# Multiple Exciton Generation in Semiconductor Quantum Dots

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ABSTRACT: Multiple exciton generation in quantum dots (QDs) has been intensively studied as a way to enhance solar energy conversion by utilizing the excess energy in the absorbed photons. Among other useful properties, quantum confinement can both increase Coulomb interactions that drive the MEG process and decrease the electron−phonon coupling that cools hot excitons in bulk semiconductors. However, variations in the reported enhanced quantum yields (QYs) have led to disagreements over the role that quantum confinement plays. The enhanced yield of excitons per absorbed photon is deduced from a dynamical signature in the transient absorption or transient photoluminescence and is ascribed to the creation of biexcitons. Extraneous effects such as photocharging are partially responsible for the observed variations. When these extraneous effects are reduced, the MEG efficiency, defined in terms of the number of additional electron−hole pairs produced per additional band gap of photon excitation, is about two times better in PbSe QDs than that in bulk PbSe. Thin films of electronically coupled QDs have shown promise in simple photon-to-electron conversion architectures. If the MEG efficiency can be further enhanced and charge separation and transport can be optimized within QD films, then QD solar cells can lead to third-generation solar energy conversion technologies.
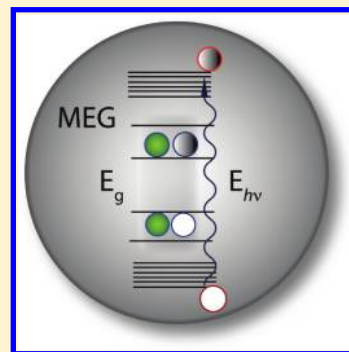
Power conversion efficiency is one of the most important parameters that can directly affect the overall cost of a PV installation. In the Shockley−Queisser (SQ) detailed balance analysis, the power conversion efficiency (PCE) is limited to ∼33% for a single light-absorbing layer.[1] The major energy loss occurs from the excess photon energy, energy greater than the semiconductor band gap, which is lost as heat through electron−phonon coupling and subsequent phonon relaxation and energy dissipation. The first Si-based solar cell was introduced in 1941 by Russell Ohl[2] with PCEs of less than 1%, and advances in material processing, material quality, and device configurations have resulted in PCEs that reach ∼80% of the SQ limit for Si or GaAs.[3] Utilizing the excess photon energy to create additional electron−hole pairs increases[4] the thermodynamically allowed PCE to ∼44% for unconcentrated light,[5] while hot carrier solar cells or multijunction solar cells with an infinite number of layers perfectly matched to the solar spectrum can reach ∼66%.[6] In bulk semiconductors, electron−hole pair multiplication (EHPM) is referred to as impact ionization (II), and in QDs, it is called multiple exciton generation (MEG). Impact ionization has been studied for over 50 years in bulk semiconductors;[7−16] however, it is too inefficient to contribute to improved PCEs. In 2001−2002, Nozik proposed that EHPM maybe enhanced in nanostructures with strong quantum confinement.[17,18] Nozik realized that while for bulk semiconductors, II must conserve both energy and momentum, the conservation of momentum is relaxed in QDs. Therefore, the threshold photon energy can approach twice the threshold energy for absorption, or the effective band gap (E_g). Lowering the threshold energy allows better utilization of the available solar spectrum and, as was later realized, also increases the efficiency of the EHPM process.[19]

