# Biexciton dissociation efficiency at Quantum Dot-Oxide Interfaces

Hai Wang [1,2], Mischa Bonn[1] and Enrique Cánovas[1,*]

*[1] Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany*

*[2] Graduate School of Material Science in Mainz, University of Mainz, Staudingerweg 9,*

*55128 Mainz, Germany*

*Correspondence to: canovas@mpip-mainz.mpg.de*

## Abstract

Harvesting multiexcitons populating semiconductor quantum dots (generated by carrier multiplication, CM) has been proposed as a path towards efficiencies beyond the shockley-Queisser limit in photovoltaic devices[1-2]. Carrier multiplication (also referred as multi exciton generation - MEG) is a phenomenon in which absorption of one high energy photon (with energy at least doubling the QD absorber bandgap onset, $h\nu/E_g>2$) is capable to produce at least two electron-hole pairs in the absorber[3-4] by impact ionization[5-6]. Although CM efficiency has been widely interrogated in colloidal QD solutions and QD solids, less focus has been placed on the physics regarding biexciton collection at electrodes. Given that the contribution of biexcitons towards the overall device photocurrent will be ultimately determined by the kinetic competition between transfer toward the electrode material and Auger relaxation within the QDs, is then imperative to harvest information about the nature of the interfacial charge collection process (e.g. regarding transfer rate and process efficiency).

Quantum dot sensitized systems could be an appealing architecture for the exploitation of CM in photovoltaic applications. In a sensitized system, ultrafast extraction of multiple charges before exciton-exciton annihilation (e.g. via Auger recombination) can be in principle achieved by tuning interfacial chemistry between QD donor and oxide acceptor (e.g. by enhancing donor-acceptor coupling strength). Indeed CM effects contributing to the overall photocurrent have been reported in complete devices employing a flat oxide

surface with QDs anchored by short molecular bridges[7]. While this work serves as a proof of principle, more relevant towards device applications is to analyse CM effects (particularly the carrier dynamics for both, CM generation and CM collection efficiency) in the more complex mesoporous oxide architectures. In this respect, so far, interfacial multi-exciton dynamics in a QD sensitized mesoporous oxide system have been only interrogated under excitation conditions not allowing CM[8] (for photon energies $hv<2Eg$; hence generating multi-excitons in the QDs by light concentration).

In this work we investigate interfacial biexciton transfer dynamics from PbS quantum dots directly nucleated onto mesoporous $SnO_2$ films as a function of impinging photon flux and photon energy. Although a priori, this system seemed very well-suited for achieving efficient biexciton dissociation, as the ultrafast QD-to-oxide transfer rate for photon energies $hv<2Eg$ is substantially faster than Auger relaxation within the QDs. We found that, remarkably, when exciting the sample with photon energies allowing CM ($hv>2Eg$), the CM biexciton collection efficiency at the oxide electrode is essentially zero. This seemingly counterintuitive result is rationalized by noting that efficient hot electron transfer at the QD-oxide interface can compete with CM within the QDs. Efficient hot electron transfer is resolved to occur on sub-100 fs timescales for the PbS/$SnO_2$ sensitized system, nulling the CM generation efficiency. Modelling allow us to conclude that for the efficient harvesting of multiple-excitons in a QD sensitized system, the QD-to-oxide electron transfer rate ($K_{ET}$) have to be kinetically compatible not only with recombination processes taking place within the QDs (the Auger relaxation rate; $K_{ET}>K_{Aug}$) but also with CM generation (impact ionization rate; $K_{II}>K_{ET}$). Implications of these results for solar energy conversion are discussed.

1.  Hanna, M. C.; Nozik, A. J. *J Appl Phys* **2006,** 100, (7).
2.  Klimov, V. I. *Appl Phys Lett* **2006,** 89, (12).
3.  Schaller, R. D.; Klimov, V. I. *Phys Rev Lett* **2004,** 92, (18).
4.  Klimov, V. I. *Annu Rev Phys Chem* **2007,** 58, 635-673.
5.  Franceschetti, A.; An, J. M.; Zunger, A. *Nano Lett* **2006,** 6, (10), 2191-2195.
6.  Allan, G.; Delerue, C. *Phys Rev B* **2006,** 73, (20).
7.  Sambur, J. B.; Novet, T.; Parkinson, B. A. *Science* **2010,** 330, (6000), 63-66.
8.  Zidek, K.; Zheng, K. B.; Abdellah, M.; Lenngren, N.; Chabera, P.; Pullerits, T. *Nano Lett* **2012,** 12, (12), 6393-6399.