

Photosensitization of TiO₂ Layers with CdSe Quantum Dots: Correlation between Light Absorption and Photoinjection

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Injection of photoelectrons from colloidal CdSe quantum dots (QDs) capped by thioglycolic acid into compact ultrathin TiO₂ layers was investigated by direct detection of modulated charge separation with surface photovoltage spectroscopy. A size-dependent peak related to light absorption in the CdSe QDs and charge transfer to TiO₂ was observed for QDs of different sizes. Correlation between CdSe QDs absorption and photoelectron injection into TiO₂ has been demonstrated. Our results show that surface photovoltage spectroscopy is a valuable tool to determine the effectiveness of carrier injection from colloidal semiconductor QDs to electron transport materials in advanced solar cell configurations.

Semiconductor nanocrystals (colloidally synthesized quantum dots, QDs) have the potential to increase the efficiency of conversion of solar photons to electricity up to about 66%, overcoming the efficiency limit caused by carrier thermalization in the conventional solar cells.¹ Recent experiments reported quantum efficiency of carrier multiplication in QDs higher than 100%,^{2–4} due to impact ionization,⁵ reaching even seven excitons per absorbed high-energy photon in PbSe colloidal nanocrystals.⁴ In addition to photocarrier generation, separation of the electronic charges is needed to realize the photovoltaic energy conversion, i.e., the charge carriers generated in the QDs must be injected into separate electron and hole transport materials. Further, owing to the high absorption cross section and the broad size tunability of absorption spectra within the visible and near-infrared spectral range, QDs have been used as photosensitizers of polymers⁶ and fullerenes.⁷

One of the most likely configurations able to attain charge separation by injection is the dye-sensitized solar cell⁸ with semiconductor QDs as sensitizer instead of organic dyes. A nanocrystalline film of a wide band gap oxide semiconductor (i.e., TiO₂) is sensitized with QDs to visible light. Electrons generated in the QD are injected into the oxide semiconductor while holes are removed by a redox couple in an electrolyte solution or by a solid hole transport material. There are several studies of complete solar cells based in this concept,^{9–12} but it is quite complex to characterize the fundamental step of charge transfer from QDs to oxide semiconductor if the whole device is analyzed, and ultrafast techniques are needed to study it separately.^{10,13} Furthermore practical, stable configurations of cells require a solid, nonvolatile hole transport medium that usually enhances notably the recombination.¹⁴ Therefore, for the design of such devices it is very important to separately control the different steps of interfacial charge transfer of the photogenerated carriers.

In this work we describe a tool for the analysis of the effectiveness of electron injection from QDs into a metal oxide and subsequent back-transfer, by means of spectral-dependent surface photovoltage (SPV) measurements. We first report on optical absorption of differently sized CdSe QDs deposited on ultrathin TiO₂ layers, and then on the injection of electrons from the QDs into TiO₂ electrically measured by SPV. We show that the SPV signal conclusively indicates quantitative separation of photogenerated carriers to different media. We find an excellent correlation between the optical and the electrical determination of, respectively, light absorption and carrier injection characteristics.

SPV measurements detect illumination-induced charge separation.¹⁵ For the formation of a SPV signal charge generation must necessarily be accompanied by net spatial charge separation. SPV can be split up into two contributions: total amount of charge, and distance between the centers of charge of the positive and negative carriers.¹⁶ This makes SPV an outstanding tool to study the charge separation in photoinjection processes, being also sensitive to the sign of the transferred charge. QD films, where the QDs are tangentially interconnected in the 3D film, have been studied using the Kelvin probe technique as SPV method,^{17,18} but not the injection from QDs.

