

Quantum dot sensitized solar cells an effective material for photovoltaic applications

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ABSTRACT

Nanomaterials are effectively used for solar energy conversions. Out of which quantum dot (QD) solar cells have thermodynamic conversion efficiency of solar photon conversion above 60%. This was achieved by hot photogenerated carriers produced when electromagnetic radiation falls on solar cells. This produces photovoltages or photocurrents by photoelectric effect. The former effect is based on miniband transport and collection of hot carriers in QD array photoelectrodes before they relax to the band edges by phonon emissions. The latter effect is based on utilizing hot carriers in QD solar cells to generate and collect additional electron-hole pairs through enhanced impact ionization processes.

Keywords: Nanomaterials, quantum dot (QD) solar cells, photoelectrodes.

INTRODUCTION

Shockley and Queisser [1] calculated the maximum thermodynamic efficiency for the conversion of unconcentrated solar irradiance into electrical free energy in the radiative limit assuming detailed balance and a single threshold absorber found [1] to be about 31%, this is also valid for the conversion to chemical free energy [2,3]. Since conversion efficiency is important parameters to optimize for implementing photovoltaic and photochemical cells on a truly large scale [4], several schemes for exceeding the Shockley-Queisser (S-Q) limit have been proposed and are under active investigations.

Like tandem cells [5], hot carrier solar cells [6–8], Solar cells producing multiple electron–hole pairs per photon by impact ionization [9,10], multiband and impurity solar cells [4,11], and thermo-photonic cells using thermal and electromagnetic energy [4]. Here hot carrier and impact ionization solar cells, and the effects of size quantization on the carrier dynamics that control the probability of these processes is discussed. It is well known that solar spectrum is continuous one and have photons with energies between 0.5 to 3.5 eV. When such photon incident on semiconductor, then photons with energies below the semiconductor band gap are not absorbed, while those with energies above the band gap create electrons and holes with a total excess kinetic energy equal to the difference between the photon energy and the band gap this may be given by energy conservation equation 1.

$$h\nu = E_g + E_{kin.}$$

---(1)

where, $h\nu$ is energy of incident photon, E_g is energy gap of semiconductor and $E_{kin.}$ is total excess kinetic energy in above equation. This excess kinetic energy creates an effective temperature for the carriers which are much higher than the lattice temperature, such carriers are called “hot electrons and hot holes”, and their initial temperature upon photon absorption can be as high as 3000 K with the lattice temperature at 300 K. The distribution of this kinetic energy between electrons and holes is decided by effective masses, with the carrier having the lower effective mass receiving more of the excess energy [6]. A major factor limiting the conversion efficiency in single band gap cells to 31% is that the absorbed photon energy above the semiconductor band gap is lost as heat through electron phonon scattering and subsequent phonon emission, as the carriers relax to their respective band edges means bottom of conduction band for electrons and top of valence for holes. To reduce this loss in efficiency has been to use a stack of cascaded multiple p–n junctions with band gaps better matched to the solar spectrum, in this way higher-energy photons are absorbed in the higher-band-gap semiconductors and lower-energy photons in the lower-band-gap semiconductors, thus reducing the overall heat loss due to carrier relaxation by phonon emission. In the limit of an infinite stack of band gaps perfectly matched to the solar spectrum, the ultimate

conversion efficiency at one sun intensity can increase to about 66%. Another approach to increasing the conversion efficiency of photovoltaic cells by reducing the loss caused by the thermal relaxation of photo generated hot electrons and holes is to utilize the hot carriers before they relax to the band edge by phonon emission [6]. There are two fundamental ways to utilize the hot carriers for enhancing the efficiency of photon conversion. One way produces an enhanced photo-voltage, and the other way produces an enhanced photocurrent. The former requires that the carriers be extracted from the photo converter before they cool [7,8], while the latter requires the energetic hot carriers to produce a second (or more) electron–hole pair through impact ionization [9,10]—a process that is the inverse of an Auger process where by two electrons–hole pairs recombine to produce a single highly-energetic electron–hole pair. In order to achieve the former, the rates of photo generated carrier separation, transport, and interfacial transfer across the contacts to the semiconductor must all be fast compared to the rate of carrier cooling [8,12–14]. The latter requires that the rate of impact ionization (i.e. inverse Auger effect) be greater than the rate of carrier cooling and other relaxation processes for hot carriers. Hot electrons and hot holes generally cool at different rates because they generally have different effective masses; for most inorganic semiconductors, electrons have effective masses that are significantly lighter than holes and consequently cool more slowly. One more important factor is hot carrier cooling rates are dependent upon the density of the photo generated hot carriers (viz., the absorbed light intensity) [15–17]. Here, most of the dynamical effects will be discuss are dominated by electrons rather than holes; therefore, discussion is restricted on primarily to the relaxation dynamics of photo generated electrons. Finally, in recent years it has been proposed [8,12,13,18–21], and experimentally verified in some cases [6], that the relaxation dynamics of photo generated carriers may be marked by quantized effects in the semiconductor known as semiconductor quantum wells, quantum wires, QDs, super lattices, and nanostructures. That is, when the carriers in the semiconductor are confined by potential barriers to regions of space that are smaller than or comparable to their deBroglie wavelength or to the Bohr radius of excitons in the semiconductor bulk, the relaxation

