The Links toward Highly Efficient Quantum Dot Solar Cells

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Abstract

Quantum dots (QDs) semiconductors have been used since 1990 [Vogel, 1990] in solar cells due to the ability to generate multi-exciton upon absorption of a single photon. A typical device structure of a quantum dot solar cell (QDSC) consists of metal oxide/ligand/QDs/electrolyte is used similar to that of dye solar cells (DSCs); nonetheless the efficiency of QDSCs are still lower than DSCs. We investigated the fundamental differences in the optical properties of QDs and dyes using density functional theory (DFT) calculations to understand the overall effect to the final solar cell performance. Quantum chemical calculations under the framework of DFT were employed to study the difference in ground and excited state properties of dyes and quantum dots. The $RuL_2(NCS)_2.2H_2O$; L = 2,2'–bipyridyl-4,4'-dicarboxylic acid (N3) dye and CdSe QDs are archetypical materials in the sensitized solar cells; therefore, these two materials were chosen as typical examples in this study. DFT calculations were performed with the use of Becke's three parameter hybrid method [Becke, 1993] with the Lee, Yang and Parr (B3LYP) gradient corrected correlation functional [Lee et al, 1988] using the Gaussian 09 W program packages [Frisch et al, 2009]; calculates geometries and binding energies very well at low computational cost. Geometry optimizations were carried out using the standard double-ζ quality lanl2dz basis sets [Hay and Wadt, 1985] followed by harmonic frequency calculations and simulating their IR spectra. Discrete spectra of excitation energies and corresponding oscillator strengths were obtained by the time-dependent DFT (TDDFT) method including n energy singlet transitions.[Scalmani et al, 2006] Molecular volumes of clusters were obtained from the Gaussian output file of the optimized geometry. The CdSe clusters were modeled with and without bifunctional ligands such as mercaptoacetic acid (MAA),[Mora-Seró et al, 2008] mercaptobenzoic acid (MBA),[Lee et al, 2007] mercaptopropanoic acid (MPA) [Leschkies et al, 2007] and mercaptosuccinic acid (MSA) which are conventionally used to conjugate the quantum dots to the MOS. The B3LYP/lanl2dz level of DFT is shown to be ideal to study ligand-QDs interactions and provide accurate description of binding energy, surface states, trap states and surface stabilization. [Fischer et al, 