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In 2004, Schaller and Klimov[20] noticed that when photoexciting a colloidal suspension of PbSe QDs at high photon energies ($h\nu > 3E_g$), a fast component persisted in the transient absorption (TA) dynamics even when the laser fluence was adjusted so that the average number of photoexcited excitons, $\langle N_0 \rangle$, was <0.1. For pulsed laser excitation of a solution of QDs with pulses of sufficiently short duration, the average occupation level follows Poisson statistics,[21] such that the fraction P_m of QDs within the excitation volume with m photogenerated excitons is $P_m = \exp[-\langle N_0 \rangle]\langle N_0 \rangle^m/m!$, where $\langle N_0 \rangle$ is the average number of photons absorbed per QD per pulse, given by $\langle N_0 \rangle = \sigma_a j_p$, with
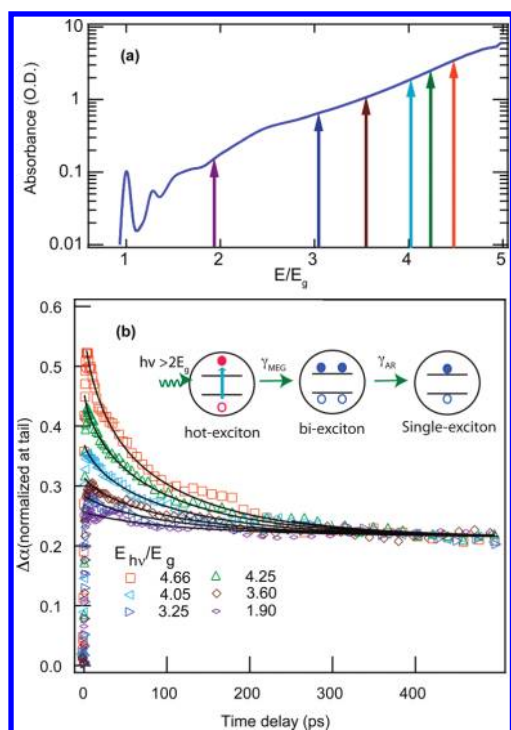
Figure 1. Typical MEG transient absorption experiment. (a) Linear absorption of PbSe QDs. The arrows show the excitation energies used to investigate MEG and correspond to the traces in (b). (b) Transients for a constant $\langle N_0 \rangle$ but increasing the photon energy from $1.9E_g$ to $4.6E_g$. The amplitude of the fast component increases with increasing photon energy. The inset shows the excitation of QDs with a photon energy greater than $2E_g$ to produce a hot exciton; the hot exciton undergoes MEG to produce a biexciton, and the biexciton undergoes Auger recombination to produce a cold single exciton. Reprinted with permission.[31]

a per-QD absorption cross section of σ_a (cm^2) and a photon pump fluence of j_p (photons$\cdot cm^{-2}\cdot pulse^{-1}$). The per-dot absorption cross section is measured in a separate experiment using ICP-MS[22] or other analytical analysis[23] and has been measured and tabulated for a variety of QD materials.[22−26] When QDs have more than one exciton, Auger recombination,[27] which describes multiparticle interactions, governs the relaxation dynamics.

Schaller and Klimov analyzed the fast component that they observed for $\langle N_0 \rangle < 0.1$ and $h\nu > 3E_g$ and found that it had the same characteristics of the biexciton lifetime, τ_2, measured in a separate experiment for an average occupation level $\langle N_0 \rangle > 1$ and relative photon energy of $h\nu < 2E_g$. The biexciton lifetime, τ_2, for typically sized QDs is in the range of ~10 to ~100 ps and is mainly governed by the volume of the QDs,[28,29] while single-exciton lifetimes are at least an order of magnitude longer. The amplitude corresponding to the fast component increased with increasing photon energy after exceeding a photon energy threshold ($h\nu_{th}$) (see Figure 1), indicating a larger biexciton population. Upon investigating QDs with different band gaps, the fast component tracked the expected linear dependence of τ_2 with QD volume. The appearance of the fast component was ascribed to efficient multiexciton generation with a threshold photon energy of $3E_g$, which is lower than what is required by momentum conservation considerations in bulk PbSe ($\sim 4E_g$)[28] and ~2 times lower than what was reported for impact ionization in bulk PbSe, $\sim 6E_g$.[30] The evidence that multiple excitons were

