

Light Energy Conversion by Mesoscopic PbS Quantum Dots/TiO₂ Heterojunction Solar Cells

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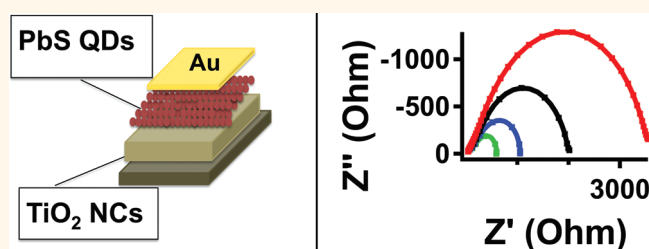
Quantum dots (QDs) have attracted great research attention due to their attractive opto-electronic properties, in particular large optical cross sections and tunable band gap due to the quantum size effect.^{1–6} QDs have been intensively investigated in a variety of photovoltaic device architectures, including nanocrystal (NC)–polymer hybrid solar cells, NC–Schottky solar cells, NC–sensitized titanium dioxide (TiO₂) solar cells, and NC hybrid bilayer solar cells.^{7–18}

Semiconductor QDs belonging to group IV–VI such as PbS and PbSe are known as good absorbers in the visible and in the near IR regime. They have high dielectric constants and a small electron and hole effective mass, corresponding to excitons with a relatively large effective Bohr radius (18 and 46 nm, respectively).^{19–23} Interband optical studies of PbS and PbSe QDs reveal band-edge excitonic transitions tuned between 0.3 and 2 eV, relatively large ground state cross section of absorption ($\sim 10^{-15}$ cm²), long excitonic lifetime (*ca.* 200–800 ns), and exceptionally high quantum efficiency of the luminescence (80%).²⁴

Recent reports of PbS and PbSe QD Schottky solar cells show power conversion efficiencies (PCEs) of 1.8–2.1% under AM1.5G illumination.^{7,25,8} These results suggest that PbS and PbSe QDs films exhibit p-type semiconductor behavior after thiol treatment and form Schottky junctions when contacted with metals.

While QD Schottky solar cells reach high short circuit current densities (J_{sc}) their open circuit voltage (V_{oc}) remains low. For example a V_{oc} of ~ 0.05 V was obtained in a PbSe QD Schottky solar cell with an Au contact, due to the high work function of the Au.⁸ As a result air sensitive contacts of Ca or Mg metal coated with Al were required to increase the

ABSTRACT



Solid state PbS quantum dots (QDs)/TiO₂ heterojunction solar cells were produced by depositing PbS QDs on a 500 nm thick mesoscopic TiO₂ films using layer-by-layer deposition. Importantly, the PbS QDs act here as photosensitizers and at the same time as hole conductors. The PbS QDs/TiO₂ device produces a short circuit photocurrent (J_{sc}) of 13.04 mA/cm², an open circuit photovoltage (V_{oc}) of 0.55 V and a fill factor (FF) of 0.49, corresponding to a light to electric power conversion efficiency (η) of 3.5% under AM1.5 illumination. The electronic processes occurring in this device were investigated by transient photocurrent and photovoltage measurements as well as impedance spectroscopy in the dark and under illumination. The investigations showed a high resistivity for the QD/metal back contact, which reduces drastically under illumination. EIS also indicated a shift of the depletion layer capacitance under illumination related to the change of the dipole at this interface.

KEYWORDS: quantum dots · photovoltaic · impedance · transient

V_{oc} of the Schottky junction (0.2–0.3 V of V_{oc}).⁸ Further increase in the QD Schottky solar cell efficiency was reported lately reaching a V_{oc} of 0.51 V by introducing an Al/LiF contact.²⁶

Recently Alivisatos and co-workers have developed Schottky solar cells incorporating PbS_xSe_{1-x} ternary QDs, in order to improve the V_{oc} and J_{sc} . These ternary Schottky solar cells yield PCEs of 3.3% under AM 1.5 illumination.⁹ In addition two recent works employ a heterojunction device architecture of placing oxide NCs as a thin spacer layer between the QDs and the FTO.^{27,28}

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The present work employs PbS QDs as light harvesters in conjunction with films composed of 18 nm-sized TiO₂ nanocrystals containing both meso- and macropores. The PbS acts at the same time as a hole conductor, rendering superfluous the use of an additional p-type material for transporting positive charge carriers. Strikingly, this very simple PbS (QD)/TiO₂ heterojunction solar cell prepared and measured in ambient air achieves remarkable photovoltaic performance, with an impressive short circuit photocurrent of 13.04 mA/cm² and a light to electric power conversion efficiency of 3.5% under AM1.5 illumination using a metal mask with an aperture area of 0.12 cm². EIS as well as transient photocurrent and photovoltage measurements are used here for the first time to unravel the mechanism of photoelectric conversion occurring in these very interesting new photovoltaic energy conversion systems.

