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Generation of hot carriers for photon management in future photovoltaics

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ABSTRACT

The most important limitation for the efficiency of photovoltaic energy conversion is related to the mismatch between the broadband character of the solar radiation and the spectral sensitivity of solar cells. Large losses appear at both sides of the solar spectrum. Low-energy photons are not absorbed and escape conversion, whereas high-energy photons can only be utilized partially. Here, we discuss how the loss related to low-energy photons can be reduced by spectral conversion, making use of active layers of Si nanocrystals in an SiO_2 matrix. As a possible solution, we consider generation of hot carriers upon sequential intraband absorption of two or more low-energy photons and present experimental data in support of this. Configurations are proposed in which efficient spectral conversion could be achieved, and their feasibilities are discussed. We also address the fast emission from Er^{3+} ions, purposefully introduced into the active layer, which can be used to trace the successful generation of hot carriers, and in that way serve to evaluate specific excitation schemes.

1. Introduction

Efficient photovoltaic (PV) conversion presents a major fundamental challenge. This is mainly related to the mismatch between the broadband character of sunlight and the spectral sensitivity of current, usually single-junction, solar cells. Low-energy (i.e., sub-bandgap) solar photons cannot be absorbed and are lost entirely, whereas higher energy photons are absorbed, but the generated electron-hole pairs quickly lose energy by cooling down from their initial energetic position to the band-edge by emitting phonons. Therefore, a conventional single-junction solar cell can only be very efficient in a narrow range of photon energies and has large inherent losses for conversion of broadband light. This leads to the fundamental efficiency limit for the PV conversion – the Shockley–Queisser (SQ) limit – of approximately 30% for an optimal material with a bandgap of 1.1 eV,,close to that of bulk Si [1]. The common way to (partially) overcome these losses is by using stacks of materials with different bandgaps (tandem or multijunction devices), but at the disadvantage of increased process complexity and cost, making them so far only suitable for concentrator and space applications [2].

There are several (other) ways to enhance the efficiency of PV devices above the SQ limit, often referred to as the third-generation PVs [3]. In that context, nanostructured materials are frequently investigated. Compared to bulk materials, nanostructures offer interesting new possibilities for device applications induced by quantum confinement, such as (i) bandgap tuning, (ii) lower density of states and reduction of hot carrier cooling by phonon scattering (the "phonon bottleneck"), (iii) enhancement of surface-related effects, (iv) enhancement of Coulomb interaction between carriers, and (v) relaxation of momentum conservation, among others. The latter is especially impactful in case of Si because of its indirect bandgap. As Si is the major PV material, this makes also Si nanostructures interesting for PV applications [4].

2. Si nanocrystals for PV solar shapers

The quantum confinement effect in nanostructures offers several possibilities to overcome photon-to-electron conversion limits. A particularly attractive option with the potential to realize a substantial efficiency enhancement of solar cells is offered by "shaping" the solar spectrum, so as to make it fit better with the sensitivity of a PV device. To realize that, procedures for efficient down-conversion (cutting) of high-energy photons from the ultraviolet range of the solar spectrum, and up-conversion ("pasting" together) of the low-energy photons in the near-infrared (NIR), need to be developed. It turns out that layers of high-quality

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Si nanocrystals (NCs) in SiO_2 offer attractive opportunities for these purposes.

2.1. Photon down-conversion

Originally, photon cutting has been demonstrated in rare-earth systems [5] and found its application in fluorescent tubes. A similar idea involves carrier multiplication (CM) by generation of multiple electron-hole pairs by absorption of a single high-energy photon in a NC, in which the efficiency of CM is enhanced by stronger Coulomb interaction (compared to bulk) [6]. This process of *multiple exciton generation* (MEG) has been observed for NCs of different semiconductor materials [7–9] – see Ref. [10] for a recent review. In the past, we had reported on an interesting variation of the MEG process for Si NCs – called *space-separated quantum cutting* (SSQC). In this case, the excitons generated by a single high-energy photon reached their ground states not in the same, but in the neighboring NCs [11–13]. The SSQC effect adds an additional virtue to MEG: It considerably increases the excitonic lifetime above the picosecond range, characteristic for multi-excitonic Auger processes, and allows for radiative recombination, and hence emission of multiple photons with lower energy. In that way photon "cutting" is realized, with a potential for application in solar shapers, for the high-energy end of the solar spectrum.

