

Material Properties – Short Circuit Current Correlations in Quantum Dot Solar Cell

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Abstract— Quantum dots (QDs) semiconductor of size below its exciton Bohr radius shows fascinating effect of quantum confinement i.e., multiple exciton generation (MEG) upon absorption of single photon with sufficient energy. However despite of the remarkable properties, application of QDs for replacement of dye molecules as light absorber in quantum dot solar cell (QDSC) is still doubtful due to inferior power conversion efficiency (~8.6%) in comparison with the dye-sensitized solar cell (DSSC) (~13%). In order to study the drawback that arises from the light absorber, three QDs were employed for QDSC fabrication viz., CdSe, CdTe and CuInS₂; layered onto TiO₂ photoelectrode by direct attachment, ligand-functionalization and paste-layering. Additionally, Z907-based DSSC was fabricated in order to strengthen the conclusion on the correlation between absorption cross-section of fluorophore and the short circuit current of cell. Five efficiency-affecting parameters are studied i.e., (i) ligand usage, (ii) QDs size distribution, (iii) redox potential of electrolyte, (iv) electronic stability of QDs and (v) absorption cross-section by electrochemical measurements, absorption spectroscopy, photoluminescence spectroscopy and quantum chemical ab-initio calculations. Significant setbacks were observed, i.e., (i) inefficient electron injection through ligand, (ii) unnecessary self-injection from small to big cluster of QDs, (iii) inefficient electron replenishment at HOMO_{QDs} by electrolyte, (iv) non-uniform and uneven excited-state electron distribution of QDs cluster that leads to inefficient electron injection from LUMO_{QDs} to LUMO_{photoelectrode} and (v) low absorption cross-section than that of Z907 dye.

Keywords—quantum dots solar cell, density functional theory, photoelectrochemical, absorption, photoluminescence spectroscopy

I. INTRODUCTION

Semiconducting materials exhibit interesting change of properties due to one, two or three dimensional confinement of electron movement; typically observed in nano-sheet, nano-rod and QDs respectively [1]. A significant change is the thicker color of the quantum confined material than that of the bulk; corresponds to a widen bandgap. This is due to expansion of continuous valence and conduction band to discretely quantized energy level of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) respectively [2]. Upon illumination of incident light with energy higher than that of the bandgap, electron in the HOMO absorbs the radiation and excited to the

higher level of energy state in LUMO; leaving positively charged hole in HOMO thus formed an exciton. The excited electron with excess energy later cools down e.g. from LUMO+2 and falls to lower energy states of LUMO+1 by photon emission with wavelength comparable to the energy level difference ($\Delta\text{LUMO}+2 - \text{LUMO}+1$) [3]. If the wavelength is the same or higher than that of the bandgap ($\Delta\text{HOMO} - \text{LUMO}$), another electron will be excited; makes at least the total number of exciton formed is two upon absorption of a single incident photon. However, in bulk semiconductor the excited electron only cools down to conduction band via phonon emissions. Excess energy from the electron transfers into the crystal lattice by vibration, rotation and translation [4]; which makes the total exciton formed is one upon absorption of one incident photon. From Shockley – Queisser thermodynamic limit calculations, the maximum theoretical efficiency of a solar cell fabricated using bulk semiconducting material as fluorophore is limited to ca. 32%. Whereas a solar cell employing quantum-confined structure semiconductor is hypothesized to boost the power conversion efficiency exceeding ca. 60% due to multi exciton generation upon absorption of single photon [5-6].

However, the highest power conversion efficiency achieved by QDSC ($\eta = 8.6\%$) [7] is still lower than that of the DSSC ($\eta = 13\%$) [8-9]. Based on our previous work, the absorption cross-section (α_A) of fluorophore shows substantial correlation with the power conversion efficiency of the fabricated cell; such that a material with high absorption cross-section absorbs large fraction of solar light [10]. By comparison of CdSe QDs with N3 dye molecule, a CdSe cluster with diameter ~4 nm is forecasted to have a larger absorption cross-section than that of the N3 dye molecule; fabricated solar cell is speculated to have higher efficiency than that of N3 dye-based solar cell. However, another obstacle arises in this particular size of CdSe QDs is the non-uniform and uneven excited state electron distribution; only the uniform and even distribution of (CdSe)₁₃ with size ca. 1.90 nm ensures efficient excited state electron injection to photoelectrode. In this work, we include CdTe and CuInS₂ QDs for comparison with Z907 dye molecule in terms of (i) absorption cross-section, (ii) HOMO–LUMO energy levels,

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(iii) excited state electron distribution and (iv) short circuit current of fabricated solar cell.

