

Generating Free Charges by Carrier Multiplication in Quantum Dots for Highly Efficient Photovoltaics

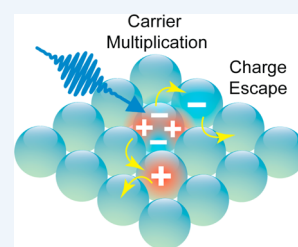
Sybren ten Cate,[§] C. S. Suchand Sandeep,[§] Yao Liu,[†] Matt Law,[†] Sachin Kinge,[#] Arjan J. Houtepen,[§] Juleon M. Schins,[§] and Laurens D. A. Siebbeles^{*,§}

[§]Optoelectronic Materials Section, Department of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

[†]Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States

[#]Toyota Motor Europe, Functional Nanomaterials Lab, Advanced Technology, Hoge Wei 33, B-1930 Zaventem, Belgium

CONSPECTUS: In a conventional photovoltaic device (solar cell or photodiode) photons are absorbed in a bulk semiconductor layer, leading to excitation of an electron from a valence band to a conduction band. Directly after photoexcitation, the hole in the valence band and the electron in the conduction band have excess energy given by the difference between the photon energy and the semiconductor band gap. In a bulk semiconductor, the initially hot charges rapidly lose their excess energy as heat. This heat loss is the main reason that the theoretical efficiency of a conventional solar cell is limited to the Shockley–Queisser limit of ~33%. The efficiency of a photovoltaic device can be increased if the excess energy is utilized to excite additional electrons across the band gap. A sufficiently hot charge can produce an electron–hole pair by Coulomb scattering on a valence electron. This process of carrier multiplication (CM) leads to formation of two or more electron–hole pairs for the absorption of one photon.



In bulk semiconductors such as silicon, the energetic threshold for CM is too high to be of practical use. However, CM in nanometer sized semiconductor quantum dots (QDs) offers prospects for exploitation in photovoltaics. CM leads to formation of two or more electron–hole pairs that are initially in close proximity. For photovoltaic applications, these charges must escape from recombination. This Account outlines our recent progress in the generation of free mobile charges that result from CM in QDs. Studies of charge carrier photogeneration and mobility were carried out using (ultrafast) time-resolved laser techniques with optical or ac conductivity detection.

We found that charges can be extracted from photoexcited PbS QDs by bringing them into contact with organic electron and hole accepting materials. However, charge localization on the QD produces a strong Coulomb attraction to its counter charge in the organic material. This limits the production of free charges that can contribute to the photocurrent in a device.

We show that free mobile charges can be efficiently produced via CM in solids of strongly coupled PbSe QDs. Strong electronic coupling between the QDs resulted in a charge carrier mobility of the order of $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This mobility is sufficiently high so that virtually all electron–hole pairs escape from recombination.

The impact of temperature on the CM efficiency in PbSe QD solids was also studied. We inferred that temperature has no observable effect on the rate of cooling of hot charges nor on the CM rate.

We conclude that exploitation of CM requires that charges have sufficiently high mobility to escape from recombination. The contribution of CM to the efficiency of photovoltaic devices can be further enhanced by an increase of the CM efficiency above the energetic threshold of twice the band gap. For large-scale applications in photovoltaic devices, it is important to develop abundant and nontoxic materials that exhibit efficient CM.

1. INTRODUCTION

Electrons in a semiconductor can be excited across the band gap by absorption of a photon. Absorption of a photon with energy equal to the band gap, E_g , leads to the production of an electron–hole pair at the band edge, with the electron at the bottom of the conduction band and the hole at the top of the valence band. A photon with energy exceeding the band gap yields an initially hot electron–hole pair with an excess energy equal to the difference between the photon energy and the band gap. The hot electron and hole subsequently relax to the band edge states by energy dissipation, see Figure 1. This charge cooling process can occur by transfer of excess energy to lattice vibrations (phonons). Another possibility is that a hot

charge undergoes one or more Coulomb scattering events on valence electrons, leading to the production of additional electron–hole pairs. This phenomenon of carrier multiplication (CM, also known as “multiple exciton generation” or “impact ionization”) allows a single photon of sufficient energy to generate two or more electron–hole pairs. Understanding the way in which material composition and (nano)structure affect CM is of fundamental scientific interest and is important for exploitation of CM in highly efficient third-generation solar cells.^{1–3}

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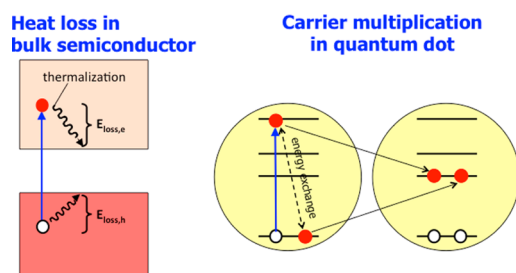


Figure 1. (left) Photoexcitation of a bulk semiconductor leads to formation of a hot electron and hole that usually lose their excess energy as heat due to phonon emission. (right) Carrier multiplication in a quantum dot results in excitation of additional electrons across the band gap.

