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A.J. Nozik

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1617 Cole Boulevard
Golden, Colorado 80401-3393

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A.J. Nozik

Center for Basic Sciences, National Renewable Energy Laboratory
1617 Cole Blvd., Golden, CO 80401

ABSTRACT

Quantum dot (QD) solar cells have the potential to increase the maximum attainable thermodynamic conversion efficiency of solar photon conversion up to about 66% by utilizing hot photogenerated carriers to produce higher photovoltages or higher photocurrents. Three quantum dot solar cell configurations are described.

1. Introduction

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 was calculated by Shockley and Queisser in 1961 [1] to be about 31%. Because conversion efficiency is one of the most important parameters to optimize for implementing photovoltaic and photochemical cells on a truly large scale [2], several schemes for exceeding the Shockley-Queisser (S-Q) limit have been proposed and are under active investigation. These approaches include tandem cells, hot-carrier solar cells [3-5], solar cells producing multiple electron-hole pairs per photon through impact ionization [6, 7], multiband and impurity-band solar cells [2, 8], and thermophotovoltaic/thermophotonic cells [2]. Here, we will discuss only hot carrier and impact ionization solar cells and the effects of size quantization on the carrier dynamics that control the probability of these processes.

A major factor limiting the conversion efficiency in single-bandgap cells to 31% is that the absorbed photon energy above the semiconductor bandgap is lost as heat through electron-phonon scattering and subsequent phonon emission, as the hot photogenerated carriers relax to their respective band edges. The main approach to reduce this loss in efficiency has been to use a stack of cascaded multiple p-n junctions with bandgaps better matched to the solar spectrum. In the limit of an infinite stack of bandgaps perfectly matched to the solar spectrum, the ultimate conversion efficiency at one-sun intensity can increase to about 66%.

Another approach is to use the hot carriers before they relax to the band edge via phonon emission [3]. There are two fundamental ways to use the hot carriers for enhancing the efficiency of photon conversion. One way produces an enhanced photovoltage, and the other way produces an enhanced photocurrent. The former requires that the carriers be extracted from the photoconverter before they cool [4, 5], while the latter requires the energetic hot carriers to produce a second (or more) electron-hole pair through impact ionization [6, 7]. To achieve the former, the rates of photogenerated carrier separation, transport, and interfacial transfer across the contacts to the semiconductor must all be

fast compared to the rate of carrier cooling [5, 9, 10]. 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. Here we will restrict our discussion primarily to the relaxation dynamics of photogenerated electrons.

In recent years it has been proposed [5, 9, 11-14], and experimentally verified in some cases [3], that the relaxation dynamics of photogenerated carriers may be markedly affected by quantization effects in the semiconductor (i.e., in semiconductor quantum wells, quantum wires, quantum dots, superlattices, 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 hot-carrier cooling rates may be dramatically reduced, and the rate of impact ionization could become competitive with the rate of carrier cooling [3].

2. Quantum Dot Solar Cell Configurations

The two fundamental pathways for enhancing the conversion efficiency (increased photovoltage [4, 5] or increased photocurrent [6, 7]) can be accessed, in principle, in three different QD solar cell configurations; these configurations are shown in Fig. 1 and they are described below.

2.1. Photoelectrodes composed of quantum dot arrays

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 minibands are formed to allow long-range electron transport (see Fig. 1A). The system is a 3-D analog to a 1-D superlattice and the miniband structures formed therein [3]. The delocalized quantized 3-D miniband states could be expected to slow the carrier cooling and permit the transport and collection of hot carriers to produce a higher photopotential in a PV cell or in a photoelectrochemical cell in which the 3-D QD array is the photoelectrode [15]. Also, impact ionization might be expected to occur in the QD arrays, enhancing the photocurrent (see Fig. 1). However, hot-electron transport/collection and impact ionization cannot occur simultaneously; they are mutually exclusive and only one of these processes can be present in a given system.

2.2. Quantum dot-sensitized nanocrystalline TiO₂ solar cells

This configuration is a variation of a recent promising new type of photovoltaic cell that is based on dye-sensitization of nanocrystalline TiO₂ layers [16, 17]. For the

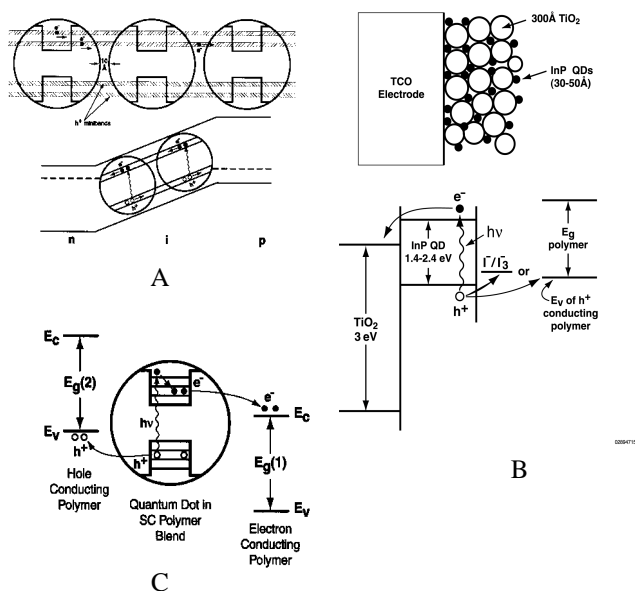


Fig. 1. Configurations for quantum dot solar cells. (A) a QD array used as a photoelectrode for a photoelectrochemical or as the i-region of a p-i-n photovoltaic cell; (B) QDs used to sensitize a nanocrystalline film of a wide bandgap oxide semiconductor (viz. TiO_2) to visible light. (C) QDs dispersed in a blend of electron- and hole-conducting polymers.

QD-sensitized cell, QDs are substituted for the dye molecules; they can be adsorbed from a colloidal QD solution [18] or produced in situ [19-22]. Successful PV effects in such cells have been reported for several semiconductor QDs, including InP, CdSe, CdS, and PbS [18-22]. A unique potential capability of the QD-sensitized solar cell is the production of quantum yields greater than 1.0 by impact ionization (inverse Auger effect) [23]. Dye molecules cannot undergo this process.

2.3. Quantum dots dispersed in organic semiconductor polymer matrices

Recently, photovoltaic effects have been reported in structures consisting of QDs forming junctions with organic-semiconductor polymers [24]. A variation of this configuration is to disperse the QDs into a blend of electron and hole-conducting polymers [25]. This scheme is the inverse of light-emitting diode structures based on QDs [26-28]. In the PV cell, each type of carrier-transporting polymer would have a selective electrical contact to remove the respective charge carriers.

All of the possible QD organic-polymer photovoltaic cell configurations would benefit greatly if the QDs could be coaxed into producing multiple electron-hole pairs by the inverse Auger/impact ionization process [23]. This is also true for all the QD solar cell systems described above. The most important process in all the QD solar cells for reaching very high conversion efficiency is the multiple electron-hole pair production in the photoexcited QDs; the various cell configurations simply represent different modes of

collecting and transporting the photogenerated carriers produced in the QDs.

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