

More Efficient Solar Cells
via
Multi Exciton Generation

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Introduction

Sunlight is the most abundant source of energy available on Earth and if properly harnessed, could significantly reduce the world's dependency on fossil fuels. In fact, current commercial solar cell technology could easily produce enough electricity to supply the United States for an entire year. This would require only a ~60,000 sq. km patch of land in Nevada. The reason that efforts aren't being made to build a solar farm at such scales is that the total cost would be in the trillions, likely surpassing the total U.S. national debt. The primary challenge with solar cells is thus improving its efficiency and reducing manufacturing and materials cost to make it cost competitive with conventional fossil fuel plants.

In terms of efficiency, conventional silicon solar cells, utilizing a single p-n junction, are limited to a maximum efficiency of 33% under AM1.5G sunlight, as defined by the Shockley-Queisser limit. For a given band gap (1.1 eV for silicon) photons with energies smaller than the band gap energy will not be absorbed. For photons with energies larger than the bandgap, the excess energy of photoexcited carriers (electrons and holes) is usually dissipated as heat via carrier-phonon scattering. If these unused regions in the solar spectrum can be utilized, it is possible to break the Shockley-Queisser limit [1].

In fact, the development of tandem solar cells is based on this notion where multiple p-n junctions composed of different active layer materials with different band gap energies are stacked on top of one another to better match the solar spectrum. In the limit of a stack composed of infinite layers, where the largest band gap material is placed at the top, the limit in efficiency then becomes 66%. Unfortunately, such tandem solar cells, despite their gains in efficiency, are cost prohibitive [1].

Another development has proposed the use of high energy carriers, excited via photons with energies larger than the band gap energy, to improve the energy conversion efficiency of solar cells. In essence, if the high energy carriers can excite additional electron-hole pairs and can be successfully transported to the electrical contacts, a greater photocurrent will be achieved. The primary draw of this phenomenon is that if these high energy carriers can be fully utilized without any heat loss, the theoretical thermodynamic efficiency will improve from 33% to 66% while only using a single junction [1,2]. The primary challenge is thus developing a means of enabling these carrier transport and multiplication processes to occur at a higher rate compared to the innate carrier cooling processes. Significant effort has been invested in this field and, as will be discussed, not without controversy.

Hot Carrier Enhancement

Carrier Excitation Process

Generally, when a photon with energy greater than the band gap energy is absorbed in a semiconductor, the excess energy will be redistributed in the form of kinetic energy amongst the photoexcited electrons and holes according to their respective effective masses. The effective mass of electrons is typically much smaller than the effective mass of holes, thus the electrons will receive a greater portion of the excess kinetic energy. Hence, the initial relaxation dynamics, prior to any scattering processes, will be dominated by electrons [1,2].

To establish equilibrium, the excited electrons will undergo thermal relaxation in two phases. In the first phase, electrons will redistribute amongst themselves via inelastic carrier-carrier scattering to form a quasi-equilibrium Fermi-Dirac distribution. A temperature can thus be associated to each carrier distribution which corresponds to the excess kinetic energy gained by each carrier. If the excess kinetic energy is greater than the band gap energy by at least kT ,

then electrons will have an initial temperature greater than the surrounding lattice. The term hot electron is used to describe these high energy carriers after the initial relaxation process where temperatures can be as high as 3000K with a lattice temperature of 300K [3]. Note that carrier-carrier scattering is quite fast (< 100 fs) [1,2].

In the second phase, once the electrons have redistributed amongst themselves, they will then equilibrate with the lattice. Generally, in semiconductors, equilibration will occur via longitudinal optical phonon emission from electron-phonon scattering. In other words, the excess energy initially gained by each electron will be lost as heat. This process is typically on the order of a ~ 100 fs time scale as well and will occur until the carrier temperature and lattice temperature equal [1,2]. Assuming no electrons are extracted, the electrons and holes will recombine in a radiative or non-radiative manner. In the non-radiative case, the electron-hole pairs can recombine and emit a phonon directly or they may undergo Auger recombination where the energy of one carrier is transmitted to another carrier before phonon emission occurs. Equilibrium is then reached once the populations of electrons and holes equal the original populations prior to the absorption of the photon.

