Analysis of Size Dependent Quasi Particle Gap and Electron-hole Columbic Energy of CdTe/ZnS Core/shell Quantum Dots

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Abstract—*In this work the cyclic voltammetry (CV) measurement is used as a tool for electrochemical characterization of CdTe/ZnS core/shell (CS) quantum dot (QD) synthesized by an aqueous method. The band structure parameters such as; conduction and valence band edge, quasi particle gap and electron hole columbic energies are estimated on the basis of semi empirical pseudo potential method(SEPM). A comparative study of our findings with CV and spectroscopic methods is done and found well agreed with each other. It is also found that as the size of the CS grows, the electron hole columbic energy or the difference between the quasi particle gap and optical band gap increases.*

1. INTRODUCTION

The semiconductor nanoparticles having size quantization effect have been widely studied in the recent time due to their various applications in different fields of science [1 - 6]. The confinement of the charge carriers in the semiconducting nano crystalline particles is one of the important properties among the microscopic properties. Particle in a box model shows that the band gap of nanoparticles decreases with increasing the particle size, in which the nanoparticles can compared with the box and the exciton with particles, hence the photoluminescence of the nanoparticles is shifted towards red wavelength on increasing the particle size [7, 8]. These electro-optic features and band edge positions are the basis of various potential applications of the nanoparticles.

Characterization of the various properties of the Nanomaterials are important and which requires serious instrumentation and lots of sample preparation protocol. Several attempts have been made to characterize and study the electronic and spectroscopic properties semiconductor NCs on surfaces by using the scanning tunneling microscope (STM) which depend on the surroundings and in particular, on its contact with the surface [9-11]. Hence this type of experiments have been performed on perfectly clean and well-ordered surfaces under ultrahigh vacuum conditions. Cyclic

voltammetry (CV) has been successfully used by different groups for several decades in the characterization electro-active molecular species which are soluble in suitable solvents where current-potential curves are recorded at well-defined scan rates for the determination of HOMO and LUMO levels [12]. CV can be operated in the mild experimental conditions to perform the measurements as compared to the photoelectron and tunneling spectroscopy techniques [13]. Haram *et al.* shows a correlation between optical band gap and electrochemical band gap [14] obtained from CV measurement. Spectroscopic methods are also employed to determine the band structure parameters such as the band gap of the nanoparticles using the Tauc's plot [15] . The present work is motivated by the objective to study the basic electro-optic properties of the CdTe/ZnS CS QD to develop new ideas to design photovoltaic cell, electroluminescent devices and Sensors as well as new building block of QD-polymer nanocomposites for micro opto-eloctronic devices. For such devices the electron transfer between the QD ensembles, polymer and electrodes used is very crucial. To enable the electron transfer in a suitable manner through the device, the band of the QD ensemble, polymer and the electrode used should align in favorable positions. This kind of information cannot be obtained from UV/vis spectroscopy. Cyclic voltammetry is a very easy technique which is very closer to the targeted applications The present work is motivated by the objective to study the basic electro-optic properties of the CdTe/ZnS CS QD to develop new ideas to design photovoltaic cell, electroluminescent devices and Sensors as well as new building block of QD-polymer nanocomposites for micro opto-eloctronic devices. For such devices the electron transfer between the QD ensembles, polymer and electrodes used is very crucial. To enable the electron transfer in a suitable manner through the device, the band of the QD ensemble, polymer and the electrode used should align in favorable positions. This kind of information cannot be obtained from

UV/vis spectroscopy. Cyclic voltammetry is a very easy technique which is very closer to the targeted applications.

In the present paper we determine the band structure parameters such as quasi particle gap electron hole columbic energy and optical band gap of the CdTe/ZnS CS QDs having different sizes. The correlation of the electrochemical band gap and optical band gap of CS structure is explained in this piece of work. As far as knowledge goes such kind of study is not done for CS structure, the results obtained from our experiment is well matched with the theoretical semi-empirical pseudopotential method (SEPM) calculations for the quasi-particle gap [16].