2.2. Photon up-conversion

In addition to SSQC, investigations of the optical properties of Si NCs in an SiO_2 matrix also revealed features that open perspectives for "pasting" of IR photons with sub-bandgap energies, which are lost in a standard PV cell.

The most significant of these are:

- Direct bandgap-related emission: The most spectacular observation is the increased efficiency of phonon-less radiative recombination (*direct bandgap-related* emission), which has been identified due to its unique fingerprint – the red-shift for smaller NC sizes [14].
- Reduction of the hot carrier cooling rate: The phonon-less recombination in Si NCs corresponds to "hot" photoluminescence (PL) and is enabled by slower thermalization of hot carriers (depending on the NC size, up to $\sim 10^3$ times slower than in bulk Si) [14].
- Efficient Auger interaction, with the characteristic time constant of ~20 ps for two excitons in a single Si NC of 4.5 nm diameter, d_{NC} ~4.5 nm [15].
- Prominent emission band at ~2.95 eV (~420 nm), possibly (interface-)defect related [14,16–18].
- Increased cross-section of the excited state absorption in the NIR range, exceeding that of the linear band-to-band absorption [19].

Based on the above findings, two specific approaches toward up-conversion of low-energy photons can be proposed:

- Exploration of nonlinear properties of Si NCs: combined absorption of two (or multiple) low-energy photons for the generation of a single low-energy electron–hole pair [20].
- Absorption of low-energy photons by free carriers for the generation of a hot exciton (e.g., sequential absorption of over- and below-bandgap photons).

In the following, we will concentrate on the latter effect, which, in our opinion, is most promising for PV applications.

3. Multicolor sequential absorption in Si NCs for spectral conversion

3.1. Induced absorption in Si NCs

The linear (band-to-band) absorption of Si NCs is characterized by a steady increase toward higher photon energies, appearing due to the higher density of states and the enhanced transition probability, as the impulse mismatch reduces. This is demonstrated in Fig. 1 for two materials with a different average d_{NC}. As can be expected, for the sample with the smaller NCs (red curve), the absorption has a higher onset value (due to its larger bandgap). For both materials absorption below ~2 eV is very low, in the 0.1–1.0% range, as the (linear) absorption for sub-bandgap energies is (practically) zero and for just over-bandgap values the optical transition is mainly "indirect"; for a better illustration a zoom-in for the low-energies is shown in panel (b). At higher

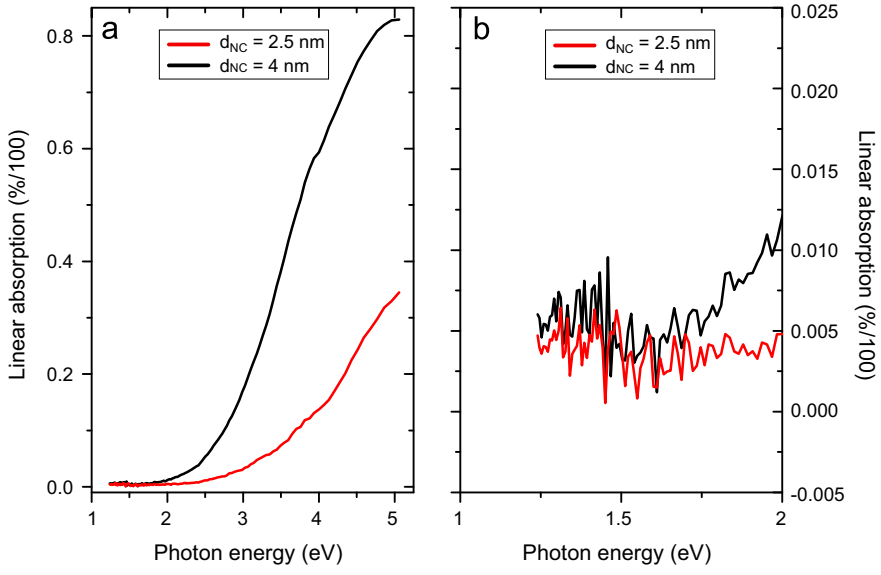

Fig. 1. (Color online) Linear absorption of two samples with different average NC diameter (black: d_{NC} ~4 nm, red: d_{NC} ~2.5 nm). In panel (b), the regime for 1.2–2.0 eV has been zoomed in to show very low values for the absorption at photon energies close to the bandgap (~1.5 eV and ~1.7 eV for d_{NC} ~4 nm and d_{NC} ~2.5 nm, respectively).

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