

Materials for downconversion in solar cells: Perspectives and challenges

M.B. de la Mora^{a,*}, O. Amelines-Sarria^{b,c}, B.M. Monroy^{d,†}, C.D. Hernández-Pérez^e, J.E. Lugo^f

^a CONACyT Fellow- CCADET Universidad Nacional Autónoma de México (UNAM), México D.F. C.P. 04510, Mexico

^b Centro de Investigación y Desarrollo Tecnológico en Energías Renovables, Universidad de Ciencias y Artes de Chiapas, Libramiento Norte Poniente No. 1150, Col. Lajas Maciel, Tuxtla Gutiérrez, Chiapas, Mexico

^c Facultad de Ingeniería Mecánica, Universidad Pontificia Bolivariana - Seccional Bucaramanga, Autopista Piedecuesta, Km 7. Bucaramanga, Santander, Colombia

^d Instituto de Investigaciones en Materiales, UNAM, Cd. Universitaria, A.P. 70-360, Coyoacán 04510, D.F. Mexico, Mexico

^e Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa, A.P. 55-534, 09340 Mexico D.F., Mexico

^f Visual Psychophysics and Perception Laboratory, School of Optometry, University of Montreal, C.P. 6128 succ. Centre Ville, Montreal, Quebec, Canada H3C3J7

ARTICLE INFO

Keywords:

Downconversion
Solar cells efficiency
Lanthanides
Nanomaterials

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, multi-junction, an intermediate-band, multiple exciton generation (**MEG**), hot-carriers and spectral modification trough upconversion or down-conversion mechanisms [7].

* Corresponding author.

E-mail addresses: betarina@gmail.com, maria.delamora@ccadet.unam.mx (M.B. de la Mora).

† Deceased author.

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 Förster (1948) [17] and Dexter (1953) [18]. This first model contemplated the following mechanisms:

- 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.
- 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.
- 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 Förster 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

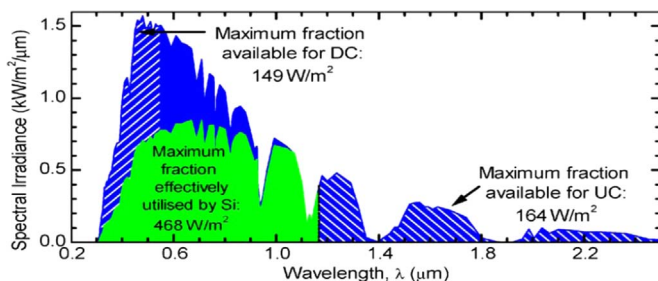


Fig. 1. Regions of the AM1.5G spectrum that can be used in a solar cell through DC and UC (blue with lines). The fraction absorbed by a thick solar silicon device is shown in green ([14] with permission of Elsevier). (For interpretation of the references to color in this figure legend, the reader is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

transfer becomes more complicated due to a variety of multiphoton processes. At this respect, Andrews and Robert D. Jenkins developed a theoretical framework by using quantum electrodynamics [23]. They showed that in general, the accretive mechanism is responsible for sensitization, and particularly in **DC** processes the interplay between site geometry and optical selection rules will determine the dominant contributory mechanism [23].

To describe the impact of **DC** in a conventional solar cell Trupke et al. [24] added a layer that exhibited **DC** effect and used a detailed energy balance following the Shockley and Queisser formalism to calculate its efficiency. An ideal condition was considered for this model. A more realistic model, which includes changes in radiation fluxes when light passes through interfaces of different refractive indices, can be found in Badescu et al. work [25,26]. Cooperative energy transfer (**CET**) is a **DC** process of major importance in solar cells performance [19,27,28]. In this process, a luminescent center splits its excited state energy in two by simultaneously transferring its energy to two nearby acceptor centers yielding two low-energy photons for each high-energy photon absorbed [28]. Monte Carlo (**MC**) methods were widely used to model **CET** dynamics [29–31]. Typically **MC** methods are employed to place the dopants randomly at allowed lattice positions and subsequently generate different configurations to simulate averaged luminescence decay curves [32]. This approach has been used for a better understanding of the transfer rate between nearest neighbors in systems as ($\text{Nd}^{3+}, \text{Yb}^{3+}$) coupled in YF_3 [30], $\text{NaYF}_4:\text{Tb}^{3+}, \text{Yb}^{3+}$ [31], $\text{Ce}^{3+}-\text{Yb}^{3+}$ codoped **YAG** phosphors [33], among others.