Although CM does occur in traditional solar cell materials such as bulk silicon, it has no practical benefit due to the high energetic threshold for CM near 4 eV and consequently insignificant occurrence under solar illumination.^{1,4} The prediction in 2002^{5,6} that CM may be more efficient in nanometer-sized semiconductor crystals (nanocrystals) than in bulk has prompted a highly active field of research on CM in nanocrystals, with the first experimental observation of CM in colloidal PbSe quantum dots in 2004.⁷ For nanocrystals, a CM threshold energy $<3E_g$ has been found, which is significantly less than the onset of $4E_g$ or more for bulk semiconductors.^{1,4,8,9}

Recent reviews on effects of size, composition, and shape of nanocrystals on CM can be found elsewhere.^{2,8} Briefly, CM has been observed in a variety of nanocrystals consisting of a single semiconductor material (lead chalcogenides,^{10–12} cadmium chalcogenides,¹³ indium phosphide,¹⁴ and silicon^{15–18}) and alloy or core–shell structures.^{19–22} The efficiency and threshold energy of CM depend on the nanocrystal material, due to variations in the effective masses of electrons and holes and in the strength of the electron–phonon interaction.^{12,23} The efficiency of CM in lead chalcogenide nanocrystals increases on variation of the shape from quantum dots to elongated nanorods with moderate aspect ratio, due to enhancement of Coulomb interactions.^{8,24–26} The observed reduction of the CM efficiency in longer nanorods could result from restrictions due to momentum conservation.⁸ Interestingly, in thin two-dimensional (2D) PbS nanosheets virtually the entire excess photon energy above the CM threshold is used for CM.²⁷ The benefit of a 2D system could be due to enhanced Coulomb interactions compared with 0D quantum dots and a higher density of electronic states than for 1D nanorods.

For solar cell applications, it is essential that the multiple electron–hole pairs generated via CM are able to escape from recombination and can be transported to external electrodes. For optimal exploitation of the solar spectrum, the band gap of the nanocrystals should be close to 1 eV.¹ Extraction of multiple electron–hole pairs for the absorption of a single photon has been realized in solar cells.^{28,29} Generating multiple free mobile charges produced by CM requires electronic coupling of nanocrystals with each other or with electron or hole accepting materials, while maintaining the effects of quantum confinement that are essential for efficient CM.

The effects of nanocrystal size, shape, and composition on CM within a nanocrystal in colloidal dispersion have been reviewed recently.^{2,8} This Account reviews our studies of the generation of free mobile charges from photoexcited lead

chalcogenide quantum dots (QDs) in thin films. These QDs can be tuned to have a band gap near 1 eV, which is suitable for exploitation of CM in a solar cell. We photoexcited thin-film samples containing PbS or PbSe QDs with short laser pulses with tunable photon energy. The yield and mobility of photogenerated charges were monitored with time using transient optical absorption measurements and electrodeless AC conductance techniques at microwave and terahertz frequencies of the oscillating electric field.^{30,31} The advantage of using these AC conductivity techniques over DC device studies is that we probe the motion of charges over relatively short distances within the thin-film sample containing the QDs. Consequently, the charge mobility that we probe with the AC techniques is not influenced by negative effects of long-range transport over grain boundaries in the sample and charge extraction at external electrodes.

2. EXTRACTING CHARGES FROM QUANTUM DOTS IN THIN-FILM HETEROJUNCTIONS WITH ORGANIC MATERIALS

Extracting charges from photoexcited QDs can be realized by bringing them into contact with electron or hole accepting materials. Fullerene derivatives can be used as electron acceptor due to their high electron affinity, while conjugated polymers can act as hole accepting materials due to their low ionization energy. These materials have been extensively used in organic solar cells, are cheap and solution processable (like colloidal QDs), and exhibit efficient charge transport.³² However, solar cells consisting of QDs with organic charge acceptor exhibit low performance,³³ with an unexplained exception involving PbS QDs blended with the polymer PDTPQ.³⁴ Interestingly, photodiodes based on QDs in a ternary heterojunction with both electron and hole acceptors have shown high performance.³⁵ The ternary heterojunction consisted of a blend of PbS QDs with the fullerene-derivative [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as electron acceptor and the polymer regioregular poly(3-hexylthiophene) (P3HT) as hole acceptor, see Figure 2.