2. EXPERIMENTAL SECTION

2.1 Synthesis of Quantum Dot Core/Shells

The CdTe/ZnS CS QDs were synthesized by a methods similar to that employed in [2] including an additional step for the formation of a shell. Where during the synthesis, 3mM CdCl$_2$ (Merck, 98%), 0.75mM Na$_2$TeO$_3$ (Loba Chemie, 98%) and 9mM MSA (Loba Chemie, 99%) of equal volume of solutions were mixed with a buffer containing Borax (Fischer Scientific, 98%) and Citric acid (Fischer Scientific, 99.5%). The reaction mixture is kept in a round bottom two neck flask and stirred it for about 5 minutes to mix the solutions completely and the pH of the solution is balanced at pH 8. As an appropriate amount of NaBH$_4$ (Merck, 95%) is added to the mixture, the colorless mixture turns into light yellow color indicating the initiation of nucleation of QD. This colored solution is then set for further reflux at about 100℃ for 20 minutes. Soon after 20 minutes of refluxing, 3mM 20 ml solutions of each ZnCl$_2$ (Merck, 95%) and Na$_2$S (Merck, >50%) are added to the reagent followed by the addition of 0.1M 1.8ml of MSA solution. Samples are taken at intervals of 20 min (sample a), 40 min (sample b), 60 min (sample c), 90 min (sample d) and 120 min (sample e) after the addition of the ZnS stock solution.

The absorption spectra of the as synthesized samples are recorded by using 1800 SHIMADZU UV-vis spectrophotometer and photoluminescence spectra are recorded by Cary Eclipse spectrophotometer. Cyclic voltammetry (CV) measurements were carried out on a CH instruments electrochemical workstation having three-electrode system consisting working electrode of a glassy carbon, reference electrode of Ag/Ag+ and counter of a platinum wire electrode with 0.5 M KCl in water as an electrolyte.

3. RESULTS AND DISCUSSION

The Cyclic Voltammetry (CV) measurement has been widely used to characterize QDs, they shows a size dependent voltammetry responds, which is associated with the size quantization effect. Considering the dielectric constant of QD

material be $\in_i$ and $\in_o$ the dielectric constant of the surrounding material. There are three process for the charge transfer with QD namely electron addition, creation of electron hole pairs and optical excitation [17]. E_0 and $E_1[e_1^1]$ be the energy of the QD before and after addition of one electron to the conduction level e_1, then

$$E_1[e_1^1] = E_0 + \varepsilon_{e1} = E_0 + \varepsilon_{e1}^0 + \sum {}_{e1}^{pol} \qquad (1)$$

Where, $\varepsilon_{e1}, \varepsilon_{e1}^0$ and $\sum {}_{e1}^{pol}$ are the quasi particle energy, single particle contribution which describes the quantum confinement and dielectric confinement which describes the polarization contribution that arise due to the discontinuity in the dielectric constant at the interface of the QD and the surrounding [9]. This energy corresponds to the energy of a non-interacting electron-hole pair known as quasi-particle gap.

$$\varepsilon_{gap}^{qp} = E_1[e_1] + E_{-1}[h_1] - 2E_0 \qquad (2)$$

Here, the energy of the QD with a hole in the highest occupied orbit h$_1$ is given by,

$$E_{-1}[h_1] = E_0 - \varepsilon_{h1}^0 + \sum {}_{h1}^{pol} \qquad (3)$$

From equation (1), (7) and (6) we will have the quasi-particle gap given by,

$$\varepsilon_{gap}^{qp} = (\varepsilon_{e1}^0 - \varepsilon_{h1}^0) + \sum {}_{e1}^{pol} + \sum {}_{h1}^{pol} \qquad (4)$$

Here $\varepsilon_{gap}^{qp} \equiv \varepsilon_{e1}^0 - \varepsilon_{h1}^0$ is the single particle (HOMO-LUMO) gap. For a particle of relatively large size the single particle gap is almost equal to the bulk single particle gap. The energy required in exciting an electron from the highest occupied molecular orbital h$_1$ to the lowest unoccupied molecular orbital e$_1$ is the optical gap and it is equal to the difference of quasi particle gap and total electron hole interaction.

$$\varepsilon_{gap}^{opt} = \varepsilon_{gap}^{qp} - (J_{h1,e1}^{coul} + J_{h1,e1}^{pol}) \qquad (5)$$

Here $J_{h1,e1}^{coul}$ is the direct electron-hole columbic interaction and $J_{h1,e1}^{pol}$ is the polarization contribution which strongly depends upon $\in_o$ whereas $J_{h1,e1}^{coul}$ is independent of $\in_o$. Where $J_{h1,e1} = (J_{h1,e1}^{coul} + J_{h1,e1}^{pol})$ electron hole columbic energy. The charging energies and the addition energies depend sensitively on the dielectric constant $\in_o$ of the surrounding material via the self-energies $\sum {}_i^{pol}$ and the polarization energies $J_{i,j}^{pol}$. For $\in_i >> \in_o$ in the charging energies are widely spaced in energy, and depend strongly on $\in_o$. If $\in_{i \leq} \in_o$ in

the charging energies are more closely spaced [18].The polarization contribution $J_{h1,e1}^{pol}$ of equation (9) trends to cancel the self-energy contribution $\sum_{e1}^{pol} + \sum_{h1}^{pol}$ of equation (8) to the quasi particle gap. Thus the dielectric environment weakly affect the optical gap.