produced per absorbed photon, therefore, is the appearance of the fast multiexciton decay component with the identical time constant of τ_2 when photoexciting above the energy conservation threshold (>$2E_g$) and at low intensity so that each photoexcited QD absorbs at most one photon. The photon-to-exciton QY at different photon energies was obtained from analyzing the amplitude of the fast and slow components. They further reported that when plotting their quantum yield (QY) data versus the normalized band gap (plotted as $h\nu/E_g$), the data from various sized PbSe samples collapsed onto a single line. Reports confirming efficient MEG in PbSe QDs quickly followed,[31] and was also reported in PbS[31] and PbTe QDs.[32] MEG has been reported for PbSe,[33,34] CdSe,[35,36] InAs,[37,38] Si,[39] InP,[40] CdTe,[41] (6,5) SWCNTs,[42] and CdSe/CdTe core/shell QDs.[43]

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Following the discovery of MEG in QDs along with optical measurements of this phenomenon in a wide variety of QD material systems, there were several groups who reported some discrepancies. In 2007, Nair and Bawendi[44] reported that while investigating CdSe and CdTe QDs, they did not observe a signature of MEG; the carrier dynamics were independent of excitation wavelength. In their study, they used a transient photoluminescence (TRPL) experiment rather than TA, but the general idea is the same; a biexciton has a faster decay than a single exciton. Their result was in contrast to a previous report from Schaller and Klimov that found positive MEG results for CdSe QDs also using TRPL.[35] Nair and Bawendi followed their study on CdSe QDs with a TRPL study of PbS and PbSe QDs.[45] Here, they did observe MEG but found smaller QYs than previous reports. Following these reports, a study of InAs core/shell/shell QDs also did not observe MEG,[46] in contrast to a Klimov report.[35] Pijpers et al.[47] reported that they could not reproduce their earlier positive MEG results using similarly prepared InAs QDs. Beard et al.[48] reported a wide variation in the QYs of PbSe QD films; the variations depended on how the QDs were treated and the different surface chemistries used to produce conductive QD films.

Because of the discrepancies and various negative reports, doubts arose surrounding all of the MEG measurements. Therefore, efforts were directed toward understanding the variations in the reported QYs. The situation began to be clarified when McGuire et al.[49,50] proposed that due to the repetitive nature of the pulsed laser experiments, a steady-state population of

1283

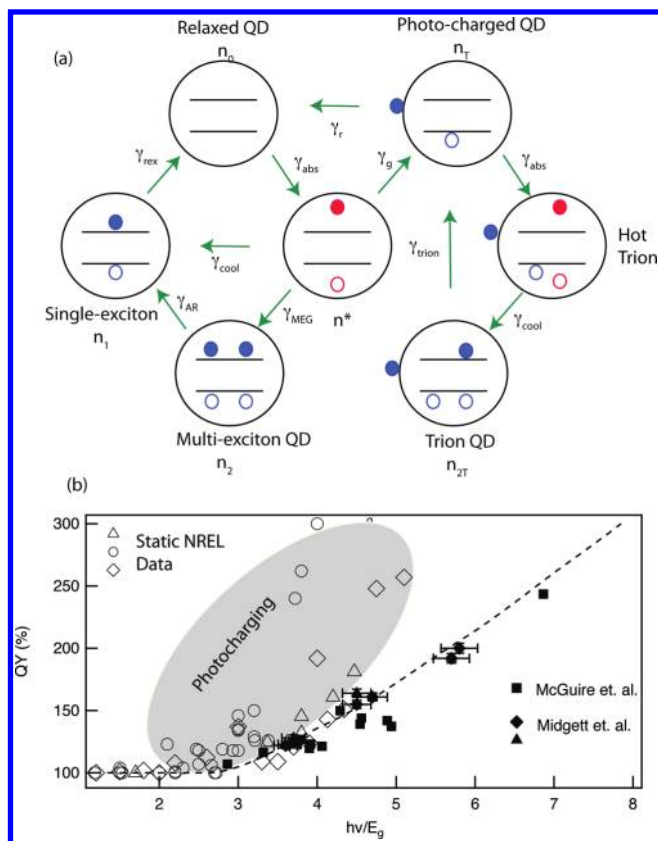dx.doi.org/10.1021/jz200166y |*J. Phys. Chem. Lett.* 2011, 2, 1282–1288