RESULTS AND DISCUSSION

Device Performance. Figure 1A shows a scheme of the device architecture. The bottom layer is composed of compact and mesoporous TiO₂ layers acting as electron collectors. Light is absorbed by the 1.39 eV band gap PbS QDs with Au as the top contact without additional electron blocking layers. The energy level diagram of the solid state QDs solar cell (ss-QDs SC) is shown in Figure 1B; the conduction and valence bands of the 1.39 eV PbS QDs permit electron injection and hole transportation to the TiO₂ and the gold, respectively. Figure 1C shows the cross section of the device where the different layers can be observed. The PbS QDs form a NC layer on top of the TiO₂ film, very few of the QDs penetrating into the porous network of the TiO₂ film as can be seen by the energy-dispersive X-ray spectroscopy (EDX) measurements in Figure 1D.

Figure 2 presents the photovoltaic results obtained for 1.39 eV PbS QDs. We obtain the best performance with quantum dots having a diameter of about 3.2 nm (1st excitonic peak at 895 nm, $E_g = 1.39$ eV). These PbS quantum dots produce an open-circuit voltage of 0.548 V, a short circuit current density of 13.04 mA cm⁻², and a fill factor of 49% corresponding to a power conversion efficiency of 3.5% under AM1.5. The PCE at a light intensity of 10 mW/cm² was 4.4% with a V_{oc} of 0.47 V, a fill factor of 49.5% and a J_{sc} of 1.9 mA/cm². The photocurrent density at full sun is significantly lower than the extrapolated value of 19 mA/cm² expected for a device with linear response to light intensity. This is due to a charge carrier collection problem as will be shown later by the impedance experiments.

The open circuit voltage, fill factor, and photocurrent decrease with increasing the QDs size, however interparticle electron transfer is facilitated in films made of the larger QDs, because for a given film

thickness there is a smaller number of particle boundaries to cross until the electrons arrive at the TiO₂. According to Matt Law and co-workers,²⁹ the mobility of electrons and holes increase by 1–2 orders of magnitude with increasing QD diameter. The size-mobility trends seem to be driven primarily by the smaller number of hops required for transport through arrays of larger QDs but may also reflect a systematic decrease in the depth of trap states with decreasing QD band gap. These authors also observed that the carrier mobility is independent of the polydispersity of the QD samples. This fact is rationalized in terms of the smaller-band gap, that is, larger diameter QDs carrying most of the current in these QD solids, if they can form a percolation network.

The number of QD layers deposit on the TiO₂ plays an important role for the photovoltaic performance. If the QD layer is too thick, the collection of photogenerated charge carriers will be incomplete, while too thin QD layers show poor light harvesting. It appears that depositing 12 layers of QDs as described in the Experimental Section is a reasonable compromise to satisfy both the light absorption and carrier collection criteria.

The incident photon to current conversion efficiency (IPCE), or external quantum efficiency, specifies the ratio of extracted electrons to incident photons at a given wavelength. The IPCE spectrum and the PbS QDs absorption spectrum (Figure 3A) are plotted as a function of wavelength of the light. Figure 3B shows the absorption spectrum of the PbS QDs deposited on the TiO₂ film. The solid state QDs cell shows a good response from the visible through the near-infrared (NIR), the IPCE reaching its maximum of 80% at 470 nm. Photons of these wavelengths are converted most efficiently as they are absorbed by PbS particles located close to the TiO₂ interface. A wide size distribution of the QDs can be seen in the IPCE spectrum. The excitonic peak of the PbS QDs can be observed at 970 nm corresponding to an IPCE of 14%, this peak was red-shifted as a result of the device preparation. The peak at 810 nm can be assigned to an optical interference fringe as a result of optical mode in this thin film solar cell as described previously by M. Law *et al.*³⁰ Integration of the IPCE spectrum over the AM1.5 solar emission yields a photocurrent density of 15 mA/cm² in reasonable agreement with the measured value.

EIS and Transient Photovoltage and Photocurrent Decay.

