfactant molecules were densely-assembled at high surfactant concentration region. This can be observed from Fig. 1; lamellar phase dominated the region of surfactant concentration > 50 wt % (labelled as point a-q in the phase diagram). Woolly, streaky or mosaic-like structures are clearly observable under light polarized microscope; reveals the characteristic property of lamellar phase liquid crystal as presented in Fig. 2.a. However, small portion of lamellar phase is also observed in the region of surfactant concentration < 50 wt %; which physically appeared as diluted lamellar known as swollen lamellar (see Fig. 2.b).

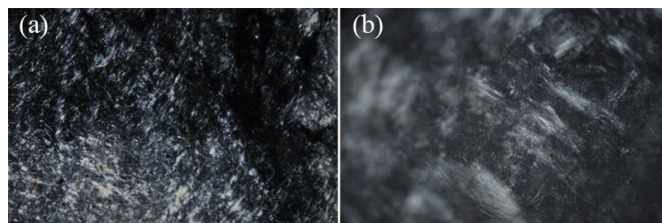


Fig. 2. (a) Densely-packed woolly structure and (b) swollen lamellar phase liquid crystal upon polarization of light for sample 70/10/20 (weight ratio of surfactant, oil and water respectively) and 30/10/60 respectively

C. Determination of W/O Microemulsion Phase

In general the microemulsion phase region formed in the region of (i) low to medium weight ratio of surfactant, (ii) medium to high weight ratio of oil and (iii) low weight ratio of water. Water in oil microemulsion phase formation as indicated in Fig. 1 confirmed by conductivity measurements and light polarized optical microscope observations (Fig. 3). Based on surfactant molecular structure (i.e., HLB value)-interfacial topology concept [9], water in oil microemulsion is formed due to bigger hydrophilic moiety than that of the lipophilic part. Curvature of surfactant film towards water is governed by relative areas of the hydrophilic head and lipophilic tail of S1670 molecule. Surfactant bilayers encapsulate water into small droplets in a continuous phase of 1-heptanol. Size of water droplets differs by water, surfactant and 1-heptanol weight ratio.

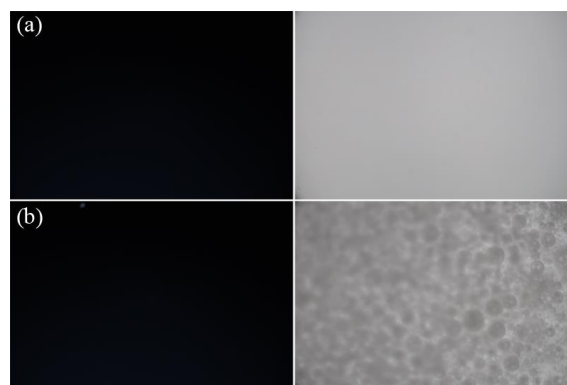


Fig. 3. Polarized (left) and non-polarize (right) optical microscope images of (a) microemulsion phase composed by 10/90/0 wt % and (b) emulsion phase

composed by 10/60/30 wt %. Note that the water droplets in emulsion phase are observable

D. Evolution of CdSe Cluster in Microemulsion Template

Absorption spectra of aliquots taken from the growth microemulsion mixture at reaction time of 1, 5, 10, 15, 30, 60 and 120 minutes are recorded; first excitonic peak in that time region is determined. Evolution of first excitonic peak position is observed; shifted to longer wavelength with increment of reaction time. This concluded that the size of yielded CdSe is increasing with reaction time as well (Fig. 4).