Ligand–functionalization of QDs has three purposes i.e., (i) QDs stabilization, (ii) binds QDs cluster to photoelectrode and (iii) electron channelling medium. TOP–functionalization of freshly synthesized CdSe cluster in nano-emulsion template preserves the size significantly over time [10]. Using quantum chemical calculations under framework of DFT at B3LYP/lanl2dz level, –SH bearing ligand i.e., mercaptoacetic acid (MAA), mercaptobenzoic acid (MBA), mercaptopropionic acid (MPA) and mercaptosuccinic acid (MSA) were estimated successfully chemisorbed on the external Cd atom. However, by comparison of the energy levels of the ligands with CdSe clusters, only MBA energy levels (HOMO and LUMO) match the energy levels of CdSe cluster; i.e., $LUMO_{MBA} < LUMO_{CdSe}$; whereas the LUMO energy level of other stated ligands are higher than that of $LUMO_{CdSe}$. LUMO energy level comparison is needed in order to predict the possibility of efficient electron injection from QDs to photo electrode; which is ideally $LUMO_{QDs} > LUMO_{ligand}$.

Five parameters have been proven to have significant effect on the efficiency of the cell i.e., (i) ligand usage, (ii) QDs size distribution, (iii) redox potential of electrolyte, (iv) emitting state of QDs and (v) absorption cross section [10]. In this work we hypothesize the same effect to happen in our fabricated CdTe and CuInS₂–based QDSC, and Z907–based DSSC; as a one step closer to derive the generalized equation of efficiency of a sensitized solar cell that writes as:

$$\eta = f(\alpha_A, \Phi_{IN}, \sigma_{TR}, \delta_{DR}) \quad (1)$$

where α_A is the absorption cross-section of the sensitizer, Φ_{IN} is the electron injection efficiency from the sensitizer to photoelectrode, σ_{TR} is the electron transport efficiency through the photoelectrode and δ_{DR} is the efficiency of electron regeneration in $HOMO_{sensitizer}$ by electrolyte.

II. MATERIALS AND METHOD

All solar cells employed in this study were fabricated using the same technique and materials. ~12 μ m photoelectrode layer was made by commercial TiO₂ paste (Solaronix Tinanoxide) using thin-layer stencil on transparent conductive glass (Solaronix TCO) and annealed at 450 °C for 30 minutes with ramp of 1.5 °C/min. The glasses were cleaned by immersion in surfactant solution and followed by sonication for 30 minutes. This step was repeated using ethanol in the second cycle of sonication and dried in room temperature before fabrication. Bare CuInS₂ and CdSe QDs without ligand–functionalization were synthesized and published elsewhere. Additionally, octadecylamine–stabilized QDs (CdTe 620, CdSe 520 and CdSe 620) were supplied by NN–Labs and Z907 dye from Solaronix. QDs and dye were attached onto TiO₂ using four methods which elaborated as the following [11]. (i) QDs were directly attached onto the surface of freshly annealed layer of TiO₂–layered conducting glass by