Previously we have applied the time-resolved SPV techniques to study the injection, recombination, and transport in ultrathin and nanoporous TiO₂ layers sensitized with N3 (Ru(dcbpyH₂)₂-(NCS)₂) dye molecules.^{19,20} In the present work we have investigated CdSe QDs of different sizes in a similar configuration, studying their spectral-dependent SPV. Figure 1 shows the sample configuration with the QD layer on top of a compact TiO₂ layer. The CdSe QDs are coated with thioglycolic acid, whose carboxylic groups are bound to the TiO₂ surface. For ultrathin layers the mean charge separation length and consequently the SPV signals increase with increasing layer thickness as indicated by arrows in Figure 1.^{16,20} The strategy of the application of the SPV spectroscopy is the following: electrons are injected from the QDs into the TiO₂ where they can diffuse. By this way the electrons are separated from the QDs in a well-

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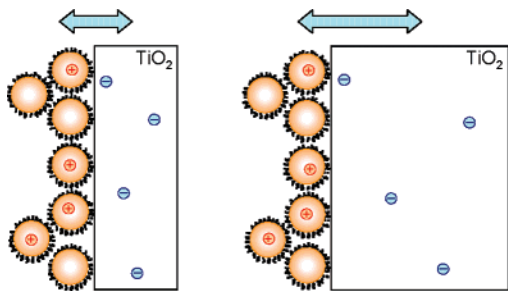


Figure 1. Sample configuration under charge separation. Photogenerated electrons are injected from CdSe QDs (shown as spheres, with thioglycolic acid as a capping layer) into a compact TiO₂ layer. The arrows mark the increased charge separation length with increasing thickness of the compact TiO₂ layer.

defined manner (electron transport in the TiO₂ controls the charge transport).^{19,20} Therefore, the TiO₂ layer is used as a probe. The sensitivity of the SPV measurements can be increased by increasing the thickness of the compact TiO₂ layer if the screening length is larger than the layer thickness.^{19,20}

Compact ultrathin TiO₂ layers were deposited on conductive SnO₂:F/glass by ion layer gas reaction technique. The thickness of the TiO₂ layer is adjusted by the number of dip cycles in a precursor salt solution. One dip cycle corresponds to the subsequent dipping of the sample into the precursor salt solution (0.03 M TiCl₄ in tetrahydrofuran), oxidation in a stream of aqueous NH₃ at 400 °C for 45 s, cooling in a N₂ stream for 40 s, rinsing in water, and drying in tetrahydrofuran. The thickness of the TiO₂ layer is about 1–2 nm for one dip cycle.

CdSe QDs capped with thioglycolic acid were synthesized in water as previously described.²¹ For the studies reported in this paper, we have used four aqueous samples of CdSe QDs, which we denote as QD1 (2.24 nm diameter, concentration in solution 0.26 mM), QD2 (2.36 nm diameter, concentration 0.26 mM), QD3 (2.48 nm diameter, concentration 0.19 mM), and QD4 (2.56 nm diameter, concentration 0.16 mM) further in text. Sizes and concentrations of samples were determined as described in ref 22. Absorption spectra of CdSe QD samples in solutions were measured with a Cary 50 spectrophotometer (Varian) and are shown in Figure 2a (dilution of original solutions 1:100). The absorption peak positions shift to longer wavelength with increasing sizes of QDs, as the quantum confinement weakens.

CdSe QDs were deposited on TiO₂ layers by dipping the substrates into colloidal solution of CdSe QD1–4 of the above indicated concentration. Spectra of optical density (OD) of the resulting films (Figure 2b) are strongly influenced by light scattering; thin lines in Figure 2b give the correction functions for light scattering. It should be remarked that the scattering of the substrate is not well defined from the point of view of a certain model and different approaches giving rather similar results for correction of scattering can be applied. Figure 2c shows the OD spectra corrected to light scattering by the substrate. The peak positions are red-shifted in comparison to the spectra in solution. The red shift is about 50 meV and practically the same for all samples. Possible reasons are the change of the dielectric constant of the QDs surrounding media, comparing QDs in water solution with QDs closed-packed layers on TiO₂, and dipole–dipole interactions of QDs in close-packed films, as discussed in detail in ref 23. Estimation of the number of deposited monolayers of CdSe QDs (taking into account that values of the OD presented in Figure 2c are for adsorption at two TiO₂ surfaces) provides a value of 1–2 monolayers.²²