Two different small perturbation measurement techniques have been applied to analyze the internal electrical parameters of the QD/TiO₂ solar cell, that is, electrochemical impedance spectroscopy (EIS) and the photocurrent and photovoltage decay technique developed by O'Regan *et al.*⁴⁴ The latter technique was applied to crosscheck the EIS results obtained under illumination since the EIS measurements are made

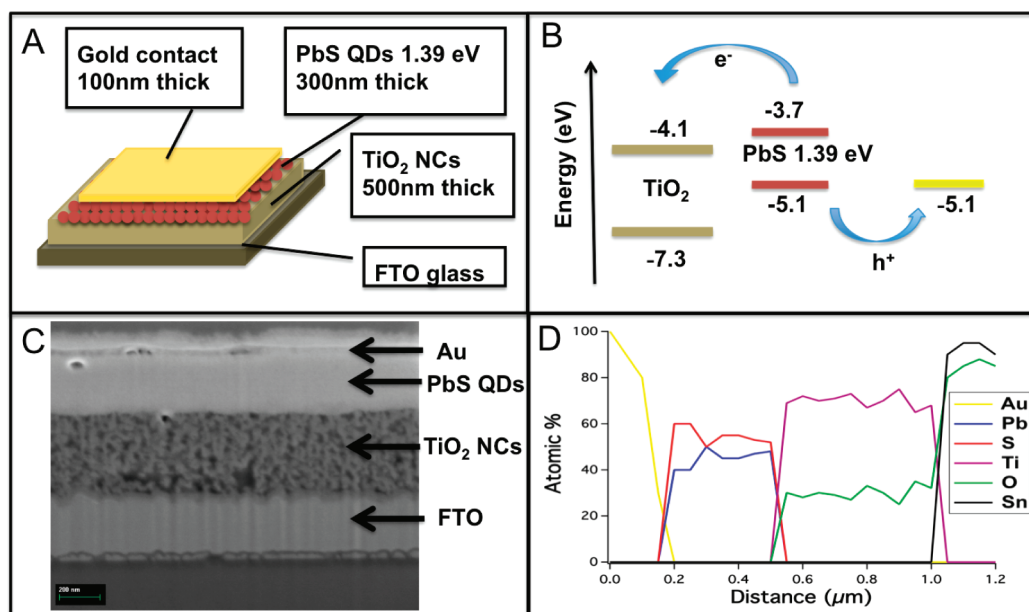


Figure 1. (A) The architecture of the PbS(QD)/mesoscopic TiO₂ photovoltaic device; the light is incident through the glass. (B) Energy level diagram of the solar cell for PbS quantum dots of 3.2 nm size. (C) Cross sectional HR-SEM of the photovoltaic device. It can be seen that the PbS QDs form a nanocrystalline layer on top of the TiO₂ film with very few of the QDs penetrating into the porous network of the TiO₂ film. The scale bar is 200 nm. (D) EDX measurement. The elemental distribution through the cross section of the device can be observed.

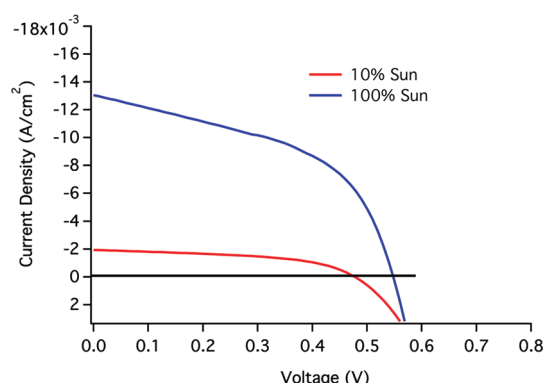


Figure 2. Measured $J-V$ characteristics for the solid state PbS QDs device. An aperture area of 0.12 cm² was placed over the device. The horizontal line parallel to the voltage axis is for guiding your eye.

over time periods of many hours, which could affect the properties of the QD/TiO₂ solar cell.

Few investigations on the internal electrical parameters of this type of QD/metal oxide heterojunction devices can be found in the literature (Beard³¹ and Sargent²⁸). Beard *et al.* investigated PbS/ZnO nanocrystal solar cells on the basis of a two-diode model, one diode describing the TiO₂/QD heterojunction interface whereby the other diode describes a Schottky junction at the QD/metal contact. The authors observed a “roll over” and a “cross over” effect in the JV characteristic of their devices commonly observed also in other systems like CdTe thin film³² or CuInS₂–TiO₂ heterojunction solar cells.³³ These effects appear depending on QD size and back contact material, which control the formation of a back contact hole-injection

barrier due to alignment of the Fermi level of the hole conductor with that of the metal contact.