immersion in 0.1 M QDs solution in toluene for 24 hours. (ii) Ligand–functionalization of TiO₂ layer was made by immersion of TiO₂–layered conducting glass in 0.1 M ligand solution in acetonitrile for five hours; followed by rinsing and immersion in 0.1 M QDs solution overnight. (iii) QDs pastes were made by mixture of 100 μ L of 0.1 M QDs solution in toluene, 0.157 g ethyl cellulose and 1.1729 g terpineol; layered on the top of TiO₂ using thin-layer stencil and annealed at 200 °C for 30 minutes with ramp of 1.5 °C/min. (iv) Dye loading procedure was done by immersion of TiO₂–layered conducting glass in Z907 dye solution in ethanol overnight. A sealing film with thickness of ~6 μ m (Solaronix Meltonix) was used to cover the non-sensitized layer of conducting glass from exposure to electrolyte. Platinum catalyst layer (Solaronix Platisol) was made on a blank conducting glass by thin-layer stencil and annealed at 380 °C for 30 minutes with ramp of 1.5 °C/min. Two types of electrolyte were used i.e., Ionic BMII and Iodolyte AN-50 (Solaronix) in order to observe the effect of redox potential. The electrolyte, sensitized area and thickness of TiO₂ layer, QDs layer and sealing film were not optimized for the best solar cell efficiency. Absorption and emission spectra of the fluorophore suspensions were recorded using Shimadzu UV-2600 spectrophotometer and Edinburgh PL2600 respectively. The HOMO and LUMO energy level of CuInS₂ QDs and the short circuit current of fabricated cells were estimated using potentiostat-galvanostat (PGSTAT 30, Autolab). Ab-initio density functional theory (DFT) with additional time dependent DFT (TD–DFT) were employed at B3LYP/lanl2dz level to calculate the lowest energy structure and simulate the excited state electron distribution of the QDs, Z907 dye and ligand molecules.

III. RESULTS AND DISCUSSIONS

A. Effect of Electronic Stability of QDs

Two different sizes of CdSe QDs were chosen i.e., CdSe 520 and CdSe 620 (NN–Labs) with average diameter of ~2.36 and 5.49 nm respectively; utilized as fluorophore. The diameter of CdSe QDs was calculated based on the first excitonic peak position (ca. 502 and 618 nm) using the following equation [12]

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

where D is diameter of CdSe and λ is the first excitonic peak position. Both types of CdSe were estimated smaller than the exciton Bohr radius of CdSe; estimated 4.93 nm ($\varnothing = 9.86$ nm) using equation

$$a_{exc} = 4\pi\epsilon_0\epsilon_r\hbar^2 \left(\frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \frac{1}{q^2} \quad (3)$$

where ϵ_0 is the permittivity of free space (8.85×10^{12} F/m), ϵ_r is the dielectric constant of CdSe (~9.4), $\hbar$ is the Planck

constant (1.054×10^{-34} J.s), m_e^* is the effective mass of electron ($0.13 m_0$ kg) in CdSe, m_h^* is the effective mass of hole ($0.45 m_0$ kg) in CdSe, m_0 is the electron rest mass ($\sim 9.1 \times 10^{-31}$ kg) and q is the charge of an electron (1.602×10^{-31} C).

Three QDSCs were fabricated with cell properties as summarized in Table 1. Iodolyte AN-50 (Solaronix, I^-/I_3^- redox couple) was used as electrolyte to regenerate electron in $HOMO_{QDs}$. Low power conversion efficiency is expected due to unoptimized fabrication.

Table 1. Properties of fluorophore and the fabricated QDSC

Type & QDs' size	Fabricated cell properties			
	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	η (%)
CdSe 520 (2.36 nm)	0.3713	0.0109	33.1246	0.001334
CdSe 620 (5.49 nm)	0.3639	0.0062	37.0112	0.000832
CdTe 620 (3.63 nm)	0.3932	0.0105	20.3518	0.000838