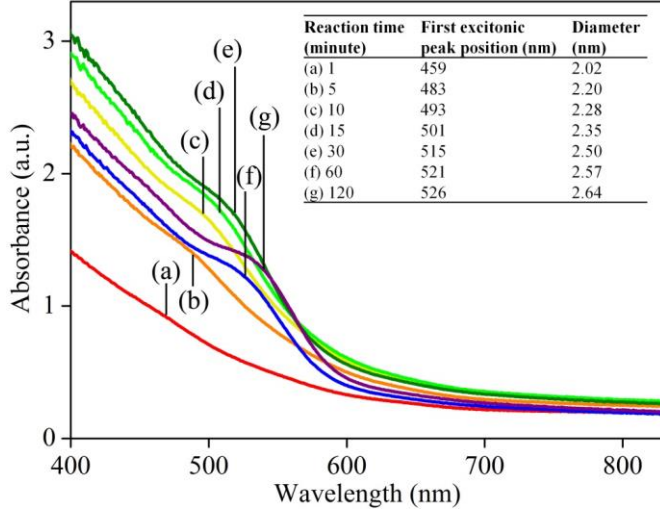


Fig. 4. Temporal evolution of the first excitonic peak position is observed for CdSe synthesized in 40/50/10 microemulsion template within (a) 1, (b) 5, (c) 10, (d) 15, (e) 30, (f) 60 and (g) 120 minutes of reaction time. Inset shows the properties of CdSe synthesized at each reaction time.

The diameter of CdSe is calculated based on the first excitonic peak position using the following equation [10]

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (4.277 \times 10^{-1})\lambda + 41.57 \quad (10)$$

where D is diameter of CdSe and λ is the first excitonic peak position. By comparison, CdSe synthesized in microemulsion and without using any microemulsion template (Fig. 5) produced different size of CdSe clusters; i.e., in the range of (i) strong quantum confinement region and (ii) bigger than the exciton Bohr radius respectively. This proves that microemulsion provide fine structure of reactor that able to inhibit rapid nucleation of CdSe cluster and preserves the size of the cluster significantly over time. Extinction coefficient of the yielded CdSe is determined using an empirical function of size due to lack of information of concentration of the yielded CdSe in the template. The function reads as [10]:

$$\varepsilon = 5857(D)^{2.65} \quad (11)$$

Bandgap of these nanocrystals is estimated using Tauc's plot (Fig. 6). The absorption coefficient is calculated by the following equation [11]:

$$\alpha = \frac{1}{t} \frac{A}{\log e} \quad (12)$$

where t is the thickness of quartz cell, A is the absorbance of the samples and e is the charge of an electron. The bandgap of CdSe is determined by extrapolating the exponential part of the curve to the x-axis. The bandgap energies of CdSe synthesized in 40/50/10 microemulsion template within 1, 5, 10, 15, 30, 60 and 120 minutes of reaction time have been estimated to be ca. 2.61, 2.29, 2.24, 2.21, 2.18, 2.15 and 2.09 eV respectively.

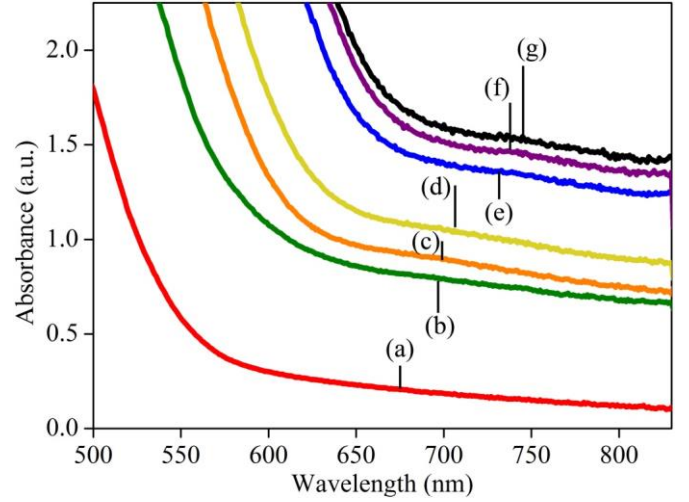


Fig. 5. Temporal evolution of the first excitonic peak position is observed for bulk CdSe synthesized without microemulsion template within (a) 1, (b) 5, (c) 10, (d) 15, (e) 30, (f) 60 and (g) 120 minutes of reaction time

