

Large improvement of electron extraction from CdSe quantum dots into a TiO₂ thin layer by N3 dye coabsorption

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Abstract

Extraction of electrons and holes photogenerated in CdSe quantum dots (QD) of 2.3 nm diameter, is monitored by Surface Photovoltage Spectroscopy. The extraction of electrons into a thin TiO₂ layer increases five-fold by absorption of N3 dye molecules on top of the QD layer. This process is facilitated by efficient hole extraction from the valence band of the QDs to the ground state of the N3 dye. Our results represent a direct measurement of charge separation in the N3/QD/TiO₂ system.

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1. Introduction

Colloidally synthesized quantum dots (QDs) are promising candidates for replacing the molecular dyes in dye-sensitized solar cells (DSC) [1] based on nanocrystalline TiO₂ networks, in order to reach higher conversion efficiencies, owing to the high absorption cross section and the broad size tunability of absorption spectra of QDs within the visible and near-infrared spectral range. Studies of complete solar cells based on this concept [2–5] have had a very limited success so far. However it has been demonstrated that QDs allow the generation of multiple excitons from a single photon due to impact ionization [6–8], reaching even 7 excitons per absorbed high energy photon in PbSe colloidal nanocrystals [8]. Therefore QDs also have the potential to overcome the loss of energy of high energy photons caused by carrier thermalization in the conventional solar cells. Advanced solar cell architectures based on QDs require to clarify

the issues of electron and hole extraction from specific QD sensitizers towards the electron and hole conducting materials that channel the carriers towards the external contacts.

We have previously reported the use of Surface Photovoltage (SPV) Spectroscopy as an excellent tool to monitor electron injection, recombination and transport of electrons in TiO₂ layers sensitized with N3 (Ru(dcbpyH₂)₂(NCS)₂) dye molecules [9,10]. Electron injection from CdSe QDs to ultrathin TiO₂ layers has been successfully studied by SPV technique as well [11]. It has been reported that Ru-polypyridine complexes are efficient acceptors for holes from CdSe QDs [12]. It has also been shown by electrochemical studies that such Ru-complexes readily transport holes in the ground level [13]. In this work we demonstrate the improvement of carrier extraction efficiency from CdSe QDs to ultrathin TiO₂ layers by attaching the N3 dye molecules on the QDs. We show that N3 molecular species effectively assist the removal of holes from CdSe QD sensitizers, which is an essential step for highly efficient solar cell operation. In addition we formulate a simple model that demonstrates that SPV can provide important information on energy level alignment and charge transfer between QDs and contacting materials. To the best of our knowledge this is the

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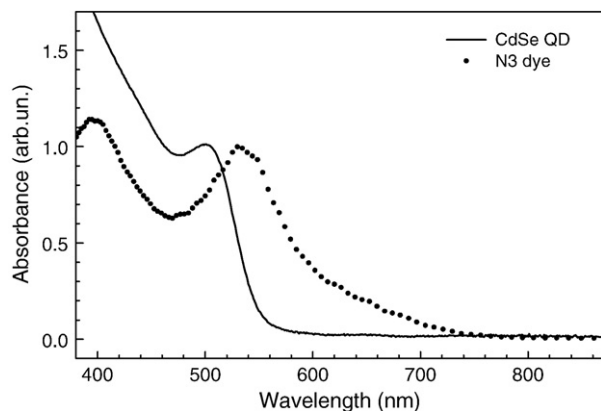


Fig. 1. Absorbance spectra of N3 dye molecules in ethanol and CdSe QDs in water.

first report on simultaneous extraction of both electrons and holes from QDs studied by SPV.

2. Experimental

Compact ultrathin TiO_2 layers (30 nm thickness) were deposited on conductive $\text{SnO}_2:\text{F}/\text{glass}$ supports by ion layer gas reaction (ILGAR) technique. CdSe QDs capped with thioglycolic acid (2.3 nm mean diameter as estimated from data of Ref. [14]), were synthesized in water as reported previously [15]. The CdSe QDs were deposited on TiO_2 -coated substrate layers by dipping the substrates into colloidal solution of CdSe QDs into 0.26 mM aqueous solution of CdSe QDs. After the measurement of the QD-sensitized sample, the sample was dipped in a N3 solution during 10 s. Fig. 1 shows the absorbance spectra of the CdSe and N3 dye in water and ethanol solutions, respectively.