We studied the factors that govern the above-mentioned performance characteristics of photovoltaic devices based on heterojunctions of PbS QDs with PCBM or P3HT.³⁶ The blends were prepared by drop-casting from solution with equal weight ratio of PbS, PCBM, and P3HT. In the resulting blend films, PCBM and P3HT exhibit phase segregation and form larger domains with a high degree of crystallinity.³⁷ The PbS QDs contain bulky oleic acid ligands on their surface that prevent electronic coupling of QDs.³⁶ We carried out ultrafast transient optical absorption measurements to determine the efficiency of charge transfer from photoexcited PbS QDs to the organic acceptors. Using ultrafast time-resolved terahertz conductivity measurements, we monitored the mobility of the charges that were transferred to the organic acceptors.

To ensure that transfer of electrons and holes from band edge states in PbS QDs to PCBM and P3HT is energetically allowed, we studied small QDs with a diameter of 2.5 nm, giving a photoluminescence peak at 820 nm, which corresponds to a band gap of 1.5 eV.³⁶ The films were photoexcited at photon energy of 1.55 eV (800 nm) to avoid complexities due to absorption by PCBM and P3HT. As further addressed below, some absorption occurs in a P3HT/PCBM blend due to direct electron excitation from P3HT to PCBM. Note that for this pump photon energy at the band gap of the PbS QDs, the process of CM cannot occur. We have not studied CM at

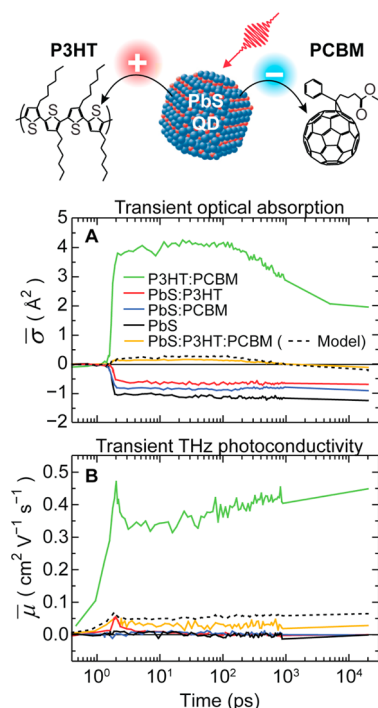


Figure 2. Extracting charges from photoexcited PbS QDs in a heterojunction with PCBM as electron acceptor and P3HT as hole acceptor. (A) The transient change of the optical absorption cross section per absorbed pump photon $\bar{\sigma} \equiv \sum_i \phi_i \Delta \sigma_i$, with ϕ_i being the quantum yield for photogeneration of species i and $\Delta \sigma_i$ being the cross section of the photoinduced change in absorption cross section due to this species. The species involved are an electron, a hole, or both in a PbS QD, an electron in PCBM, and a hole in P3HT. (B) Time-resolved terahertz conductivity per absorbed excitation photon: $\bar{\mu} \equiv \sum_i \phi_i \mu_i$ with μ_i being the mobility of charged species i . The dashed lines were obtained as a weighted superposition of signals for PbS QDs and the binary blends, as described in ref 36. Reprinted with permission from ref 36. Copyright 2012 American Chemical Society.

higher photon energy in blend films with PbS QDs, since we did not observe generation of free mobile charges, as discussed below.

Photoexcitation of a film of the PbS QDs with oleic acid surface passivation ligands leads to an optical bleach at the band gap, due to generation of long-lived excitons, see the black curve in Figure 2A. Addition of PCBM reduces the bleach amplitude (blue curve, Figure 2A), due to electron transfer from PbS QDs to PCBM, yielding PCBM anions with a quantum yield of 0.41. Adding P3HT to a PbS QD film also reduces the bleach (red curve, Figure 2A), due to hole transfer from PbS QDs to P3HT, yielding P3HT cations with a quantum yield of 0.09. The step-like kinetics of the transient bleach observed for blends of PbS QDs with PCBM or P3HT implies that charge transfer occurs within our experimental time resolution of 100 fs, while the charge recombination time exceeds the 20 ns time scale of our measurements. Ultrafast charge transfer from PbS QDs to P3HT has also been observed by others.³⁸ We attribute the ultrafast charge transfer from the QDs to the organic acceptors to a Marcus-type charge transfer process close to the optimal regime, where the driving force for charge separation cancels the reorganization energy.³⁶ The magnitude of the quantum yields of charge transfer is likely limited by the bulky oleic acid ligands on the surface of a QD, which hinder access of PCBM and P3HT to the QD surface. In

