ULTRAFAST CHARGE TRANSFER DYNAMICS IN SUPER-SENSITIZED QUANTUM DOT SOLAR CELL

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Abstract

Working principle and charge transfer dynamics in ultrafast has been demonstrated in quantum dot (QD) /dye composite materials where dye and composite form strong charge transfer (CT) complex in the ground state. Charge separation processes found to take place in three in three different pathways: by transferring photo-excited hole of QD to dye, electron injection from photo-excited dye to QD and direct electron transfer from HOMO of dye to conduction band of QD. Charge transfer dynamics was monitored by direct detection of dye cation radical and electron in the QD in the transient absorption spectra. Electron injection and electron transfer process are found to be pulse width limited (< 100 fs) however hole transfer time measured to be sub-picosecond. Charge recombination dynamics has been found to be very slow. Photovoltaic response of CdS/DBF super sensitized TiO2 quantum dot solar cell found to be improved drastically due to spatial charge separation (electron in CdS QD and hole in DBF).

Augmentation of current conversion efficiency in dye sensitized solar cell (DSSC) is one of the most challenging tasks. So far the record conversion efficiency of above 13% in DSSC has been reported by Graetzel and co-workers using specially synthesized Zn−porphyrin and cobalt (II/III)- based redox electrolyte, which is believe to be lower for commercial application. In this regard design and development of quantum dot sensitized solar cell (QDSSC) has been started world-wide for the next generation solar module. It is believed that single photon can generate more than one electron-hole pair multiple exciton generation (MEG) in quantum dot which in turn can drastically increase the efficiency of the devices. It has been verified that efficiency of quantum dot solar module can be enhanced significantly by dissociating or separating the multi-exciton before ultrafast exciton-exciton annihilation. However, so far the highest conversion efficiency in QDSC has been reported by Kamat and co-workers to be ~ 5.2 %. By introducing inorganic−organic heterojunction and hybrid passivation the efficiency could increased upto ~7 %, which is still much lower than conventional dye-sensitized solar cells (DSSCs). In QD materials majority of exciton recombines before it dissociates...
as a result efficiency realized in QDSC is much lower than expected. By using suitable molecular adsorbate (electron or hole acceptors) exciton dissociation in QD materials can be reality. In addition to that it has been realized that limited absorption of solar radiation of QDs and slow hole transfer rate are the main reasons for overall low efficiency of QDSC. These problems can be tackled by introducing super sensitizer in QDSC, where quantum dot and molecular adsorbate can exchange charge carriers on photo-excitation. In super sensitization in addition to photosensitizing the quantum dot material, molecular adsorbate also can act as hole transporting materials for photosensitized quantum dot, as a result grand charge separation takes place in QD-molecular composite material.

In this article we intend to demonstrate charge transfer mechanism and grand charge separation of super-sensitized solar cell materials. For this purpose we have chosen CdS QD and di-bromo fluorescene (DBF) dye molecule where both CdS QD and DBF individually can sensitize TiO2 nanoparticles. Redox energy levels of CdS QD and DBF molecule imply that conduction band (CB) of CdS lies below LUMO level which allows photo-excited DBF to inject electron in to the CB of CdS QD and HOMO level of DBF lies above the valence band (VB) of CdS QD allowing photo-excited hole transfer to DBF molecule. Interestingly CdS QD and DBF forms strong charge transfer (CT) complex where on photo-excitation direct electron transfer from DBF to CdS QD is feasible. We have carried out steady state and time-resolved emission measurements to confirm hole and electron transfer processes following different path ways in the above system. Femtosecond transient absorption spectroscopy and Fluorescence Up-conversion techniques have been employed to monitor the charge (both electron and hole) transfer dynamics in ultrafast time scale and to demonstrate grand charge separation in CdS QD/DBF composite system.

Oleic-capped CdS QDs were synthesized by following the previously reported method of high-temperature reaction of precursors in hot noncoordinating solvent ODE. Fig. 1 shows the high resolution TEM images of CdS QD particle and particle size were determined to be 2.5 nm.

