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Free Charges Produced by Carrier Multiplication in Strongly Coupled PbSe Quantum Dot Films

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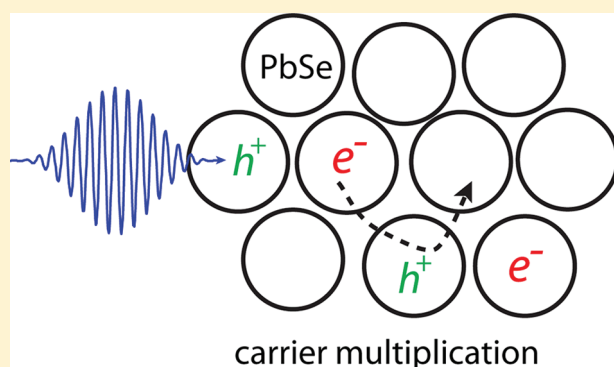
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 Supporting Information

ABSTRACT: We show that in films of strongly coupled PbSe quantum dots multiple electron–hole pairs can be efficiently produced by absorption of a single photon (carrier multiplication). Moreover, in these films carrier multiplication leads to the generation of free, highly mobile charge carriers rather than excitons. Using the time-resolved microwave conductivity technique, we observed the production of more than three electron–hole pairs upon absorption of a single highly energetic photon ($5.7E_g$). Free charge carriers produced via carrier multiplication are readily available for use in optoelectronic devices even without employing any complex donor/acceptor architecture or electric fields.

KEYWORDS: Carrier multiplication, multiple exciton generation, charge generation, quantum dot solids, solar cells



The occurrence of multiple exciton generation (MEG), creating multiple electron–hole pairs from single photon absorption, has been reported in several studies on solutions of semiconductor quantum dots (QDs).^{1–4} A large amount of research involves PbSe QDs, for which the occurrence of MEG has been well established.^{2,5–8} Lead chalcogenide QDs are of particular interest, since their size can be tuned to obtain a band gap $E_g = 0.7–1.0$ eV, which is optimal for exploitation of MEG in a solar cell under AM1.5 conditions.^{3,9,10,13,14} In photovoltaic devices QDs are applied in the form of thin films. Films of electronically coupled PbSe QDs have been prepared by spin-coating and chemical treatment and were investigated for MEG using ultrafast transient absorption spectroscopy.^{11,12} In optoelectronic devices harvesting of free mobile charge carriers produced by a MEG-type process in lead chalcogenide QDs has been realized by application of an external electric field¹³ or by bringing the QDs in contact with TiO_2 as electron acceptor.¹⁴

According to recent time-resolved spectroscopic studies, photoexcitation of strongly coupled PbSe QD films leads to formation of free mobile charge carriers with unity quantum yield on a sub-picosecond time scale.¹⁵ Since there is no need to invoke an excitonic state as precursor to free charge carriers, we use the term carrier multiplication (CM) rather than multiple exciton generation (MEG), for production of multiple mobile electron–hole pairs by absorption of a single photon. The work of ref 15 involves photoexcitation at energies below the threshold of CM. In the time-resolved microwave photoconductance studies described

below, the photoexcitation energy is increased with the aim to study the efficiency of CM in strongly coupled PbSe QD films. We found that the efficiency of CM in these films exceeds that for QDs in colloidal solution. The direct generation of mobile charge carriers implies that exploitation of CM in a photovoltaic device does not require introduction of hybrid donor/acceptor material systems.

Monodisperse oleic acid capped PbSe nanocrystals were synthesized according to procedures reported in the literature.¹⁶ The synthesis procedure is outlined in the Supporting Information. After synthesis, the QDs were dispersed in tetrachloroethylene (TCE) for optical absorption measurements and hexane for film preparation. Figure 1A shows that the absorption spectrum of QDs with a diameter of 5.4 nm exhibits the first absorption peak at 1620 nm (0.76 eV), while for QDs of 6.9 nm the first absorption peak occurs at 1890 nm (0.66 eV, not included in the figure).