The present work employs PbS QDs with an energy gap of 1.39 eV and gold as contacting material, which showed only very few cases of cross over in the $J-V$ characteristic. These results are in accordance with the observations of Beard *et al.*³¹ for this QDs size contacted to gold. However roll over effects may appear at higher forward bias voltages than those applied in the present study.

The transient measurements determined the current and voltage decay at a given bias potential or current, respectively. The voltage decay is in this case only dominated by recombination and thus gives direct access to the electron lifetime. The lifetime of the current decay is a combination of electron transport time (τ_{trans}) and electron lifetime (τ_e) and enables with the τ_e of the voltage decay the calculation of the transport time ($1/\tau_{signal} = 1/\tau_{trans} - 1/\tau_e$).⁴⁴

Figure 4 compares the electron lifetimes and the electron transport times measured by the time-resolved perturbation techniques. We can observe an initially constant electron lifetime of about 5 ms which decreases from 0.3 V on. The transport time is at low bias potentials nearly 10 times lower, securing >90% charge collection. It is also constant up to 0.3 V and starts then to increase. Similar shapes of the lifetime and transport time could be observed also for solid state dye sensitized solar cells.^{45,34}

The Nyquist plots of an EIS measurement are presented in Figure 5. On closer examination of Figure 5B three different features can be observed, a high frequency

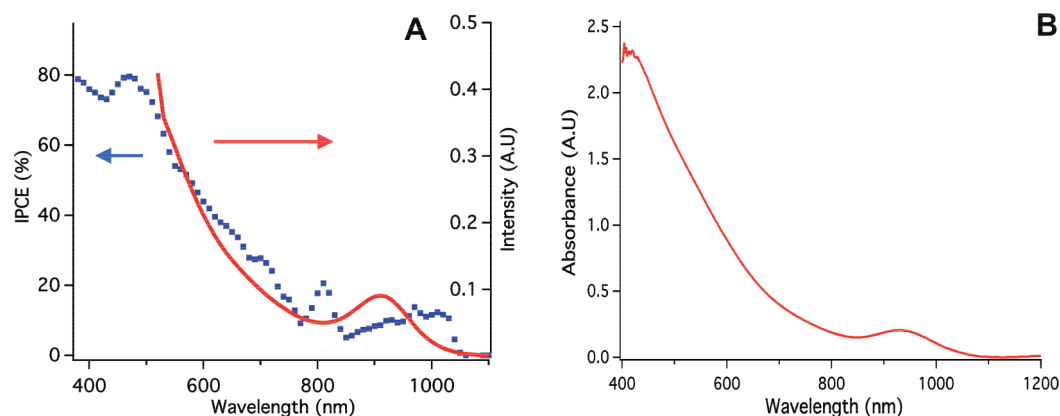


Figure 3. (A) Spectral response curves of the photocurrent for the solid state PbS QDs device. The external quantum efficiency or incident photon to current conversion efficiency is plotted as a function of wavelength of the incident light (blue) and the absorbance spectra of the PbS QDs measured in solution of tetrachloroethylene at a low concentration of approximately 3 mg/mL. (B) Absorption spectrum of the PbS QDs deposited on the TiO₂ film.

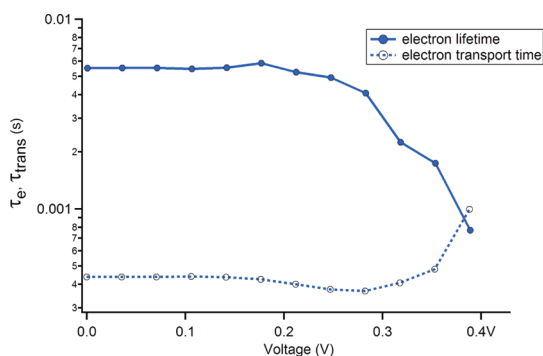


Figure 4. Comparison of electron lifetimes and the electron transport times measured by time-resolved perturbation techniques at 50% sun.

arc (frequency range ~ 1 MHz to 100 kHz), whose size depends strongly on the applied bias potential, an intermediate element visible at medium to higher forward bias (frequency range ~ 100 kHz to several kHz) and a low frequency arc (frequency range \sim kHz to mHz). Owing to lack of an overall model describing all processes and interfaces in the device, we focused on the high and the low frequency response of the EIS. Both elements in these frequency ranges can be separately fitted by a simple RC element (with the R and C in parallel). Surely the low frequency response can be assigned to the TiO₂/PbS interface since the resistance of this element mirrors the observed dark or photocurrent, respectively. The high frequency response can be either related to the Au/QDs interface²⁸ or to the transport in the QD layer (similar to the transport in a polymer like P3HT³⁵). We adopt in this publication the "classical" interpretation used also by Sargent *et al.*²⁸ which assumes full or nearly full depletion in the QD layer and attributes the high frequency response to the Au/QD interface. Further investigations are conducted for clarification.