The SPV method is a well-established material characterization technique which relies on analyzing the illumination-

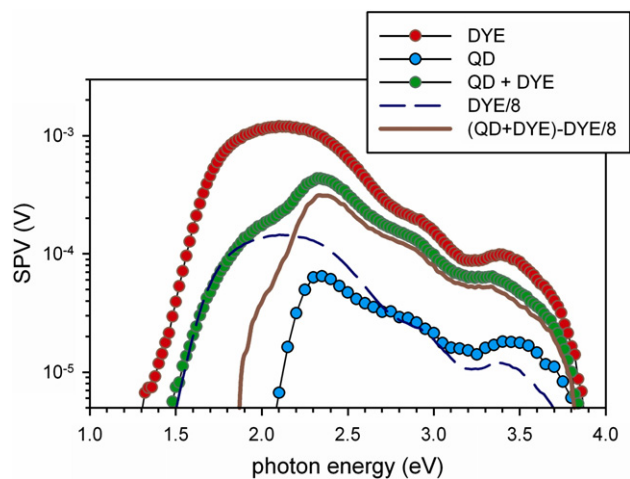


Fig. 2. SPV for different species (N3 dye, CdSe QDs, and CdSe QDs+N3 dye) attached on the surface of 10 nm thick compact TiO_2 . The graph plots the direct measurement of SPV without any normalization to the light intensity. The dashed line is the spectrum of dye rescaled to fit the low energy part of the QD+dye spectrum. The thin solid line is the QD+dye spectrum with the dye contribution subtracted.

induced charges in the surface photovoltage [16]. To obtain a SPV signal two consecutive processes are needed, first, light absorption inducing excess charge carriers in the analyzed sample and second, separation of charge carriers in space that produce a net electrical field and consequently an induced photovoltage. If the sample is placed, for example, between two conducting plates, the SPV could be measured as the voltage induced in the formed capacitor. The spectral dependent SPV measurements were carried out in the arrangement of parallel-plate capacitor [17]. SPV spectra were measured in high vacuum by using a halogen lamp with a quartz-prism monochromator for the excitation and a chopper for modulation (modulation frequency 2.5 Hz, signal detected with a lock-in amplifier).

3. Results and discussion

Fig. 2 shows the results of spectral SPV measurements of the thin and compact TiO_2 layers with different species attached at the surface: $\text{TiO}_2/\text{N3 dye}$, $\text{TiO}_2/\text{CdSe QD}$, and

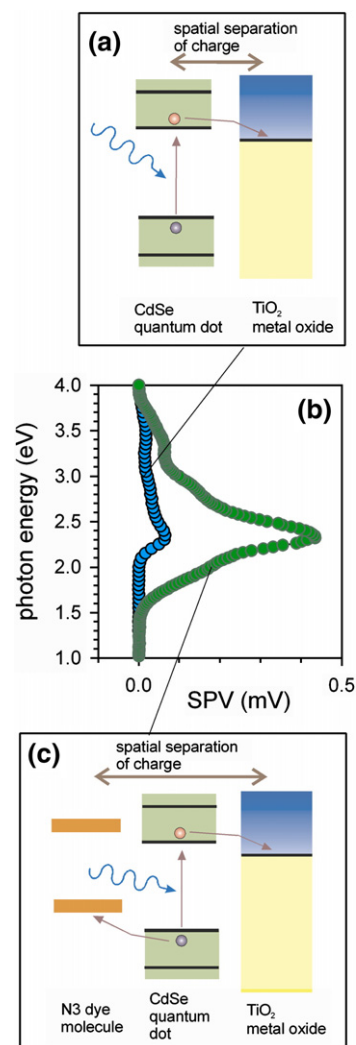


Fig. 3. SPV for different species (CdSe QDs, and CdSe QDs+N3 Dye) absorbed at the surface of 10 nm thick compact TiO_2 layer (b). The schemes (a) and (c) show the models for the charge separation responsible for the observed SPV signal.