In our previous work on DFT, the most electronically stable magic size CdSe is ca. 1.90 nm of diameter [13-15]; belongs to $(CdSe)_{13}$ cluster (Fig. 1.a). Extended growth of the cluster makes the excited state electron distribution becomes non-uniform and uneven (Fig. 1.b). Localization of excited state electron at internal atoms are observed; inhibited from being channelled efficiently to the photoelectrode [10]. By diameter comparison, $(CdSe)_{13}$ (1.90 nm) < CdSe 520 (2.36 nm) < CdSe 620 (5.49 nm) < exciton Bohr radius (9.86 nm); it is hypothesized such that both of the utilized fluorophores (CdSe 520 and CdSe 620) have non-uniform and uneven excited state electron distribution. This is proved by inferior short circuit current of QDSC fabricated using CdSe 620 QDs in comparison with CdSe 520 as fluorophore; leads to lower power conversion efficiency ($\eta = 0.000832\%$) than that of CdSe 520-based QDSC ($\eta = 0.001334\%$). It is clearly observed that as the QDs cluster grows bigger than the magic size cluster, i.e., magic size < x < exciton Bohr radius; the setback effect of non-uniformity and localization of LUMO becomes dominant in the fabricated QDSC. The same effect is observed in CdTe-based QDSC; fabricated using CdTe 620 (Solaronix) as fluorophore; with diameter ~ 3.63 nm < exciton Bohr radius 7.34 nm ($\phi = 14.68$ nm) [12]. A realistic cluster model is optimized at B3LYP/lanl2dz level of DFT. The geometry was identified as real cluster model using procedure reported before [10]. By comparison, experimental absorption spectra of CdTe 620 and calculated oscillator strength of $(CdTe)_{16}$ are well matched (Fig. 2). Transition marked with “•” is assigned to the HOMO (-6.124 eV) – LUMO (-3.931 eV) gap; consists of two identical oscillator strengths with small separation of 0.0002 eV i.e., dark and bright exciton. The calculated bandgap of the cluster is 2.193 eV consistent with the experimental bandgap ~ 2.2 eV. Additional TDDFT clearly mapped the excited state electron distribution reveals localization of LUMO distribution dominantly at Te atoms

with one surface Cd and Te atom without electron density (Fig. 3); thus categorized as electronically unstable cluster. This electronic instability are the cause of poor electron injection from QDs to photoelectrode; thus low short circuit current (~ 0.0105 mA/cm²) and efficiency ($\sim 0.000838\%$) of the fabricated cell is observed upon illumination of light (Table 1).

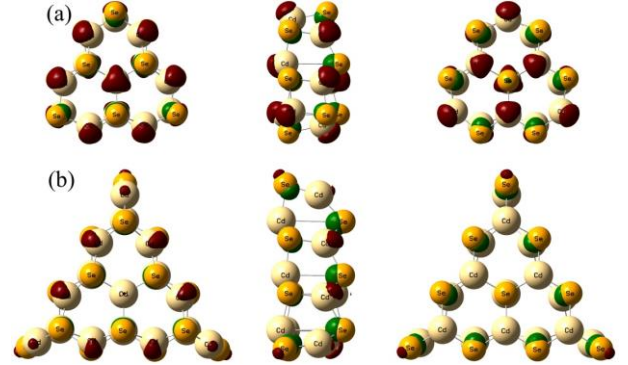


Fig. 1. (a) Uniform and even LUMO distribution of $(CdSe)_{13}$ and (b) non-uniform and uneven LUMO distribution of $(CdSe)_{16}$ cluster; observed from front, side and rear view respectively [10]

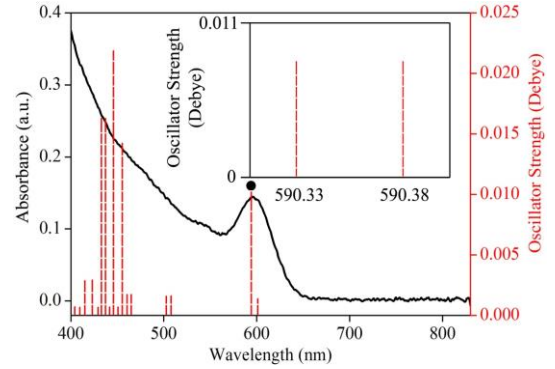


Fig. 2. Comparison of experimental UV-Vis absorption spectra (solid line) of CdTe 620 with calculated oscillator strength (dashed lines) of $(CdTe)_{16}$. Inset is a magnified view of HOMO-LUMO transition at ~ 590.38 nm (top right). The oscillator strength marked with “•” is the HOMO-LUMO transition.

