Materials for downconversion in solar cells: Perspectives and challenges

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ABSTRACT

Solar energy has an enormous potential to solve society energy needs in a sustainable way. Notably, photovoltaic systems (**PV**) permit to obtain electricity based on solar energy. However, some issues must be addressed to establish **PV** as a reliable source of electrical power, for example, its low energy density. One of the approaches to improve the performance of **PV** systems is to utilize the solar spectrum in solar cells efficiently. Downconversion (**DC**) is a process where a high energy photon is converted into two or more photons with lower energy. Trough downconversion is possible to use a wider portion of the solar spectrum raising the efficiency in different kinds of solar cells. The present paper reviews the state of the art of materials and methods used to take advantage of downconversion processes in solar cells. Here we discuss some of the pros and cons of different designs in solar cells as well as the main characteristics of the materials utilized.

1. Introduction

In a society with a global population now exceeding 7 billion satisfying energy requirements in a sustainable way is a major challenge. Photovoltaic (**PV**) systems provide the possibility to generate electricity with environmental advantages as zero carbon dioxide emission during operation as well as scale flexibility, simple operation, and low-cost maintenance. Solar energy is especially appropriate for smart energy networks with distributed power generation, operating and maintenance costs for **PV** panels are considered to be low compared to costs of other renewable energy systems [1]. Due to its benefits, the total **PV** installed capacity at the end of 2014 amounted to at less 177 gigawatts (**GW**) as stated by the International Energy Agency Photovoltaic Power System Program (**IEA PVPS**) [2]. According to **IHS** technology analysis, an enterprise specialized in market technology studies, the total global solar photovoltaic capacity is forecast to reach 498 **GW** in 2019 [3]. This scenario can be affected by weak commodity prices, a slowing world economy and still very low oil prices [4].

Despite its numerous advantages, there are still issues to overcome to establish **PV** technologies as an important source of energy in the global perspective. The two principal problems are the intermittent nature of environmental conditions and the low energy yield in **PV** systems that increase area-relate costs. Typically a **PV** system consists of four basic building blocks: solar cells, organized to form a solar panel or module, inverter, utility meter and performance monitoring. The energy yield in **PV** systems is affected by the fulfillment of each component especially from the efficiency of the solar cells.

A theoretical efficiency limit for an homojunction solar cell around 31% was calculated for Shockley and Queisser through the assumption that for a single semiconductor absorber, under standard AM 1.5 solar spectra and external quantum efficiency (**EQE**) equal to 1, one absorbed photon would result in one photogenerated electron [5]. Conventional solar cells exhibit lower efficiencies due to reflection losses, lattice thermalization, recombination, junction and contact voltage, among others [6]. Different strategies are proposed to address this low-efficiency problem, as the concentration of sunlight, multijunction, an intermediate-band, multiple exciton generation (**MEG**), hot-carriers and spectral modification trough upconversion or downconversion mechanisms [7].

The spectral modification approach refers to the ability to manipulate the solar cell to suit the solar spectrum better. There is a mismatch between the solar spectrum and the response of solar cells. When an incoming photon enters a solar cell, only those whose energy is equal or slightly higher than the band gap of the semiconductor can be converted into an electron-hole required to generate electricity. Photons with lower energy cannot be absorbed by the solar cell, while photons with so much higher energy produce a "hot" electron–hole pair that relaxes to the band edges being lost to heat [6,7]. For optimal energy conversion is important that the majority of the solar spectrum can be used.

Conventional solar cells are fabricated to use the visible range, which contains a substantial fraction of the solar energy spectrum. *If we could also use the ultraviolet (UV) or/and infrared (IR) parts of the spectrum, solar cells* efficiency could be increased. Some materials are capable of generating more than one visible or near infrared photon after absorbing a **UV** photon. This process is called downconversion **(DC)** [6,8]. Also for materials that exhibit anti-Stokes photoluminescence is possible to obtain emitted photons with higher energy than the incoming one [9]. This process is known as upconversion **(UC)** and can be used to profit the near and far infrared region of the solar spectrum. Both schemes are useful to harvest the efficiency of solar cells. To better illustrate these concepts Fig. 1 displays the parts of the AM 1.5 spectrum than can be utilized by a standard silicon solar cell (green zone) in comparison of the fraction of light which could be employed to **DC** and **UC** process (blue with lines).

The present work highlights the latest advances in **DC** materials to improve the performance of different solar cells. This paper is organized as follows: In Section 2 a brief overview of the theoretical framework and fundamental aspects of **DC** is presented. The materials and methods developed to fabricate solar cells by using downconversion effect are analyzed in Section 3. In Section 4, present-day solar cells devices that use downconversion approaches are discussed. Finally, this work ends with a summary of the perspectives and challenges related to the use of different materials for **DC** in solar cells.

