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Quantum Dot Solar Cells: High Efficiency through Multiple Exciton Generation

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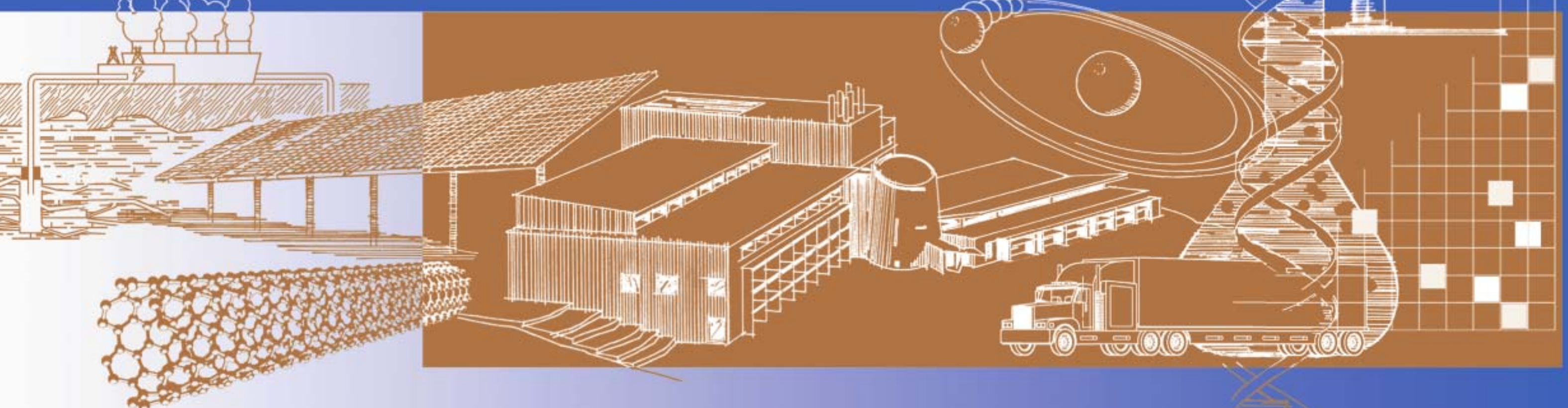

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ABSTRACT

Impact ionization is a process in which absorbed photons in semiconductors that are at least twice the bandgap can produce multiple electron-hole pairs. For single-bandgap photovoltaic devices, this effect produces greatly enhanced theoretical thermodynamic conversion efficiencies that range from 45 - 85%, depending upon solar concentration, the cell temperature, and the number of electron-hole pairs produced per photon. For quantum dots (QDs), electron-hole pairs exist as excitons. We have observed astoundingly efficient multiple exciton generation (MEG) in QDs of PbSe (bulk $E_g = 0.28$ eV), ranging in diameter from 3.9 to 5.7nm ($E_g = 0.73$, 0.82, and 0.91 eV, respectively). The effective masses of electron and holes are about equal in PbSe, and the onset for efficient MEG occurs at about three times the QD HOMO-LUMO transition (its "bandgap"). The quantum yield rises quickly after the onset and reaches 300% at 4 x E_g (3.64 eV) for the smallest QD; this means that every QD in the sample produces three electron-hole pairs/photon.

1. Objectives

This work addresses MEG and carrier energy relaxation processes in semiconductor QDs. Our aim is to determine how the efficiency of MEG is influenced by the change in physical properties related to quantum confinement in semiconductor nanoparticles. The ultimate objective is to use a QD semiconductor system with highly efficient MEG to fabricate a high-efficiency solar cell.

2. Technical Approach

We are studying MEG quantum yields and energy relaxation rates in QDs using fs pump-probe transient absorption techniques [1].

3. Results and Accomplishments

To study MEG processes in QDs, we detect multiexcitons created via exciton multiplication (EM) by monitoring the signature of multiexciton decay in the transient absorption (TA) dynamics, while maintaining a pump photon fluence lower than that needed to create multiexcitions directly. The Auger recombination rate is proportional to the number of excitons per QD with the decay of a biexciton being faster than that of the single exciton. By monitoring the fast-decay component of the TA dynamics at low pump intensities we can measure the population of excitons created by MEG. The transients are detected with either a band-edge probe photon that monitors the band-edge bleach or a mid-IR photon that probes intraband transistions in the newly created excitons.

We have measured the MEG quantum yield (QY) in colloidial PbSe QDs with diameters ranging from 3.9 to 5.7 nm, corresponding to QD bandgaps ranging from 0.91 to 0.73 eV. For all the PbSe QD samples the onset for efficient MEG occurs at about three times the energy gap, a result in agreement with that reported by Schaller and Klimov [2]. Our data show that QYs > 2 can be achieved at higher photon energy, meaning that three electron/hole pairs per photon have been created by MEG.

For the 3.9 nm QD ($E_g = 0.91$ eV), the QY reaches a surprising value of 3.0 at $E_h / E_g = 4$. This means that on average every QD in the sample produces three excitons/photon. The sharper rise of the QY in the smallest diameter sample compared to the other two larger samples may be due to the different surface passivation conditions. The 3.9 nm QD sample was treated with oleic acid and oleylamine to improve the surface passivation, which greatly increased the single-exciton lifetime. More work is warranted to understand what role the surface plays in efficient MEG.

