Built-in Quantum Dot Antennas in Dye-Sensitized Solar Cells

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ABSTRACT A new design of dye-sensitized solar cells involves colloidal semiconductor quantum dots that serve as antennas, funneling absorbed light to the charge separating dye molecules *via* nonradiative energy transfer. The colloidal quantum dot donors are incorporated into the solid titania electrode resulting in high energy transfer efficiency and significant improvement of the cell stability. This design practically separates the processes of light absorption and charge carrier injection, enabling us to optimize each of these separately. Incident photon-to-current efficiency measurements show a full coverage of the visible spectrum despite the use of a red absorbing dye, limited only by the efficiency of charge injection from the dye to the titania electrode. Time resolved luminescence measurements clearly relate this to Förster resonance energy transfer from the quantum dots to the dye. The presented design introduces new degrees of freedom in the utilization of quantum dot sensitizers for photovoltaic cells. In particular, it opens the way toward the utilization of new materials whose band offsets do not allow direct charge injection.

KEYWORDS: quantum dots · semiconductor nanocrystals · Förster resonance energy transfer (FRET) · sensitized solar cells · organic dye

Harvesting energy directly from sunlight using photovoltaic technology is being increasingly recognized as an essential component of future global energy production. Dye-sensitized solar cells (DSSCs) originally introduced by Grätzel *et al.*[1] are promising devices for inexpensive, large-scale solar energy conversion. Photo conversion efficiencies greater than 11% have been reported for DSSC based on nanoporous TiO_2 electrodes, dye sensitizer, and an iodide/triiodide redox system. The most successful dyes employed are ruthenium complexes,[2,3] (Ru(dcbpy)$_2$(NCS)$_2$), N$_3$ (dcbpy = 4,4-dicarboxy-2,2'-ipyridine), or the bistetrabutylammonium salt N719. In DSSCs, dye molecules absorb photons and inject electrons from their excited state into the conduction band of a mesoporous TiO_2 film where they diffuse to a transparent conducting front contact while the oxidized dye is recharged by a redox electrolyte, which transports the positive charge to a back electrode.

Many attempts have been made to improve DSSCs. These include different geometrical structures of the nanoporous electrodes to provide higher surface area and better charge transport,[4] replacement of the liquid electrolyte by a solid one in order to prevent the electrolyte evaporation,[5] and synthesis of alternative molecular dyes to extend the spectral response. In particular, several solutions to the difficulties associated with narrow absorption spectra of molecular dyes were proposed. The so-called "black dye" offered a broader absorption spectrum,[6] but low absorption cross section and instability under strong illumination inhibited significant efficiency increase.[7] Dye cocktails enable broad absorption spectra,[8] but in the absence of efficient dyes for the red part of the spectrum result in lower cell efficiencies compared with the standard DSSCs. A new approach reported recently utilizes Förster resonance energy transfer (FRET) from donor dye molecules that are added to the redox solution. Upon absorption of light, the donor molecules transfer the excitation energy to an acceptor dye adsorbed on the electrode followed by the standard charge separation process. For liquid electrolytes, donor molecules are heavily quenched.[9,10] Therefore, this strategy has very recently been employed using solid electrolytes.[11]

Similar geometries using other sensitizers, such as inorganic semiconductor nanocrystals (quantum dots, QDs), have been proposed.[12−22] QDs have the advantage of a broad absorption spectrum, stretching from the band edge to higher energies, in contrast with the narrow absorption spectra typically exhibited by molecular dyes. On the other hand, charge collection in quantum dot sensitized solar cells (QDSSCs) has proven to be significantly more difficult,

See the accompanying Perspective by Basham *et al.* on p 1253.

probably due to charge trapping on QD surfaces and the availability of more recombination channels. Moreover, photochemical reactions, particularly with the liquid electrolyte can induce significant degradation of the QD sensitizers. A detailed account of these can be found in two recent reviews.[12,18]