agreement with this, the quantum yield for charge transfer to bulky P3HT is much lower than that for the smaller PCBM molecules. The positive transient absorption for the P3HT/PCBM blend is due to holes in P3HT that are generated by electron excitation directly from P3HT to PCBM. The positive transient absorption of the ternary blend of PbS QDs with both PCBM and P3HT (yellow curve in Figure 2A) at times shorter than 1 ns is due to a contribution of holes produced by direct excitation of P3HT/PCBM (green curve), which dominates over the bleach due to charges in PbS QDs. The transient for the PbS/P3HT/PCBM blend can be well described as a superposition of the transient absorption for the P3HT blend and the PbS QDs weighted by the fraction of absorbed pump photons in each material component (see the dashed curve in Figure 2A). This implies that the quantum yields of charge transfer from PbS QDs to PCBM and P3HT in the ternary blend are similar to those in the binary blends. This is likely due to the small probability of having both PCBM and P3HT at the surface of a PbS QD.

The mobility of charges produced by transfer from PbS QDs to PCBM and P3HT was studied by using time-resolved terahertz conductivity measurements.³⁶ The terahertz conductivity is highest for P3HT/PCBM blends, see Figure 2B. The high terahertz conductivity in this blend is due to phase segregation of P3HT and PCBM leading to formation of large domains with high degrees of crystallinity. The high mobility of holes and electrons in P3HT and PCBM domains, respectively, gives rise to the observed terahertz conductivity in Figure 2B, similar to the microwave conductivity reported before.³⁹ The terahertz conductivity for blends containing PbS QDs is much smaller. In blends with PbS QDs, the majority of the excitation photons is absorbed by the PbS QDs. Apparently, charges originating from PbS QDs do not contribute significantly to the terahertz conductivity. Using the charge-transfer yields determined from the transient absorption data in Figure 2A, we found the mobilities of electrons and holes originating from PbS QDs to be on the order of $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is about 30 times smaller than those for charges generated directly within P3HT/PCBM. From this, we infer that electrons and holes resulting from a photoexcited PbS QD remain Coulombically bound across the QD–acceptor interface.³⁶ This can be understood, since the large oleic acid molecules on the QD surface prevent mutual electronic coupling. As a consequence, the PbS QDs do not provide domains in which charge can move away from its sibling countercharge in PCBM or P3HT. The resulting electron–hole Coulomb attraction between a charge on a PbS QD and the countercharge in PCBM or P3HT explains the small yield of mobile charges in photovoltaic devices based on PbS QDs with PCBM or P3HT operated without external electric field^{34,40,41} and the larger yield in photodiodes operated with an external field.³⁵ To produce a photocurrent in a device, an external electric field is needed to separate the electron and hole that are initially Coulombically bound across the interface between a PbS QD and the organic acceptor. The lack of free charge carriers in the absence of an external electric field makes these blends unattractive for application in solar cells, and therefore the studies of ref 36 were not extended to CM.

The yield of free charge carriers in blends of PbS QDs and conjugated polymers has recently been enhanced by replacing the bulky oleic acid ligands on the PbS QDs by much smaller 3-mercaptopropionic molecules.⁴² The presence of these small ligand molecules promotes the formation of domains of