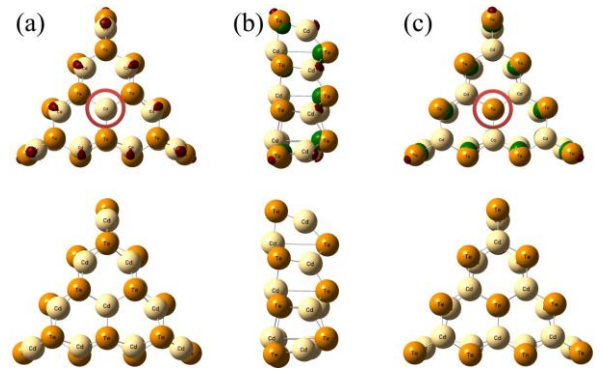


Fig. 3. Optimized structure (bottom) and excited state electron distributions (top) of $(CdTe)_{16}$ cluster as observed from (a) front, (b) side and (c) rear view. Circles show external Cd and Te atoms without LUMO density

B. Effect of Absorption Cross-Section of Light Absorber

Four cells were fabricated using Z907 dye, CdSe 520, CdSe 620 and CdTe 620 as fluorophore. The absorption cross-section of each fluorophore and properties of fabricated cells are presented in inset of Fig. 4.

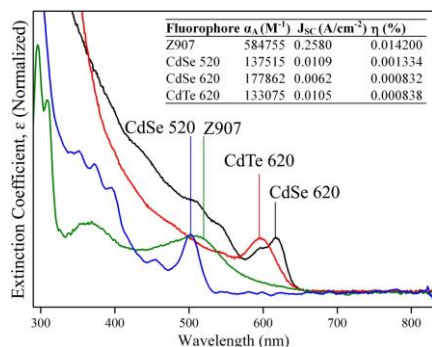


Fig. 4. Experimental absorption spectra of CdSe 520, CdSe 620, CdTe 620 and Z907 dye. Inset is the properties of the fabricated cells

Two significant observations were noted from the comparison of the cells. (i) By comparison in between Z907, CdSe 620 and CdTe 620-based solar cells, a clear correlation of the absorption cross-section of each fluorophore and the short circuit current is observed. Such that Z907 dye with the highest α_A possess the largest absorption wavelength dispersion; generating more exciton and increasing J_{SC} and η significantly by 20 folds than the other fluorophores. Fluorophores with lower absorption cross-section generate lesser number of exciton; produce lower J_{SC} and η than that of Z907 dye-based cell. (ii) By comparison in between two fabricated cells using same type of fluorophore with different size, i.e., CdSe 520 and CdSe 620; it is found that CdSe 620 holds lower J_{SC} and η even though it has higher α_A than that of CdSe 520. This is another prove of our hypothesis in previous section that CdSe 620 experience more setback effect than CdSe 520 due to non-uniform and uneven excited state electron distribution. This also proves that the ability to generate more exciton is meaningless if electron injection mechanism is inhibited by the structure of fluorophore itself. It is concluded that electronic stability more dominant than the absorption cross-section in affecting the short circuit current. The discussion of the excited state electronic structure of Z907 dye is included in the next section.

C. Effect of Functional Group and the Distance to the Nearest LUMO (in Ligand and Z907)

CuInS₂ QDs with estimated average size of 5.24 nm were used in this section [16]. Three CuInS₂-based QDSCs were fabricated using ligand-functionalization route; utilizing MAA, MPA and MSA. Energy level alignment i.e., HOMO and LUMO of fluorophores, ligand molecules and photoelectrode material were estimated using combination of cyclic voltammetry (CV) experiment and ab-initio DFT [17]. Cyclic voltammogram was recorded for CuInS₂ QDs solution in toluene (1 mg/ml) at scan rate of 50 mVs⁻¹ in a three-electrode system (Fig. 5). Glassy carbon (3 mm diameter), Ag wire and Pt loop were utilized as working electrode, reference

electrode and counter electrode respectively. The LUMO energy level of CuInS₂ 0.8135 V vs Ag/AgCl (-3.4296 eV vs vacuum) was determined successfully using CV technique. The HOMO energy level -1.0323 V vs Ag/AgCl (-5.2753 eV vs vacuum) was estimated based on a comparison between the LUMO and bandgap value (estimated using Tauc's plot which presented in Fig. 6) due to indistinctly observable cathodic peak.