Hot Carrier Enhancement

In conventional p-n junction solar cells, these heat losses typically comprise 47% of total losses [2]. Thus, if the hot electrons can be better utilized to generate photocurrent, thus reducing heat losses, then the overall energy conversion efficiency will correspondingly improve as well. This can occur if the high energy electrons can transfer its excess kinetic energy to excite an additional electron-hole pair in a process known as impact ionization. Impact ionization is the inverse of Auger recombination [2]. For practical use, the rate of impact ionization must occur at a higher rate compared to the carrier cooling processes. In the case where the excess energy of an

electron is insufficient to excite additional carriers, it would be desirable to ensure electron transport is also faster than the cooling processes so as to minimize heat loss. Generally, the different effective masses for electrons and holes will lead to different relaxation dynamics, resulting in additional complexity, which will become particularly important when carrier-carrier scattering processes occur. It should be noted that because of this disparity in carrier effective mass, the threshold energy necessary to excite an additional exciton will not necessarily be $2E_g$ as follows,

$$h\nu_{thresh} = \left(2 + \frac{m_e}{m_h} \right) E_g \quad (1)$$

where it is assumed that the effective mass of the holes, m_h , is greater than or equal to the effective mass of electrons, m_e [2]. As an example, in the case of a PbSe nanocrystalline material, the effective masses of holes and electrons are approximately equal. Thus, the threshold energy to initiate carrier multiplication is actually $3E_g$.

The key challenge to utilizing these effects in real solar cell systems require developing a means of improving transport and impact ionization rates relative to the carrier cooling rates. Thus far, effort has been made to slow the cooling processes by altering the relaxation dynamics via quantum confinement. Despite initial experimental results supporting this belief, subsequent experimentation has led to contradictory results, causing significant debate over the mechanism behind enhancement and whether quantization truly has an effect on the cooling rate.

Mechanism for Multi Exciton Generation

The original motivation behind the use of quantum confinement was based on experiments showing the occurrence of multiple exciton generation in bulk materials. These materials include PbSe, PbS, CdSe, InAs and Si [2]. It was believed that quantization could alter the band structure of the material to further increase the number of excited excitons by reducing

the carrier cooling rate via a phonon bottleneck. This phonon bottleneck is achievable for both quantum well structures (1D confinement) and quantum dots (3D confinement), albeit using different carriers [1]. It was also believed that stronger Coulombic coupling of electrons and holes, the primary cause of increased Auger recombination, would also allow impact ionization to occur at a higher efficiency [1,2,4]. For these effects to occur, the proposed nanostructures would require a characteristic dimension smaller than the Bohr exciton radius, the physical distance between an electron in a conduction band and a hole in the valence band. This would lead to larger band energies and increasingly discretized interband transitions [5]. In order to determine the effect of quantum confinement on the cooling rate, the relaxation time constant, corresponding to the electron temperature decay rate via phonon emission, can be studied using the following expression,

$$\tau_c \sim \omega^{-1} \exp\left(\frac{\hbar\omega}{kT}\right) \quad (2)$$

where τ_c is the hot carrier cooling time, ω is the phonon frequency, and T is the carrier temperature.

For quantum well or superlattice structures, a hot phonon bottleneck can be produced if the carrier density is sufficiently high. As mentioned previously, longitudinal optical phonons are the primary carrier involved in electron-phonon scattering. Equation (2) was used to compare a bulk sample of GaAs and a multi quantum well sample of GaAs at different carrier densities. The results are shown in Figure 1 [6].

The results show that higher carrier densities will result in a longer time constant, thus resulting in a slower cooling rate. This decrease in cooling rate is the hot phonon bottleneck. The reasoning for this effect is that for large carrier densities, a large nonequilibrated population of longitudinal optical phonons will be produced in such a manner that they cannot equilibrate with

the lattice quick enough due to the more sparse electronic structure of the material. Some of the optical phonons will thus be reabsorbed by the electrons, slowing the temperature decay and the cooling rate [1,6]. Unfortunately, this bottleneck effect requires large carrier densities to occur, as indicated in Figure 1 where the difference in the time constant between the bulk sample and the multi quantum well sample are only apparent at high carrier densities. This high carrier density requirement corresponds to very high solar concentrations on the order of 10^4 [1]. For practicality, this is unsuitable.

In the case of 3D quantum confinement, such as in quantum dots or nanocrystalline materials, it is also believed a phonon bottleneck can occur without the requirement of a high carrier density. This is possible due to the quantization effects on the energy band structure, where the changes in the electronic structure limit the phonon modes capable of intraband transition. Such modes will consist of simultaneous emission of multiple phonons or the emission of a high energy phonon.