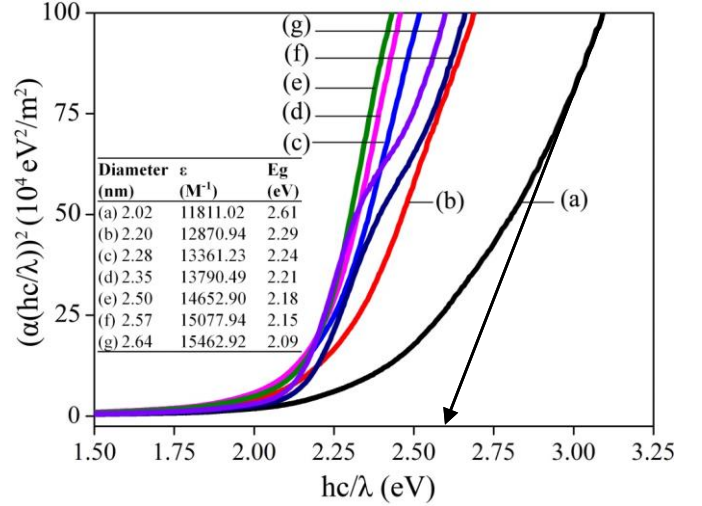


Fig. 6. Tauc's plot for CdSe synthesized in 40/50/10 microemulsion template within (a) 1, (b) 5, (c) 10, (d) 15, (e) 30, (f) 60 and (g) 120 minutes of reaction time. Inset shows the absorption coefficient and bandgap of CdSe synthesized at each reaction time

Emitting state of CdSe is studied using Photoluminescence spectrometer at excitation and emission wavelength of 500 nm and 590 nm respectively; 530 nm filter was used to eliminate noise. Evolution of broad emission spectra is observed (Fig. 7). Stoke's shift decreases as the clusters grow; indicates the

existence of deep trap which arises from irregular surface of CdSe similar to the literature property of small-medium sized clusters [12-13]. Asymmetric PL spectra with an obvious tail in the short wavelength region is observed at 1 and 5 minutes of reaction time; indicates fast nucleation of smaller particle than that of the average size. This is due to rapid increment of average diameter ~ 0.045 nm/min within 1 to 5 minutes of reaction time region. However, the cluster size stabilizes after 5 minutes of reaction time. The growth slowed down steadily from ~ 0.016 nm/min at 10 minutes of reaction time to ~ 0.00117 nm/min at 120 minutes of reaction time. This is observed by the symmetric PL spectra at reaction time of higher than 5 minutes.

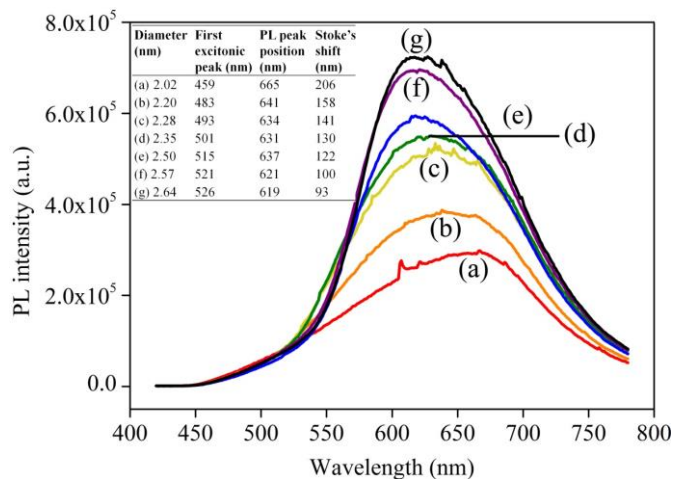


Fig. 7. Temporal evolution of the photoluminescence property of CdSe synthesized in 40/50/10 microemulsion template within (a) 1, (b) 5, (c) 10, (d) 15, (e) 30, (f) 60 and (g) 120 minutes of reaction time. Inset shows the Stoke's shift of CdSe synthesized at each reaction time.

E. Extraction of CdSe QDs from Microemulsion Template

Yielded CdSe QDs from 30 minutes of reaction time were extracted by centrifugation and washing process. The precipitated CdSe QDs were then dried in 80 °C ambience for 12 hours. The XRD pattern presented broad peaks that are difficult to discriminate between wurtzite (hcp) and zinc blende (fcc) crystal structures (Fig. 8). The quenched intensity of [102] and [103] peaks is due to stacking fault along the [002] plane in CdSe QDs that made the diffraction pattern appears as zinc blende (Zhang et al., 2002 and Jose et. al., 2005). The broadening of the diffraction peaks is due to very small size of CdSe.

