Activating Carrier Multiplication in PbSe Quantum Dot Solids by Infilling with Atomic Layer Deposition

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Supporting Information

ABSTRACT: Carrier multiplication—the generation of multiple electron–hole pairs by a single photon—is currently of great interest for the development of highly efficient photovoltaics. We study the effects of infilling PbSe quantum-dot solids with metal oxides by atomic layer deposition on carrier multiplication. Using time-resolved microwave conductivity measurements, we find, for the first time, that carrier multiplication occurs in 1,2-ethanedithiol-linked PbSe quantum-dot solids infilled with Al₂O₃ or Al₂O₃/ZnO, while it is negligible or absent in noninfilled films. The carrier-multiplication efficiency of the infilled quantum-dot solids is close to that of solution-dispersed PbSe quantum dots, and not significantly limited by Auger recombination.

Non-Infilled

Infilled by ALD

C olloidal semiconductor quantum dots (QDs) currently receive a great deal of interest for applications in photovoltaics. 1−3 This is due to their tunable band gap, cheap solution-based synthesis and processing, and, most promisingly, the occurrence of carrier multiplication (CM; also called multiple exciton generation), 4−9 where the absorption of one photon of sufficiently high energy results in the generation of multiple electron–hole pairs of lower energy. In the presence of CM, the optimal band gap for harvesting the solar spectrum shifts from 1.34 eV (Shockley–Queisser limit: no CM) to 0.7 eV (ideal CM). 5,9,10 Lead chalcogenide QDs have a band gap tunable over this range, 11 which makes them ideal candidates for utilizing CM in photovoltaics. CM has been observed for PbSe QDs in dispersion. 6,12−14

In thin-film QD solids for photovoltaic applications, QDs are electronically coupled by replacing the bulky passivating ligands used during synthesis by shorter molecules. In this way, band gap tunability is maintained, and charge mobility is increased due to the decreased width of inter-QD tunneling barriers. 15,16 Applications suffer from the rapid degradation in air of such films because the short linker molecules provide almost no protection against oxidation. 17 Recently, infilling the interstitial space of 1,2-ethanedithiol-linked PbSe (PbSe-EDT) QD solids with inorganic matrices (Al₂O₃ or Al₂O₃ followed by ZnO) by atomic layer deposition (ALD) was shown to produce air-stable films by suppressing oxidative and photo-thermal degradation of the QDs. 17,18 Furthermore, infilling PbSe-EDT QD solids enhances charge mobility by up to an order of magnitude, attributed to a passivation of charge trap states. 18

Here we investigate the yield of multiple free electrons and holes that result from CM in PbSe-EDT QD solids infilled with Al₂O₃ or Al₂O₃ followed by ZnO. Note that this multiple free charge generation (MFCG) yield is not necessarily the same as the CM yield. CM leads to the generation of multiple electrons and holes that initially reside in close proximity. These charges can undergo Auger recombination unless they quickly move away from each other. The MFCG yield is determined by the extent to which the latter occurs. MFCG thus requires both CM and a subsequent escape of charges from Auger recombination. We find that ALD infilling activates the MFCG efficiency: from weak or absent before infilling, due to negligible CM, 19−21 to approaching the intrinsic CM efficiency reported for isolated PbSe QDs in dispersion. 4 Infilling is thus an important technique for the realization of cheap, robust CM-enhanced photovoltaics.

Three infilled PbSe-EDT QD solids were prepared (6.3 nm QD diameter; see Methods section). One QD solid was infilled with Al₂O₃, a second with Al₂O₃(1 nm)/ZnO(5 nm) (i.e., 1 nm of Al₂O₃ followed by 5 nm of ZnO), and a third with Al₂O₃(3 nm)/ZnO(5 nm). The films were then overcoated with 20−30 nm Al₂O₃ to guarantee their stability in air. The resulting QD solids have a band gap energy of 0.64 eV (λ = 1930 nm) and retain quantum confinement on infilling (cf. Figure S1, Supporting Information). A noninfilled PbSe-EDT QD solid (6.0 nm QD diameter) was studied as a control.

Received: April 8, 2013
Accepted: May 8, 2013
The charge mobility of the QD solids was determined by time-resolved microwave conductivity measurements (TRMC; see Methods), similar to a previous study on films of PbSe QDs with 1,2-ethanediame ligands. The samples were mounted in a microwave cavity (8.5 GHz resonance frequency) and excited with a 3 ns laser pulse of tunable wavelength. Photogeneration of mobile charge carriers leads to absorption of microwave power. The latter can be related to the product of the mobility $\mu$ and yield of mobile charge carriers per incident photon $\eta$, summed for photogenerated electrons and holes: $\eta_i(t)\mu_e + \eta_h(t)\mu_h$; see Methods. Figure 1 shows typical microwave conductivity transients for photoexcitation of the Al$_2$O$_3$-infiltrated PbSe-EDT QD solid at varying excitation density. The signal initially rises due to the generation of mobile charges during the laser pulse, reaches a maximum at time $t = t_{max}$ and subsequently decays due to first-order processes or higher-order Auger recombination of electrons and holes. Auger recombination becomes faster at higher excitation density, as expected, and it becomes negligible for photoexcitation densities below $2 \times 10^{-4}$ photons per QD (see Methods). The decay kinetics are independent of photoexcitation energy at low excitation density. The noninfiltrated PbSe-EDT QD solid behaves similarly (data not shown).