On the basis of this mechanism alone, the cooling rate should decrease. However, experimentation on several nanocrystalline materials, such as InP and CdSe, has resulted in cooling rates that are still relatively fast when compared to a true bottleneck situation [2]. The reason is due to the presence of additional scattering mechanisms. The most prominent mechanism is believed to be an Auger process where the excess kinetic energy of an electron is transferred to a hole. Because the hole generally has a larger effective mass, the valence band structure will be correspondingly denser compared to electrons, thus facilitating phonon emission. In fact, experiments on InP nanocrystals have shown cooling rates will increase as the size of the nanocrystal decreases. This is believed to be due to greater Auger cooling resulting

from the stronger Coulombic interaction between electrons and holes. This trend is shown in Figure 2.

In order to exploit the altered band structure to slow cooling, this Auger process must be reduced. Two possible solutions have been experimentally shown. The first solution consists of choosing a material where the effective mass of the electrons and holes are nearly equivalent. This will cause a bottleneck effect for both electrons and holes, thus inhibiting the Auger process. It has been shown that lead salts, such as PbS, PbSe or PbTe, are amongst the better materials for carrier multiplication since the effective masses of the electrons and holes are nearly equal [1]. The second solution is limited to quantum dots, where a polymer coating is applied to trap a hole at the surface of the quantum dot. If the hole is rendered immobile, the Auger process will be eliminated. It should be noted that these trapping dynamics will also alter electron transport [1,7]. Several experiments have purportedly supported this mechanism of carrier multiplication in materials such as PbSe and PbS salts, PbTe, CdSe, Si and InAs quantum dots as listed in reference [1,2,8]. In fact, a record of 7 excitons per photon was reported by Schaller, et. al for PbSe quantum dots [9].

Although several experiments supported this theoretical enhancement mechanism, additional experiments following the initial reports failed to reproduce the same results and in fact, exhibited significantly lower carrier multiplication efficiencies. This was reported for CdSe, InAs, PbS, and PbSe as listed in reference [1,2,8]. The inability to rectify these contradictory results has called into question whether quantum confinement does in fact improve carrier multiplication efficiency.

Recently, a report published by Pijpers, et. al provided experimental results and theoretical calculations which refute the claim that quantization will result in higher carrier

multiplication [8]. It was believed that previous experimentation on quantum dots overestimated the number of excited excitons due to high excitation fluence, sample-to-sample variability and the lack of stirring of quantum-dot suspensions. In their experiment, they measured the carrier multiplication for bulk samples of PbS and PbSe and compared their results to previously published data on quantum dots of the same material, as shown in Figures 3 and 4. They found that bulk samples exhibited higher carrier multiplication than quantum dots, contradicting the conventional belief that bulk materials are less efficient at producing additional excitons.

From their calculations, they believe the reason for this contrary result is that the mechanisms originally believed to enable enhancement fail to account for additional limiting factors. As discussed, the suppression of the Auger processes in quantum dots should enable slower cooling of the hot carriers. However, they argue that at higher energy levels, the density of states will increase such that phonon emission via intraband transition will still be favorable despite quantum confinement. Thus, the ability to slow the cooling rate is limited. They also contend that the impact ionization rate depends on not only the Coulomb interaction, but the density of bi-exciton states as well. In quantum dots, they argue that the stronger Coulomb interaction is negated by a decrease in the density of states. Finally, they also contend that surface defects in the quantum dots may enable additional relaxation pathways, further reducing carrier multiplication.

Although these results indicate bulk materials are superior to quantum dots or nanocrystalline materials, a following paper by Delerue, et. al show that bulk materials and their corresponding quantum dots will in fact yield a similar energy conversion efficiency [10]. Their results show that despite the occurrence of higher carrier multiplication in bulk materials, the energy efficiency, defined as the fraction of photon energy used to generate excitons instead of

heat, is greater in quantum dots. The reason is that the density of states in quantum dots above the energy threshold for impact ionization will quickly increase, resembling bulk values. Thus, the impact ionization rate is nearly identical for bulk materials and quantum dots. The difference between both cases is the change in the energy threshold where quantum dots will exhibit a higher energy threshold due to quantum confinement. Therefore, it is likely that more excitons will be generated in bulk materials due to the lower energy threshold while the energy of the additional excitons in quantum dots will be larger due to the higher energy threshold. Thus, despite the higher energy efficiency in quantum dots, they determined that increases in efficiency in solar cells will be small.

