

Esselen Award Report

Prospects and Novel Approaches for the Low Cost Power Conversion of Solar Photons to Electricity and Solar Fuels

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I. Introduction

The well-being of global society requires a large and constantly increasing supply of energy, 86% of which is presently provided by the utilization of fossil fuels (oil, natural, and coal). This has resulted in a high probability for highly disruptive, and perhaps even catastrophic, climate change induced by the CO₂ released from burning fossil fuels, the destruction of natural ecosystems, and politico- economic problems caused by major dependencies upon finite fossil fuel supplies from a relative small number of politically unstable or hostile countries. Substituting alternative renewable energy that is affordable, carbon-free, clean and sustainable is considered by many thought leaders to be the number one challenge currently facing humanity.

Solar energy capture, conversion and storage is widely considered to be one renewable energy approach that could be a potential major contributor to meeting this challenge. The Earth receives approximately 120,000 terawatts (TWs) (1 TW=10¹²W) of solar energy annually in a highly reliable and distributed fashion. This vastly exceeds the current annual worldwide energy consumption of ~15 TW and any conceivable future needs. However, sunlight is dilute; the yearly-averaged solar power striking the Earth's surface is about 170 watts per square meter and dependent upon location and season. Devising methods for efficiently and cost- effectively capturing and storing this energy for use by mankind is indeed one of the great challenges of our age.

Third Generation solar photon conversion[1-3] for the production of electricity (photovoltaic (PV) cells) or fuels involve solar cells that have two characteristics: (1) a power conversion efficiency greater than the Shockley-Queisser thermodynamic limit[3,4] (32% for single junction PV cells) and ~31% for cells producing solar fuels[5]) and (2) a very low cost per unit area.[1] Since PV cells are commercially produced in the fastest growing global industry at the present time (averaging about 45% over the past 5 years), while cells for the direction formation of solar fuels from sunlight is still in the R&D phase and a commercial industry has not yet been established, this short summary will focus on PV cells. However, it is to be noted that energy consumption nationally and internationally is dominated by liquid and gaseous fuels, which represent about 2/3 to 3/4 of all energy consumed annually. Thus, it is critical to ultimately produce solar fuels at low energy cost, comparable or lower than fossil fuels; this also requires high conversion efficiency and low cost/unit area of the solar conversion system, and the new approaches we discuss here for TGPV can also be

applied to solar fuels production.

II. Third Generation Photovoltaics

According to Green,[1] in order to be classified as a Third Generation PV (TGPV) cell the value of the PV module cost/unit area divided by the peak watts delivered/unit area should yield a cost per peak watt (Wp) for the module of about \$0.20 - \$0.30 /Wp . Thus, for example, this goal would be achieved for a PV module having a cost of \$100/m² and an efficiency of 50% (i.e., 500 watts/m² since the peak solar intensity at the earth's surface is 1 Kw/m² at high noon with no clouds); any combination of efficiency and area cost yielding \$0.20-\$30/Wp would thus be classified as a TGPV cell. To obtain the yearly-averaged energy cost for the PV system (\$/kWh), the balance of systems (BOS) cost (\$/m²) needs to be added to the module cost, and then the annual-averaged capacity factor for the PV system together with other operating costs (e.g., interest rates, maintenance, taxes) need to be considered.

A simple, rule-of thumb conversion is to simply multiple the total \$ per peak watt cost (module + BOS) by 0.04 to 0.05 (depending upon geographical location) to obtain \$/kWh. If the module and BOS costs for the TGPV systems remain about equal, as they are today, then a \$0.20/Wp module cost would result in a total system cost of \$0.40/Wp and this would represent an energy cost of about \$0.02/kWh— a cost competitive with or even lower than that of energy from coal.

One route to achieve TGPV cells that is now being extensively investigated is to use semiconductor nanostructures in PV cells.[6-12] Nanostructures of semiconductor materials exhibit quantization effects when the electronic particles of these materials are confined by potential barriers to very small regions of space. The confinement can be in one dimension (producing quantum films, also termed quantum wells in the early 1980s as the first examples of quantization in nanoscale materials), in two dimensions (producing quantum wires, rods, or tubes), or in three dimensions (producing quantum dots (QDs)). Some authors refer to these three nanostructure regimes as 2D, 1D, or 0D, respectively, although these terms are not as precise. Nanostructures of other classes of materials, such as metals and organic materials are also possible, but the present discussion will be limited to semiconductor nanostructures. Nanostructures of crystalline materials are also referred to as nanocrystals (NCs); and this term includes a variety of nanoscale shapes with the three types of spatial confinement, including spheres, cubes, rods, wires, tubes, tetrapods, ribbons, discs, cups, and platelets. The first six shapes are all being studied for renewable energy applications, but the focus here will be on the use of spherical semiconductor NCs (QDs).