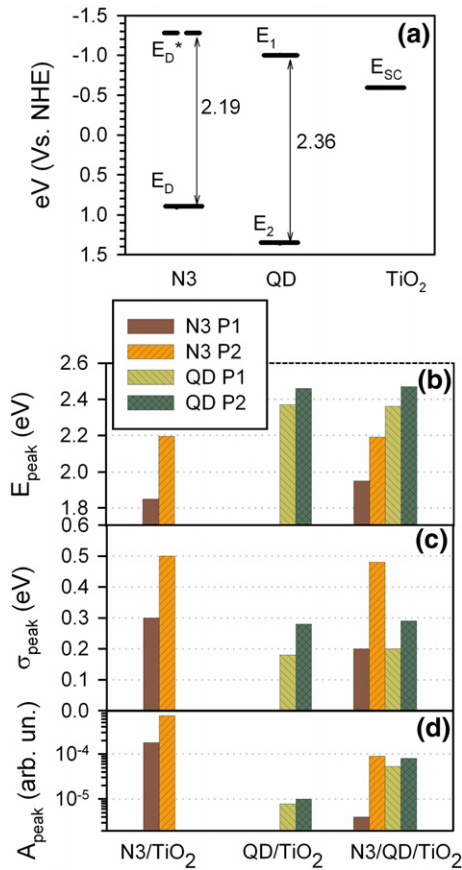


Fig. 4. Energy diagram of the system N3/CdSe QD/TiO₂ (a). Results of the fits of experimental SPV peaks: Energy (b), dispersion (c) and amplitude (d).

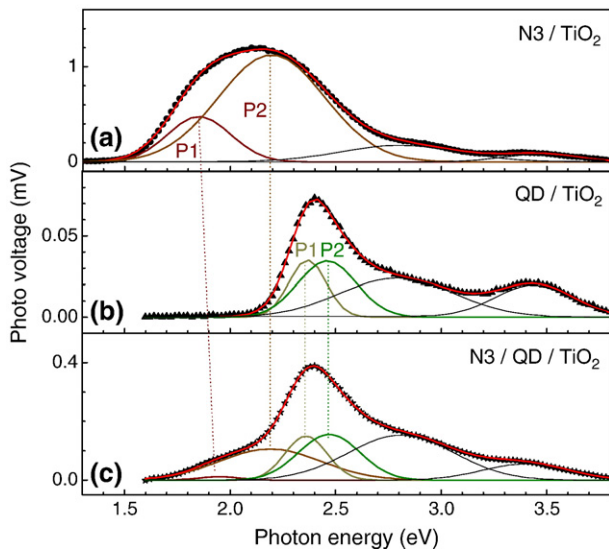


Fig. 5. Measured SPV spectra (symbols) for the N3/TiO₂ (a), CdSe QD/TiO₂ (b) and N3/CdSe QD/TiO₂ (c). The two brownish and the two greenish lines give the Gaussians (P1, P2) for the fits of the peaks related to charge separation related to absorption by dye molecules and QDs, respectively. The black Gaussians fit the rest of the spectra. The red lines represent the fitted SPV spectra. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

TiO₂/CdSe QD/N3 dye. The PV signal of the TiO₂/N3 sample is stronger by more than one order of magnitude in comparison to the TiO₂/QD sample. This indicates the importance of recombination pathways in complex nanostructured systems sensitized with QDs. When the N3 dye is attached to the QDs that are absorbed at the TiO₂ surface, an eight-fold increase of the PV signal is observed with respect to the QD-only signal, Fig. 2. In principle the larger signal may be attributed to increased injection from the N3 dye. However, the major peak of the spectrum of the QD+dye configuration occurs at the position of the QD absorption, which is an evidence that the injection into TiO₂ occurs from electrons photogenerated in the QD, as will be discussed in more detail later. A minor part of the signal of the QD+dye configuration is due to the injection of electrons from the N3 dye towards the TiO₂, this part can be removed by fitting the low energy part of the SPV spectrum (dashed line), where the QD show no absorption. The result of such fitting and subtraction, shown in Fig. 2 in thin line, indicates that attaching the dye to the QDs increases the PV signal of the QDs by a factor larger than five.