Conclusion

The debate over the benefits of quantum confinement enhancement on multi exciton generation is still ongoing. Further experimentation is needed to verify recent claims that quantization effects will not improve carrier multiplication relative to bulk materials due to the proposed mechanisms.

Although only alluded to in this paper, significant work has also been conducted in the extraction of multiple excitons before exciton-exciton annihilation occurs (10~100 ps). One approach has been the use of ultrafast interfacial electron transfer using electron donors and acceptors to separate electrons and holes generated in quantum dots. For example, Huang et. al demonstrated exciton dissociation for CdSe quantum dots, where additional excitons were absorbed into methylene blue, an electron acceptor with life times greater than 1 ns [7]. Additional gains must be made to improve charge transport within the junction in order to better utilize the additionally generated excitons.

Clearly, significant work still remains, both in determining the mechanism of multi exciton generation as well as improving electron transport for use in real devices. Additionally, considerations must be made to the integration of such structures into the solar cell. For example, Nozik proposed the integration of quantum dots in the space charge region of a p-i-n junction in a solar cell or as a substitute for dye molecules in Graetzel cells to create a quantum dot sensitized cell. If such goals can be achieved, the impact would be significant as this would enable a means of improving efficiency without drastically increasing cost.

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Appendices

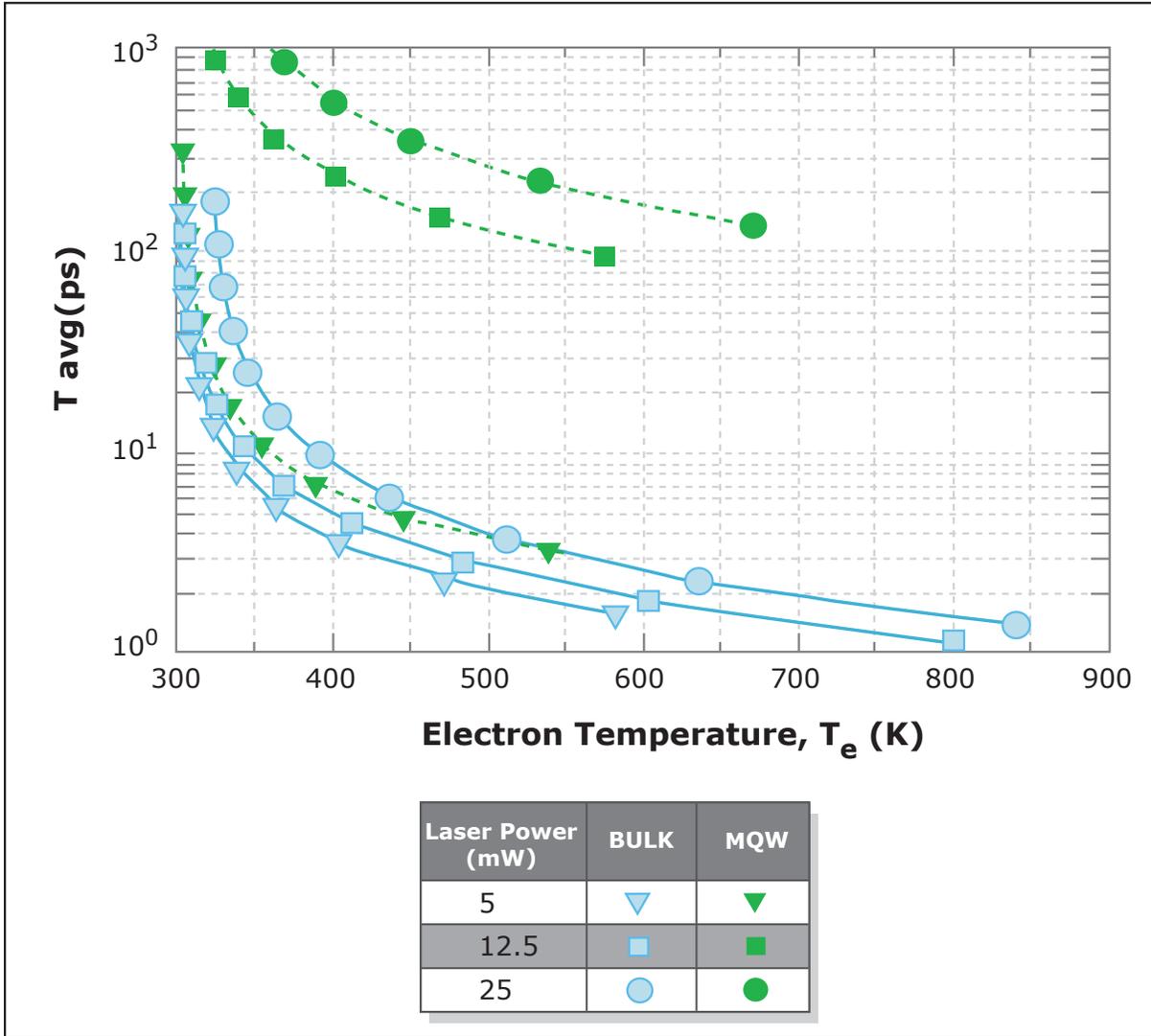


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Figure 1: The time constant for hot electron cooling as a function of electron temperature. This data corresponds to bulk GaAs and GaAs multi quantum wells. Increases in laser power correspond to greater carrier densities. [Reference 6]