The assignment of the EIS response in the medium frequency range requires further analysis. At this stage

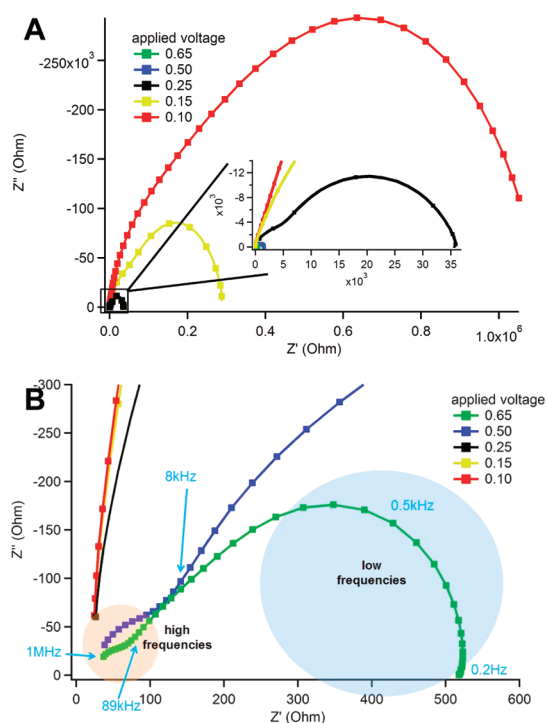


Figure 5. Nyquist plots derived from the EIS measurements in the dark at different bias potentials with the indication of the frequencies employed (A) at low bias potentials and (B) at high forward bias.

it is clear that the resistance associated with this circuit element decreases with increasing forward bias.

Figure 6A presents results from the fitting of the impedance measurements in the dark and under illumination for the low frequency element.

Taking a closer look at the low frequency RC element in the dark we can observe the following: The low frequency capacitance (C_{LF}) at potentials up to 0.3 V is nearly constant and increases slowly with forward bias. At about 300 mV the capacitance starts to increase to reach a plateau at about 500 mV. This capacitance originates from the depletion layer capacitance at the QD/TiO₂

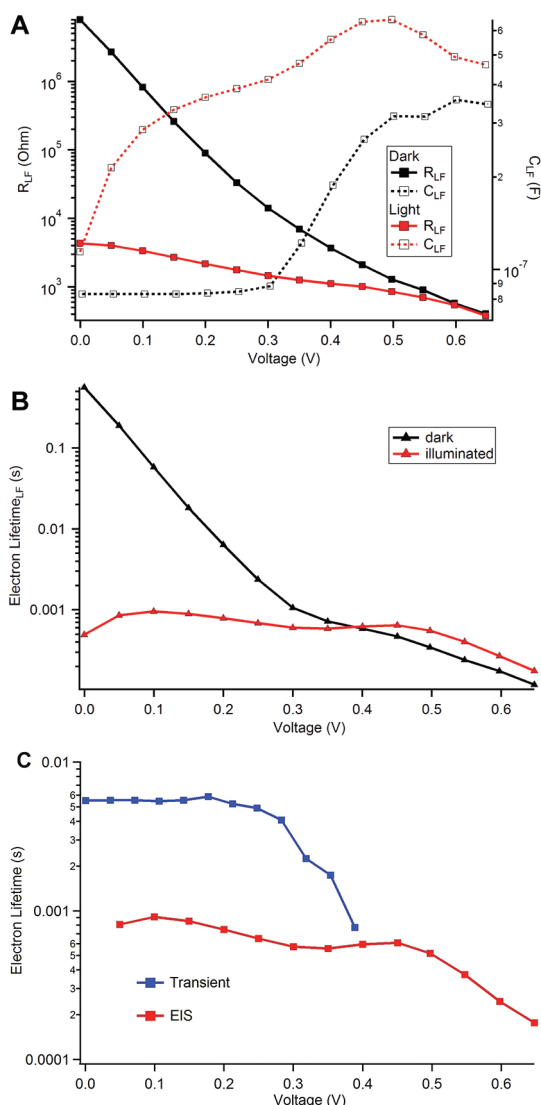


Figure 6. Results of the EIS measurements in the dark and under illumination for the low frequency response (A) and the calculated lifetimes (B); the lifetime under illumination by transient measurements and EIS (C).