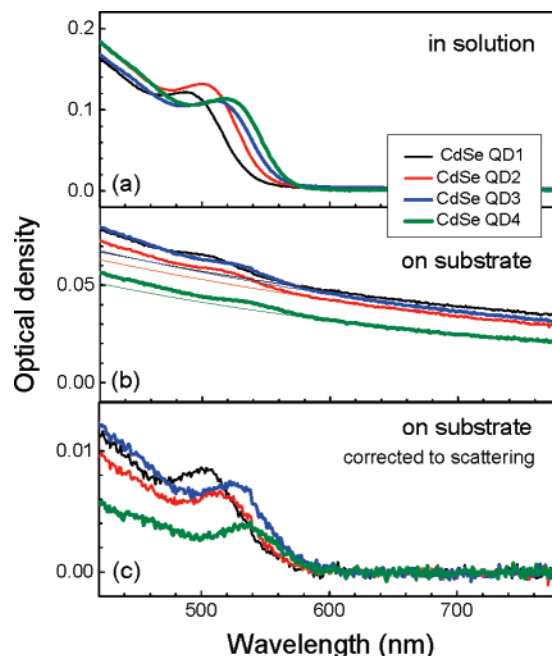


Figure 2. Optical density spectra of CdSe QDs 1–4 in solution (a) and on TiO₂ substrate without (b) and with (c) correction to scattering. Thin lines in (b) give the approximations of the scattered light.

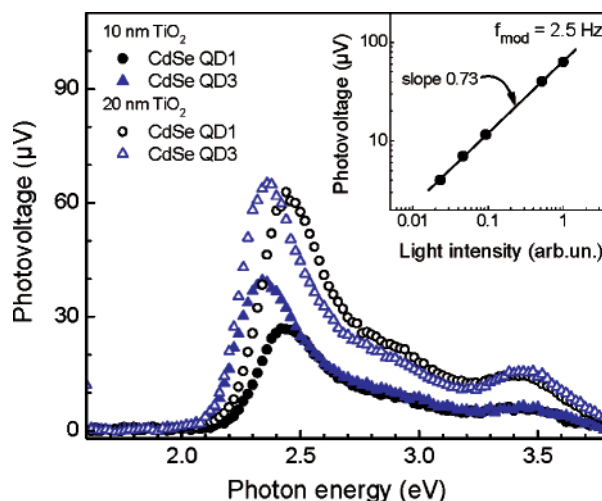


Figure 3. SPV for CdSe QD1 and CdSe QD3 deposited on 10 and 20 nm thick compact TiO₂ layers. The graph plots the direct measurement of SPV without any normalization to the light intensity.

Spectral-dependent SPV measurements were carried out in the arrangement of parallel-plate capacitor.²⁴ 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).

Figure 3 shows SPV spectra of TiO₂ layers with different thicknesses, sensitized with CdSe QD1 and QD3. The in-phase SPV signals are only considered, because no change in phase for QDs has been observed. All in-phase SPV signals have a positive sign implying that the surface has been positively charged under illumination due to injection of electrons into the TiO₂. The SPV spectra show two peaks related to light absorption in the QDs (maximum at 2.36 and 2.46 eV, for QD1 and QD3, respectively) and in the TiO₂ (sets on at 3.2 eV). We point out that these peak energies are equal to those of the OD