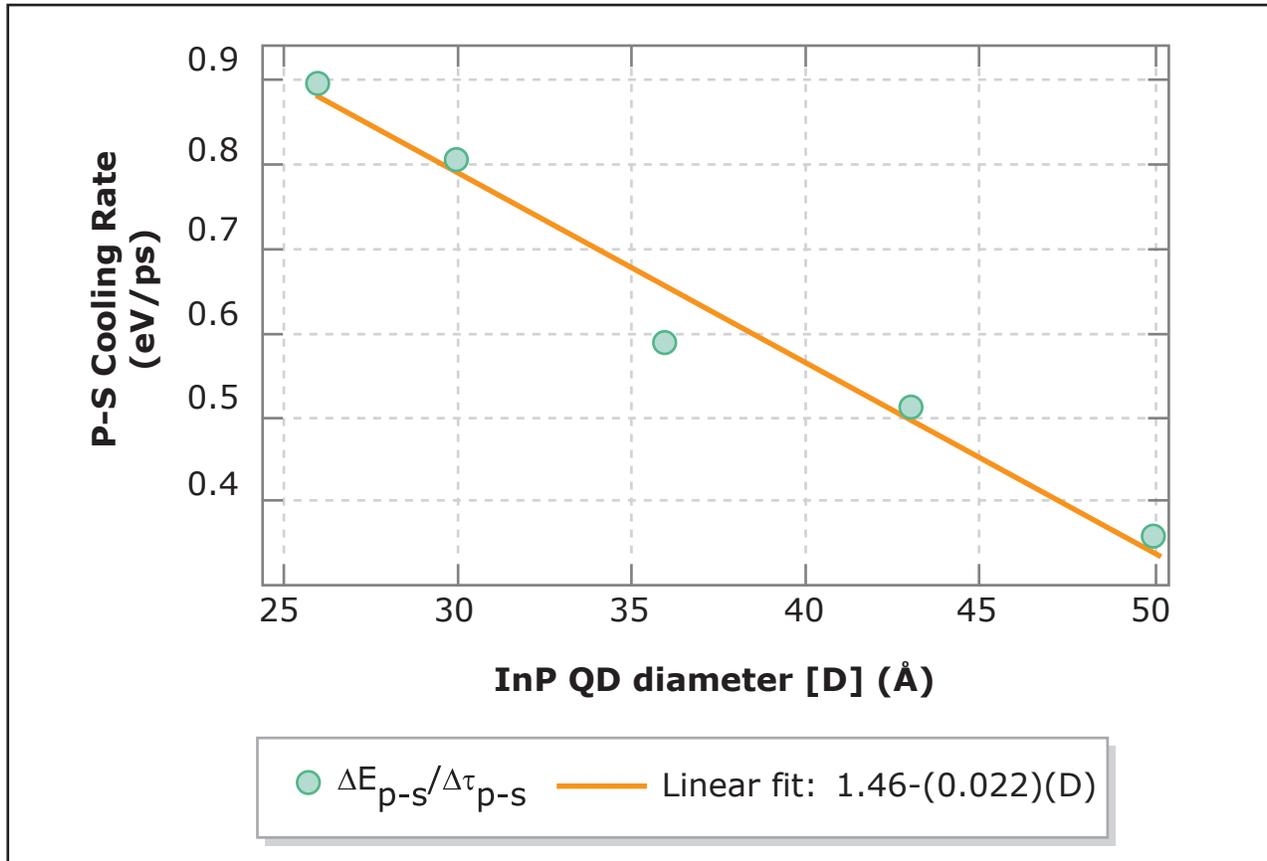