As discussed elsewhere the SPV is sensitive to the charge separation [18], in terms of two contributions: total amount of charge, and distance between the centers of charge of the positive and negative carriers. Fig. 3(b) compares in the linear

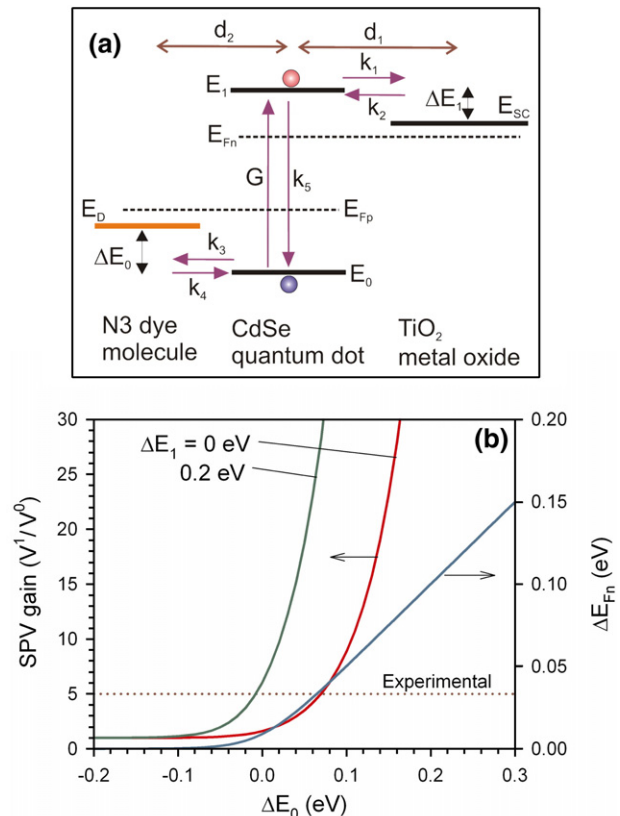


Fig. 6. (a) Kinetic model for electron–hole pair generation and recombination in a QD, and carrier extraction to TiO₂ and dye molecules. (b) Gain in SPV by inclusion of the dye molecules, with respect to QDs only at TiO₂ surface, according to the model described in text, as a function of difference of energy levels in the system. The right scale shows the increase of the electron quasi-Fermi level by inclusion of the dye molecules in the system.

scale the measured SPV with and without N3 dyes attached to the QDs. The change of signal is interpreted in terms of the models in the schemes (a) and (c): In Fig. 3(c) the holes injected to the dye introduce an additional distance of the charge separation with respect to the no-dye situation in Fig. 3(a). However, since the dye molecule size is much smaller than the TiO₂ thickness, this effect alone cannot explain the large increase of SPV observed. We show below that in addition, a large increase of electron density in TiO₂ is obtained due to the removal of holes from the CdSe QD.

Let us consider in more detail the energy diagram of the system. Values taken from the literature are indicated in Fig. 4 (a), converted to the electrochemical scale of Normal Hydrogen Electrode (NHE). E_{SC} is the conduction band edge of TiO₂, and E_D is the ground level of the dye; these were estimated from electrochemistry measurements in Ref. [19]. E_1 is the conduction band level of the CdSe QDs, estimated from electrochemical measurement in Ref. [20]. Calculation of E_1 using the method of Ref. [12] gives a slightly higher value of -1.36 (NHE). E_2 , the valence band of the CdSe QDs, is taken from the injection peak.

