Nanoscience and Nanostructures for Photovoltaics: Quantum Dots, Multiple Exciton Generation, and Third Generation Solar Cells

M.C. Beard, J.M. Luther. M.C. Hanna, A. G. Midgett, and A. J. Nozik
National Renewable Energy Laboratory
Golden, Colorado 80401
and
University of Colorado
Department of Chemistry and Biochemistry
Boulder, CO 80309

ABSTRACT

Nanostructures of crystalline materials, also referred to as nanocrystals; includes a variety of nano-scale shapes with the three types of spatial confinement, including spheres (termed quantum dots (QDs)), cubes, rods, wires, tubes, tetrapods, ribbons, cups, discs, and platelets. The first six shapes are being intensively studied for renewable energy applications, but the focus here will be on the use of semiconductor QDs.

In 1961 Shockley and Queisser (S-Q) calculated the maximum possible thermodynamic efficiency of converting solar irradiance into electrical free energy in a PV cell assuming : (1) complete carrier cooling, and (2) that the only other free energy loss mechanism was radiative recombination. This detailed balance calculation in the radiative limit yields a maximum thermodynamic efficiency of 31-33% with optimum bandgaps between about 1.1 to 1.4 eV. One approach to exceed the S-Q limit is to use the excess kinetic energy of the hot carriers to produce additional electron-hole pairs . In bulk semiconductors this process is called impact ionization and is an inverse Auger type of process. However, impact ionization (I.I.) cannot contribute to improved quantum yields in present solar cells based on bulk Si, CdTe, $CuIn_xGa_{1-x}Se_2$, or III-V semiconductors because the maximum QY for I.I. does not produce extra carriers until photon energies reach the ultraviolet region of the solar spectrum. In bulk semiconductors, the threshold photon energy for I.I. exceeds that required for energy conservation alone because crystal momentum (**k**) must also be conserved. Additionally, the rate of I.I. must compete with the rate of energy relaxation by phonon emission through electron-phonon scattering. It has been shown that the rate of I.I. becomes competitive with phonon scattering rates only when the kinetic energy of the electron is many multiples of the bandgap energy (E_g) ($4.4E_g$).

In QDs, electrons and holes are spatially confined and exhibit quantization effects. This leads to the following: (1) the e^-–h^+ pairs are correlated and thus exist as excitons rather than free carriers, (2) the rate of hot electron and hole (ie, exciton) cooling can be slowed because of the formation of discrete electronic states, (3) momentum is not a good quantum number and thus the need to conserve crystal momentum is relaxed, and (4) Auger processes are greatly enhanced because of increased e^-–h^+ Coulomb interaction. Because of these factors it has been predicted that the production of multiple e^-–h^+ pairs will be enhanced in QDs compared to bulk semiconductors; both the threshold energy ($h\upsilon_{th}$) for electron hole pair multiplication (EHPM) and its efficiency, η_{EHPM} (defined as the number of excitons produced per additional bandgap of energy above the EHPM threshold energy) are expected to be greatly enhanced. In QDs we label the formation of multiple excitons *Multiple Exciton Generation* (MEG); free carriers can only form upon dissociation of the excitons, for example in various PV device structures. The possibility of enhanced MEG in QDs was first proposed in the 2001-2002 and experimentally confirmed in 2004. Experiments observing MEG have now been reported for PbSe, CdSe, PbTe, InAs, Si, InP, CdTe and CdSe/CdTe core-shell QDs. S-Q detailed balance calculations in the radiative limit for conventional solar cells compared to QD solar cells exhibiting various MEG characteristics regarding the threshold photon energy $h\upsilon_{th}$ and η_{EHPM} (Fig 1) confirm that the power conversion efficiency of QD solar cells significantly exceeds that of conventional cells if the threshold photon energy for MEG is between $2E_g$ and $3E_g$. It has also been shown very recently that the threshold photon energy for MEG to occur and its efficiency (defined as the additional photon energy in bandgap units required to create an additional e^-–h^+ pairs) are related by the expression:

$$\mathbf{h\upsilon_{th}}/E_g = 1 + 1/\eta_{EHPM} = 1 + 1/\eta_{MEG}$$

Recent work also shows why the appropriate parameter to use when comparing the efficiency of MEG in QDs vs impact ionization in bulk materials is $h\upsilon/E_g$ and not just the absolute photon energy $h\upsilon$. When $h\upsilon/E_g$ is used, the slope of plots of MEG QY vs $h\upsilon/E_g$ is the MEG efficiency, η_{MEG}. The use of just $h\upsilon$, as proposed by some researcher, led to the invalid conclusion that there is no efficiency difference between MEG in QDs and I.I. in bulk semiconductors.

A few years ago several published reports could not reproduce some of the reported early positive MEG results or if MEG was indeed observed the efficiency was claimed to be much lower and in one report MEG efficiency was claimed to be only equivalent to impact ionization in bulk materials. Thus, some controversy arose about the efficiency of MEG in QDs. This controversy has recently been resolved. One reason for it has been attributed to the influence of QD surface treatments and surface chemistry on MEG dynamics compared to cooling dynamics; a 2nd reason is that in some cases QD charging produced during transient pump-probe spectroscopic experiments confounded the MEG quantum yield analysis. Long-lived charge could produce trions in the QDs after the absorption of an additional photon in the QDs in a pump-probe experiment, which then could confound the fast early time decay of transient absorption or bleaching signals that is the signature of MEG, and lead to over-estimation of the MEG QY. However, recent work shows that charging effects may not always be significant, and they are dependent upon the specific QD surface chemistry, photon fluence, photon energy, and QD size. In any case, the possibility of photocharging effects can be eliminated in MEG experiments based on time-resolved TA spectroscopy by flowing or stirring the colloidal QD suspension to refresh the sample volume of QDs being probed. MEG experiments where photocharging is eliminated and the surface chemistry is the same now produce consistent and reproducible MEG QYs in different laboratories (Fig 2).

In one possible QD solar cell configuration the QDs are formed into an 3-D array with inter-QD spacing sufficiently small such that strong electronic coupling occurs to allow long-range electron transport and good carrier mobility. Such arrays have been formed into nanocrystalline p-n junction QD solar cells with certified efficiencies of ~ 3% and recent non- confirmed efficiencies of > 5%.

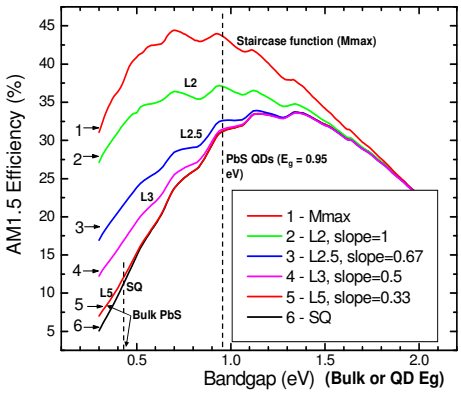

Fig 1. S-Q Calculations for different linear MEG characteristics L(n), where n is the MEG threshold energy hυ/Eg.

$h\upsilon_{th}/E_g = 1 + 1/\eta_{EHPM} = 1 + 1/\eta_{MEG}$

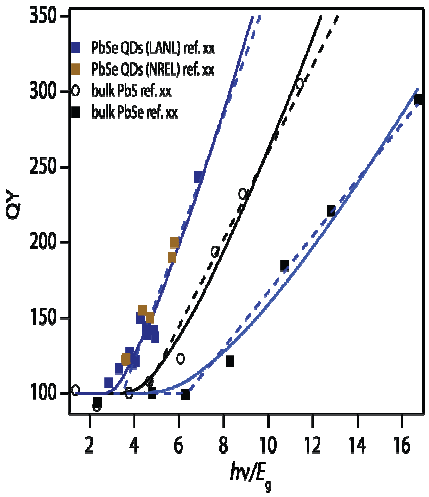

Fig. 2. QY vs hυ/Eg for PbSe QDs where no photocharging is possible and QD surface chemistry is constant; results from NREL and LANL.