Herein, we present a design which combines the benefits of QDs in terms of their broad absorption spectrum with the evolved charge transfer mechanism of DSSC. In this design, QDs serve as "antennas", funneling absorbed energy to nearby dye molecules *via* FRET, rather than being used directly as sensitizers. The QDs are incorporated into the nanoporous TiO₂ electrode with total isolation from the redox electrolyte, as schematically shown in Figure 1. This concept allows separating between the efficient photon absorption by the nanocrystalline quantum dot and the charge separation (electron injection to the TiO₂ and hole transfer to the electrolyte) by the adjacent dye molecule. It offers a viable alternative to the limitations of carrier injection and collection of both DSSCs and QDSSCs. Most importantly, the new design, by which the QD "antenna" is incorporated into the solid titania electrode, provides several critical benefits: the isolation of the QD "antenna" from the electrolyte solution prevents donor quenching; the geometry resembling parallel donor−acceptor layers with short distance increases the energy transfer efficiency; finally, QDs isolation significantly improves their photostability as compared with traditional designs that involve charge transfer between the iodine electrolyte and the QDs.[17]

The mechanism of FRET involves a donor in an excited electronic state, which may transfer its excitation energy to the nearby acceptor in a nonradiative fashion through long-range dipole−dipole interaction.[23] The theory is based on the concept of treating an excited donor as an oscillating dipole that can undergo an energy exchange with a second dipole having a similar resonance frequency. In principle, if the fluorescence emission spectrum of the donor molecule overlaps the absorption spectrum of the acceptor molecule, and the two are within a minimal distance from one another (typically 1−10 nm), the donor can directly transfer its excitation energy to the acceptor *via* exchange of a virtual photon.

The selection of donor and acceptor chromophores is of high importance. Herein, we used new unsymmetrical squaraine dye,[24] 5-carboxy-2-((3-(1,3-dihydro-3,3-dimethyl-1-ethyl-2H-indol-2-ylidene)methyl)-2-
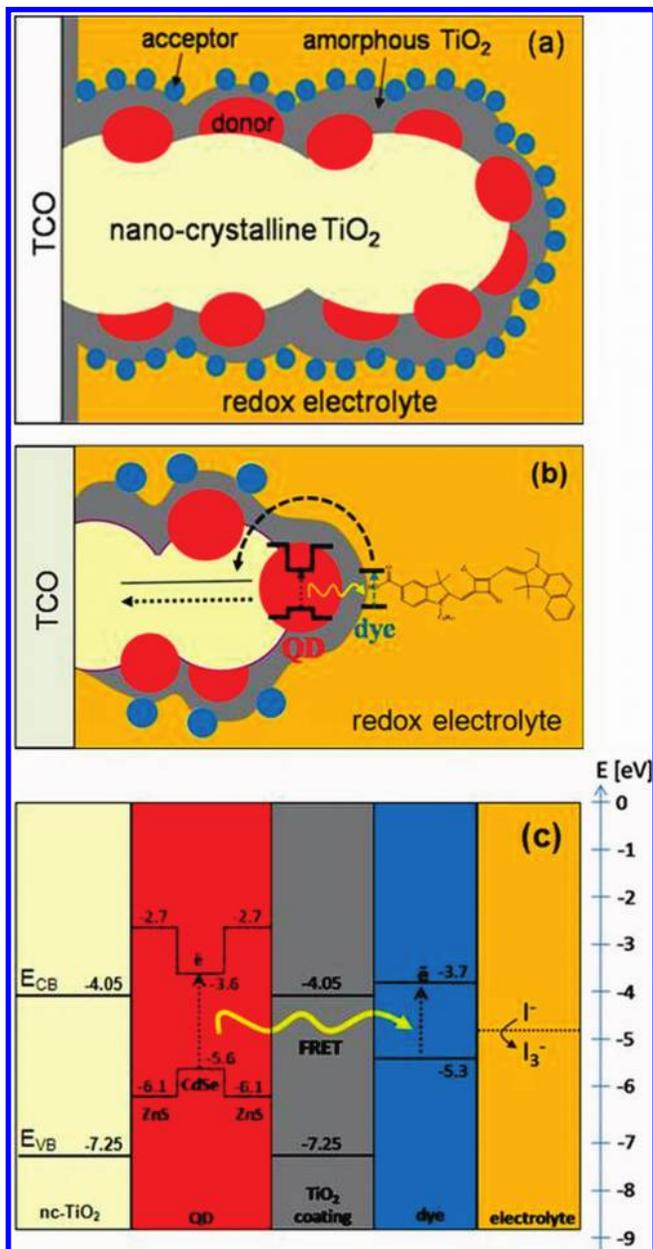