The peaks of injection from N3 molecules or QDs into TiO₂ in the photovoltage spectra, can be fitted by two Gaussians which excellent accuracy. The measured and fitted SPV spectra are given in Fig. 5. The results of the fits are summarized in Fig. 4(b)–(d). For the N3/TiO₂ sample the peak positions are 1.85 and 2.19 eV; the latter is denoted as E_D^* in Fig. 4(a). The widths of the distributions amount to 0.3 and 0.5 eV. For the N3/QD/TiO₂ sample the position of the peak at 2.19 eV remains practically unchanged whereas the position of the peak at 1.85 eV is shifted to 1.95 eV. At the same time the widths of the distributions decrease to 0.2 and 0.47 eV and the amplitudes of the peaks decrease by 45 (for the peak with the lower energy) and 8 (for the peak at 2.19 eV) times. The strong blue shift and the decrease of the width of the distribution parameter of the peak at the lower energy show that electron injection sets on at significantly higher energy (at least of the order of 0.2 eV) when the N3 dye molecules are adsorbed on top of the QD layer. Therefore the energy level E_1 is about 0.2 eV above the lower limit of the first excited state of N3. The peak positions of the QDs remain unchanged after N3 adsorption and the widths of these peaks increase, but not much. The electron injection from TiO₂ sets on at about 1.6 eV. If counting 1.6 eV from E_D and adding 0.2 eV we get a value which is only slightly below E_1 as indicated in Fig. 4(a).

Overall, the energy levels in Fig. 4(a) taken from literature values and the injection peaks of SPV show that the considerations of Fig. 3 for the interpretation of the changes of the SPV of QDs are plausible. However, it is clear that Fig. 4(a) is only an estimation, since the different energy levels indicated in the figure may change due to surface conditioning in a particular situation. In order to discuss the increase of SPV shown in Fig. 3(b) in more quantitative terms, we formulate a simple model that describes the occupation of the different parts of the system, by generation and recombination of excitons in the QDs and extraction of carriers, comparing the presence and absence of the dye molecules attached to the TiO₂. Such a

simple model is outlined in Fig. 6(a) and is given by the set of kinetic equations

$$\frac{dn_Q}{dt} = G - k_5 n_Q p_Q - k_1 n_Q + k_2 n_{SC} \quad (1)$$

$$\frac{dp_Q}{dt} = G - k_5 n_Q p_Q - k_3 p_Q + k_4 p_D \quad (2)$$

$$\frac{dn_{SC}}{dt} = k_1 n_Q - k_2 n_{SC} \quad (3)$$

$$\frac{dp_D}{dt} = k_3 p_Q - k_4 p_D \quad (4)$$

$$n_Q + n_{SC} = p_Q + p_D \quad (5)$$

Here n_Q and p_Q are the electron and hole number in the QDs, n_{SC} is the electron number in the TiO₂ semiconductor, and p_D is the hole number in the dye. G is the generation rate, proportional to the light intensity. By introducing $n_Q = N_Q e^{-(E_1 - E_{Fn})/k_B T}$, $n_{SC} = N_{SC} e^{-(E_{SC} - E_{Fn})/k_B T}$, $p_Q = N_Q e^{+(E_0 - E_{Fp})/k_B T}$, $p_D = N_D e^{+(E_D - E_{Fp})/k_B T}$, where N_s are total number of states for each part of the system, E_{Fn} , E_{Fp} are electron and hole Fermi levels, and $k_B T$ the thermal energy, we can impose a detailed balance conditions that give the following results:

$$\frac{k_1}{k_2} = \frac{N_{SC}}{N_Q} e^{-\Delta E_1/k_B T} = A \quad (6)$$

$$\frac{k_3}{k_4} = \frac{N_D}{M_Q} e^{+\Delta E_0/k_B T} = B \quad (7)$$

where $\Delta E_0 = E_D - E_0$ and $\Delta E_1 = E_1 - E_{SC}$. The last equalities in Eqs. (6) and (7) are definitions. Solving the above set of equations in steady state conditions gives:

$$n_Q^1 = \left(\frac{1+B}{1+A} \right)^{1/2} c; \quad p_Q^1 = \left(\frac{1+A}{1+B} \right)^{1/2} c; \quad (8)$$

$$n_{SC}^1 = A n_Q^1; \quad p_D^1 = B p_Q^1;$$

where $c = (G/k_5)^{1/2}$.