The PbSe QD films were produced by layer-by-layer dip coating using a mechanical dip coater (DC Multi-8, Nima Technology) mounted inside a nitrogen glovebox. A silanized quartz substrate was dipped alternately into a solution of PbSe QDs in hexane for 60 s and a 1 M solution of 1,2-ethanediamine (EDA) in acetonitrile for 60 s and rinsed in acetonitrile for 30 s. The dipping procedure was repeated 20 times, resulting in homogeneous

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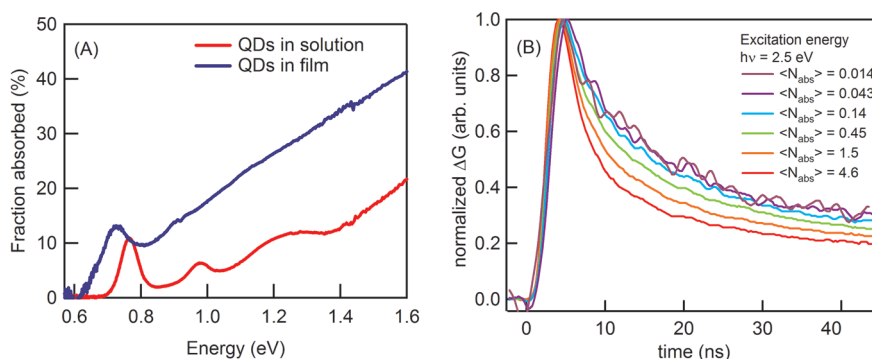


Figure 1. (A) Fraction absorbed photons for 5.4 nm PbSe QDs in tetrachloroethylene solution (red) and in a film with EDA ligands (blue). (B) Normalized photoconductance, ΔG , at different average numbers of excitations per QD for $h\nu = 2.5$ eV, normalized at their maximum. For $\langle N_{\text{abs}} \rangle \leq 0.04$, the decay of charges exhibits first-order kinetics and higher-order recombination is not important.

thin films. Films were placed at the entrance of the integrating sphere of a Perkin-Elmer Lambda 900 spectrometer to obtain the transmittance, F_t , and behind it to determine the reflectance, F_r . The fraction of absorbed light is $F_a = 1 - F_r - F_t$.

The excitation wavelength dependence of the photoconductance was investigated using the time-resolved microwave conductivity (TRMC) technique.^{17,18} The samples were mounted in an X-band microwave cell (8.4 GHz). The samples were photoexcited with 3 ns laser pulses from a Q-switched Nd:YAG laser (Opotek Vibrant 355 II). The average number of photons absorbed per QD is obtained as $\langle N_{\text{abs}} \rangle = I_0 \sigma$, where σ is the absorption cross section.¹⁹ Note that this is an upper limit, since the photon fluence decreases due to optical absorption along the depth in the sample.

Upon photoexcitation the change in microwave power reflected from the cell was measured. For small photoinduced changes in the real conductance of the sample, $\Delta G(t)$, and negligible change in imaginary conductance, the relative change in microwave power is

$$\frac{\Delta P(t)}{P} = -K \Delta G(t) \quad (1)$$

where K is a sensitivity factor which has been determined previously.¹⁷ The photoconductance $\Delta G(t)$ can be expressed as

$$\Delta G(t) = e \beta I_0 F_a \Phi(t) \sum \mu \quad (2)$$

where e is the elementary charge, β is the ratio between the broad and narrow inner dimensions of the waveguide, I_0 is the photon fluence in the laser pulse, F_a is the fraction of light absorbed by the sample, $\Phi(t)$ is the number of mobile charge carriers at time t per absorbed photon, and $\sum \mu$ is the sum of the electron and hole mobilities. The mobile charges giving rise to the photoconductance correspond to electrons in a conduction band state or holes in a valence band state that can be delocalized over different QDs in a film and perform a drift motion with a velocity at least partially in-phase with an oscillating microwave electric field. By contrast, excitons consist of a pair of an electron and a hole that are strongly bound by their mutual Coulomb attraction to form a neutral species. Excitons do not contribute to the real component of the microwave photoconductance measured in the current study.