Figure 2. (a) Relaxation pathways for excitons produced with high-energy photons. The photocharging pathway complicates the analysis of MEG yields and depends on the photon energy, photon fluence, and QD surface quality. The effects of photocharging on MEG yields can be reduced by flowing or stirring the samples during the experiment. Reproduced with permission.[52] (b) Photon-to-exciton QYs deduced from transient absorption data and results obtained on static solutions compared to flowing or stirring solutions.

charged QDs can be established through a low-probability photoionization event if the lifetime of the photoionized state is longer than the time between excitation pulses (2 ms).[51] The proposed scheme is illustrated in Figure 2a. Unexcited QDs (labeled n_0) in the top panel are excited to n*, a hot exciton state produced by absorption of a photon with $h\nu > 2E_g$. The hot exciton may cool (labeled γ_{cool}) to the band gap, creating a single exciton in its lowest-energy state, or undergo MEG to create two or more excitons. However, the hot exciton state may also undergo photocharging with rate γ_g. These QDs accumulate during the experiment because their lifetime exceeds that of the laser repetition rate. If a QD in the n_T state absorbs another photon from the next laser pulse, a trion-like state (labeled n_{2T}) is produced that undergoes a nonradiative Auger recombination (γ_{trion}) process with similar dynamics to biexciton recombination. Thus, yielding a similar dynamical signature that if otherwise is ascribed solely to MEG leads to an artificially high QY.[49,50,52] This alternative pathway can be avoided by not exposing the QDs to multiple laser pulses either by stirring or carefully flowing the QD solution. Thus, the small fraction of QDs that undergo photocharging are swept away and not allowed to accumulate.

McGuire et al. found that the photoionization event must have a very low probability and that the ionized QD lifetime must be

very long.[49] Midgett et al. further analyzed the photocharging in PbSe QDs and found that the photocharging occurred with a probability of 1×10^{-5} for absorption of photons with $\sim 4E_g$ of energy but that once photocharged, their lifetime could be between 10 and 30s.[52] They reported that some of the variations in the QYs could be traced to different surface conditions of the QDs. Differences in the surface chemistry could affect either the competition between cooling and MEG or the degree of photo-charging. Varying QD surface conditions, excitation fluence, and photon energy leads to variations in the degree of photocharging. McGuire et al.[53] proposed an energetic barrier between the lowest single-exciton state and a localized surface trap state that can be accessed by the initially hot exciton.[53] Figure 2b compares the QYs obtained under static and flowing conditions.[19] The static conditions produced results that differed between three different samples,[31] while under flowing conditions, reproducible results are obtained. Whether photocharging plays a role in other QD systems such as Si, CdSe, InAs, and InP remains an open question.