interface similarly to a p–n junction.²⁸ A Mott–Schottky plot ($1/C^2$) of this capacitance yields the built in potential of this junction (~ 440 mV). As also observed by Sargent *et al.*³⁶ this measured built in potential is slightly lower than the actual observed photovoltage although the deviation in our devices is higher. The recombination resistance (R_{LF}) decreases from 0 V on showing ineffective blocking and therefore a shunt which reduces the FF and therefore the overall efficiency of the device.

Under illumination the capacitance rises earlier (about 200 mV) then in the dark to reach its plateau at about 300 mV bias potential. Such a displacement of the capacitance under illumination could also be observed for organic bulk heterojunction solar cells. The reason is so far not fully understood but could be due to the accumulation of minority charge carriers at slow reacting surface states. This can induce a change at the ionic dipole layer present at the interface and leads

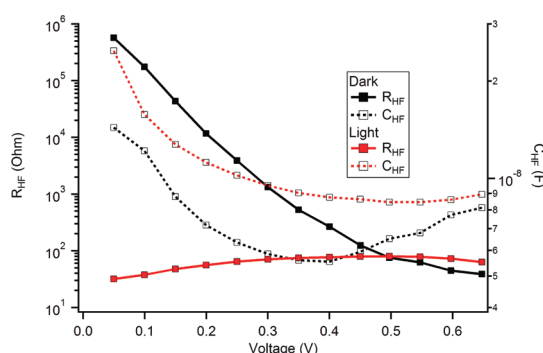


Figure 7. Resistance and capacitance of the high frequency RC element from EIS in the dark and under illumination.

consequently to an unpinning and shifts of the bands.^{37,38} Though if we compare the slope of the plot of $1/(C_{LF})^2$ in the dark and the slope of the illuminated sample, we observe the same slope indicating no change in doping.

The determined recombination resistance at the interface is as expected drastically reduced under illumination. The recombination at this interface is fast. We can calculate the effective lifetimes (Figure 6B) by the product of R_{LF} and the C_{LF} and observe the strong change of lifetime from dark to illumination conditions.³⁹ The lifetime under illumination itself is relatively constant from 0 to 450 mV, reducing with increasing dark current. Comparing the electron lifetime determined by transient techniques and the impedance (Figure 6C) one can see that the lifetime determined by the latter is shorter than by the former technique. The reason is the change of the device performance under continued illumination leading to higher V_{oc} and lower J_{sc} and FF (for an explanation see the following).

In Figure 7 one can observe the behavior of the high frequency resistance R_{HF} and capacitance C_{HF} attributed to the Au/PbS QDs interface. The contact between the gold and the QDs should match by its work function and Fermi level yielding an ohmic contact. Though what we observe for this interface in the dark is a strongly potential-dependent behavior indicating that this interface is more complicated than expected as also observed by Beard *et al.*³¹ The band alignment at this interface shows a more Schottky-type character (which can be due to surface states) in the dark⁴⁰ resulting in an unfavorable band bending and therefore in a partial blocking of the charge carriers at this contact. This is reflected in the high R_{HF} . The situation changes drastically under illumination. The R_{HF} under illumination reduced near short circuit conditions several decades and is nearly constant over the whole potential range (around 10 ohm cm^2). Although the resistance at this interface reduced due to illumination it still represents part of the overall series resistance of the device, thus reducing the FF.

In conclusion we can say that although still a lot of unknown effects in these devices appear and more experiments have to be performed to finally understand the processes taking place, the EIS and transient measurements offered a deeper view inside the TiO_2/PbS heterojunction solar cell.

The increase in the V_{oc} after longer illumination time can be explained in terms of a photoinduced proton consumption reaction, which was revealed by FTIR spectroscopy as shown in Figure 8. The FTIR data presented include a reference spectrum for MPA methanol solution. The rest of the data are FTIR spectra of MPA attached to the PbS (QDs) / TiO_2 films without the gold contact measured at different illumination times.