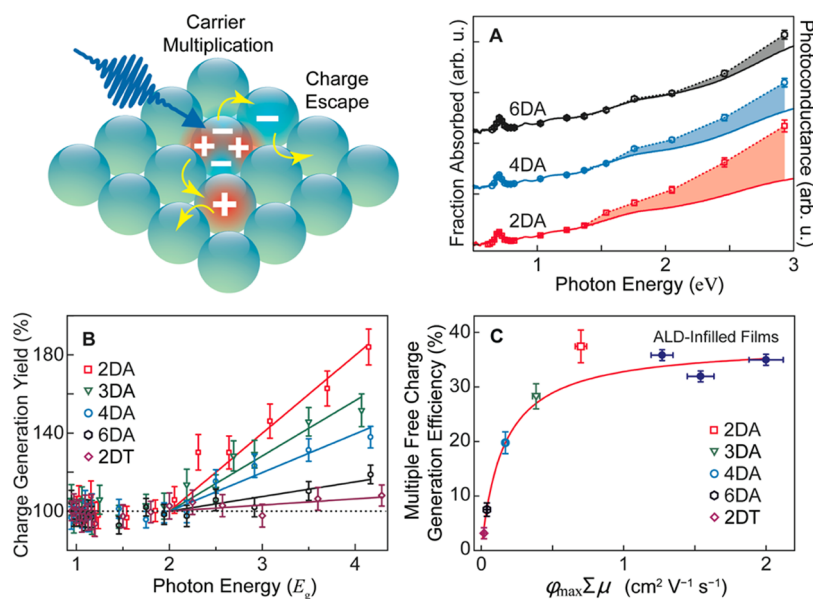


Figure 3. Carrier multiplication produces multiple charges in close proximity. The charges must be sufficiently mobile to escape from Auger recombination. (A) Fraction of absorbed photons (solid lines, offset for clarity) and microwave photoconductance per incident photon (markers) for PbSe QD solids with 2DA, 4DA, and 6DA ligands; shaded areas indicate MFCG yields exceeding one. (B) Charge generation yield versus photon energy; straight lines are linear fits to determine the MFCG efficiency. (C) MFCG efficiency versus $\phi_{\max} \Sigma \mu$ for PbSe QD solids with organic ligands (open markers) and for ALD-infilled films from ref 47 (solid blue markers). The data can be described by a theoretical model (red curve) of charge escape and Auger recombination.⁴⁵ Reproduced from ref 45. Creative Commons license (CC BY 3.0).

electronically coupled PbS QDs in which electrons can move from one QD to another and escape from the hole in the polymer. In thin films of strongly coupled PbSe QDs, the quantum yield for photogeneration of free mobile charges has been found to be close to unity.³¹ Such films are ideal candidates for use as the active layer in a photovoltaic device with selective electron and hole accepting electrodes. As will be discussed below, in films with sufficiently high charge mobility, virtually all electron–hole pairs produced via CM can escape from Auger recombination.

3. GENERATION OF FREE MOBILE CHARGES PRODUCED VIA CARRIER MULTIPLICATION IN THIN FILM QUANTUM DOT SOLIDS

Electron–hole pairs that are photogenerated in the active layer of a photovoltaic device must dissociate into free mobile electrons and holes that can be extracted at external electrodes. A promising approach to generate free charges from photoexcited QDs involves using a thin film solid of QDs with strong mutual electronic coupling.^{31,33,43} Strong coupling can be achieved by replacing the bulky ligands on the QD surface (resulting from synthesis) by smaller ligands. Smaller ligands reduce the distance between the QDs, which leads to enhanced overlap and coupling between electron wave functions on adjacent QDs. It has indeed been found that the mobility of charge carriers in a QD solid can be varied by changing the ligand length and the nature of the anchor group with which a ligand binds to the QD surface.^{44–46} CM produces multiple electron–hole pairs that are initially in close proximity. To exploit CM in a photovoltaic device, these charges must be sufficiently mobile to escape from Auger recombination.

We studied effects of the mobility of charges in QD solids on the efficiency of generating free electrons and holes that are produced via CM. The mobility was systematically varied in solids of identical PbSe QDs (6.0 nm diameter), so that the

initial CM efficiency is the same.⁴⁵ The mobility was tuned using organic surface ligands with varying anchor groups or length, including 1,2-ethanedithiol (2DT) and 1,2-*n*-alkanediamines (*n*DA) with *n* = 2, 3, 4, or 6. Figure 3A shows the optical absorption spectra of PbSe QD solids with 2DA, 4DA, and 6DA ligands against the left axis. The peak due to the first optical transition is clearly discernible, which shows that quantum confinement effects have remained after coupling of the QDs in the solid. We studied the efficiency of multiple free charge carrier generation (MFCG) by time-resolved microwave photoconductance measurements.^{30,45} Charges were generated by photoexcitation with a 3 ns laser pulse at variable photon energy. The photoconductance increases during the laser pulse and reaches a maximum (with MFCG yield ϕ_{\max}) at a time that is determined by the competition between charge photo-generation and their decay by recombination or trapping.