dynamics can be dramatically altered; specifically, the hot carrier cooling rates may be dramatically reduced, and the rate of impact ionization could become competitive with the rate of carrier cooling [6] shown in Fig1.

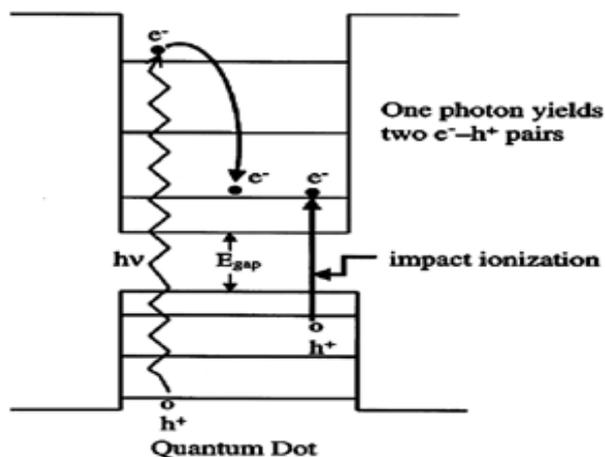


Fig1. Enhanced photovoltaic efficiency in QD solar cells by impact ionization (inverse Auger effect).

Greatly, slowed hot electron cooling in InP, CdS, CdSe and CdTe QDs has been observed by the different research group[22]. For QDs, one mechanism for breaking the phonon bottleneck that is predicted to slow carrier cooling in QDs and hence allow fast cooling is an Auger process. Here a hot electron can give its excess kinetic energy to a thermalized hole via an Auger process, and then the hole can then cool

quickly because of its higher effective mass and more closely spaced quantized states. However, if the hole is removed from the QD core by a fast hole trap at the surface, then the Auger process is blocked and the phonon bottleneck effect can occur, thus leading to slow electron cooling. This effect was first shown for CdSe QDs [23,24]; it has now also been shown for InP QDs, where a fast hole trapping species (Na biphenyl) was found to slow the electron cooling to about 7 ps [22]. This is to be compared to the electron cooling time of 0-3 ps for passivated InP QDs without a hole trap present and thus where the holes are in the QD core and able to undergo an Auger process with the electrons [22]

QUANTUM DOT SOLAR CELL CONFIGURATIONS

The two fundamental pathways for enhancing the conversion efficiency (increased photovoltage [7,8] or increased photocurrent [9,10]) can be accessed, in principle, in three different QD solar cell configurations, and are described below. However, it is emphasized that these potential high efficiency configurations are speculative and there is no experimental evidence yet that demonstrates actual enhanced conversion efficiencies in any of these systems. Absorption and photoluminescence spectra of such CdS quantum dots are shown in figure 2.