The C=O mode of the carboxylic acid group is assigned to the band at 1703 cm^{-1} , and the CO_2^- asymmetric and symmetric stretching modes of PbS and TiO_2 coordinated carboxylate group appear at 1520 and 1400 cm^{-1} respectively.⁴¹ The intensity of those bands is changed during illumination of the PbS (QD)/ TiO_2 film. The C=O mode decreases, while the CO_2^- asymmetric and symmetric stretching modes increase in intensity. The asymmetric stretching mode also does not appear in the MPA solution spectrum.

These changes in peak intensity suggest that carboxylic acid groups are converted to carboxylate groups under illumination of the device. As the environment becomes less acidic due to proton consumption the conduction band of the TiO_2 shifts upward and hence the V_{oc} increases.⁴² An upward shift of the conduction band edge of the metal oxide leads to a barrier formed in the depletion region in between the QDs to the TiO_2 , which should ultimately reduce the photocurrent as is indeed observed. While the detailed mechanism for the light induced proton consumption remains to be unraveled it is likely to involve photocorrosion of PbS, producing sulfur and excess conduction band electron that could reduce protons to hydrogen.

FTIR spectra over a wider frequency range are shown in the inset of Figure 8. The solution spectrum exhibits CH_2 stretching vibrations of MPA at 2900 cm^{-1}

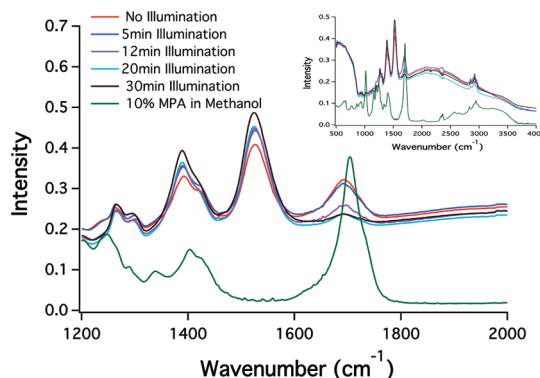


Figure 8. FTIR spectra of the MPA solution in methanol and the solid state QD solar cell without the gold contact under different illumination times. Inset: the complete measured range of the FTIR spectra.

and the S—H stretching band at 2550 cm^{-1} in the MPA spectrum. The latter disappears once the MPA is associated with the PbS QDs. There are two absorption bands appearing in the MPA spectrum that are due to the MPA molecules forming dimers in the liquid state. These are the bands at 2669 and 941 cm^{-1} , which are ascribed to the O—H stretching and out-of-plane bending modes, respectively.⁴¹

CONCLUSIONS

The salient features of PbS QD/ TiO_2 solar cells were examined to elucidate the principles of operation of these intriguing new mesoscopic devices. These cells are composed of a layer of PbS quantum dots deposited onto a mesoporous TiO_2 , a transparent conducting oxide, and gold forming the front and back contact of the device, respectively. The cells give a J_{sc} of 13.04 mA/cm^2 , a V_{oc} of 0.548 V , a FF of 0.49 corresponding to a solar to electric power conversion efficiency (η) of 3.5% under AM1.5 light intensity. The electronic properties of the cell were scrutinized by electrochemical impedance spectroscopy and transient photocurrent and photovoltage measurements. Though not all features of these devices could be understood so far and more investigations have to follow, a deeper understanding of the internal processes could be achieved.

EXPERIMENTAL SECTION

Methods and Device Fabrication. Colloidal PbS QDs were synthesized according to the method reported by Hines *et al.*²⁰ As-prepared PbS QDs were capped with oleic acid (OA). The first excitonic absorption bands of QDs were tuned by controlling reaction temperatures and the concentrations of precursors. The PbS QDs were stored in nitrogen glovebox.

During device fabrication, a thin blocking layer of compact TiO_2 was first deposited by spray pyrolysis onto a precleaned FTO glass substrate using a solution of titanium diisopropoxide bis(acetylacetonate) in ethanol as precursor. Subsequently, a porous TiO_2 layer was deposited by doctor blading from a dilute aqueous paste containing a mixture of 18 nm sized TiO_2

particles and 500 nm sized polystyrene beads. The polystyrene was burned during the subsequent sintering step performed for 30 min at $450\text{ }^\circ\text{C}$ producing macropores of 200 nm pore size. In addition, the $500 \pm 50\text{ nm}$ thick titania film contained 23 nm -sized mesopores generated from the TiO_2 nanoparticle network.⁴³

The procedure for the deposition of the PbS QDs film is similar to the one reported by Sarjent *et al.*²⁸ with several changes. The PbS QDs were subsequently deposited layer by layer on the porous TiO_2 film by spin coating a 50 mg mL^{-1} solution in octane under ambient atmosphere. Each layer was cast at a spinning rate of 2500 rpm applied for 10 s and treated thereafter briefly with a solution of 10% 3-mercaptopropionic acid (MPA, $\geq 99.0\%$ from Sigma Aldrich) in methanol using again