![Fig. 1: The HRTEM image of synthesized CdS QD. Particle size was measured to be 2.5 nm (scale bar 5 nm). Inset: The SAED pattern of CdS QD (scale bar 5 nm).](image)

To understand charge transfer interaction in the excited state it is very important monitor ground state interaction between dye and QD materials. Fig. 2 shows the optical absorption spectra of DBF sensitizd CdS QD. Pure DBF molecule shows weak optical absorption up to 550 nm with a peak at 465 in addition to an absorption band below 280 nm as depicted in Fig. 2a. Fig. 2b depicts the optical absorption spectrum of 0.49 µM CdS QD and 0.3 mM DBF dye.
$\mu$M CdS QD in chloroform which shows an exciton at 433 nm and corresponding band gap can be calculated to be $-2.69$ eV. Now on addition of CdS quantum dot (QD) in DBF solution the optical absorption band become broader and shifted to the red region of the spectrum (Fig. 2c). The color of the solution becomes deep red (while the color of free DBF and CdS is light orange and yellow respectively) indicating formation of strong charge transfer (CT) complex between CdS QD and DBF. High extinction co-efficient of the CdS-DBF complex suggest that the composite materials form strong CT complex where partial charge transfer takes place in the ground state. This observation clearly suggests that CdS-DBF composite material is a potential material for super-sensitizer, which can absorb more solar radiation as compared to that of the individual CdS QD and DBF molecule.

To understand charge transfer dynamics steady state and time-resolved emission studies for both CdS QD and DBF molecule separately and also in the composite system by selective excitation. Figure 3a shows steady state luminescence spectra of CdS QD in chloroform after exciting the sample at 375 nm, which consist an emission peak at 450 nm with high quantum yield ($\phi_f=0.24$). Fig. 3b shows the emission spectra of CdS QD in presence of 0.3 mM DBF. It is clearly seen that CdS emission is completely quenched in presence of DBF. As we have already mention that the valence band (1.35 V vs NHE) of CdS lies below the HOMO (0.8 V vs NHE) of DBF (Scheme 2), so photo-excited hole can be captured by DBF which is thermodynamically viable. Hole transfer reaction can be expressed by the equations below:

$$\text{CdS} + h\nu \rightarrow \text{CdS} (e^- + h^+) \quad (1)$$

$$\text{CdS} (e^- + h^+) + \text{DBF} \rightarrow \text{CdS} (e^-) + \text{DBF}^+ \quad (2)$$

To find the hole transfer dynamics time-resolved emission studies has been carried out of free CdS QDs and also in presence of DBF and shown in Fig. 3 inset (upper panel). The emission decay traces of CdS QD and CdS/DBF composite have been monitored at 450 nm after exciting the samples at 406 nm. The emission decay traces can be fitted multiexponentially with time constants of $\tau_1 = 0.58 \text{ ns (39\%)}$, $\tau_2 = 23.8 \text{ ns (32\%)}$, $\tau_3 = 5.2 \text{ ns (29\%)}$ with $\tau_{avg} = 9.4 \text{ ns for CdS QD and of } \tau_1 = 0.12 \text{ ns (61\%)}$, $\tau_2 = 0.94 \text{ ns (22\%)}$, $\tau_3 = 3.4 \text{ ns (17\%)}$ with $\tau_{avg} = 0.9 \text{ ns}$ for CdS/DBF system. The average lifetime of CdS/DBF system is ten times shorter as compared to that of CdS QD, which confirms hole transfer process in the composite materials as suggested in equation 2. Presumably the observed decrease in lifetime arises due to hole transfer (HT) from CdS QD to DBF molecule, then the HT rate constant can be determined through the following expression

$$k_{HT} = 1/\tau_{\text{CdS+DBF}} - 1/\tau_{\text{CdS}} \quad (3)$$

Using the average lifetime values of 9.4 ns (CdS) and 0.9 ns (CdS-DBF) the hole transfer rate constant can be determined to be $1.1 \times 10^9 \text{ sec}^{-1}$. 