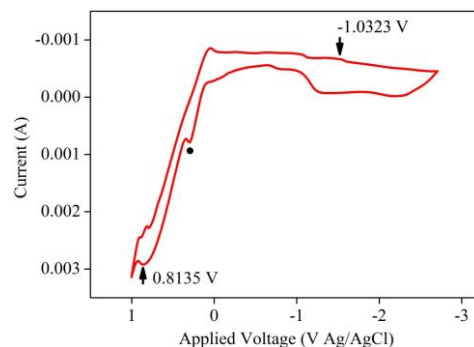


Fig. 5. Cyclic voltammogram of CuInS₂ QDs reveals the anodic peak corresponds to LUMO energy level at 0.8135 V vs Ag/AgCl (-3.4296 eV vs vacuum). HOMO energy level, -1.0323 V vs Ag/AgCl (-5.2753 eV vs vacuum) is estimated by comparison of the LUMO with the bandgap value; which estimated using Tauc's plot due to indistinctly observable cathodic peak. The anodic peak marked with "•" is corresponds to the low energy deep trap states in the QDs

The estimated HOMO and LUMO energy levels are comparable with experimental work by Zhong et. al [18]. Additional anodic peak is observed at 0.2690 V vs Ag/AgCl (-3.9740 eV vs vacuum); corresponds to a low energy deep trap states in the QDs. Fig. 7 shows the powder absorption and PL spectra of CuInS₂ QDs; a broad deep trap emission at 732 nm is observed [19].

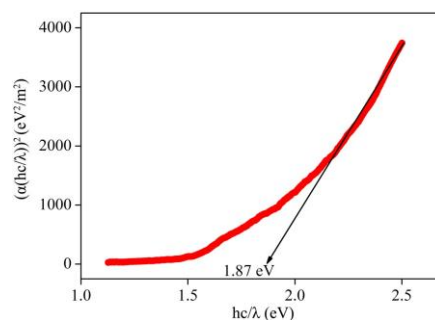


Fig. 6. Bandgap of CuInS₂ QDs (1.87 eV) is estimated from the absorption spectra using Tauc's plot

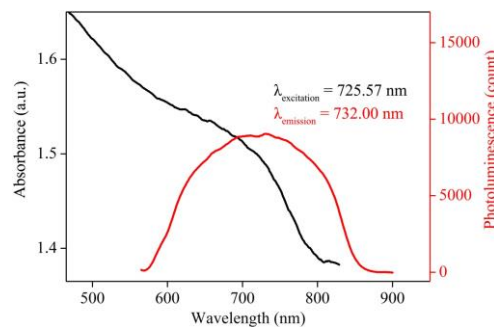


Fig. 7. Powder absorption and emission spectra of CuInS₂ QDs shows the first excitonic absorption peak at 725.57 nm and a broad emission from a low energy deep trap states at 732 nm

The HOMO and LUMO energy levels of ligand viz., MAA, MPA and MSA are calculated using ab-initio DFT framework at B3LYP/lan12dz level with additional TDDFT that mapped the excited state electron distribution efficiently; presented in our previous work [10]. The energy levels of the ligands and ligands are compared as in Fig. 8; the LUMO energy levels of the ligands are found lower than that of the QDs. Efficient electron channelling from QDs to ligand are expected from such LUMO energy level alignment i.e., $LUMO_{QDs} > LUMO_{ligand}$.

Table 2. HOMO, LUMO energy levels and bandgap of MAA, MPA and MBA

Ligand	HOMO (eV) ^a	LUMO (eV) ^b	Bandgap (eV) ^c
MAA	-7.11	-3.61	3.50
MPA	-7.14	-3.63	3.51
MSA	-7.24	-3.90	3.34