Figure 1. (a,b) Schematic presentation of a system. The system consists of a transparent conducting oxide (TCO) on which nanocrystalline (nc) TiO₂ (off-white big circles) is grown. QDs (red circles) bound to nc-TiO₂ *via* a MPA linker (not shown) and covered by a thin layer of amorphous TiO₂ (gray coating) to which dye molecules (small blue circles) are connected. This entire structure is immersed in a liquid redox electrolyte (I⁻/I₃⁻). (c) Band alignment of each component in the system relative to the vacuum level.

hydroxy-4-oxo-2-cyclobuten-1-ylidene)methyl)3-3-dimethyl-1-octyl-3H-indolium (SQ02) as the acceptor chromospheres since it is an organic dye with substantially high molar extinction coefficient (319000 M⁻¹ cm⁻¹) that absorbs strongly in the red edge of the visible spectrum (unlike most common dyes used in DSSCs). CdSe/CdS/ZnS QDs (core/shell/shell) were chosen as a donor for several reasons: First, its light absorption is complementary to that of SQ02 dye. Second, its emission spectrum can be easily tuned for good spectral overlap by tailoring the CdSe core size. Third,
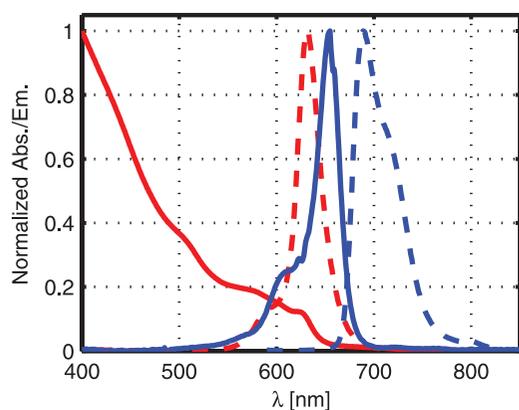
Figure 2. Absorption (solid lines) and emission (dashed lines) spectra of CdSe/CdS/ZnS core/shell/shell quantum dots (red) in water at pH10 and SQ02 dye molecules (blue) in ethanol. The figure shows a large overlap between emission spectrum of the QDs and absorption spectrum of dye molecules.

the ZnS shell creates a barrier which practically inhibits direct charge injection to the titania electrode.

RESULTS AND DISCUSSION

A schematic description of the system is presented in Figure 1a,b. QDs are first deposited on the nanocrystalline titania electrode and then overcoated with a thin (~4 nm) layer of amorphous titania. QDs are thus completely incorporated within the solid electrode and isolated from the electrolyte. The sensitizer dye is then deposited on the amorphous layer and is later immersed in the liquid electrolyte. Figure 1c demonstrates energy level diagram of the system. As specified previously, the ZnS shell prevents direct charge injection from the QD, leaving FRET as the main decay channel of the excited QDs. In regular dye solar cells, light is directly absorbed by the sensitizer dye, exciting an electron from the HOMO level to the LUMO level. In the new configuration a second, "indirect injection" channel is introduced, by which, an electron is promoted from the valence band to the conduction band of the QD, followed by energy transfer from the excited state of the QD into the LUMO of the dye *via* FRET. Thereafter, charge separation occurs exactly as it does in a regular DSSC, whereby the electron is injected from the excited state of the dye into the conduction band of the electrode through the amorphous TiO_2 coating. The electron is thus transported to the charge collector, while holes are transported to the back contact *via* the electrochemical mediator.

Figure 2 presents the absorption and emission spectra of CdSe/CdS/ZnS QDs, along with the absorption and emission spectra of the unsymmetrical squaraine dye, SQ02. For donor−acceptor pair there is a significant overlap between the emission spectrum of CdSe/CdS/ZnS QDs and the absorption spectrum of SQ02.

The rate of the FRET interaction is given by $K_{FRET} = 1/\tau_D(R_0/r)^6$ where r is the distance between the

donor−acceptor pair, R_0, the Förster radius, is the distance by which probability of energy transfer is 50%, and τ_D is the excited state lifetime of the donor molecule in the absence of acceptor. The Förster radius is given by[25]