The maximum photoconductance is plotted in Figure 3A against the right axis. For photon energies below ~ 1.5 eV, the photoconductance follows the absorption spectrum. This simply reflects that the number of charges is proportionate to the number of absorbed photons. Interestingly, at higher photon energies, the photoconductance increases faster with photon energy than the fraction of absorbed photons. This is a signature of an increasing MFCG yield due the occurrence of CM. Above the CM threshold, the photoconductance deviates more from the optical absorption for shorter ligands. The higher mobility of charges for shorter ligands facilitates escape from Auger recombination and enhances the MFCG yield.

Figure 3B shows the MFCG yield as a function of photon energy for different ligands. The rise of the MFCG yield for photon energies above the energetic threshold for CM also depends strongly on the nature of the ligand. For *n*DA ligands, the MFCG yield rises faster with photon energy for shorter ligands (smaller *n*). However, for 2DT ligands (purple diamonds), there is hardly any effect of CM on the MFCG

yield. This is due to the low mobility of charges in a PbSe QD solid with 2DT ligands.⁴⁸ We define the MFCG efficiency as the slope of the linear fits in Figure 3B. The MFCG efficiency obtained in this way is the increase in MFCG yield per unit photon energy normalized to the band gap of the material, analogous to the well-known CM efficiency.^{1,49} Figure 3C shows the MFCG efficiency versus the product of $\varphi_{\max} \sum \mu$, with $\sum \mu$ being the sum of the electron and hole mobility. It is clear that the MFCG efficiency increases strongly with the charge mobility for the organic ligand series 2DT, 6DA, 4DA, 3DA, and 2DA. The experimental results can be reproduced by a theoretical model (red curve) with the initial CM efficiency taken as 0.4 (as in solution) and multiple electron–hole pairs escaping from Auger recombination with a rate that scales linearly with the sum of the electron and hole mobilities. According to recent studies,⁵⁰ 2DT binds to the QD surface much more strongly than amine ligands. Amine ligands were found to strip lead oleate from the QDs, resulting in necking of QDs to an extent that increases as the ligand becomes shorter. Hence, the increase of the charge mobility for the ligand series mentioned above is at least partially due to enhanced necking.

To further establish the relation between the charge mobility and the MFCG efficiency, we also varied the charge mobility by infilling PbSe QD solids with 2DT ligands with Al₂O₃ or Al₂O₃/ZnO.⁴⁷ Figure 4 shows the MFCG quantum yield for a

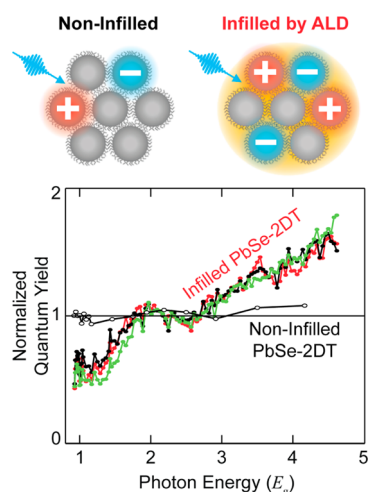


Figure 4. Effect of interstitial treatment on yield of free mobile charges produced by carrier multiplication in PbSe QD solids. In a PbSe QD solid with 1,2-ethanedithiol (2DT) ligands (black curve), multiple charges produced via carrier multiplication do not escape efficiently from Auger recombination. The higher charge mobility obtained by infilling with Al₂O₃ (black curve) or Al₂O₃/ZnO (red and green curves) allows charges to escape from recombination, and carrier multiplication contributes to the yield of free charges at higher photon energy. Reprinted with permission from ref 47. Copyright 2013 American Chemical Society.

PbSe QD solid with 2DT ligands and for the same QD solid after infilling. As already discussed above, CM does not give a significant contribution to the MFCG efficiency for a PbSe QD solid with 2DT ligands. However, after infilling the MFCG yield steeply rises for photon energies above $2.7E_g$. The MFCG efficiencies obtained from the data in Figure 4 for the infilled PbSe QD solids are also shown in Figure 3C. The MFCG efficiency can now be seen to saturate at a value near 0.35 for a charge mobility near $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The saturation value of the

MFCG efficiency is close to the initial CM efficiency value of 0.41, as measured for solution-dispersed PbSe QDs on picosecond time scale prior to Auger recombination.¹ This similarity implies that most charges produced via CM in PbSe QD solids with higher mobility can escape from Auger recombination. We have recently infilled PbSe QD solids with 2DA ligands with Al₂O₃ and found the charge mobility to increase by a factor five.⁵¹ The effect of infilling on the charge mobility for 2DA ligands is much smaller than that for 2DT ligands. This can be understood from the necking in the 2DA films, which already enhances the mobility prior to infilling. According to the data in Figure 3C, further increase of the mobility in 2DA films by a factor five after infilling will not have a significant effect on the MFCG efficiency.