For MEG to be the dominant cooling process, its rate must be much faster than the competing cooling rates of excited excitons by phonon emission. In PbSe QDs, the fast cooling by the Auger process is expected to be inhibited because of the large spacing between both hole and electron levels which is a consequence of the nearly equal electron and hole effective mass in PbSe. With Auger cooling inefficient, we may expect cooling rates of a few ps, as is observed in other QD systems where the phonon bottleneck is operative. A new and unique model to explain the details of MEG in QDs has been proposed [1]

In theoretical efficiency calculations [3] of solar cells with impact ionization (II) included as a charge generation process, a stair step QY, representing the energetic maximum QY that can be obtained from II, is used with an idealized detail balance model to calculate the maximum expected efficiency vs Eg. We have developed an alternate approach to incorporate idealized or experimentally determined II QYs into a numerical device simulator, which allows us to explore the potential benefits of II on cell performance. This approach also allows us to incorporate deviations from ideal behavior (Auger, trap and surface recombination, finite-carrier mobilities, incomplete absorption, etc.) into the device model. When II is active in a material, the total generation rate (optical plus II) can be written as:

$$G(x) = \Sigma(1+QY_{II}) \quad \exp(- \quad x) \qquad (1)$$

where is the absorption coefficient, is the solar photon flux, and the summation covers the energies above the bandgap.

Through simulations, we have compared the performance of an idealized device having the different QY_{II} models shown in Fig. 1.

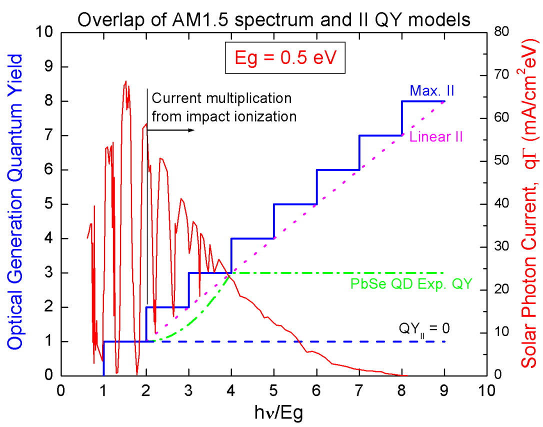

Fig. 1. QY models used in the device simulations.

We investigated four II QY models: the case of no II, the experimentally measured QY_{II} of PbSe QDs shifted to Eg, a linear QY_{II}, and the energetic maximum QY that can be obtained from II. Charge generation from II for absorbed photons above twice the bandgap will add to the usual optical generation from absorbed photons with h > Eg.

To calculate theoretical efficiencies with the above II models, we used a simple, idealized pn-junction configuration with a total length of 3.7 m. The absorption coefficient was taken to have a square-root energy dependence rising to 10^5 cm^{-1} at h = 4 eV, which insured ~100% absorption of photons with h > Eg. Both radiative and Auger recombination mechanisms were included with a radiative B coefficient of 10^{-10} cm^6/s and and an Auger coefficient of $8x10^{-28}$ cm^3/s. The mobility of electrons and holes was taken to be 100 cm^2/Vs and the n- and p-side doping was 10^{17} cm^{-3}. In these initial calculations, we neglected minority carrier surface recombination and trap recombination. The cell efficiency vs. Eg over the range 0.5 to 1.5 eV is shown in Fig. 2.

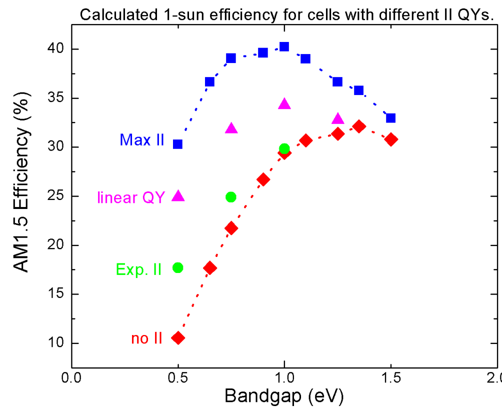

Fig. 2. Calculated efficiencies for different QY_{II} models.

Under unconcentrated AM1.5 illumination, a cell with maximal II has the potential to reach ~41% efficiency at Eg ~ 1 eV. The efficiencies calculated using the experimentally determined II QY of PbSe QDs are lower than the maximum values, because of the slow rise of the QY above 2xEg. The improvement over the “no II” case is much better, however, for lower bandgaps. This implies that lower-gap QDs with a fast turn-on in QY_{II} will be required for significant efficiency enhancements in QD solar cells.

4. Conclusions

We have observed very high QYs because of multiple exciton generation in PbSe QDs, reaching up to 300% at 4xEg. Future work will explore the dependence of QD size, electronic structure, and related semiconductor properties on MEG, and will also model the performance of QD-sensitized mesoporous solar cells that are based on impact ionization in QDs.

REFERENCES

1. R.J. Ellingson, M.C. Beard, P.Yu, O.I. Micic, A.J. Nozik, A. Shaebev, and Al.L. Efros. *Science*, 2004 (submitted).

[2] R.D. Schaller and V.I Klimov. “High-efficiency carrier multiplication in PbSe nanocrystals: implications for solar energy conversion” PRL **92**, 186601 (2004).

[3] A. DeVos and B. Desoete. “On the ideal performance of solar cells with larger-than-unity quantum efficiency,” *Solar Energy Mater. Solar Cells*, **51** 413 (1998).

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