Fig. 3: Upper panel: Photoluminescence (PL) spectra of CdS QD (a) in absence and (b) in presence of DBF in chloroform solution after exciting at 375 nm. Inset: Emission decay traces of (c) CdS QD and (d) CdS-DBF composite after exciting at 406 nm and monitoring at 450 nm. Lower panel: Photoluminescence (PL) spectra of DBF (e) in absence and (f) in presence of CdS QD after exciting at 500 nm. Inset: Fluorescence upconversion traces of (g) DBF and (h) CdS-DBF composite after exciting at 435 nm and monitoring at 560 nm. [CdS] = 0.49 $\mu$M and [DBF] = 0.3mM.
Now from Scheme 2 it is clear that photo-excited DBF molecule can inject electron into the conduction band of CdS QD. To monitor this electron transfer process from photo-excited DBF to CdS QD we have carried out emission spectroscopy in the present investigation after exciting DBF molecule. Electron injection dynamics from photo-excited xanthenes dyes (DBF is a xanthenes dye) to the conduction band of TiO₂ have been demonstrated by us. Since xanthenes dye molecules are highly luminescent, it is easy to demonstrate electron transfer process by monitoring the luminescence quenching measurements. Fig. 3 lower panel depicts the emission spectra of DBF and DBF-CdS composite after exciting the samples at 500 nm. Fig. 3e shows the emission spectra of DBF which has emission peak at 557 nm with a hump at 584 nm. However in presence of CdS the emission intensity drastically reduces as shown in Fig. 3f. Again as we have already mentioned that LUMO (-1.5 V) of DBF lies above the conduction band (-1.3 V vs NHE) of CdS QD (Scheme 2), so photo-excited DBF can inject electron into the conduction band of CdS. The emission quenching can be attributed to electron injection from photoexcited DBF to CdS, and can be expressed by the equations below:

$$\text{DBF} + h\nu \rightarrow \text{DBF}^* \quad (4)$$

$$\text{DBF}^* + \text{CdS QD} \rightarrow \text{DBF}^+ + \text{CdS QD} (e^-) \quad (5)$$

Now to monitor electron injection dynamics we have carried out fluorescence upconversion measurements for free DBF and also in presence of CdS QD after exciting the samples at 435 nm laser pulse and monitoring at 560 nm and shown in Figure 3 inset (lower panel). We would like to make a point that exciting pure CdS at 435 and monitoring at 560 nm, no emission signal was observed. It is clear from emission decay trace of pure CdS (Fig. 3g) that emission lifetime of DBF is too long to measured in fluorescence up-conversion technique. So to measure the emission lifetime of DBF we performed nanosecond life time measurements (TCSPC) and determined to be 1.6 ns. Fig. 3h depicts the emission kinetics of DBF in presence of CdS QD which can be fitted bi-exponentially with time constants of \(\tau_1 = 618\) fs (85%) and \(\tau_2 = 1.8\) ps (15%) with average life time \(\tau_{avg} = 800\) fs. If we presume that the observed decrease in lifetime arises due to electron injection from photoexcited DBF to CdS QD, then we can determine the electron injection time constant by the following expression.

$$\text{kinj} = 1/\tau_{DBF} + \text{CdS} - 1/\tau_{DBF} \quad (6)$$

By following the above expression electron injection rate can be determined to be \(1.2 \times 10^{12}\) sec⁻¹. With the help of time-resolved emission technique we have demonstrated both electron injection from photoexcited DBF to CdS QD and also hole transfer from photo-excited CdS QD to DBF molecule.

To substantiate charge (both electron and hole) transfer dynamics in early time scale with accuracy femtosecond transient absorption spectroscopic measurements has been carried out by exciting CdS QD, DBF and DBF-CdS QD/composite system at 400 nm laser light. Fig. 4 shows the transient absorption spectra of photoexcited CdS/DBF QD composite materials in different time delay, which comprises a bleach below 550 nm and two broad absorption bands at 550-750 nm and 750-900 nm respectively. The broad
spectral absorption in the 750-900 nm regions can be attributed to the electrons in the conduction band in CdS QD. The transient absorption band at 550-750 nm can be attributed to DBF cation radical. The band having maximum at 650 nm is assigned to DBF cation radical (DBF+). We have already demonstrated that at 400 nm photo-excitation both electron injection and hole transfer process can occur in DBF/CdS composite materials. Now to understand the charge transfer and charge recombination dynamics we have monitored the kinetics at 500 nm (bleach wavelength) and 650 nm (DBF cation radical) and shown in Figure 4 inset. It is clearly seen that charge recombination dynamics is extremely slow where electrons and holes are spatially separated.