4. COMPETITION BETWEEN CARRIER MULTIPLICATION AND COOLING OF HOT CHARGE CARRIERS

The decay of a hot electron or hole via CM competes with cooling by phonon emission, as studied experimentally^{8,49} and theoretically.^{52–55} Cooling of a hot charge carrier limits the time window during which CM can take place. The cooling process involves stimulated and spontaneous phonon emission in competition with phonon absorption. The amplitude of nuclear lattice vibrations increases with temperature, which enhances electron–phonon coupling. Thus, the rate of hot-carrier cooling by phonon emission can be affected by temperature. In which way, however, is not known a priori, since phonon absorption and stimulated emission occur with different rates. The rate of CM can be affected by temperature, since at higher temperature more phonons are available that can be absorbed to compensate for energy mismatches in electronic transitions, see sketch in Figure 5. The net result of the above-mentioned factors determines the effect of temperature on the efficiency of CM.

We carried out a study of the effect of temperature on the CM efficiency in PbSe QD solids infilled with Al₂O₃ or Al₂O₃/ZnO using the time-resolved microwave conductivity technique introduced above.⁵⁶ Figure 5 shows the measured quantum yield of mobile electrons and holes, $\phi_i(t)$, weighted by their mobilities, μ_i , which is given by $\bar{\phi}(t) = \phi_e(t)\mu_e + \phi_h(t)\mu_h$. The temperature dependence is shown in Figure 5 for a photon energy below the CM threshold ($1.9E_g$, red), together with data for higher photon energy where CM is known to be significant ($4.6E_g$, black). Their identical slopes imply that the CM efficiency is independent of temperature. On the basis of theoretical considerations, the cooling rate of hot charges in PbSe QDs is predominantly due to the temperature-independent process of spontaneous phonon emission,⁵⁶ which implies that CM is also a temperature-independent process. Thus, it is deduced that phonons do not assist CM in PbSe QD solids from 90 to 295 K and that apparently phonons do not notably compensate energetic mismatches in electronic transitions.⁵⁶ Although the rate of spontaneous phonon emission does not significantly depend on temperature, it varies with the properties of the QD parent material. This underlines the importance of the choice in QD material in reducing the cooling rate and thereby increasing the CM efficiency.^{8,12}

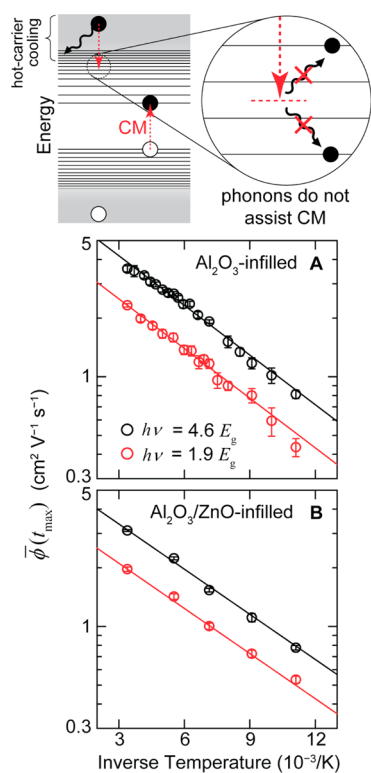


Figure 5. Carrier multiplication competes with hot-carrier cooling. The effect of temperature on the microwave photoconductance has been measured in the absence (red) and presence (black) of carrier multiplication for a PbSe QD solid infilled with Al_2O_3 (panel A) or $\text{Al}_2\text{O}_3/\text{ZnO}$ (panel B). It has been inferred from these data that the efficiency of carrier multiplication is temperature independent.⁵⁶ Reprinted with permission from ref 56. Copyright 2013 American Chemical Society.

5. SUMMARY

This Account outlines the recent progress in generation of free mobile charges resulting from carrier multiplication in QDs for highly efficient photovoltaics. It has been found that charges must be sufficiently mobile to escape from mutual (Auger) recombination. This has been realized by strong electronic coupling of PbSe QDs via introduction of short 1,2-ethanediamine ligands or by infilling of the interstitial space of QD solids with metal oxides via ALD. A future challenge involves realization of efficient CM at the threshold energy of twice the band gap in abundant and nontoxic materials.

AUTHOR INFORMATION

Corresponding Author

*E-mail: l.d.a.siebbeles@tudelft.nl.