The yield of mobile charge carriers per incident photon, $\eta$, is proportional to the magnitude of the transients as shown in Figure 1. The latter was determined at sufficiently low excitation density so that nongenerate charge recombination does not play a role within the 3 ns time resolution. The results are displayed in Figure 2 (red symbols, left axis) together with the fraction of absorbed photons, $F_A$ (black curve, right axis), as a function of photon energy. The curve of $\eta$ follows the shape of the low-energy absorption peak (due to the 1S$_0$1S$_0$ transition), implying a constant quantum yield of free charges per absorbed photon, $\phi \equiv \eta/F_A$ for this transition. At higher photon energies $\eta$ increases faster than the fraction of absorbed photons, $F_A$, implying an increase of the quantum yield, $\phi$.

Figure 3 shows the quantum yield, $\phi$, for the Al$_2$O$_3$-infiltrated PbSe-EDT QD solid, normalized to the mean value in the interval (1.75–2.70)$E_g$. Photogeneration of the 1S$_0$1S$_0$ and 1P$_0$1P$_0$ transitions ($h\nu \leq 1.25E_g$) gives an identical quantum yield to within experimental uncertainty. For photon energy in the range (1.25–1.75)$E_g$ the quantum yield undergoes a sigmoid rise centered at the third electronic transition. Since CM is energetically forbidden at these energies, this implies that third-transition electron–hole pairs more easily lead to mobile charges than 1S$_0$1S$_0$ or 1P$_0$1P$_0$ pairs. Such an effect has been observed previously in devices of noninfiltrated PbSe-EDT QD solids, and was tentatively attributed to the production of more trapped excitons at lower photon energy. It could also be that electron–hole pairs of the third transition and higher have a larger spatial delocalization, thus increasing the effective distance between electron and hole and decreasing the Coulomb attraction. For photoexcitation in the range (1.75–2.70)$E_g$ the quantum yield shows no further increase with photon energy. This is likely due to a saturation of the dissociation yield at unity, a value as reported for a 1,2-ethanediame (EDA)-linked PbSe QD solid excited at 1.75$E_g$. $^2$ For photoexcitation above a threshold energy $h\nu_{th} = 2.70E_g$ the quantum yield increases with photon energy. This is attributed to MFCG (note: carrier mobility is independent of excitation energy since hot charges thermally relax within the present time resolution). It has an associated MFCG efficiency of 0.35 ± 0.01 (standard deviation), quantified by the slope for $h\nu \geq 2.70E_g$ in Figure 3: $\Delta\phi/\Delta(h\nu/E_g)$, analogous to the CM efficiency as defined in the literature. While CM has not been observed for noninfiltrated PbSe-EDT QD solids (cf.

Figure 1. Effect of varying photoexcitation density on charge decay in an Al$_2$O$_3$-infiltrated PbSe-EDT QD solid. The vertical axis displays the product of the mobility $\mu$ and yield of mobile charge carriers per incident photon $\eta$, summed for photogenerated electrons and holes: $\eta_i(t)\mu_e + \eta_h(t)\mu_h$ (see Methods). Photogeneration ($\lambda = 500$ nm, i.e., $h\nu = 3.9E_g$) was performed with a density varied from $2 \times 10^{-4}$ to $6 \times 10^{-2}$ photons per QD.

Figure 2. Action spectrum of the Al$_2$O$_3$-infiltrated PbSe-EDT QD solid. The left axis shows the yield of mobile charge carriers per incident photon: $\eta$, which is proportional to $\eta_i(t = t_{max})\mu_e + \eta_h(t = t_{max})\mu_h$. The right axis shows the fraction of incident photons absorbed by the sample, $F_A$. The horizontal axis displays $h\nu/E_g$ with $E_g$ the band gap energy of the QD solid (determined from Figure S1). The yield of mobile charge carriers per incident photon increases more strongly with photon energy than $F_A$ does. Inset: for excitation near the band gap, the yield is proportional to $F_A$.

Figure 3. Normalized quantum yield versus band gap normalized photon energy for the Al$_2$O$_3$-infiltrated PbSe-EDT QD solid. The quantum yield, $\phi$, is the yield of free charges per absorbed photon: $\phi \equiv \eta/F_A$. The first three electronic transitions of the film are indicated by dashed lines (see Note 1, Supporting Information). The normalized quantum yield saturates to unity at 1.75$E_g$ and MFCG occurs with threshold energy 2.70$E_g$. $^2$
Figure 4,19–21 the present results show for the first time that infilling leads to the generation of free charges by CM.

