Spectroscopic Characterization of Multi-Exciton Generation Efficiency in Nano-Structured Materials

Investigators

Stephen Connor, Graduate Student, Department of Chemistry and Department of Materials Science and Engineering, Stanford University, Minbiao Ji, Graduate Student, Department of Physics and PULSE Institute, SLAC National Accelerator Laboratory, Stanford University, Sungnam Park, Postdoctoral Researcher, PULSE Institute, SLAC National Accelerator Laboratory, Stanford University, Taleb Mokari, Staff Scientist, Molecular Foundry, Lawrence Berkeley National Laboratory, Michael Yi Cui, Professor, Department of Materials Science and Engineering, Stanford University, Michael McGehee, Professor, Department of Materials Science and Engineering, Stanford University, Kelly Gaffney, Professor, Photon Science, SLAC National Accelerator Laboratory, Stanford University

Abstract

The ability of single photons to generate more than one electronic excitation (exciton) when the energy of the photon is more than twice the minimum electronic excitation energy (band gap) presents a potentially useful approach increasing the efficiency of solar cells. Studies predating our work had indicated that multi-exciton generation (MEG) from a single photon occurred with much higher efficiency in quantum confined materials (quantum dots) than in bulk materials, but these measurements have received significant skepticism, bringing into question the viability of MEG as a means of increasing solar cell efficiency.

While multiple concerns regarding these claims of high efficiency have been raised, we proposed to perform a careful spectroscopic characterization of the multiple exciton generation efficiency. We used a UV laser pulse to generate multiple excitons from single UV photons and measured the average number of excitons generated per photon by spectrally resolving the UV induced intraband absorption in colloidal PbSe quantum dots. These measurements demonstrated that the spectral distribution, as well as the amplitude, of the transient spectrum depends on the number of excitons excited in a quantum dot. The accurate quantification of the average number of excitons per absorbed UV photon requires the full transient intraband spectrum be measured and spectrally integrated.

Utilizing this methodology, we observed multiple exciton generation in colloidal PbSe quantum. In parallel with our work, multiple other experimental and theoretical studies have been attempted to assess the efficiency of MEG. Our finding indicates higher efficiency than some and lower than others. While quantitative consensus has not been achieved, the majority of scientists do not think that MEG in quantum dots provides a likely route to more efficient solar cell devices.

Introduction

The generation of cost effective and environmentally benign sources of energy represents a critical challenge for sustaining and advancing human well fair throughout the world while simultaneously reducing greenhouse gas emissions. The sun baths our planet with an average power of 120,000 TW, making the conversion of solar power to electrical power with

photovoltaic cells a very promising and environmentally sustainable approach to energy production. Despite the tremendous potential of solar energy, the high cost of solar energy relative to conventional sources of electrical power limits solar energy to a minor component of the present global energy supple. Coal burning electrical power plants operated in the US in 1999 produced 2.1 lb of CO_2 per kWh of electrical power. Replacing coal with sunlight as an important source of electrical power has enormous potential to reduce greenhouse gas emissions, but solar energy must become more cost effective for this goal to be achieved.

The cost of solar energy can be shrunk by reducing solar cell manufacturing costs or increasing solar cell conversion efficiency. We propose to use the special properties of nanostructured materials to greatly increase the efficiency of cost effective solar cells. An enormous range of conversion efficiencies have been achieved with a wide variety of photovoltaic materials. Standard methods for calculating the maximum theoretical efficiency of a photovoltaic solar cell assume only one electron-hole pair can be generated for each absorbed photon[1]. This leads to a maximum single band gap solar cell conversion efficiency of un-concentrated sunlight into electricity of 31%, termed the Shockley-Queisser limit [1].

The Shockley-Queisser limit assumes all energy contained by a single photon in excess of the semiconductor band gap will be converted from electronic- to vibrational-energy and dissipated as heat. In bulk, inorganic semiconductors this limitation has been shown to be an accurate assumption [2], but the increased interaction between excitons in nano-structured inorganic semiconductors makes multiple exciton generation (MEG) potentially more efficient [3]. Should efficient MEG and carrier extraction be achievable in a solar cell, the theoretical photovoltaic device efficiency could be increased significantly from 31% to 43% [4,5].