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Notes

The authors declare no competing financial interest.

Biographies

Sybre ten Cate received his masters degree in Physics (University of Amsterdam, the Netherlands) in 2010, graduating on the computational research of magnetohydrodynamics. In 2014, he completed his Ph.D. research (Foundation for Fundamental Research on Matter, the Netherlands) at the Delft University of Technology. His Ph.D. work comprised the experimental and theoretical research on carrier multiplication, electron–hole-pair recombination and dissociation, and subsequent charge diffusion and trapping in systems of semiconductor nanocrystals (quantum dots).

C. S. Suchand Sandeep obtained his masters degree in physics from IIT Madras and his Ph.D. from the Raman Research Institute, Bengaluru, India, in 2010. He was a visiting researcher at the Universita Politecnica delle Marche, Ancona, Italy, during 2006–2007. After completing his Ph.D., he joined Delft University of Technology, the Netherlands, as a postdoctoral researcher. His research interests include solar energy conversion, multiple exciton generation, nanoscience and nanotechnology, ultrafast spectroscopy, and nonlinear optics.

Yao Liu studied chemistry at Beijing Normal University and obtained his Ph.D. degree at the Institute of Photographic Chemistry, Chinese Academy of Sciences, in 1995. He was promoted as research professor at the Institute of Photographic Chemistry, Chinese Academy of Sciences, in 1999. He worked as a postdoctoral researcher at the University of Uppsala in Sweden and at the University of Florida in the USA. He worked as a research associate at The Ohio State University and as specialist at University of California at Irvine. His research involves low-structured semiconducting materials including quantum well, superlattices, quantum dots, and conjugated organic materials. He is also interested in solar cells and photodynamic therapy related metal complexes.

Matt Law joined the Chemistry Department at the University of California, Irvine, in 2008 and was promoted to Associate Professor with tenure in 2014. He obtained his Ph.D. in Chemistry from the University of California, Berkeley in 2006, where he studied the synthesis, properties, and device applications of oxide nanowires under the direction of Peidong Yang. His postdoctoral research with Arthur Nozik at the National Renewable Energy Laboratory focused on the development of quantum dot solar cells and photoelectrochemical water splitting devices. Matt's research group at UC Irvine focuses on the development of new materials and devices for solar energy conversion, including nanostructured solar cells, earth-abundant thin-film photovoltaics, and water splitting cells.

Sachin Kinge is leading the Functional Nanomaterials laboratory in Toyota Motor Europe. His research is about future advanced technology on new materials for energy conversion/storage. Before joining Toyota, he earned a Ph.D. from The Max Planck Institut für Kohlenforschung, Germany, in 2004 and was a postdoctoral researcher in MESA+ Institute of Nanotechnology at the University of Twente in the Netherlands.

Arjan J. Houtepen studied chemistry at Utrecht University. He obtained his Ph.D. in 2007 under supervision of Prof. Vanmaekelbergh at Utrecht University and subsequently became tenure track assistant professor in Delft. In 2009–2010, he was a visiting scientist in the group of Prof. Feldmann in Munich. At present, he is tenured assistant professor in the Optoelectronic Materials Section of the Department of Chemical Engineering at Delft University of Technology and guest professor in the Physics and Chemistry of Nanostructures group at

Ghent University. His research focuses on the generation, transport, and decay of charges in films of colloidal quantum dots.

Juleon M. Schins received his Ph.D. degree in 1992 at the University of Amsterdam, the Netherlands. After postdoctoral research in France (Laboratoire d'Optique Appliqué, ENSTA, Palaiseau) and the Netherlands (Universiteit Twente), he joined the Optoelectronic Materials Section of the Department of Chemical Engineering at Delft University of Technology. His current research interests include charge carrier mobility and exciton dynamics in photoexcited semiconductor nanostructures (dots, rods, and platelets), studied by means of pump-probe spectroscopy, probing in the visible, infrared, terahertz, and gighertz regimes.

Laurens D. A. Siebbeles studied chemistry at the Free University in Amsterdam and obtained his Ph.D. degree at the FOM-institute for Atomic and Molecular Physics (AMOLF) in Amsterdam in 1991. He was a postdoctoral researcher at the University of Paris-Sud in France. Currently, he is leader of the Optoelectronic Materials Section of the Department of Chemical Engineering at the Delft University of Technology in the Netherlands. His research involves time-resolved spectroscopic studies on excitons and charges in novel nanostructured materials, including organic materials, semiconductor quantum dots, nanorods, and two-dimensional materials.

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