The size of the extracted CdSe is found bigger than the estimated value by UV-Vis absorption spectra (Fig. 9); due to possible effects of breakage of surfactant assembly at the surface of water droplets that leads to coalescence of water droplets while content exchange still occurs; caused by high speed centrifugation ($\sim 12\ 000$ rpm) of 15, 30 and 60 minutes impregnated samples. To overcome this drawback, fresh aliquots are injected into trioctylphosphine (TOP) with volume ratio of TOP to aliquot $\sim 1:7$; to encapsulate and strengthen the structure of the cluster before centrifugation and washing process.

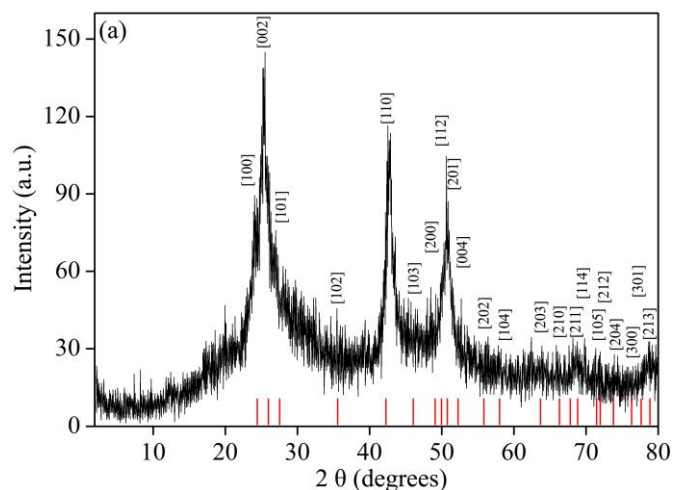


Fig. 8. Broad XRD peaks of wurtzite CdSe QDs synthesized using microemulsion procedure extracted at 30 minutes of reaction time. Vertical lines indicate the possible Bragg reflections (JCPDS-ICDD 60630)

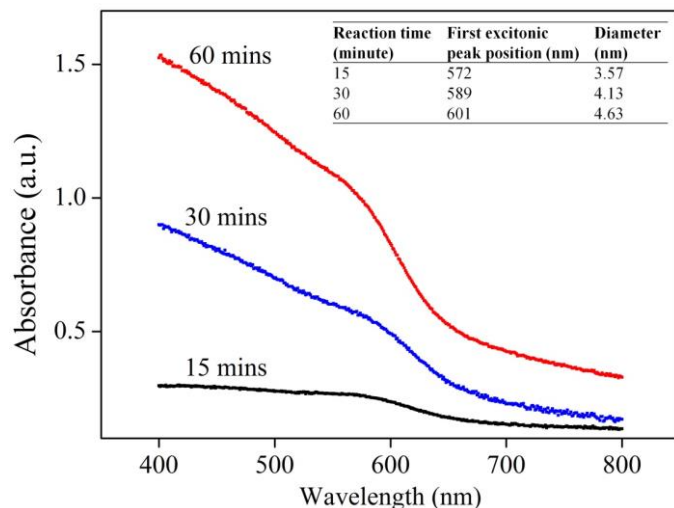


Fig. 9 UV-Vis absorption spectra of extracted and washed CdSe synthesized using 40/50/10 microemulsion template at 15, 30 and 60 minutes of reaction time respectively. Inset shows the estimated size of extracted CdSe

Fig. 10 shows a comparison of absorption spectra (40/50/10 microemulsion template) between the (i) freshly taken aliquots (ii) extracted CdSe without TOP and (iii) extracted CdSe with TOP. By comparison of the first excitonic peak position, extracted CdSe without TOP–functionalization is found to extend the growth till 4.13 nm (Fig. 10.b); even though it was extracted and washed from aliquot that contains 2.50 nm cluster (Fig. 10.a). Extracted CdSe with TOP–functionalization clearly shows size perseverance; determined by the same position of the first excitonic peak with that of the fresh aliquots (Fig. 10.c).