Researchers also questioned the notion that MEG in QDs was actually enhanced over II in bulk semiconductors; the argument of an enhanced Coulomb interaction in QDs may be offset by a lower density of final states in QDs relative to that for bulk semiconductors.[30,45] Nair and Bawendi[45] and later Pijpers et al.[30] argued that plotting the enhanced QY versus the reduced photon energy ($h\nu/E_g$) overestimated the contribution of quantum confinement, and they showed that when plotting the QYs versus $h\nu$, neglecting the band gap, the results from bulk semiconductors were higher than those obtained from QDs. To compare the measured results from QDs with II measured in bulk semiconductors, Beard and Ellingson[28] plotted $(QY - 1)$, or the extra carriers produced, versus $(h\nu/E_g - 2)$, or the amount of excess energy above the energetic minimum. Pijpers et al. defined an energy efficiency and concluded that while the QY found for bulk semiconductors could be higher at a fixed photon energy, the energy efficiency is higher in the QDs because the amount of energy needed to produce an (electron–hole) e–h pair is larger for QDs. McGuire et al. used two different "figures of merit" to compare the measured QYs, an energy figure of merit defined as the $QY*E_g$ and a M figure of merit that compares the measured QYs to that of an ideal MEG material. The ideal behavior was assumed to be a straight line starting with a photon energy threshold ($h\nu_{th}$) of $2E_g$ and a slope corresponding to the formation of each additional e–h pair at each additional increase of E_g; thus, the CM figure of merit is $QY/QY_0 = (QY - 1)/[h\nu/E_g - 2]$, similar to the analysis of Beard and Ellingson. Beard et al.[19] considered the energy losses that occur with and without EHPM. For absorption of a photon with energy greater than E_g but in the absence of EHPM, all of the excess energy is lost as heat, $E_{loss} = h\nu - E_g$. When the EHPM efficiency, η_{EHPM}, is equal to 1, the amount of excess energy needed to produce an additional EHP is just the band gap energy, E_g. The amount of energy lost at a photon energy $h\nu = xE_g$, where $x > 1$, is $E_{loss} = (x - m)E_g$, where $m = \lfloor h\nu/E_g \rfloor$ and the "floor" operator, $\lfloor\ \rfloor$, denotes rounding down to the nearest integer. The maximum QY exhibits a "staircase" where QY = 2 at $2E_g$, 3 at $3E_g$, and so forth and is plotted as trace M_{max} in Figure 3. When the EHPM efficiency is less than 1, the amount of energy required to produce an additional EHP defined as the e–h pair creation energy, ε_{EHPM},[49,54,55] is greater than the band gap energy $\varepsilon_{EHPM} \geq E_g$. Therefore, η_{EHPM} is defined as the minimum amount of energy required to produce an EHP (i.e., the band gap) divided by the
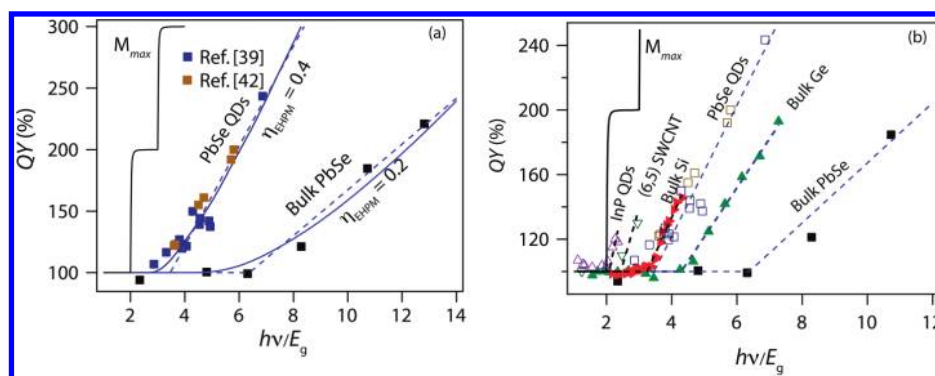
Figure 3. (a) QYs for PbSe QDs,[39,52] compared to bulk PbSe.[30] (b) EHPM in bulk Ge[7] ($\eta_{EHPM} = 0.3$), bulk Si[15] ($\eta_{EHPM} = 0.4$), and bulk PbSe ($\eta_{EHPM} = 0.2$) are compared to available EHPM results for PbSe QDs ($\eta_{EHPM} = 0.4$), InP QDs[40] ($\eta_{EHPM} = 0.9$), and (6,5) SWCNTs[42] ($\eta_{EHPM} = 0.7$).