The obtained UV-vis absorption and PL spectra are shown in the Fig. 1 and CV plot for the samples is shown in the Fig. 2. For CdTe/ZnS CS QD there is excitonic absorption peak at 563 nm which shows a blue shift compared to the bulk CdTe owing to the effect of quantum confinement. With the increase of the size of the CS QD absorption and emission spectra are red shifted, this results also shows the size quantization effect which shows similar type of behaviors as that of the cyclic voltammetry measurement.
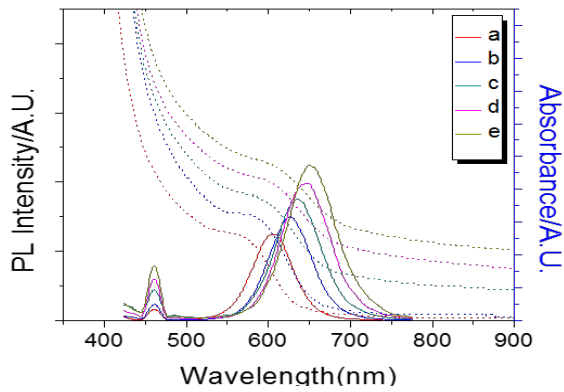

Fig. 1: Absorption (dash) and corresponding emission (solid) spectra of MSA-capped CdTe/ZnS QD. The size of the Q-dots was varied by changing the refluxing time.
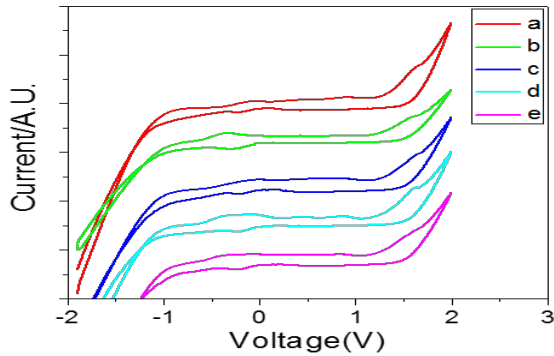

Fig. 2: An overlay of cyclic voltammograms (CVs) recorded on MSA-capped CdTe/ZnS CS Q-dots. These CVs are arranged in increasing order of size from top to bottom.

Optical band gap of the samples are calculated from Tauc's plot. In which the intercept of the resulting linear region of the $(\alpha h v)^2$ versus (hv) plot gives the band gap [15]. The calculated optical band gap of the samples reflects the quantum confinement effect. The diameter the QDs samples were

calculated according to the relationship[19],

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + 1.0064\lambda - 194.84 \quad (10)$$

where λ is the wavelength of the first excitonic absorption peak.

The electron transfer in QD mediated through conduction band edge e_1 and valence band edge h_1 is responsible for the cathodic (C_1) and anodic (A_1) peak in the CV curve[20, 21]. The difference between the two levels e_1 and h_1 is the quasi particle gap. The quasi particle gap of CdTe/ZnS CS is determined from the cyclic voltammetry measurement. The CV plot of the samples is shown in Fig 2. From the CV plots there are prominent anodic and cathodic peaks are observed for the several samples mentioned in Table 1.

Table 1: Band structure parameters obtained from the electrochemical method

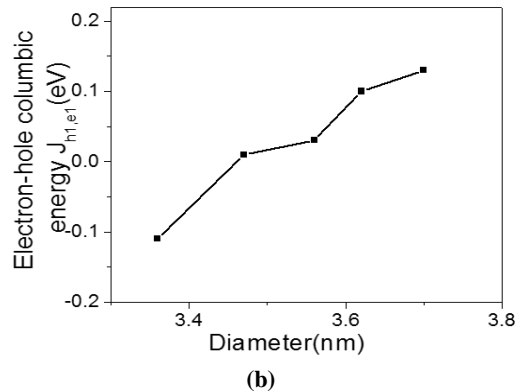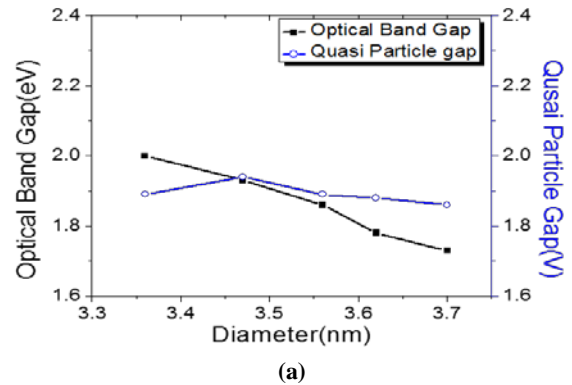| Samples	Position of A_1(V)	Position of C_1(V)	Quasi particle gap ε_{gap}^{opt} [C_1- A_1] (V)
(a)	-0.22	1.67	1.89
(b)	-0.30	1.64	1.94
(c)	-0.21	1.68	1.89
(d)	-0.24	1.64	1.88
(e)	-0.25	1.61	1.86