2500 rpm rotational speed for 10 s. This treatment displaced the oleate ligand completely and rendered the QD insoluble, which allowed thin films of 300 nm thicknesses to be created using 12 successive deposition cycles. Each layer was rinsed with anhydrous methanol and anhydrous octane (purchased from Sigma Aldrich) to remove excess of MPA and PbS QDs. Finally, a gold back contact of ca. 100 nm thick was deposited by evaporation through a shadow mask. The device was then completed by encapsulation in argon atmosphere. The encapsulation of the device was made by placing a 2 mm glass on top of the active area of the device using a piece of hot melt Surlyn (25 μ m thick) as a spacer. After encapsulation the device was stable under air.

The cell architecture and a cross section of the device measured by scanning electron microscopy are shown in Figure 1 panels A and C, respectively. The cross section of the device was measured by Zeiss Jemini FEG-SEM, using 1.8 kV with a magnification of 120KX. The SEM picture confirms that PbS QDs form an overlayer on top of the macroporous TiO₂ film. Only a few particles penetrate in the pores of the oxide.

A Cary 5000 (Varian) spectrophotometer was used to obtain the absorbance of the PbS QDs.

Photovoltaic Characterization. Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 450 W xenon lamp (model no. 81172, Oriol). Its power output was adjusted to match AM 1.5 global sunlight (100 mW/cm²) by using a reference Si photodiode equipped with an IR-cutoff filter (KG-3, Schott) in order to reduce the mismatch between the simulated light and AM 1.5 (in the region of 350–750 nm) to less than 2% with measurements verified at two PV calibration laboratories [ISE (Germany), NREL (USA)]. *I*–*V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. A similar data acquisition system was used to determine the monochromatic incident photon-to-electric current conversion efficiency. Under full computer control, light from a 300 W xenon lamp (ILC Technology, U.S.A.) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., U.K.) onto the photovoltaic cell under test. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined by $\text{IPCE}(\lambda) = 1240(J_{\text{sc}}/\lambda\phi)$, where λ is the wavelength, J_{sc} is short-circuit photocurrent density (mA cm⁻²), and ϕ is the incident radiative flux (mW cm⁻²). Photovoltaic performance was measured by using a metal mask with an aperture area of 0.12 cm².

Transient Photocurrent and Photovoltage Decay Measurements. White light bias was generated by an array of diodes (Lumiled model LXHL-NWE8 whiterstar) in combination with red light pulsed diodes (LXHLND98 redstar, 0.2 s square pulse width, 100 ns rise and fall time) for the perturbation excitation, controlled by a fast solid-state switch. The voltage dynamics were recorded via a Keithley 2602 source-meter. The light source for the perturbation was set to a low light intensity to achieve mono-exponential voltage decay kinetics. The voltage decay measurements were performed from zero current (V_{oc}) over a range of fixed currents intervals on the photocurrent–voltage curve to mimic the *I*–*V* characteristic of the device while measuring the transients. Small perturbation transient photocurrent measurements were performed in a similar way to the open-circuit voltage decay measurements but here holding a fixed potential while measuring the photocurrent transients. To check on the RC limitation of the measurement setup the pulse charge rate and the voltage decay rate were compared and showed no limitation.^{44,45}

Electrochemical Impedance Measurements (EIS). Impedance measurements employed an Autolab PGSTAT30 (EcoChemie B.V., Utrecht, Netherlands) over a frequency range from 1 MHz down to 0.1 Hz at bias potentials between 0 and 0.6 V (with a 10 mV sinusoidal AC perturbation). For the impedance measurements under illumination a LED (Lumiled model LXHL-NWE8 whiterstar) was used. All measurements were done at 20 °C. The resulting impedance spectra were analyzed with Z-view software (v2.8b, Scribner Associates Inc.).

Fourier Transform Infrared (FTIR) Measurements. FTIR measurements were performed with a Digilab FTS 7000 series spectrometer, using 64 scans with a 2 cm⁻¹ resolution step. Samples

were prepared as discussed in methods and device fabrication except that no gold was evaporated. The 10% MPA in methanol solution was measured by placing a drop on the FTIR diamond.

Conflict of Interest: The authors declare no competing financial interest.

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Supporting Information Available: Bode plots in the dark and under illumination. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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