2. Fundamental aspects

2.1. Theoretical background

As mentioned before downconversion involves converting high energy photons into lower energy photons. The concept of using **DC** to split a **UV** photon into two visible photons was first explored by Dexter in 1957 [10]. **DC** can be accomplished through the use of host lattice states or ions (single or a combination of them) which can lead to quantum efficiencies larger than unity [6,11–15]. When a similar process occurs in a material with quantum efficiency smaller than the unity the process is called downshifting [16].

In host lattices, the effect of **DC** is related to the impact ionization process. Here a single high-energy photon generates multiple electron–hole pairs attributed to an interband Auger process under appropriate

conditions can be useful to generate electricity [10,11]. It requires the absorption of photons with energy as twice or more times the host material band gap [10]. The other **DC** scheme considers a single ion as an optically active center with three energy levels. When a high energy photon is absorbed a transition to the maximum energy level takes place. Hence a sequence of two emissions happens emitting two photons with lower energy. It is also possible to obtain **DC** by using two ions. In this case, the excited ion can relax from the higher energy state into the lower energy state by energy transfer to the second ion. After the energy transfer both ions can emit a photon to reach the ground state [6–8].

Lanthanide ions are extensively used for the aforementioned purposes due to its sufficient energy level in the 4f orbital allowing several intraband transitions ($4f^n$–$4f^n$) within the f-manifold with different energies. Besides, the optical spectrum of those ions when doped into several materials are similar to free ions. This similarity is due to the fact that 4f electrons are effectively shielded from surrounding crystal fields because of the outer filled 5s and 5p shells. Therefore, 4f-4f transitions do not contribute to chemical bonding and thus have a negligible effect on the metal-to-ligand distance. The forbidden f–f transitions of trivalent lanthanide ions limit phosphors' absorption bandwidth.

Investigation in lanthanides for downconversion purposes started with single ions doped-fluorides as Pr^{3+}, Tm^{3+}, Er^{3+}, Gd^{3+} capable of cascade emission. In some lanthanide ions d-f optical transitions are present and exhibit broader emission spectra than the ions with f optical transitions [8]. Energy transfer from a lanthanide ion to another occurs by different mechanisms as: i) migration of electrons and holes; ii) immigration of excitons; iii) resonance between atoms with sufficient overlap integrals; and, iv) reabsorption of photons emitted by another activator ion or sensitizer [14]. The energy absorbed in a lanthanide ion can migrate to a host lattice defect and then *recombine non-radiatively affecting DC performance.* Therefore, luminescent host materials should be highly crystalline and have few lattice defects and impurities [10–14]. Also, the surface area of the crystals must be minimized [16].

The energy transfer between ions during the process was first considered theoretically by Föster (1948) [17] and Dexter (1953) [18]. This first model contemplated the following mechanisms:

(a) The energy excitation of a donor ion (D) is transferred to other ion named acceptor (A), which is separated by a distance R. Here the energy transfer is related to an electrostatic coupling, magnetic coupling and coupling between ions.

(b) The rate of the energy transfer induced for the dipole generated for the coupling mentioned above process decreases as R^6, and the rate of exchange as exp (−2R/L), where R is the donor-acceptor separation and L is the effective average Bohr radius for D and A ions excited and unexcited states.

(c) The energy transfer rate is proportional to the spectral overlap of the absorption and emission bandwidths of the D and A ions.

Late in 1970 Kuhn presented a complete theoretical treatment from a classical point of view [19]. The coulombic interaction proposed by Föster occurs at distances of the order of angstroms. As the distance between donors and acceptors is increased, the model considers the radiative emission-absorption character of the process. In 1989 Andrews formulated a theory that found emission-absorption roles and their interplay [20]. This theoretical approach was complemented with quantum considerations in the subsequent work of Avery [21], and Gomberoff and Power [22]. Avery work replaced the coulombic interaction with its relativistic counterpart, the Breit interaction [21]. While Gomberoff and Power take into account the effect of the retardation on the spatial dependence of the resonance transfer rate of excitation by using S-matrix theory [22].

If we consider a system with three luminescent centers the energy
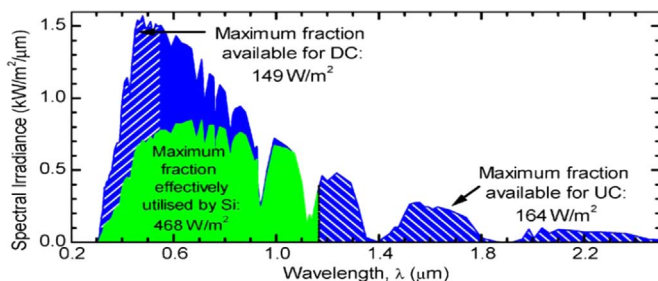

Fig. 1. Regions of the AM1.5G spectrum that can be used in a solar cell trough **DC** and **UC** (blue with lines). The fraction absorbed by a thick solar silicon device is shown in green ([14] with permission of Elsevier). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)