2012] Additional TDDFT single point energy calculation is used to map the electron density of the ground and excited states of the fluorophores. Figure 1 summarizes the results of the calculations. Four CdSe QDs, viz., $(CdSe)_6$, $(CdSe)_{13}$, $(CdSe)_{16}$ and $(CdSe)_{26}$, where the subscripts represents the number of molecules in each geometry, were considered in this study. Among them, the first three clusters were experimentally identified before.[Jose et al, 2006] The fourth cluster, i.e., $(CdSe)_{26}$, was generated by parallel stacking of two $(CdSe)_{13}$ structures and optimized its bond lengths, bond angles and dihedral angles for a minimum energy structure. Five links have been identified in the study provide numerous insights to build high efficiency QDSCs. They are (i) fundamental differences in the emitting states of the QDs in the strong and weak confinement regime were observed, which successfully explained the performance differences. (ii) The crucial role of ligand does not lead to a QD enable widening of the absorption of the photo-electrode. (iii) Wide QDs size distribution further hinders efficient electron injections, (iv) wide absorption cross-section of QDs favours photon harvesting as in Figure 2. (v) Role of redox potential of electrolyte in QD reduction process.[Saifful Kamaluddin Muzakir et al, 2013]
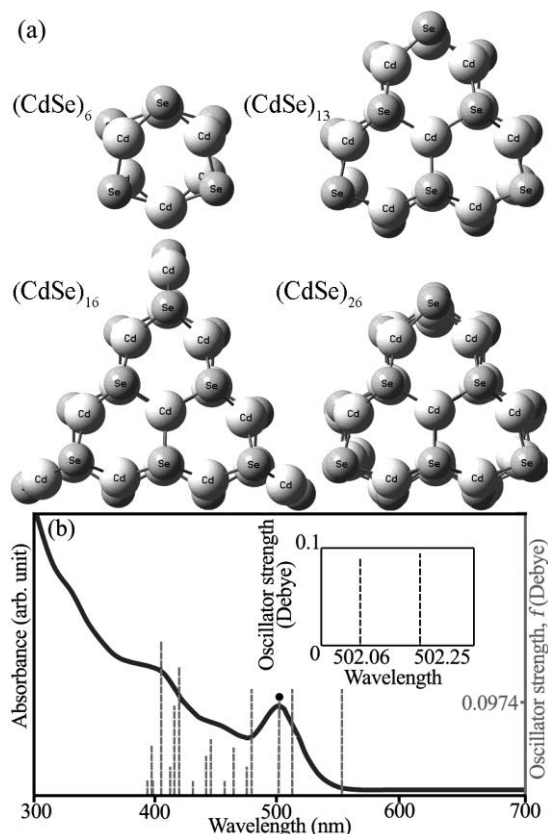
Figure 1: (a) Optimized geometries of CdSe clusters and (b) comparison of calculated transition oscillator strength (dashed lines) with experimental UV-Vis absorption spectra (solid line) of $(CdSe)_{26}$ cluster.
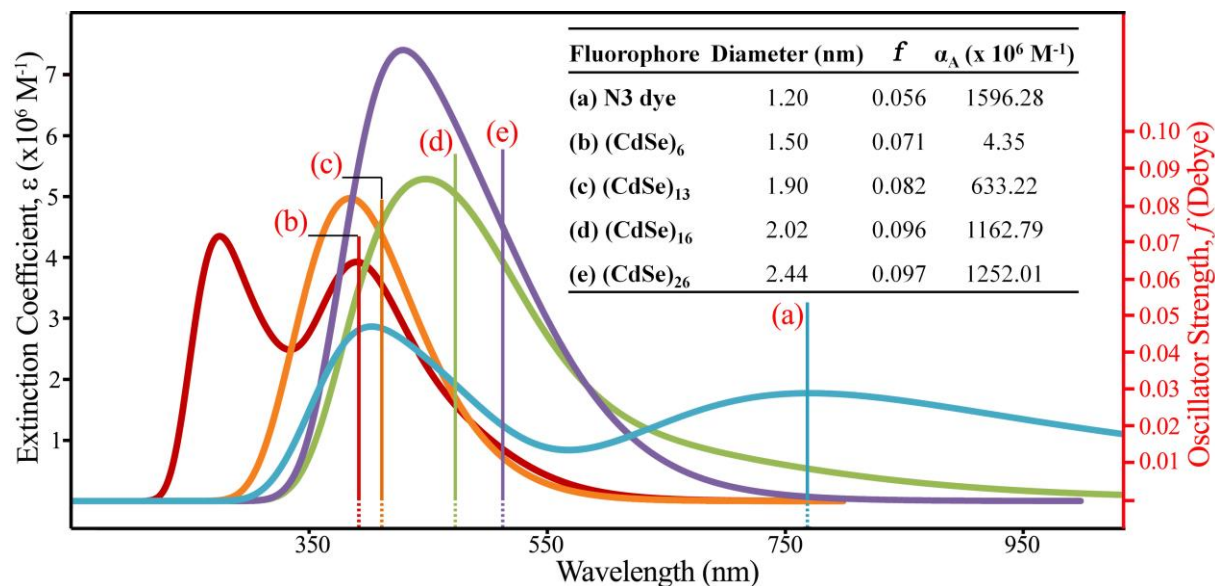

Fluorophore	Diameter (nm)	f	α_A (x 10^6 M^{-1})
(a) N3 dye	1.20	0.056	1596.28
(b) $(CdSe)_6$	1.50	0.071	4.35
(c) $(CdSe)_{13}$	1.90	0.082	633.22
(d) $(CdSe)_{16}$	2.02	0.096	1162.79
(e) $(CdSe)_{26}$	2.44	0.097	1252.01

Figure 2: Simulated absorption spectra of $(CdSe)_6$, $(CdSe)_{13}$, $(CdSe)_{16}$, $(CdSe)_{26}$ and N3 dye, generated from energy calculations of DFT show increment of oscillator strength (f) as the size of fluorophore increases (inset). N3 dye shows the widest absorption cross-section (α_A) than that of QD clusters indicates a superior photon absorption properties. Vertical lines are the calculated oscillator strengths at excitonic peak position of each fluorophore. Note that the curve for N3 dye is extended until ~1550 nm of wavelength.

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