Background

Significant experimental and theoretical efforts have been has been exerted to assess the magnitude of MEG in quantum-confined materials in specific and assess the feasibility of quantum-confined materials as active solar cell materials in general. At present, the efficiency levels of colloidal quantum-confined materials do not match that of bulk semiconductor materials or organic photovoltaics and experiment and theory are not indicating that MEG should be much more efficient in quantum-confined materials. While the fundamental physics and chemistry of electron dynamics in quantum-confined materials remain highly interesting, a compelling case for solar cell technology based on quantum-confined materials has yet to be made.

Results

We have investigated multiple exciton generation (MEG) in PbSe with laser excitation at 400 nm, which corresponds to 3.26 times the PbSe band gap energy of 0.94 eV. As we have emphasized, accurate determination of the MEG efficiency requires a probe signal that is proportional to the number of excitons per quantum dot (QD) and spectral integration of the transient signal to effectively account for population dependent spectral shifts in the transient signal. The accurate determination of the MEG efficiency also requires assurance that electron and hole trap states do not influence the transient absorption (TA) signal and robust demonstration that $N_0 \ll 1$. We do not believe trap states play an important role in our measurements for two reasons. One, we see no

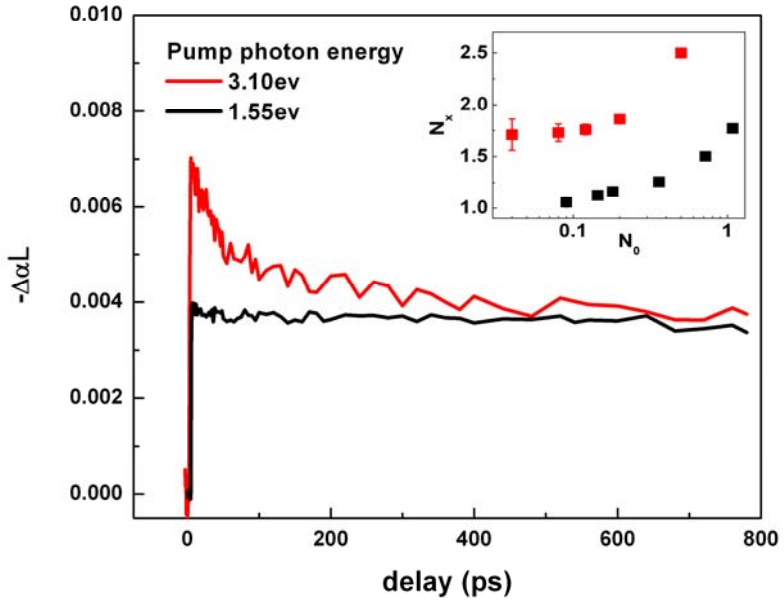

Figure 1. Data indicating the occurrence of carrier multiplication. TA traces measured with 1.55 eV and 3.1 eV pump photon energies at low photon fluence. We chose pump powers so that the long time TA tails roughly overlap. Inset shows the power scaling of the carrier multiplicities at the two pump photon energies.

evidence of traps when exciting with low fluence at 800 nm. This can be seen in **Figure 1**, where the 800 nm signal has no time dependence for short delay times. In addition, the multi-exciton decay observed when exciting with 400 nm occurs with the same rate as the multi-exciton decay observed at 800 nm, where traps have been ruled out. For the dynamics induced by absorption of 400 nm light to be the consequence of trap state dynamics would require the trap state decay to match the Auger recombination dynamics.

We have used multiple methods to insure that $N_0 \ll 1$. **Figure 1** shows the TA signal for low fluence excitation at 800 nm and 400 nm. The absence of any early time signal in the 800 nm signal insures that $N_0 \ll 1$ at 800 nm and the overlap of the 800 nm and 400 nm generated signals at long delay times provides evidence that the same number of photons have been absorbed at 400 nm [6]. However, this might be insufficient, since the average number of absorbed photons depends on the optical thickness, $\langle N_0 \rangle_L = N_0 \frac{1-e^{-\alpha L}}{\alpha L}$. Instead of using $\langle N_0 \rangle_L$, we took the more stringent quantity, N_0. This insures that the number of photons absorbed per QD at the front surface of the sample will also be much less than one. Given the different absorptions at 400 nm and 800 nm used in the experiment, $\langle N_0 \rangle_L$ must be a factor of 2 lower at 400 nm to achieve the same N_0.