$$R_0^6 = \frac{9000(\ln 10)\kappa^2 Q_D J}{128\pi^5 n^4 N_{AV}}$$

where κ^2 is the orientation factor (averaged $^2/_3$ for random orientation[23]), n is the refractive index of the medium (1.5−2.1, in between redox electrolyte and TiO_2 electrode), Q_D is the quantum efficiency of the donor molecule (24%−70%; in an organic solution QD's quantum efficiency is 70%, but in aqueous solution it drops to 24%. The real quantum yield of the donor in the electrode configuration was not measured but should be higher than 24% because of better passivation and the higher refractive index of the titania electrode), N_{AV} is the Avogadro number. $J = \int_0^\infty I_D(\lambda)\varepsilon_A(\lambda)\lambda^4 d\lambda$ is the weighted spectral overlap where I_D is the emission spectrum of the donor and ε_A is the molar extinction coefficient of the acceptor. On the basis of the above input the calculated Förster radius is between $R_0^{min} = 5.5$ nm and $R_0^{max} = 6.6$ nm. Following these considerations, and given the thin ZnS and amorphous titania coatings, efficient FRET can be expected in this system provided that the dye coverage is dense enough.

The fingerprint of efficient FRET is a significant shortening of the donor radiative lifetime in the presence of the acceptor, and a concomitant increase in the acceptor lifetime. To characterize the FRET efficiency we first measure the transient luminescence of the QD donor on a bare electrode following QD and amorphous titania deposition. The measured decay dynamics are then compared to those measured on the same electrode following deposition of the SQ02 dye. To avoid saturation effects, these measurements are performed on an electrode over which donor QDs were dilutely deposited. The QD donor emission transients, both with and without the presence of the acceptor are presented in Figure 3a. A clear shortening of the emission transient is observed upon deposition of the dye. The acceptor luminescence transient from this electrode is presented in Figure 3b, along with the decay transient from an electrode over which dye was deposited without the presence of the QD donor. FRET from the QD donor is clearly exhibited by the appearance of a slow decay component in the acceptor luminescence.

The FRET efficiency can be derived from the ratio between the lifetime of the donor in presence and absence of the acceptor:[26] $E = 1 - \tau_{DA}/\tau_D$. Note that this result neglects the distance distribution of donor−acceptor pairs—an acceptable approximation in our case due to the confinement of acceptors to the insulating layer and the immobility of the donors. On the basis of a three exponential lifetime model com-
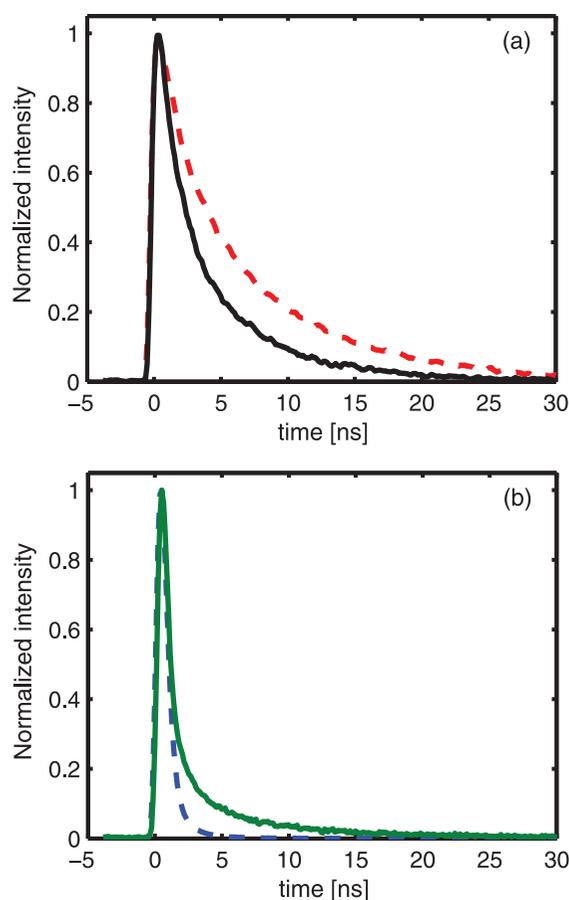
Figure 3. Lifetime measurements of different cell configurations excited at 470 nm showing efficient FRET in the measured electrode. The donor emission transient (detected using a 633 ± 30 nm band-pass filter) is presented in panel a. The dashed red curve represents the lifetime of a donor only, while the solid black curve was measured in the presence of an acceptor. The acceptor emission transient (detected using a 700 nm long-pass filter) is presented in panel b. Here the dashed blue curve represents the lifetime of an acceptor only, while the solid green curve was measured in the presence of a donor.

monly applied on the QDs, the average lifetime of each decay curve was calculated as follows:

$$I(t) = \sum_{i=1}^{3} \alpha_i e^{-t/\tau_i} \Rightarrow \tau_{AV} = \frac{\sum_{i=1}^{3} \alpha_i \tau_i}{\sum_{i=1}^{3} \alpha_i}$$

The average lifetime of the donor only decay curve is $\tau_D = 4.88$ [ns] ($\chi^2 = 1.023$) compared with faster donor decay $\tau_{DA} = 2.74$ [ns] ($\chi^2 = 0.97$) in the presence of the acceptor. As a result the given FRET efficiency is $E \approx 44\%$. As the donor is dilute, the acceptor channel exhibits transient emission due to both direct absorption (with a temporal profile resembling that of a dye-only system) and FRET, as reflected in the slower exponential tail, correlated with the decay dynamics of the donor.