From steady state and time-resolved emission and absorption studies suggest that generation of electron in the conduction band in CdS and formation of DBF cation radical might be taking place through more than one process. Recent investigation on quantum dot solar cell suggests removal of charges (holes and electrons) from photo-excited quantum dots can be key factor to improve the conversion efficiency. In CdS-DBF composite materials it is clear from Scheme 2 that DBF can extract the photo-excited hole from CdS QD (path 1, Scheme 3). In addition to that photo-excited DBF can inject electron to the conduction band of CdS (path 2, Scheme 2) suggesting CdS-DBF is a typical type II system of QD-molecular system. Over and above the formation of type II system, from steady state optical absorption measurements (Fig. 1) it is clear that CdS QD and DBF form strong CT complex with very high molecular extinction co-efficient, which has absorption band in the red region of the solar radiation as compared to both CdS QD and DBF molecule, as a result the absorption cross-section of CdS-DBF composite system towards solar radiation increase dramatically. Excitation of CT CdS-DBF complex electron from HOMO of DBF can move directly to the conduction band of CdS (path 3, Scheme 2) which ensure much higher charge separation as compared to both hole transfer from CdS to DBF and also electron injection from photoexcited DBF to the CB of CdS. We have demonstrated that blue part, green part and red part of the solar radiation will be absorbed by CdS QD, DBF and CdS-DBF CT complex respectively as shown in Scheme 2.

Steady state and time-resolved spectroscopic analysis suggest that CdS-DBF composite can be used as a great super sensitizer in quantum dot solar sell. The photo-electrochemical performance of mesoscopic TiO2 films modified with CdS, DBF, and CdS/DBF was monitored under similar illumination condition of AM 1.5 irradiation (100mWcm⁻²) using a redox couple, where Pt-coated FTO is used as counter electrode. The electrolyte composition: 0.6 M 1,2 dimethyl 3-propyl imidazolium, iodide, 0.1 M LiI, 0.05 M I₂, and 0.5 M 4-tert-butylpyridine in acetonitrile is used. It is noteworthy that Fig. 5 purely shows a comparison of solar cells based on CdS QD, DBF dye and CdS/DBF composite and actual photocurrent action spectra can be improved further by optimized fabrication of QDSC. It is interestingly to see that maximum IPCE observed for TiO₂/CdS/DBF electrode which is much higher as compared to both TiO₂/CdS electrode and TiO₂/DBF electrode, confirming efficient hole transfer from CdS QD to DBF molecule and also super sensitization through CdS-DBF charge transfer complex.
This synergy between the CdS and the dye in facilitating higher photocurrent generation indicates an additional role of the dye in shuttling holes across the CdS/dye electrolyte interface. With this proposition, it becomes quite impressive to see dramatic improvement of photovoltaic response for the CdS-DBF composite on TiO2 photo anode, which represents the high efficacy of super-sensitization in stabilizing interfacial charge separation of QDSC. This is a direct correlation of transient absorption and luminescence data and photoaction spectra which describes higher charge separation through super-sensitization. CdS-DBF composite not only effectively removes the hole from quantum dot it can also absorb more solar radiation due to formation of charge transfer complex which has very high molar extinction coefficient. Considering the fact that QDSC photoaction is exclusive outcome of kinetic competitions of electron injection, hole transfer, back electron transfer and dye-regeneration processes, this super-sensitization scheme can bring significant improvement in QDSC without much changing the devise fabrication.

In conclusion ultrafast hole and electron transfer dynamics in CdS QD/di-bromo fluorescein (DBF) composite are explored and verified as a super-sensitizer in QDSC. Optical absorption studies indicate CdS QD and DBF form strong charge transfer complex in the ground state. Steady state and time-resolved absorption and emission studies confirmed that on photo-excitation charge separation in CdS-DBF composite take place in three different pathways. As a result grand charge separation takes place in CdS-DBF composite, which confirms the usefulness as a super-sensitizer in QDSC. Ultrafast transient absorption and Femtosecond up-conversion studies indicates that path 2 and path 3 are pulse width limited (<100 fs) however path 1 time measured to be 800 fs. Charge recombination dynamics found to very slow due to spatial charge separation in the composite. Understanding the charge transfer dynamics at molecular level in ultrafast time scale has helped in achieving superior J-V and IPCE response of CdS/DBF super sensitized TiO2 quantum dot solar cell. This observation confirms the reality of multiple exciton dissociation and finally higher photo-conversion efficiency in quantum dot solar cell.

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References