As shown in the **Figure 1** inset, we observe a laser fluence independent exciton multiplicity when exciting at 400 nm greater than one, confirming the presence of MEG. For a photon energy equal to 3.26 E_g, we observe an average of 1.6±0.2 excitons per absorbed photon. This MEG efficiency matches the efficiency observed by Schaller *et al.* when exciting at 400 nm and using a PbSe QD with a similar E_g [7,8], [6, 19, 22] and exceeds the efficiency measured by Ellingson *et al.* [9] at the same photon energy in a PbSe quantum dot with a similar E_g. As emphasized by Nair and Bawendi [10], [22] this efficiency does not significantly exceed the bulk efficiency measured by Smith and Dutton at 3.1 eV photon energy [11][33]. Whether quantum confinement has a significant impact on the observed efficiency cannot be assessed yet.

The creation and harvesting of multiple carriers from a single photon absorption represents an appealing and potentially important route to increasing the efficiency of photovoltaic devices. While we remain far from identifying how to efficiently extract the generated carriers from the photoexcited quantum dots, before tackling such a difficult scientific and engineering challenge, we need to verify MEG efficiency warrants the effort. We believe the spectrally resolved intraband transition provides an excellent means of characterizing the efficiency of multiple exciton generation in PbSe and also provides an excellent opportunity to investigate the physical and chemical properties of PbSe quantum dots that determine the efficiency. At a minimum our results support further investigation and provide reason for optimism that carrier multiplication may provide a valid means of enhancing solar cell efficiency beyond the Shockley-Queisser limit.

Conclusions

Significant experimental and theoretical efforts have been has been exerted to assess the magnitude of MEG in quantum-confined materials in specific and assess the feasibility of quantum-confined materials as active solar cell materials in general. At present, the efficiency levels of colloidal quantum-confined materials do not match that of bulk semiconductor materials or organic photovoltaics and experiment and theory are not indicating that MEG should be much more efficient in quantum-confined materials. While the fundamental physics and chemistry of electron dynamics in quantum-confined materials remain highly interesting, a compelling case for solar cell technology based on quantum-confined materials has yet to be made.

Publications

1. Ji, Minbiao, Park, Sungnam, Connor, Stephen T., Mokari, Taleb, Cui, Yi, Gaffney, Kelly J., Efficient Multiple Exciton Generation Observed in Colloidal PbSe Quantum Dots with Temporally and Spectrally Resolved Intraband Excitation, Nano Lett., 9, 1217-1222, 2009.
2. Gaffney, K.J., Ji, Minbiao, Park, Sungnam, Connor, Stephen T., Mokari, Taleb, Cui, Yi, Efficient Multiple Exciton Generation Observed in Colloidal PbSe Quantum Dots with Temporally and Spectrally Resolved Intraband Excitation, poster presentation at Clusters, Nanocrystals, and Nanostructures Gordon Conference.

References

1. Shockley, W. and Queisser, H.J. J. App. Phys., 32, 510, 1961.
2. Wolf, M., *et al.*, J. App. Phys. 83, 4213, 1998.
3. Nozik, A.J., Ann. Rev. Phys. Chem. 52, 193, 2001.
4. Werner, J.H., *et al.*, Phys. Rev. Lett. 72, 3851, 1994.
5. Klimov, V.I., App. Phys. Lett. **89** (2006).
6. Trinh, M. T., Houtepen, A. J., Schins, J. M., Hanrath, T., Piris, J., Knulst, W., Goossens, A. P. L. M., Siebbeles, L. D. A., Nano Lett. 8, 1713-1718, 2008.
7. Schaller, R. D., Klimov, V. I., Phys. Rev. Lett. 92, 186601, 2004.
8. Schaller, R. D., Petruska, M. A., Klimov, V. I., Appl. Phys. Lett. 87, 3, 2005.
9. Ellingson, R. J., Beard, M. C., Johnson, J. C., Yu, P., Micic, O. I., Nozik, A. J., Shabaev, A., Efros, A. L., Nano Lett. 5, (5), 865-871, 2005.
10. Nair, G., Geyer, S. M., Chang, L. Y., Bawendi, M. G., *Phys. Rev. B* **2008,** 78, (12), 10.
11. Smith, A., Dutton, D. J. Opt. Soc. Am. 48, 1007-1009, 1958.

Contacts

Kelly J. Gaffney: kgaffney@slac.stanford.edu
Yi Cui. yicui@stanford.edu
Michael D. McGehee: mmcgehee@stanford.edu