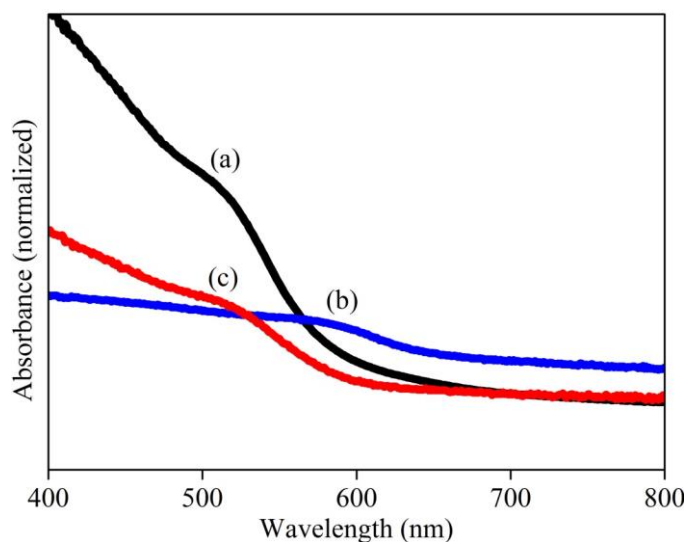


Fig. 10. Absorption spectra of (a) fresh aliquots (b) extracted without TOP and washed CdSe and (c) extracted with TOP-functionalization and washed CdSe synthesized in 40/50/10 template at 30 minutes of reaction. TOP-functionalization preserves the size of the freshly formed clusters; determined by the same first excitonic peak position (~ 515 nm) with that of the fresh aliquots

F. Electronic Structure of the Extracted CdSe Without TOP-Functionalization

Quantum chemical calculations under the framework of DFT were utilized to study the electronic structure and excited state properties of the synthesized CdSe. In this work, a new realistic cluster of $(\text{CdSe})_{32}$ was optimized at B3LYP/lanl2dz level using Gaussian 09 W program packages [14-16]; calculates geometry very well at low computational cost. Geometry optimizations were carried out using the standard double- ζ quality lanl2dz basis sets [17] followed by frequency calculations and simulating their IR spectra. Excitation energies and oscillator strengths were obtained by the time-dependent DFT (TDDFT) method including n energy singlet transitions [18]. The size of the cluster was calculated from molecular volume of the optimized geometry; which obtained from the Gaussian output file of the optimized geometry. $(\text{CdSe})_{32}$ cluster was built by parallel stacking of two $(\text{CdSe})_{16}$ structures with extensive bond lengths, bond angles and dihedral angles optimization for a minimum structure [1]. The trustworthiness of the cluster was confirmed by harmonic frequency calculations at B3LYP/lanl2dz level of DFT. The calculated IR spectrum of the optimized structure showed positive frequency. Thus confirming minimum energy structures.

Successively, the geometry was identified as real cluster using a similar procedure reported before [1]. The diameter of $(\text{CdSe})_{32}$ calculated from its molecular volume is 3.69 nm; which gives the value of the first excitonic absorption peak at ~ 576 nm calculated using Eq. 10. By comparison of experimental absorption spectra of extracted CdSe without TOP-functionalization synthesized using 40/50/10 microemulsion template at 30 minutes of reaction time; and

calculated oscillator strength of $(\text{CdSe})_{32}$ cluster are well matched (Fig. 11). A transition at ~ 576 nm marked with “•” is assigned to the HOMO (6.42 eV) – LUMO (4.48 eV) gap. The transition consists of two identical oscillator strengths with small separation of < 0.1 meV; assigned as dark and bright exciton. These fine structures confirm the $(\text{CdSe})_{32}$ cluster as a realistic cluster [19]. The estimated size of extracted CdSe from the UV-Vis absorption spectra is 3.69 nm well matched with the calculated size of $(\text{CdSe})_{32}$. The calculated bandgap of the cluster is 1.94 eV consistent with the experimental bandgap ~ 1.9 eV.