Next we consider the situation in which there is no dye molecule attached to the QD; this can be obtained from the model, setting $B=0$, with the results:

$$n_Q^0 = \left(\frac{1}{1+A} \right)^{1/2} c; \quad p_Q^0 = (1+A)^{1/2} c; \quad n_{SC}^0 = A n_Q; \quad (9)$$

The SPV without dye is (in reduced units)

$$V^0 = d_1 n_{SC}^0 \quad (10)$$

With the dye molecule included in the system, it is

$$V^1 = d_1 n_{SC}^1 + d_2 p_D^1 \quad (11)$$

Therefore the gain in SPV signal by the inclusion of the dye is

$$\frac{V^1}{V^0} = (1+B)^{1/2} + \frac{d_2 B (1+A)}{d_1 A (1+B)^{1/2}} \quad (12)$$

This function is represented in Fig. 6(b) for different values of ΔE_0 and ΔE_1 . It has been assumed that $N_D=N_Q$ (one dye molecule per QD), $N_{SC}=100N_Q$, $d_1=7$ nm, $d_2=2$ nm. In the simulations of Fig. 6(b) it is observed that if the dye ground level is lower in energy than the QD valence band level ($\Delta E_0<0$), then no SPV gain is expected, and the electron density does not increase when including the dyes in the system. Since experimentally a gain of 5 has been observed, we conclude that $E_D>E_0$, as expected from Fig. 4(a), implying an effective removal of holes from the QD, in agreement with previous observations [12].

In order to compare the situations with and without dye attached to the QDs, let us monitor the increase of number of carriers following the change of quasi-Fermi levels. This is given by

$$E_{Fn}^1 - E_{Fn}^0 = k_B T \ln \frac{n_Q^1}{n_Q^0} \quad (13)$$

$$E_{Fp}^1 - E_{Fp}^0 = -k_B T \ln \frac{p_Q^1}{p_Q^0} \quad (14)$$

Applying Eqs. (8) and (9) we obtain:

$$E_{Fn}^1 - E_{Fn}^0 = E_{Fp}^1 - E_{Fp}^0 = \frac{1}{2} k_B T \ln(1 + B). \quad (15)$$

We can see in Eq. (15) that both quasi-Fermi levels for electrons and holes are displaced upwards by the *same* amount with respect to the case of no dye. This is because the internal photovoltage in the QD (given by $E_{Fn}-E_{Fp}$) is fixed by the generation-recombination rates, independently of the outer channels for carrier extraction, as follows:

$$E_{Fn} - E_{Fp} = \Delta E_{\text{gap}} + 2k_B T \ln \frac{c}{N_Q} \quad (16)$$

The amount the Fermi level shifts is represented in Fig. 6(b). Upon inclusion of the N3 dye, the concentration of holes in the QDs decreases (E_{Fp} is higher than without dye), however the total concentration of holes increases as $p^1 = (1 + B)^{1/2} p_Q^0$, due to the new holes states supplied by the presence of the dye. In contrast to this, the concentration of electrons increases (E_{Fn} also higher than without dye), in both subsystems: TiO₂ layer and CdSe QDs. Since the spatial separation $d_1 > d_2$, the increase of number of electrons is mainly responsible for the increase of the SPV, which can be very large, as seen in the calculated values of Fig. 6(b).

4. Conclusion

Experimental results of SPV with high sensitivity to spatial charge separation show that extraction of holes is supported by N3 dye molecules attached to CdSe QDs. This reduces the hole density in the QDs, increasing largely the number of electrons and producing the observed five-fold increase in SPV signal.

Acknowledgments

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