The absorption spectra of PbSe QD films with 1,2-ethanediamine (EDA) ligands exhibit a red shift (35 meV) and broadening (50 meV) of the first absorption peak, as compared to QDs in solution; see Figure 1A. The red-shift in coupled PbSe QD films

is well-known and has recently been attributed mainly to polarization effects,²⁰ resulting from the change in the dielectric environment. The slight broadening of the absorption peak is attributed to increased electronic coupling^{21,22} and additional disorder in the site-energies due to variation of local environment. The presence of a pronounced first absorption peak in the spectrum of the film implies that quantum-confinement is maintained, indicating that the QDs remain distinct in the film.

Normalized photoconductance transients for varying excitation density are shown in Figure 1B for photoexcitation energy $h\nu = 2.5$ eV. The photoconductance increases to reach a maximum, ΔG_{max} , that is determined by the competition between charge carrier formation during the 3 ns laser pulse and charge carrier decay by recombination or trapping. For $\langle N_{\text{abs}} \rangle \leq 0.04$ the decay kinetics are independent of photoexcitation density, which implies that mobile charges decay by a first-order process such as trapping at defects. The same result is found for other photoexcitation energies; see Figure S1 in the Supporting Information. Possible effects of photocharging of the sample were studied by averaging photoconductance transients over a few to several hundred laser pulses, delivered at a repetition rate of 10 Hz. Both the magnitude per absorbed photon and the decay kinetics of the photoconductance were independent of the number of laser pulses or, equivalently, the total number of charges generated. In agreement with this, the data in Figure 1B and Figures S1 and S2 (Supporting Information) show that both the magnitude and decay kinetics become identical at lower excitation density ($\langle N_{\text{abs}} \rangle \leq 0.04$). Hence, the occurrence of artifacts due to photocharging of the sample can be excluded. For higher photoexcitation densities higher-order (Auger) recombination of charges contributes to the decay.

Figure 2 shows the photoconductance normalized by the incident laser photon fluence, $\Delta G_{\text{max}}/I_0$, for a film of 5.4 nm PbSe QDs as a function of photoexcitation energy for $\langle N_{\text{abs}} \rangle = 0.04$. The spectral shape of $\Delta G_{\text{max}}/I_0$ coincides with the optical absorption spectrum (note the inset for energies around the band gap) for photon energies $h\nu \leq 1.55$ eV. This implies that for these energies the quantum yield for charge carrier photogeneration is constant, independent of excess excitation energy. As mentioned above, a previous study has shown that photoexcitation below the energetic threshold for CM produces charges with unity quantum yield.¹⁵ Hence, for the present film the quantum yield is unity for $h\nu \leq 1.55$ eV. At higher photon energy $\Delta G_{\text{max}}/I_0$ becomes increasingly higher in comparison with the optical attenuation. The latter implies that the quantum yield for charge