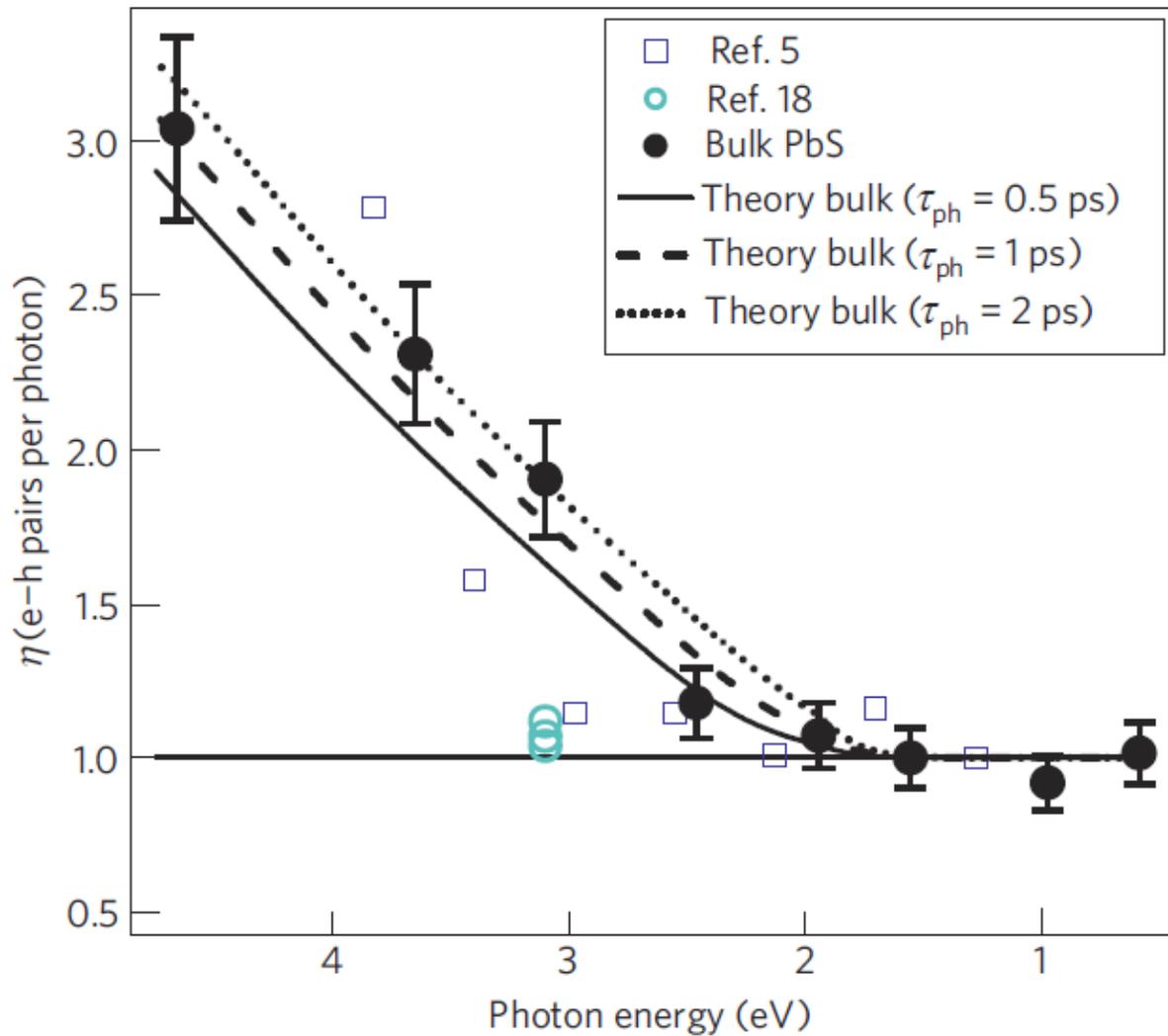