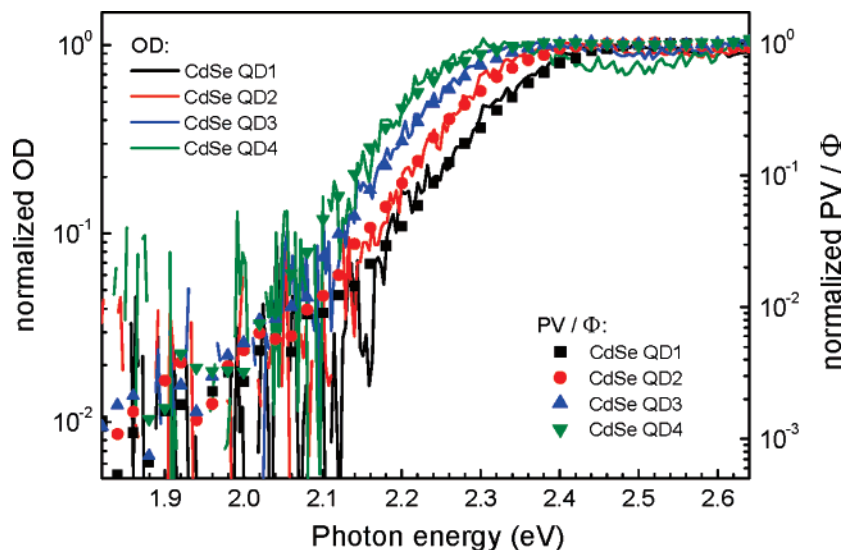


Figure 4. Normalized optical density (OD) of the CdSe QD1–4 on substrate and normalized surface photovoltage (SPV) spectra of the CdSe QD1–4 deposited on 20 nm thick TiO₂ compact layers. The power coefficient between the vertical scales of 0.7 has been introduced.

spectra obtained for the QDs deposited on the substrate and red-shifted by about 50 meV in comparison to the QDs in solution.

The SPV signal increases with increasing thickness of the compact TiO₂ layer due to the increase of the mean charge separation length.^{16,20} The observed increase of the SPV signals with increasing thickness of the TiO₂ layers gives direct evidence that injected mobile electrons dominate the mechanism of photovoltage formation in the investigated samples and that charge separation within the QD layer can be neglected.

The SPV signal increases with light intensity by a power law with a power coefficient of about 0.73 (inset of Figure 3). This shows that the transport in the TiO₂ layer and the relaxation of injected charge has to be considered for the modulated SPV signal. Accumulation of charge carriers in the TiO₂ layer causes a weaker increase of the SPV signal with light intensity. The slowest traps in TiO₂ do not follow the modulation frequency and lead to permanent negative charging of the compact TiO₂ layer even at relatively low light intensity.

For comparison with the OD the SPV spectra were normalized to the photon flux (Φ). The photon flux (in arbitrary units) was determined by measuring the light intensity with pyroelectric detector and dividing the signal by the photon energy. Both OD and PV/Φ were normalized to 1 at the maximum of absorption related to the QDs. Figure 4 shows the normalized OD and PV/Φ spectra as functions of photon energy in independent logarithmic scales. The logarithmic scales are aligned in such a way to each other that the normalized OD and PV/Φ spectra coincide in their shapes. The scales of the normalized OD and PV/Φ spectra are different by a power law with a power coefficient of about 0.7. This power coefficient is practically equal to the dependence of the PV signal on the intensity within the experimental error. Therefore, the change in the OD is equivalent to the change in the intensity. For the given scales the agreement between the normalized OD and PV/Φ spectra is very good. This means that the conditions for injection and recombination of injected electrons are very similar for all sizes of QDs analyzed.

To conclude, photoelectron injection from CdSe QDs into TiO₂ layers has been separately observed using spectral SPV measurements, showing a direct correlation between QD absorption and subsequent photoelectron injection into the TiO₂

layer. It has been shown that the injection and the recombination of injected electrons are similar for all sizes of QDs analyzed. These results indicate that SPV spectroscopy constitutes a valuable tool for the study of the injection efficiency of different QD configurations and its implication in the development of new solar cell devices. We also stress that it is possible to obtain detailed information of the relative importance of the different steps that form the spectral SPV response of QDs, namely, carrier generation by light absorption, carrier injection, and recombination, by analysis of time-resolved SPV spectra, as shown previously in our work on dye-sensitized TiO₂ layers.^{19,20} This research is in progress.

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