Following the demonstration of efficient FRET between the QD donors and the dye acceptors, we pro-

ceed to measure the incident photon to current efficiency (IPCE) of our cells. In these measurements, we compare the IPCE of the full cell, containing both QDs and dye to two reference cells. Each of the two reference cells consists of one sensitizer (either the QDs or the dye) in a configuration similar to that of the FRET based cell, including the amorphous titania layer, to allow for a fair comparison. The IPCE curves of all three cells are presented in Figure 4b. The absorption spectra of the dye and the QDs are shown, for reference, in Figure 4a. The red IPCE curve relates to the electrode containing only QDs (nc-TiO$_2$/QDs/amorphous TiO$_2$ coating). The minimal response at short wavelengths is attributed to electron excitation within the nc-TiO$_2$. We observe no electron injection from the QDs to the nc-TiO$_2$. The blue curve refers to the electrode containing only the dye sensitizer (nc-TiO$_2$/amorphous TiO$_2$ coating/SQ02 dye molecules). This electrode shows a response between 550−750 nm which resembles the absorption spectrum of the SQ02 dye. The black curve shows an IPCE response of the FRET electrode (nc-TiO$_2$/QDs/amorphous TiO$_2$ coating/SQ02 dye molecules). While maintaining the conversion efficiency in the spectral window of the dye (550−750 nm), the cell provides similar efficiency between 400 and 550 nm with a peak resembling the QDs absorption spectrum. This peak originates from the relatively strong absorption of QDs in this wavelength range, translated into efficient FRET interaction and charge separation by the dye, which thereby completes a full coverage of the visible spectrum. As is evident, the presence of the QDs contributes to the IPCE only in the presence of the relay acceptor dye.

It should be noted that the optical density of our electrode in the QDs absorption region and the high FRET efficiency associated with the new electrode configuration, should provide IPCE values much higher than the ~10% obtained. The results show that the FRET related conversion efficiency is limited by the charge injection efficiency of the (saturated) SQ02 dye. Thus, the observed IPCE at all excitation wavelengths is limited by the maximal value measured on the electrode containing only the dye. This can be improved by using a different acceptor dye and possibly by treatment of the amorphous titania layer.

