Multi-exciton generation in nanodots: a new paradigm for solar energy conversion

(I) R.D. Schaller, M. Sykora, J.F. Pietryga, and V.I. Klimov: "*Seven excitons at the cost of one: redefining the limits for conversion efficiency of photons into charge carriers*", Nano Letters, 6, 424 (2006).

(II) G. Nair and M.G. Bawendi: "*Carrier Multiplication yields for CdSe and CdTe nanocrystals by transient photoluminescence spectroscopy*", arXiv.org :0708.3866, Phys. Rev. 76, 081304 (2007).

(III) M. Tuan Trinh, A.J. Houtepen, J.M. Schins, T. Hanrath, J. Piris, W. Knulst, A. Goossens, and L. Siebelles: *"In spite of recent doubts Carrier Multiplication does occur in PbSe nanocrystals"*, Nano Letters, 8, 1713 (2008).

Recommended with a Commentary by G.T. Zimanyi, U.C. Davis

The theoretical maximum of the conversion efficiency of solar energy into electrical form in semiconductor photovoltaic cells was calculated to be a disappointing 31% by Shockley and Queisser in 1961. Photons with energies below the semiconductor gap are not absorbed and photons with energies above the gap generate an exciton, which quickly relaxes to the bottom of the conduction band. Optimizing the value of the band gap given the solar spectrum leads to the above 31%.

This calculation, however, was based on the "one-photon-in-one-electron-out" paradigm. In a remarkable recent paper, a group at the Los Alamos National Laboratory shattered this paradigm by establishing that in 3-4nm diameter PbSe nanodots a *single* incoming photon may be able to generate as many as *seven* electrons (see (I)). Since this announcement the analogous effect has been observed in a half dozen different materials, including Si nanodots.

Such Multiple Exciton Generation (MEG) was theorized and observed in bulk materials already in the late fifties, but with a very small probability. The relaxation of the high energy exciton can take place via phonon-emission or by generating additional excitons through the Coulomb interaction. Direct calculation shows that in bulk materials the phonon-channel is the dominant relaxation mechanism.

In the early nineties, however, A. Nozik argued that MEG can be more important in nanostructures than in bulk materials. The twin reasons for this are that in nanostructures: (i) the Coulomb interaction is enhanced relative to bulk materials because of the quantum confinement of the excitons - in effect, the size of the nanodot forces the excitons to overlap more extensively, suppressing screening; (ii) the phonon relaxation channel is suppressed because in nanostructures the discreteness of the energy levels suppresses the availability of electron-hole pair states which satisfy the energy conservation in phonon-assisted processes – the "phonon-bottleneck" effect.

The Los Alamos paper is the first experimental observation of such a MEG process in nanodots. A calculation of the energy conversion efficiency in MEG based solar cells, based on detailed balance, arrived at a maximum of 42% instead of the 31[1]. This is a large increase in a field where every percent gain is a tough fight.

In rapid succession, at least three theories have been proposed to account for the MEG. Strong Coulomb interactions play a central role in all of them. The Impact Ionization theory by A. Zunger and collaborators[2] captures the physics in two separate steps: first a single electron absorbs the photon leading to the formation of a high energy exciton. Then, in a subsequent step, the high energy exciton generates additional excitons via Coulomb interactions. In a calculation combining the pseudopotential and configuration interaction (CI) methods, they report exciton lifetimes and energy dependences, which appear consistent with the data.

The work of Ellingson et al.[3] proposed that the MEG results from the high energy single exciton state coherently rotating/evolving into a multi-exciton state with the same energy. The Los Alamos group itself put forward[4] the idea that during MEG the single high energy exciton is only a virtual intermediate state, which gives way to the multi-exciton final state. In recent months there were several new publications moving this debate forward.

Progress on the experimental front is equally fascinating. Last summer a group at MIT reported (see (II)) that they do not see an MEG process consistent with the original Los Alamos report. Since this group used a different measurement technique, additional checks were called for to settle the debate. A very recent paper from Cornell and Delft (see (III)) finds results in favor of the presence of MEG, albeit somewhat weaker than the original report.

Given the possibly transformational impact of MEG in nano-structures for solar applications, people in the field are looking forward to a period of intense and exciting research.

References:

[1] V. Klimov, Applied Physics Letters, 89, 123118 (2006).

[2] A. Franceschetti, J. Anh, and A. Zunger*,* Nano Letters, 6, 2191 (2006).

[3] R.J. Elligson, M.C. Beard, J. Johnson, P. Yu, O. Micic, A. Nozik, A. Shabaev, A. Efros, Nano Letters, 5, 865 (2005).

[4] R. Schaller, V. Agranovich, and V. Klimov, Nature Physics, 1, 189 (2005).