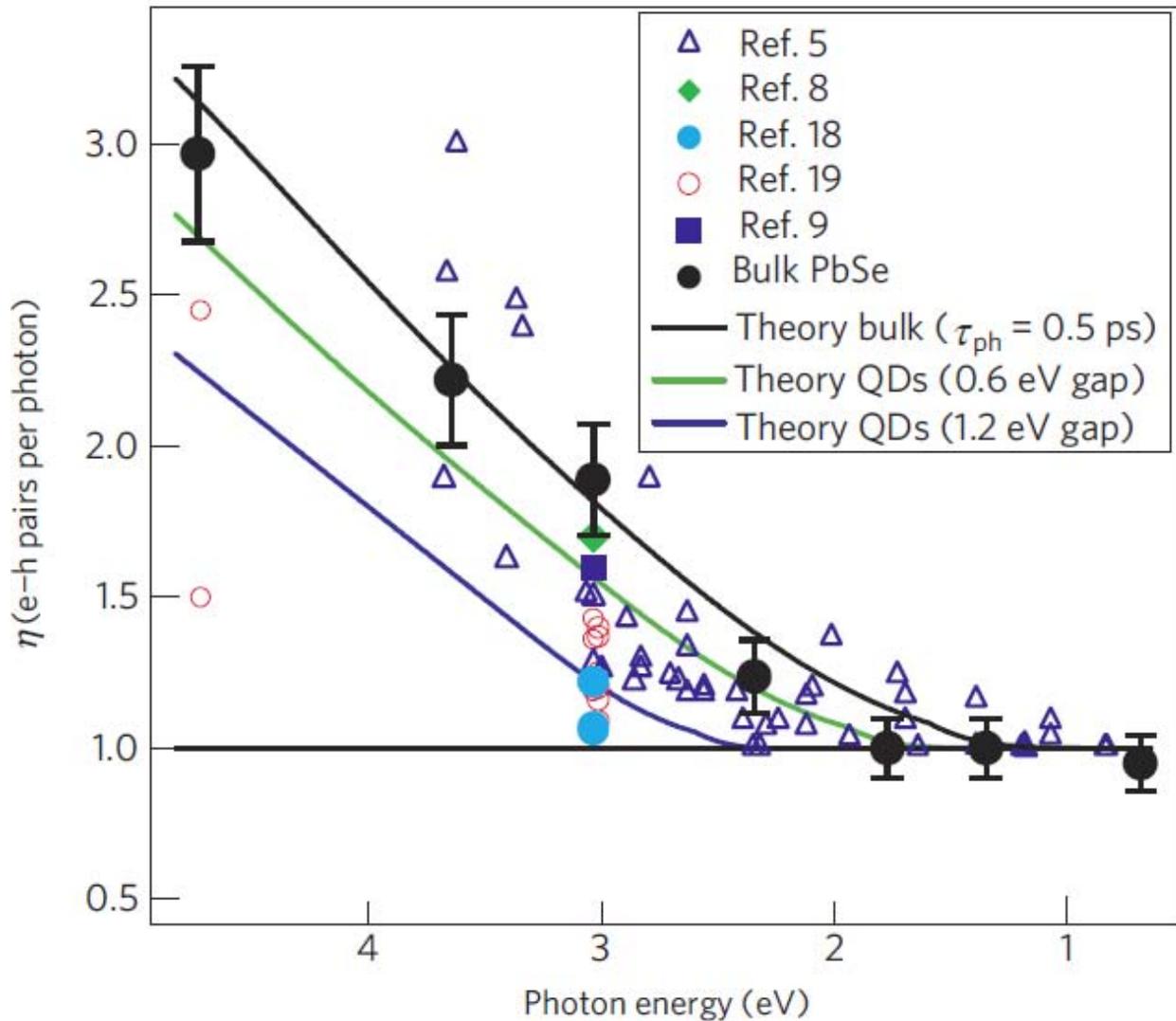
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Figure 2: Average cooling rate for an electron transitioning from a P to S state as a function of quantum dot diameter. This data is for InP quantum dots. [Reference 2]



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Figure 3: Carrier multiplication efficiency for PbS bulk material. The black dots correspond to experimental measurement and the lines correspond to theoretical calculation. This data was compared to published data for PbS quantum dots. [Reference 8]



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Figure 4: Carrier multiplication efficiency for PbSe bulk material. The black dots correspond to experimental measurement and the lines correspond to theoretical calculation. This data was compared to published data for PbSe quantum dots. [Reference 8]

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