(a)

(b)

Fig. 3: (a) Optical bandgap and Quasi Particle gap of a size series of CdTe/ZnS CSQDs, (b) Variation of $J_{h1,e1}$ with size of CdTe/ZnS CS QDs.

Scheme diagram for the addition of the electron to a neutral dots, the creation of interacting and non-interacting electron hole paire is shown in the Fig 4. The peak-to-peak separation between C_1 and A_1 gives the electrochemical band gap [21] which is well matched with the band gap calculated from optical method. Comparison of the band structure parameters of the CdTe/ZnS core/shell QD obtained by both optical and electrochemical methods are shown in the Fig 3(a). From the Fig 3(b). It is clear that as the size of the CS structures increases, the difference between the optical band gap and the quasi particle gap, *i.e.* the electron hole coulomb energy increases.
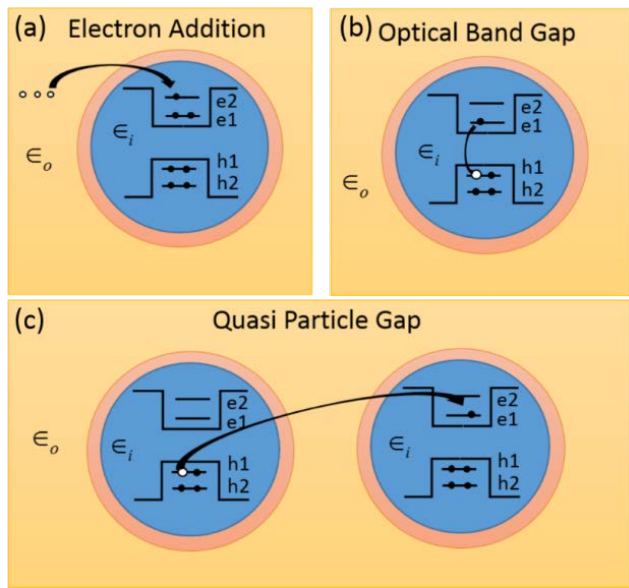

Fig. 4: (a) Addition of electrons into neutral Q-dot, (b) Creation of interacting electron-hole pairs due to optical excitation, resulting in an optical band gap, (c) Creation of non-interacting electron-hole pairs with an electron to one Q-dot and the simultaneous creation of hole in other QD resulting in a quasi-particle gap.

4. CONCLUSION

The electron transfer in QD takes place through the conduction band edge e_1 and valence band edge h_1, alignment of these levels at appropriate position is very important for the practical application of QD in the field of electronics and opto-electronics, these levels are responsible for the cathodic (C_1) and anodic (A_1) peak in the CV analysis. Here the quasi particle gap of CdTe/ZnS CS is determined from the cyclic voltammetry measurement and corresponding optical band gap are also calculated from the optical methods. Result obtained from both the two methods are in good agreement with the theoretical models. From the obtained results it is found that the charging energies and the addition energies depend sensitively on the dielectric constant ϵ_o of the surrounding material via the self-energies $\sum_i^{pol}$ and the

polarization energies $J_{i,j}^{pol}$. Thus the dielectric environment weakly affect the optical gap as a result the variation in the optical band gap and the quasi particle gap is obtained. As the size of the CS structures increases the difference between the optical band gap and the quasi particle gap increases. This may be due to the change in relative change in dielectric constant inside ϵ_i and outside of the CS structure ϵ_0 or due to the effective dielectric constant (ϵ_o).The quasi particle gap depends strongly upon ϵ_o because the electron transfer occurs through the surrounding medium for the creation of a pair of non-interacting electron hole pair whereas for an interacting electron hole pair electron transfer occurs in the QD itself.

5. ACKNOWLEDGEMENTS

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