Effects of infilling on the efficiency of charge carrier generation via CM were investigated by comparing results for three differently infilled PbSe-EDT QD solids to that of the noninfilled PbSe-EDT QD solid (see Figure 4). Note that the quantum yield values were normalized to their mean value in the interval (1.75–2.70)Eg as in Figure 3. The quantum yield for the noninfilled PbSe-EDT QD solid (black symbols, Figure 4) shows no effect of CM, in agreement with earlier findings for noninfilled PbSe-EDT QD solids.19–21 However, in contrast to earlier device measurements21 and in contrast to the three infilled QD solids, it does not increase on going from the noninfilled PbSe-EDT QD solids.19 This is close to the 0.41 CM efficiency measured with a Perkin–Elmer Lambda 900 spectrometer equipped with integrating sphere. Infilling was used to increase the quantum yield in air inside the integrating sphere. The noninfilled film was kept under N2 atmosphere. The absorption spectrum of this film was obtained from the measured transmission and reflection spectrum. The band gap energy of the QD solid, Eg, is taken as that photon energy at which the lowest-energy absorption peak shows a maximum.

Time Resolved Microwave Conductivity. Photoconductivity was measured using the time-resolved microwave conductivity technique.22,23 Samples were mounted in an Nd3+-filled microcavity (8.5 GHz resonance frequency) at the position of maximum electric field (~100 V cm⁻¹). This limits the time resolution to 16 ns due to the response time of the cavity. However, transients were deconvolved for the known cavity response function (see Supporting Information, Note 2), resulting in a time resolution limited by the 3 ns laser pulse. Samples were photoexcited at a 10 Hz repetition rate using 3 ns pulses of tunable wavelength obtained by pumping an optical parametric oscillator with the third harmonic (355 nm) of a Q-switched Nd:YAG laser (Optronik Vibrant 355 II). The laser has a wavelength accuracy of ±5 nm (determined at 1000 nm). An excitation fluence of 2 × 10¹⁴ photons per QD was found to be sufficiently low that higher-order Auger recombination of electrons and holes was insignificant. This fluence was determined as I/[(1 − Fₚ)σ], with I the incident excitation fluence, Fₚ the fraction of incident light reflected by the film surface, and σ the absorption cross section of PbSe QD in dispersion.

The product of the mobility μ and time-dependent yield of mobile charge carriers per absorbed photon ϕ(t), summed for photogenerated electrons and holes, is related to the change in probe power P as
\[ \phi(t) \mu_F + \phi_b(t) \mu_b = -\frac{1}{eK\mu_F^2} \left( \frac{P_{\text{on}}(t) - P_{\text{off}}}{P_{\text{off}}} \right) \]

with \( t \) the pump–probe delay time, \( e \) the elementary charge, \( K \) the frequency-dependent sensitivity factor, \( \beta = 2.08 \) the aspect ratio of the rectangular waveguide, \( \lambda_0 \) the fluence incident on the sample, \( F_a \) the fraction of photons absorbed by the sample, \( P_{\text{on}} \) the microwave probe power after passing through the photoexcited sample, and \( P_{\text{off}} \) the microwave probe power after passing through the ground-state sample. The yield per incident photon \( \eta \) is related to the yield per absorbed photon \( \phi \) as \( \eta = \phi F_a^\beta \). The MFCG efficiency is determined from the increase of the quantum yield \( \phi \) with photon energy. Hence a constant fraction of charge trapping does not lead to misinterpretation of the efficiency, which is also the case for ultrafast transient absorption experiments employing the peak–tail method.

**ASSOCIATED CONTENT**

Supporting Information

Steady-state absorption spectra and electronic transition energy determination; deconvolution of microwave conductivity transients and determination of lower limit to charge mobility; chemicals used. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

S.T.C. performed the time-resolved microwave conductivity and steady-state absorption experiments, analyzed the data, and wrote the manuscript. Y.L. synthesized the QDs, prepared the QD solids, and performed the ALD in-filling. C.S.S.S. provided the absorption and photoconductivity spectrum of a PbSe-EDT film. S.K. was involved in directing the research. A.J.H. advised on the interpretation. T.J.S. designed the time-resolved microwave conductivity experiment. J.M.S. advised on the experimental work. M.L. and L.D.A.S. designed and supervised the project and edited the manuscript. All authors discussed the results and implications and commented on the manuscript at all stages.

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is part of the Joint Solar Programme (JSP) of Hyet Solar and the Stichting voor Fundamenteel Onderzoek der Materie (FOM), which is part of the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). C.S.S.S. acknowledges financial support by Toyota Motor Europe NV/SA. L.D.A.S. acknowledges financial support by the 3TU Centre for Sustainable Energy Technologies (Federation of the Three Universities of Technology in The Netherlands). Y.L. and M.L. acknowledge financial support by the Center for Advanced Solar Photophysics (CASP), an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES).

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