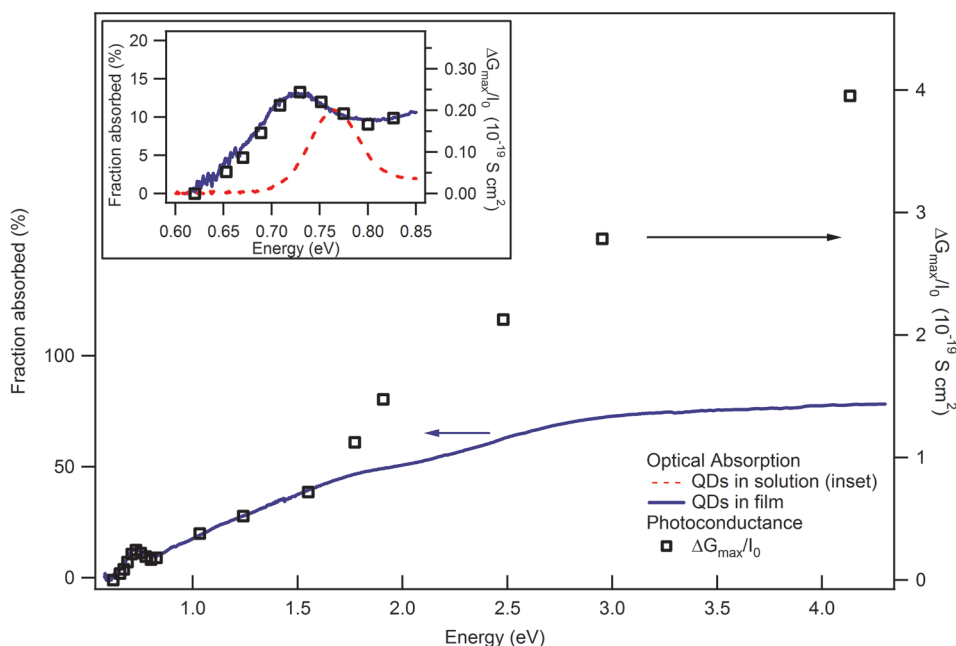


Figure 2. Left axis: Fraction absorbed photons for 5.4 nm PbSe QDs in tetrachloroethylene solution (red dotted line) and in film with EDA ligands (solid line). Right axis: Photoconductance normalized to incident laser fluence, $\Delta G_{\max}/I_0$, at $\langle N_{\text{abs}} \rangle = 0.04$ (□) as a function of photon energy. The inset shows the excitation region around the QD band gap.

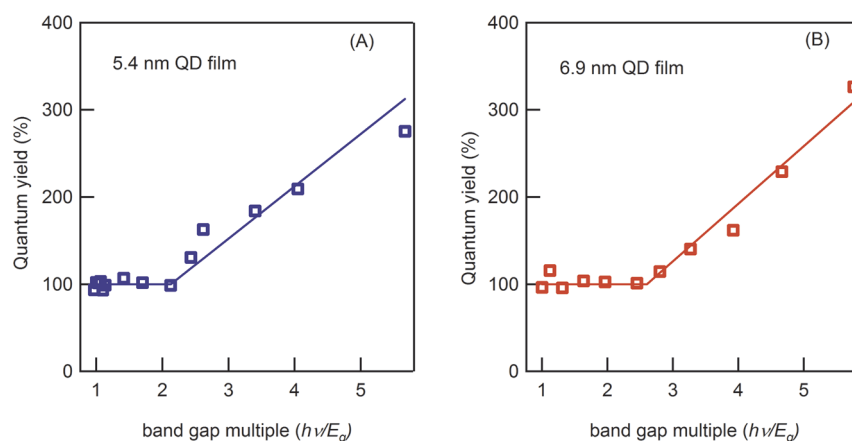


Figure 3. Quantum yield as a function of photon energy in terms of the band gap multiple (5.4 nm QDs: $E_{g,\text{film}} = 0.73$ eV, 6.9 nm QDs: $E_{g,\text{film}} = 0.63$ eV). $\langle N_{\text{abs}} \rangle = 0.04$ for both films.

carrier photogeneration increases with photon energy and reaches values exceeding 1, as a result of CM. Note, at higher energy the fraction absorbed photons saturates to $\sim 85\%$, as a result of reflectance at the front of the film and absorption of practically all photons that enter the film.

Figure S2 in the Supporting Information shows $\Phi(t = 3 \text{ ns})\Sigma\mu = [\Delta G_{\max}/I_0]/e\beta F_a$ (see eq 2) as a function of photoexcitation density for different photon energies. For photon energies $h\nu \leq 1.55$ eV the $\Phi(t = 3 \text{ ns})\Sigma\mu$ values are within 20–30% of each other, reflecting the constant (unity) quantum yield. At higher photon energies the $\Phi(t = 3 \text{ ns})\Sigma\mu$ values are higher over the entire range of photoexcitation densities, in agreement with an enhanced quantum yield due to CM. Noteworthy are the high $\Phi(t = 3 \text{ ns})\Sigma\mu$ values realized in these films. As $\Phi(t = 3 \text{ ns})$ has a maximum value of 1 at energies below the CM threshold, the lower limit to the sum of the electron and hole mobilities is

$0.8 \pm 0.1 \text{ cm}^2/(\text{V s})$. Using the Einstein–Smoluchowski relation to obtain the diffusion coefficient, together with the half-lifetime for charge decay $\tau_{1/2} = 15$ ns from Figure 1B, gives a diffusion length $LD = (6\tau_{1/2}k_B T\mu/e)^{1/2}$ as long as ~ 300 nm at room temperature.