^{a, b, & c} The calculated energy levels are with respect to vacuum

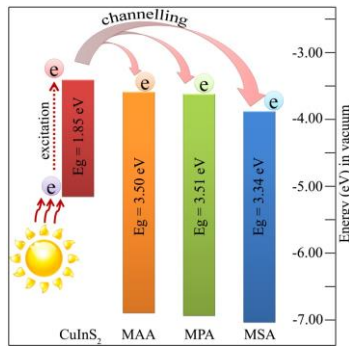


Fig. 8. Energy level comparison in between CuInS₂ QDs, MAA, MPA and MSA ligand

Nonetheless, the later process viz., electron injection from QDs–ligand conjugate to photoelectrode is dependable on two factors i.e., (i) number of adsorption site and (ii) the distance from the nearest LUMO to anchoring hydrogen at –COOH functional group of the ligand. Table 3 shows a comparison between the ligands and Z907 dye; in terms of the mentioned factors and the short circuit current of fabricated cells. The observed J_{SC} of the cells is recorded such that Z907-based > MSA-functionalized > MAA-functionalized > MPA-functionalized. By comparison of adsorption site, Z907 holds the most number (4 sites) and followed by MSA (3 sites). It is believed that the more the adsorption site the faster electron injection would be; generates higher J_{SC} . Both MAA and MPA have two adsorption sites; present lower J_{SC} than that of Z907-based and MSA-functionalized cells.

Table 3. Number of adsorption site and the distance of the nearest LUMO to the anchoring hydrogen at –COOH functional group of ligand or dye

Structure	Adsorption site	LUMO to H _{anchor} (Å)	J_{SC} (mA/cm ²)
MAA	2	1.89	0.0755
MPA	2	2.71	0.0561
MSA	3	0.98	0.0846

Z907	4	3.81	0.2580
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Further comparison of the fabricated cells out of these two ligands in terms of the distance from the nearest LUMO to the anchoring hydrogen of –COOH functional group is made. It is observed that the closer the LUMO to the anchoring hydrogen, the faster the electron injection and higher J_{SC} is attainable. Fig. 9 shows the adsorption sites and measurements of the nearest LUMO to the anchoring hydrogen at –COOH and –SH functional group of each ligand and Z907 dye molecule. It is clearly shown that the excited state electron distribution in Z907 dye is mainly localized at the functional groups; readily to be injected to the photoelectrode with suitable energy level, typically $LUMO_{dye} > LUMO_{photoelectrode}$.

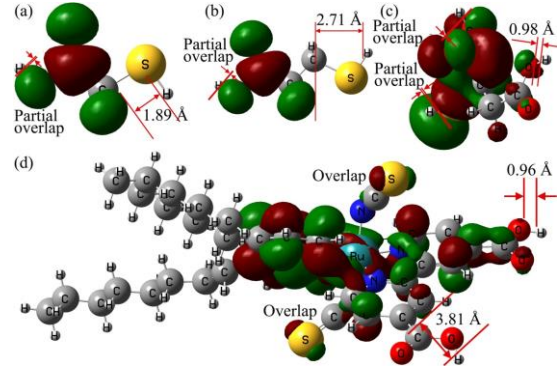


Fig. 9. Measurements of the nearest LUMO to the anchoring hydrogen at –COOH and –SH of (a) MAA, (b) MPA, (c) MSA and (d) Z907 dye molecule

D. Slowed Electron Injection due to Multi-Size QDs

In order to study the multi-size QDs effect to the J_{SC} , two cells were fabricated using CdSe 520 (average diameter 2.36 nm) and mixture of CdSe 620 (average diameter 5.49 nm) with the earlier QDs. Fig. 10 a-b shows absorption spectra of CdSe 520 and the mixed QDs; represented by peaks at 515 nm (Ø 2.36 nm) and 619 nm (Ø 5.49 nm) of wavelength. First assumption is that the mixed QDs possess wider α_A and higher J_{SC} of fabricated cell than that of the CdSe 520-based is expected. However, a detailed energy level of device structure unveils the drawback of mixed QDs sensitization; the unnecessary electron injection from small to big cluster of QDs. Fig. 10.c shows the weakness of multi-size of fluorophore sensitization; a possible injection from small to big QDs with energy level alignment of $LUMO_{small\ QDs} > LUMO_{big\ QDs}$ is hypothesized [20]. It is noted from previous section that the electron injection from the big QDs to the photoelectrode is inferior in comparison with the injection from the small QDs. Excited electron takes longer time to reach the photoelectrode, thus lower the J_{SC} (0.0095 mA/cm²) and the efficiency of the cell (0.0009%); in comparison with the CdSe 520-based cell ($J_{SC} = 0.0109$ mA/cm² and $\eta = 0.0013\%$). This proved that the unnecessary injection leads to inefficient and slowed electron injection from small QDs to the photoelectrode.