actual amount of energy required to produce an additional EHP after the MEG threshold is passed, $\eta_{EHPM} = E_g/\varepsilon_{EHPM}$. Experimentally, QYs begin to exceed 1 above an energy threshold, $h\nu_{th}$, and they increase linearly for $h\nu > h\nu_{th}$. In this nonideal case, the amount of energy lost that is not used in creating additional EHPs is $E_{loss} = h\nu_{th} - E_g = E_g/\eta_{EHPM}$ for photon energies greater than $E_g + \varepsilon_{EHPM}$, and the QY is related to η_{EHPM} by

$$ QY = \left(\frac{h\nu}{E_g} - 1\right)\eta_{EHPM} = (h\nu - E_g)\frac{1}{\varepsilon_{EHPM}} \quad (1) $$

for $h\nu > h\nu_{th}$. η_{EHPM} is be obtained from plotting the QY versus $h\nu/E_g$, while $1/\varepsilon_{EHPM}$ is obtained from plotting QY versus $h\nu$. The energy threshold is related to the efficiency by

$$ h\nu_{th} = E_g + \frac{E_g}{\eta_{EHPM}} \quad (2) $$

Improving the overall efficiency of the EHPM process results in a lower energy threshold. An expression relating the QY to the competition between cooling and EHPM was derived. Figure 3a displays enhanced QY data for PbSe QDs where the samples are flowed at 150 mL/min during the transient absorption experiment. Data from refs 49 and 50 for PbSe QDs are plotted as dark blue squares. EHPM QYs for bulk PbSe (filled black squares) are plotted and reproduced results from ref 30. EHPM is about two times more efficient for the PbSe QD samples (0.41) than that for the bulk PbSe (0.19). Similar conclusions were reached by the analysis of Beard and Ellingson,[28] Delerue et al.,[56] and McGuire et al.[50]

Some insight into how EHPM may be further improved can be gained by comparing the various available literature results for QDs and bulk semiconductors. Figure 3b displays data for bulk Ge[7] ($\eta_{EHPM} = 0.3$), bulk Si[15] ($\eta_{EHPM} = 0.4$), as well as bulk PbSe data. Data for the PbSe QDs, InP QDs[40] ($\eta_{EHPM} = 0.9$), and (6,5) SWCNTs[42] ($\eta_{EHPM} = 0.7$) are displayed. In nearly all cases, the efficiencies for the QD samples are higher than those for bulk semiconductors, with bulk Si displaying the highest efficiency among the available bulk semiconductor data, comparable to that of the PbSe QDs. While there is one promising report of MEG for Si QDs[39] with $\eta_{EHPM} = 0.9$, those measurements need to be repeated to determine the contribution of photocharging and then verified at different laboratories. The results for InP QDs are promising; however, they have too large of a band gap to be of use for photovoltaic applications; therefore, narrow band gap III−V QDs such as InN, InAs, and InSb are of interest. For the specific

case of InAs QDs, there are conflicting reports,[37,38,46,47] and further investigation to sort out the MEG efficiencies is needed. The results for the (6,5) SWCNTs where there is no bulk counterpart are also promising, and these novel absorbers require further work. In order to determine what factors influence the enhanced efficiencies in QD, all of the competing channels need to be better understood. Extraneous competing channels such as surface-mediated cooling and whether and how these channels can be reduced to lead to potentially even higher MEG efficiencies need to be understood. As an example of this approach, Pandey and Guyot-Sionnest[57] designed a QD heterostructure consisting of a CdSe/ZnS/ZnSe/CdSe core/shell1/shell2/shell3 structure that was designed to eliminate alternative carrier relaxation channels and demonstrated the slowed cooling of the electronic states within the CdSe core. The realization of slowed cooling followed many years of research into the various cooling channels within CdSe QDs, and such an approach should be fruitful for enhancing MEG efficiencies in designed QD systems.