The quantum yield can be determined quantitatively by dividing $\Delta G_{\max}/I_0$ by the fraction of absorbed photons, F_a , and scaling the average of the results for photon energies $h\nu \leq 1.55$ eV to unity quantum yield, as inferred from the work of ref 15. The quantum yield obtained in this way is shown in Figure 3 as a function of the band gap multiple $h\nu/E_g$ for films of PbSe QDs with diameters 5.4 and 6.9 nm. For 6.9 nm QDs the quantum yield reaches 350% for an excitation energy of $5.7E_g$. The electron–hole pair multiplication efficiency η_{EHMP} ,²³ defined as the increase of the quantum yield per band gap multiple, $\Delta([\Delta G_{\max}/I_0]/F_a)/\Delta(h\nu/E_g)$, is about 60%, which is significantly

higher than the values of $\sim 40\%$ reported previously for PbSe QDs in solution.^{4,8} The energetic threshold for CM in the film QDs is at similar (or even lower) energies as for PbSe QDs in solution, where CM starts to occur around $2.8 E_g$.^{4,24} The current CM efficiencies for films of PbSe QDs with EDA ligands are larger than those reported previously for PbSe QD films with other ligands.^{11,12} It should be noted, that the previously reported quantum yields were determined by the assumption that photoexcitation of electronically coupled QD films leads to formation of (multiple) excitons rather than free charges. If free charges are directly generated in (some) of the films reported in refs 11 and 12, determination of the quantum yield from the photobleaching signal at picosecond and nanosecond times would be inadequate.

On the basis of the above, our understanding of CM in these strongly coupled QD films involves, sequentially, photoexcitation of a single valence electron into the continuum of conduction states and inelastic scattering of the highly mobile hot charge carrier (electron, hole, or both) on a QD in the ground state, thereby promoting a second electron to the conduction continuum. The second process is also called impact ionization.²³ Electronic coupling between QDs in a film leads to bandlike electronic states that are delocalized over different QDs. The efficiency of CM is determined by the matrix element for Coulomb coupling between an initial state of a hot delocalized charge carrier and a final state with a second electron in the conduction continuum. These delocalized states are different from the localized exciton states for isolated QDs in solution. Therefore it is not surprising that the CM efficiency in a QD solid differs from that for QDs in solution.

The finding of efficient CM makes films of PbSe QDs with EDA ligands attractive for application in solar cells. It is therefore interesting to calculate the enhancement of the solar cell power conversion efficiency due to CM as found for the films discussed above. Taking into account only spectral losses, the output power of a solar cell is

$$R = \frac{\int_{E_g}^{\infty} \Phi(E) [P_{in}(E)/E] F_A(E) dE}{\int_{E_g}^{\infty} [P_{in}(E)/E] F_A(E) dE} \quad (3)$$

where E is photon energy and the incident solar power P_{in} is taken from ref 25. The quantum yield, $\Phi(E)$, in presence of CM is taken from Figure 3, while in absence of CM the quantum yield is taken equal to 1. The relative increase in solar conversion efficiency is then found to be $R = 24\%$ for the film of 5.4 nm PbSe QDs.

In conclusion, the current work demonstrates the occurrence of efficient CM in films of strongly coupled PbSe QDs with 1,2-ethanediamine (EDA) ligands with an efficiency that exceeds that for PbSe QDs in solution. The direct photogeneration of free mobile charges via CM in these films is attractive for photovoltaic applications, since hybrid donor/acceptor material structures for exciton dissociation are not needed.

■ ASSOCIATED CONTENT

S Supporting Information. Materials and methods and photoconductance data for different photoexcitation energies and laser fluences. This material is available free of charge via the Internet: <http://pubs.acs.org>.

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