E. Redox Potential Mismatches

Effect of redox potential of electrolyte explains the reason behind low reading of J_{SC} and η of all the fabricated cells. Two CdSe 620-based QDSCs were fabricated using paste method which explained earlier; utilizing two different electrolytes i.e., (i) IonLic BMII and (ii) Iodolyte AN-50. Redox potential of IonLic BMII is estimated using ab-initio DFT i.e., $E^0 = -2.426$ eV with respect to vacuum; the main cause of low J_{SC} (0.0128 mA/cm^2) and η (0.0008%) of fabricated cell due to energy level misalignment i.e., $E^0 > \text{LUMO}_{\text{TiO}_2}$ preventing electron regeneration of QDs [10]. The QDSC with Iodolyte AN-50 electrolyte presented slightly higher J_{SC} (0.0356 mA/cm^2) and η (0.0047%) than that of the previous cell; a better redox potential is speculated i.e., $\text{LUMO}_{\text{QDs}} > E^0 > \text{HOMO}_{\text{QDs}}$ could possibly assist the QDs regeneration process.

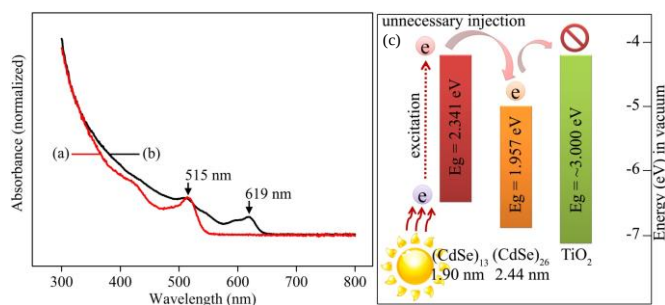


Fig. 10. Absorption spectra of (a) CdSe 520 represented by a peak at 515 nm of wavelength, (b) mixture of CdSe 520 and CdSe represented by two peaks at 515 nm and 619 nm respectively. (c) The HOMO and LUMO energy levels of $(\text{CdSe})_{26}$, $(\text{CdSe})_{32}$ clusters and TiO_2 (photoelectrode)

IV. CONCLUSIONS

In conclusion, a comparative study between CdSe, CdTe and CuInS_2 -based QDSCs and Z907-based DSSC employing ab-initio DFT calculation and experimental work has been undertaken to strengthen our answers to the reason of inferior photovoltaic parameters of QDSC compared to the DSSC. Based on the generalized equation that correlates the materials (viz., fluorophore, ligand, photoelectrode and electrolyte) properties and photoconversion efficiency, we show that unexceptional short circuit current generated in the QDSC arises from three factors which summarized as the following. (i) Inferior absorption cross-section (α_A) of the QDs with size $\ll$ exciton Bohr radius than that of the Z907-based DSSC. (ii) Inefficient electron injection (Φ_{IN}) due to electronic instability of big QDs cluster compared to the Z907 dye molecule. By another comparison between two CdSe-based QDSC, the electronic instability is dominantly affecting the photovoltaic performance; made the α_A factor becomes mediocre. (iii) Poor electron regeneration (δ_{DR}) at HOMO_{QDs} by electrolyte due to energy level mismatches; optimization of electrolyte is needed based on energy level alignment. Two additional insights gained from this work are the setback effect of multi-size QDs as fluorophore and ligand usage. First, multi-size fluorophore usage leads to unnecessary and slowed electron injection from small to big QDs cluster. Second, efficiency of electron injection in Z907-based DSSC and

ligand-functionalized QDSC with $\text{LUMO}_{\text{QDs}} > \text{LUMO}_{\text{ligand}}$, is affected by the number of absorption site and the distance from the nearest LUMO to the anchoring hydrogen at $-\text{COOH}$ functional group.

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