One ubiquitous feature of all present PV cells is that photons having energies greater than the semiconductor bandgap create free carriers or excitons that have energies in excess of the bandgap; these carriers or excitons are called “hot carriers” or “hot excitons.” This excess electron energy is kinetic free energy and is lost quickly (ps to sub-ps time scales) through electron-phonon scattering, thus converting the excess kinetic energy into heat.[9] The free carriers or excitons then occupy the lowest energy levels (the bottom and top of the conduction and valence bands, respectively) where they can be

removed to do electrical work or lost through radiative or non-radiative recombination. In 1961, Shockley and Queisser[4] (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%, depending upon the details of the AM1.5 solar spectrum utilized, with optimum bandgaps between about 1.1 to 1.4 eV . One way used presently to reduce the energy loss due to carrier cooling is to stack a series of semiconductors with different bandgaps in tandem with the largest bandgap irradiated first followed by decreasing bandgaps. In the limit of a large number of different multiple bandgaps matched to the solar spectrum the conversion efficiency can reach 67% at one-sun intensity. However, in practice only 2 to 3 bandgaps are used because for these multijunction PV cells most of the gain in efficiency is obtained with 3 bandgaps; after that there are diminishing returns. Detailed Balance calculations show that with 2 bandgaps the maximum efficiency is 43%, with 3 it is 48%, with 4 it is 52%, and with 5 it is 55%.

Another 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 well-known and is called impact ionization; it 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, $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$, 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, where solar photons do not exist or are non-abundant. In bulk semiconductors, the threshold photon energy for I.I. exceeds that required for energy conservation alone because crystal momentum (\mathbf{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 to $5E_g$).

In QDs, electrons and holes are spatially confined and exhibit quantization effects.[5-12] 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;[5-9] both the threshold energy ($h\nu_{th}$) 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 2001-2002[6,9] and experimentally confirmed in 2004-

2005.[10,11] Experiments observing MEG have now been reported for PbSe, CdSe, PbTe, InAs, Si, InP, CdTe and CdSe/CdTe core-shell QDs.[12] 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 $h\nu_{th}$ and η_{EHPM} (Figure 1) confirm that cells significantly exceeds that of conventional cells if the threshold photon energy for MEG is between $2E_g$ and $3E_g$. [5,13,14]

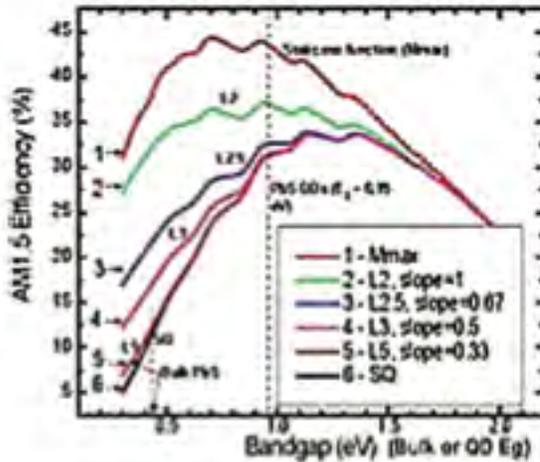


Figure 1. S-Q Calculations for different linear MEG characteristics L_n , where n is the MEG threshold energy $h\nu/E_g$ (from reference 13)

It has also been shown very recently[13] 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:

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

Recent work[13] also shows why the appropriate parameter to use when comparing the efficiency of MEG in QDs vs impact ionization in bulk materials is $h\nu/E_g$ and not just the absolute photon energy $h\nu$. When $h\nu/E_g$ is used, the slope of plots of MEG QY vs $h\nu/E_g$ is the MEG efficiency, η_{MEG} . The use of just absolute photon energy, $h\nu$, in plots of QY vs photon energy, 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. We claim that this controversy now has recently been resolved.[13-16] One reason for it has been attributed to the influence of QD surface treatments and surface chemistry on MEG dynamics compared to cooling dynamics;[17] a second reason is that in some cases QD charging produced during transient pump-probe spectroscopic experiments confounded the MEG quantum yield analysis.[14-16] Long-lived charge could produce trions in the QDs after the absorption of an additional photon in the QDs in

a pump-probe transient absorption (TA) or experiment, which $h\nu/E_g = 1 + 1/\eta_{EHPM} = 1 + 1/\eta_{MEG}$ then could confound the fast early time decay of transient absorption or bleaching signals that is the signature of MEG, and lead to overestimation of the MEG QY. However, the 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.[14] 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 by the pump pulse. MEG experiments where photocharging is eliminated and the surface chemistry is the same now produce consistent and reproducible MEG QYs in different laboratories (Figure 2).

In one possible QD solar cell configuration the QDs are formed into a 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 $\sim 3\%$ and recent non-confirmed efficiencies of $> 5\%$.

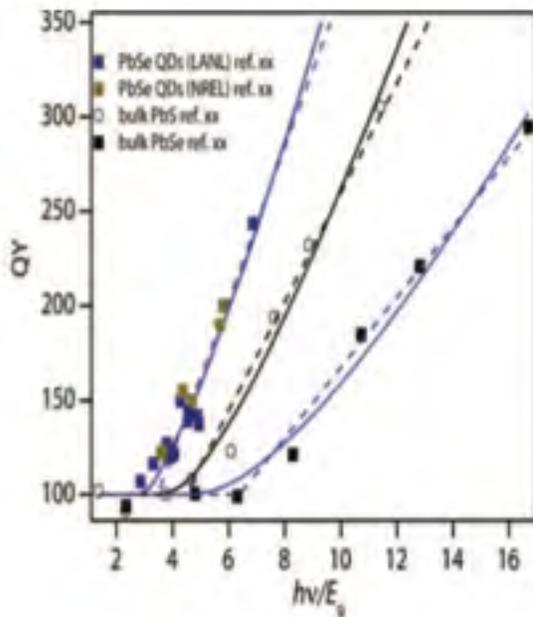


Figure 2. QY vs $h\nu/E_g$ for PbSe QDs where no photocharging is possible and QD surface chemistry is constant; results from NREL and LANL. [from Reference 13]

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