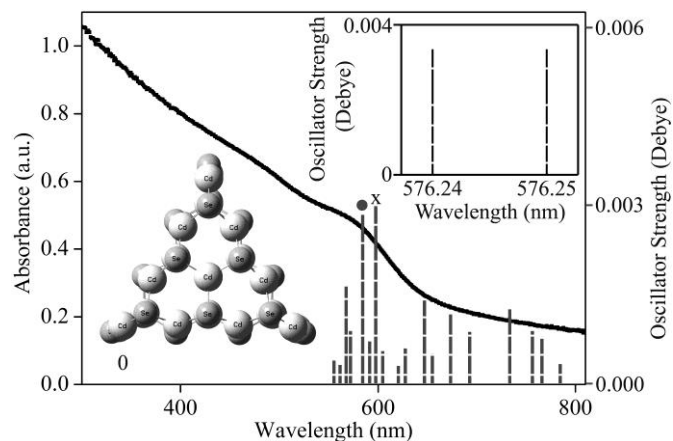


Fig. 11. (a) Electronic structure of $(\text{CdSe})_{32}$ and (b) comparison of experimental UV-Vis absorption spectra (solid line) of yielded CdSe using 40/50/20 microemulsion template at 30 minutes reaction time with calculated oscillator strength (dashed lines) of $(\text{CdSe})_{32}$. Insets are optimized geometry (bottom left) and magnified view of HOMO-LUMO transition at ~ 576.25 nm (top right). The oscillator strength marked with “•” is the HOMO–LUMO transition, whereas the other with “x” arises from surface trap

TDDFT single point energy calculation is used to map the electron density of the excited state of the cluster (Fig. 12). Electron distribution of the cluster is found mainly localized at all 32 Se atoms and only nine internal Cd atoms. No electron density is found at any external Cd atoms. CdSe nanostructures with size below the exciton Bohr radius fascinate researchers as dye replacement and fluorophore in solar cell to boost the total power conversion efficiency exceeding $\sim 60\%$ [20].

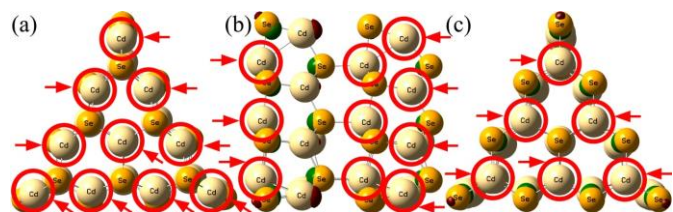


Fig. 12 (a) Non-uniform and uneven LUMO distributions at Cd and Se atom make the $(\text{CdSe})_{32}$ cluster electronically unstable as observed from (a) front, (b) side and (c) rear view. Circles show Cd atoms without LUMO density and arrows marked the external Cd atoms.

These excited state electrons, observed as green and red region (assigned for electrons with opposite spin) need to be channelled out and injected to LUMO of photoelectrode before they recombine to HOMO of CdSe. Ligand viz., mercaptoacetic acid, mercaptosuccinic acid, mercaptobenzoic

acid are used to connect CdSe and photoelectrode material; binds efficiently at external Cd atoms [21]. However, the efficiency of injection is hindered due to electron density localization at Se atoms and zero electron distribution at external Cd atoms. Small cluster with uniform and even electron distribution i.e., (CdSe)₁₃ in the range of diameter of ~1.90 nm is needed in order to fabricate a solar cell using ligand-assistance route [1]. This gives hint to reduce the size of water droplet by using low water content of template. Composition of higher content of surfactant than 40 wt % is yet to be explored in order to achieve the desired size. It is concluded in this section that determination of the most electronically stable cluster of QDs gives significant insight before fabrication of a solar cell. TOP-functionalization successfully preserves the desired cluster size; however the effect of ligand contamination needs to be studied in order to ensure efficient electron injections from fluorophore to photoelectrode material.

IV. CONCLUSIONS

CdSe QDs clusters (~4-8 nm) were successfully synthesized using microemulsion procedure at 37 °C. The QDs were characterized by low photoluminescence, size polydispersity, broad PL and quenched intensity of [103] plane in the wurtzite XRD pattern. Models of (CdSe)₃₂ QDs cluster was simulated and validated. Slight variation in size and bandgap between the QDs models and the experimentally synthesized QDs were observed due to the nature of estimation and approximation which give errors during execution of each procedure (i.e., Tauc's plot, empirical function of size – first excitonic peak, DFT calculations and peaks fitting). Thus, exact matched values are not expected; however the experimental-based and theoretical-based values are comparable.

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