To conclude, we present a new configuration for QD-sensitized DSSCs *via* a FRET process. Our results prove the general feasibility of enhancing light absorption and broadening the absorption spectrum by the addition of QDs acting as "antennas", effectively increasing the number of photons harvested by the dye sensitized solar cell. We have shown that FRET is the dominant mechanism funneling energy from the QDs to the dye, and IPCE measurements show a full coverage of the visible spectrum, limited only by the efficiency of charge injection from the dye to the titania electrode.
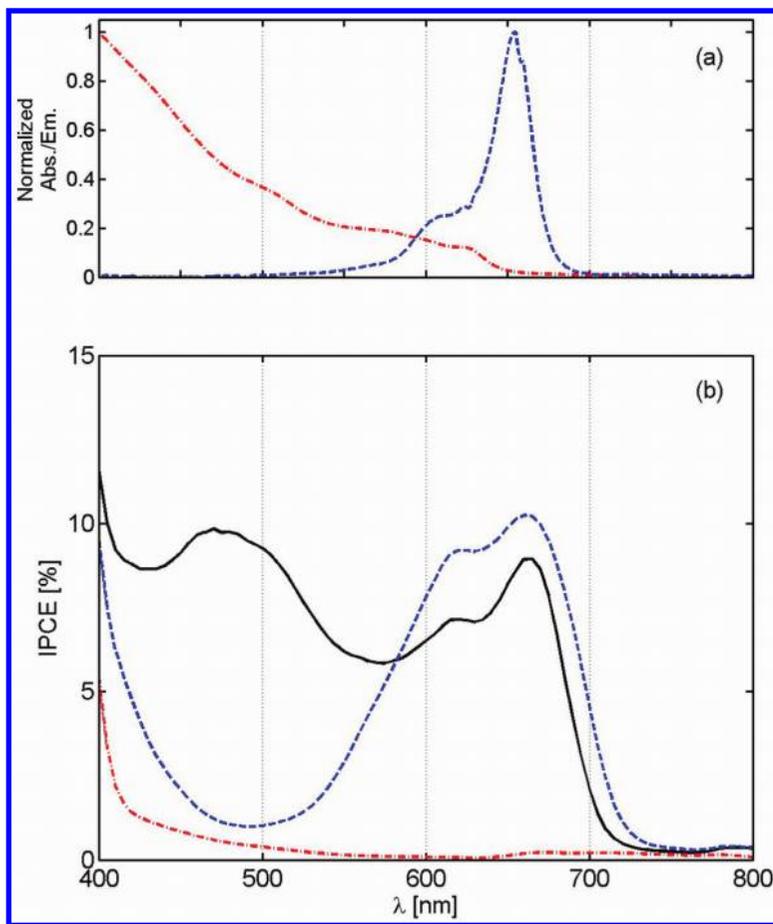
Figure 4. (a) normalized absorption spectra of QDs (dash-dotted red curve) and dye molecules (dashed blue curve). (b) IPCE curves of the three solar cells: a cell consisting of QDs only (dash-dotted red curve); a cell containing only dye molecules (dashed blue curve); the complete cell including the QD antenna layer and the dye molecules (solid black curve). The IPCE curves reveal significant contribution of the QDs to the spectral response of the cell but only in the presence of the dye.

The utilization of a FRET to transfer energy from QDs to dye molecules introduces new degrees of freedom in the design of QD sensitizers for PV cells. In particular, it opens the way toward the utilization of new materials whose band offsets (relative to the titania electrode) do not allow direct charge injection. The fact that QD donors are incorporated into the solid electrode will potentially result in a significant improvement to the stability of such systems.

METHODS

Synthesis of CdSe/CdS/ZnS QDs. To demonstrate FRET from QDs to dye molecules, CdSe/CdS/ZnS nanocrystal QDs were synthesized as follows: A mixture of cadmium oxide (CdO), n-tetradecylphosphonic acid (TDPA), and 1-octadecene (ODE) was heated under argon to 280 °C in a three-neck flask. Following, the stock solution of trioctylphosphine selenium (TOPSe) was quickly injected to the hot solution. The growth temperature was then reduced to 250 °C until the dots reached the desired diameter. The CdS and ZnS shells were synthesized using a layer-by-layer growth technique in a one-pot synthesis.[27] The resulting QDs are slightly rodlike, with aspect ratios of about 2. A TEM image can be found in the Supporting Information. The hydrophobic organic ligands of as synthesized QDs were exchanged with water-soluble MPA molecules, which also served as linker molecules to the titania electrode. Details of the synthesis and the ligand exchange procedure are given in the Supporting Information.

Preparation of Solar cells. Mesoporous TiO$_2$ films were prepared by electrophoretic deposition (EPD) of p-25 nanoparticles onto a fluorine-doped tin oxide (FTO) covered glass substrate.[28] The film was deposited in two consecutive cycles with drying between them. Following the EPD process, the electrode was dried in air at 150 °C, pressed, and sintered at 550°c. For QDs deposition, the electrode was immersed in an aqueous solution of CdSe/CdS/ZnS core/shell/shell QDs for 24 h. Then, a thin layer of TiO$_2$ coating was applied over the QDs-mesoporous by electrophoretic deposition of stabilized amorphous TiO$_2$.[29] Mild heat treatment of the coated electrode at 80 °C was applied in order to stabilize the amorphous TiO$_2$ coating which serves as both a stabilizer for the QDs and as a substrate for the dye molecules. An SQ02 sensitized organic dye was deposited by dipping. The concentration of the dye we used for the dipping solution was about 0.1 mM and 10 mM CDCA in ethanol solution. The adsorption time for the dyes was 4 h. The solar cell was fabricated using I$^-$/I$_3^-$ redox electrolyte and a Pt-coated FTO glass as a counterelectrode (see Supporting Information for more details).

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Supporting Information Available: Chemicals, synthesis of QDs, TEM image of QDs, film preparation, and photo electro-chemical measurements. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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