> **Multiple exciton generation in QDs is a very important process that, if harnessed, could lead to a new solar conversion efficiency limit.**

In order for MEG to have a large impact on solar energy conversion, the QDs must be incorporated into a suitable energy conversion architecture.[17,58] The minimum requirements are (1) the QDs must be the absorbing component, (2) the multiexcitons produced within the QDs must be separated prior to Auger recombination, and (3) the free charge carriers or excitons must be transported to electron- and hole-accepting contacts. A further requirement is that the MEG efficiency must not be degraded when the QDs are incorporated into one of these schemes. After the initial reports of MEG in QDs, intense interest in producing QD solar cells (QDSCs) followed,[59−64] with the goal of incorporating QDs such that multiple excitons can be separated and collected as photocurrent.[65] The most promising approach is based on films of electronically coupled QDs as the absorber layer in an all inorganic PV device. The QD films to date have been incorporated into Schottky barrier configurations and p−n heterojunction (see Figure 4) structures. The PCE efficiency for these
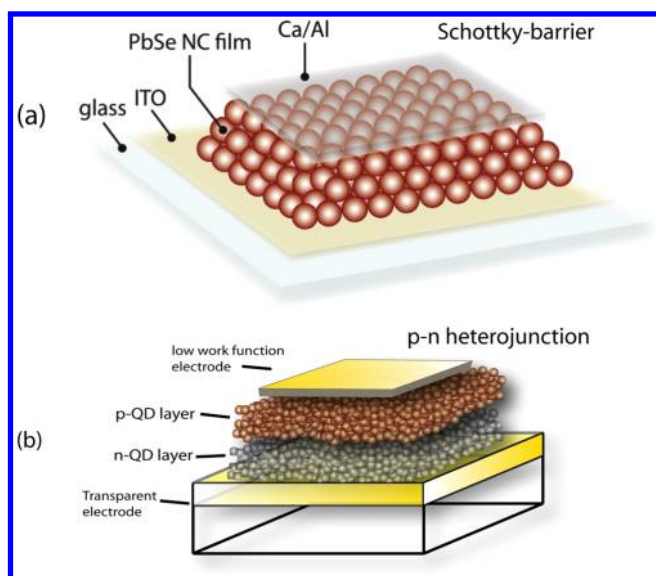
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Figure 4. (a) Schematic representation of simple Schottky barrier quantum dot solar cells; light enters through the glass/ITO layer where a thin layer (60–300 nm thickness) of QDs is deposited via a layer-by-layer approach. (b) A p–n QD heterojunction; the PbS(Se) QD-film is the p-layer. Adapted and reproduced with permission.[62,65]

approaches has increased from 1–2% in 2007 to 4–5% in 2010. The measured V_{oc} of PbS QDSCs is higher than the bulk PbS band gap,[61] demonstrating that useful quantum confinement properties can be retained in a suitably designed solar energy conversion structure. Approaches based on QD-sensitized TiO_2 and QD–polymer blends[66] have also shown promise.

To produce conductive QD films where the QDs retain some degree of their quantum confinement properties, a layer-by-layer procedure of treating the QD film with a dilute solution of 1,2-ethanedithiol (EDT) or similar thiols has received the most attention. The treatment tends to produce lightly conductive p-type QD films with modest carrier mobilities.[67] The short thiol ligands replace the longer insulating as-produced carboxylic acid ligands, bringing the QDs closer to allow for efficient communication. To investigate the effects of chemical treatment on single and biexciton lifetimes and MEG, five chemical treatments that can produce conductive QD films were studied,[48] and the authors found that three important changes occur; (1) the single-exciton lifetimes decrease, reflecting an increased rate of recombination, (2) the biexciton lifetime increases for decreasing QD–QD distance, and (3) the absorption cross section per QD increases for films with longer biexciton lifetimes.

Careful examination of the internal quantum efficiency (IQE) in a Schottky junction EDT-treated QDSC did not find evidence for collection of multiple carriers per absorbed photon.[65] In agreement, TA results found that MEG is nearly quenched in the EDT treated films. There are at least three ways in which the various chemical treatments can affect MEG, (1) changes in the surface chemistry which affect QD–ligand interactions and subsequently exciton relaxation rates, (2) doping of the QDs, causing enhanced Auger recombination, and (3) an increase in inter-QD coupling, producing diminished quantum confinement and/or charge-transfer states with higher carrier mobilities and lower inter-QD charge-transfer barriers. The degree to which each of the above contributes to modulating MEG has not been

determined, and more work is needed to sort out how best to build a QD-based PV device that preserves MEG.