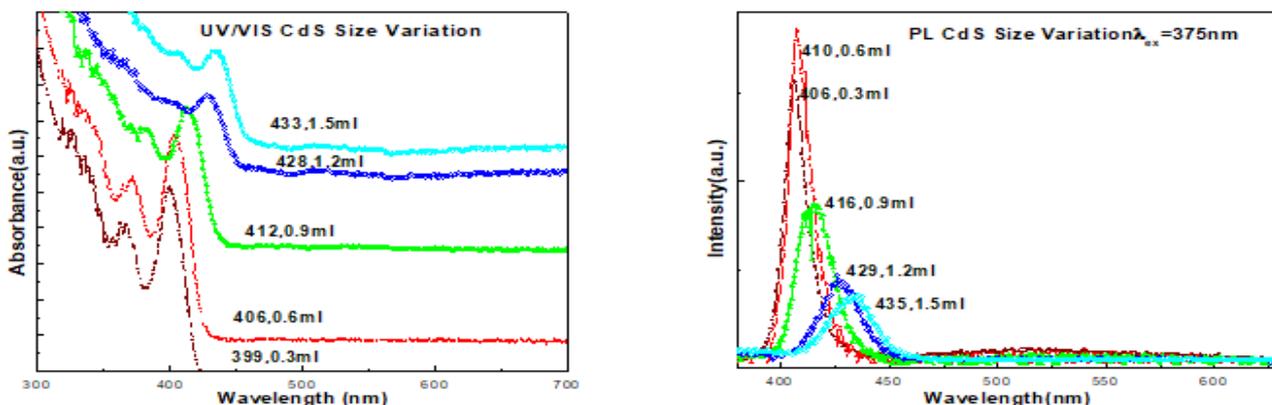


Fig.2. Absorption and photoluminescence spectrum of CdS quantum dots with varying size, absorption and photoluminescence peak positions shown in figure. The concentration oleic acid which acts as capping agent is also shown in inset. The sizes of CdS quantum dots (radius) are 2.3 nm, 2.5 nm, 2.8 nm, 3.1 nm and 3.3 nm.

1. Quantum dot arrays in p-i-n cells

In this configuration, the QDs are formed into an ordered 3-D array with inter-QD spacing sufficiently small such that strong electronic coupling occurs and mini bands are formed to allow long-range electron transport. The delocalized quantized 3D mini band states could be expected to slow the carrier cooling and permit the transport and collection of hot carriers at the respective p and n contacts to produce a higher photo potential in a PV cell or in a photo electrochemical cell where the 3-D QD array is the photo electrode [25].

Also, impact ionization might be expected to occur in the QD arrays, enhancing the photocurrent (see Fig. 1) The former have been formed via evaporation and crystallization of colloidal QD solutions containing a uniform QD size distribution; crystallization of QD solids from broader size distributions lead to close-packed QD solids, but with a high degree of disorder. Concerning the latter, arrays of epitaxial QDs have been formed by successive epitaxial deposition of epitaxial QD layers; after the first layer of epitaxial QDs is formed, successive layers tend to form with the QDs in each layer aligned on top of each other [27,28]. Theoretical and experimental studies of the properties of QD arrays are currently under way. Major issues are the nature of the electronic states as a function of inter-dot distance, array order vs. disorder, QD orientation and shape, surface states, surface structure passivation, and surface chemistry. Transport properties of QD arrays are also of critical importance, and they are under investigation.

2. Quantum dot-sensitized nanocrystalline

This configuration is a variation of a recent promising new type of photovoltaic cell that is based on dye-sensitization of nanocrystalline TiO₂ layers [29–31]. In this latter PV cell, dye molecules are chemisorbed onto the surface of 10–30 nm size TiO₂ particles that have been sintered into a highly porous nanocrystalline 10–20 nm TiO₂ film. Upon photoexcitation of the dye molecules, electrons are very efficiently injected from the excited state of the dye into the conduction band of the TiO₂, affecting charge separation and producing a photovoltaic effect. For the QD-sensitized cell, QDs are substituted for the dye molecules; they can be adsorbed from a colloidal QD solution [32] or

produced in situ [33–36]. Successful PV effects in such cells have been reported for several semiconductor QDs including InP, CdSe, CdS, and PbS [32–36]. Possible advantages of QDs over dye molecules are the tunability of optical properties with size and better heterojunction formation with solid hole conductors. Also, as discussed here, a unique potential capability of the QD-sensitized solar cell is the production of quantum yields.

CONCLUSION

Nanomaterials are effectively used in photovoltaic applications as solar energy converter. Quantum dot (QD) which have size less than Bohr exciton radius can be used in solar cells, and have thermodynamic conversion efficiency of solar photon conversion above 60% which is more than enough compared to other materials. This high efficiency achieved by a peculiar phenomenon, in which hot photogenerated carriers produced when electromagnetic radiation falls on solar cells. This produces photovoltages or photocurrents by photoelectric effect. The former effect is based on miniband transport and collection of hot carriers in QD array photoelectrodes before they relax to the band edges by phonon emissions. The latter effect is based on utilizing hot carriers in QD solar cells to generate and collect additional electron-hole pairs through enhanced impact ionization processes.

Conflicts of interest: The authors stated that no conflicts of interest.

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