Surprisingly, QYs found for some chemically treated films compare well with the results found for stirred or flowed PbSe QD solutions. For the film measurements, the samples are completely static, and therefore, any photocharging discussed above should be more severe. However, in only the pure EtOH-treated film was there an apparent increase in the MEG yield observed, while all other films studied showed a decrease in MEG relative to that measured in static solutions. The photocharging discussed above results in an apparent increase of the QY, and therefore, it was concluded that photocharging in films must be of a different nature than that observed in the isolated QDs. Photocharging in films may not occur as efficiently as that in solutions for several reasons; (1) the high mobility of carriers may allow for faster regeneration of the photocharged state, and (2) differences in surface states induced by the different surface ligands as well as increased QD–QD coupling may reduce the density of acceptor sites. Future work will be needed to understand potential charging effects in QD films. Understanding exciton dynamics and MEG efficiency in electronically coupled QD films is essential for learning how to harness MEG to convert light into electricity with high efficiency.

There are several examples of MEG measured in the photocurrent of devices incorporating either QDs or carbon nanotubes. Sambur et al.[68] found an IQE greater than 1 for a single monolayer of PbS QDs that were strongly coupled to an atomically flat TiO_2 anatase surface. Gabor et al.[69] constructed p–n junction photodiodes from SWCNTs and observed efficient EHPM in the photocurrent when the photoenergy was tuned to greater than $2E_g$. Hints of multiple carrier collection were observed in the biased IQE of a PbS QD photodiode structure.[70,71] A tandem polymer/PbSe QD device showed evidence of MEG within the PbSe layer;[72] however, the IQE of each individual layer was not extracted. These results provide ample motivation to gain a complete picture of carrier relaxation processes in QDs and QD assemblies in order to learn how to boost MEG efficiencies and extract the extra carriers as photocurrent.

Future Issues and Challenges. Multiple exciton generation in QDs is a very important process that, if harnessed, could lead to a new solar conversion efficiency limit. To make the largest impact on solar energy technologies, the MEG efficiency needs to be further improved so that the onset for MEG occurs as close to $2E_g$ as possible.[19,58] The parallel process of impact ionization in bulk semiconductors was studied for many years as a means of bypassing the SQ limit, and while II is too inefficient to be of use for solar energy conversion, it does play a major role in enhancing the sensitivity of photodetectors. Future research challenges include understanding the size-dependent MEG efficiency; how does the MEG efficiency scale with size from QDs to bulk? Is there morphology dependence to the MEG efficiency? What

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1286

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governs the MEG efficiency in different materials systems? This is related to why II efficiencies differ in bulk semiconductors, a question that still is not well understood. The competing relaxation channels need to be understood. Solar energy conversion strategies that incorporate QDs is an emerging field of research with many different approaches.[73−75] A better understanding of how surfaces of the highly faceted QDs affect energy flow and how to better control surface states is essential. The fact that MEG is enhanced in PbSe QDs is encouraging, and a better understanding of the factors that influence MEG will lead to improvements in efficiency.

■ BIOGRAPHY

Matthew C. Beard studied time-resolved THz spectroscopy at Yale University with Charles Schmuttenmaer and graduated with a Ph.D in Physical Chemistry in 2002. He joined the group of Arthur J. Nozik in 2003 at NREL using THz spectroscopy to study charge carrier generation and transport within quantum dot arrays and films. Currently, Dr. Beard is a Senior Scientist in the Chemistry and Materials Science Center at NREL. His interest includes quantum dot solar cells and exciton and charge carrier dynamics in quantum dots and coupled quantum dot films. He employs transient absorption and THz spectroscopy in his studies.

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1288

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