Inokuti-Hirayama [34] and Yokota-Tanimoto [35] models are **MC**-based methods that neglect the crystal structure of the host material. Instead, the model imposes a discrete distribution of acceptors around a single donor. Here, only the transfer from donors to acceptors in their ground state is considered. Even though the simplification of the complex energy transfer mechanisms in **DC** this model provides a good approximation of many experimental systems [36,37] and it can also be useful to understand **UC** process [38].

A model that explicitly takes into account all possible interactions between donor ions and nearest-neighbors, but averages the effect of the rest of the crystal, was developed by Rabouw and Meijerink [27,32]. The accuracy of the model is suitable for various crystal host geometries.

Nanomaterials are recently explored as novel materials for **DC** applications [39]. Size effects as quantum confinement and surface effects give some advantages compared to conventional ones such as negligible scattering for enhanced beam collimation, minimal backscatter to the source, and minimal internal scattering losses [40]. An example of nanomaterials with desirable properties for **DC** are nanophosphors such as nanocrystals doped with lanthanide ions [40]. These materials are also widely used for upconversion purposes [39]. Some magnetic nanophosphors as $\text{NdGdF}_4:\text{N}^{3+}, \text{Yb}^{3+}, \text{Tm}^{3+}$ exhibit dual mode conversion: **DC** and **UC** [41]. For applications in a single junction and multicell devices, this kind of nanomaterials can be useful to minimize incident light scattering if they are placed in front of the solar cell [42]. To analyze energy transfer behavior in these complex nanomaterials, models for study **CET** previously discussed are also useful. The intensity of emission spectra component in these materials can be interpreted by using the Judd-Ofelt formalism extensively applied in the analysis of systems that include lanthanide ions [43,44]. It is well known that lanthanide ions optical behavior depends strongly on the local crystalline structure, when the size of a crystal decrease to the nanoscale, optical properties change due to the formation of enhanced surface states [45]. Also changes in ion–ion and ion–lattice interactions are present. These characteristics must be considered for the theoretical study of **DC** in nanophosphors. Recently, some groups as Wenqin Luo et al. propose to use excitation spectrum instead the absorption spectra to calculate Judd-Ofelt parameters when considering nanosize effects [46]. In the model, nanoscale

is included through the consideration of an effective index of refraction and the filling factor occupied by nanocrystals.

Regarding the theoretical analysis of solar cells efficiency including nanoparticles as a layer on the top of a solar cell Abrams et al. developed a model [47] based on the method of Ruppel and Würfel [48]. Such model is used to calculate the open-circuit voltage and short-circuit current of the solar cell, thereby determining the efficiency. The analysis covers lossless and lossy theoretical limits, as well as a thermodynamic evaluation. A total 7% efficiency improvement was calculated in the case of a perfectly efficient down-converting material [48,49].

Theoretical calculations for different kinds of solar cells with optimized values of refractive index and emission wavelength of the **DC** layer are presented in the work of Ten Kate et al. [50]. Recently, Alharbi and Kais gave a fascinating discussion about the radiative mechanism in photosynthesis for a better understanding of the radiative process in **PV**. A similar mechanism in the coupling of photosynthetic reactions is proposed to suppress recombination in photocells giving a general enhancement of net photo-generated current by 35% [51].

Considerable advances have been made in developing a robust framework to better understand **DC** process and its influence on the solar cells performance. Theoretical models usually consider two types of energy balance. The first are based on radiative processes among two-extended-level systems. The second one is a thermodynamic approach which takes into account the balance of entropy and energy fluxes. However, the complexity of the energy transfer in different designs of solar cells and the recent inclusion of materials at the nanoscale [8,40,41] requires appropriate approaches and tools for a better develop of **PV** systems. Lately, an emerging area in computational material science called ‘high-throughput’ (**HT**) provide a new platform to study and develop materials [52]. The principle of this method is to create an extensive database containing electronic and thermodynamic properties of a material of interest and analyze it by intelligent data mining. Until now **HT** has shown its effectiveness to study complex nanomaterials and its applications such as catalysis or some **PV** systems. We consider **HT** as an idoneous approach for **PV** systems that includes **DC** materials because it allows defining the leading electronic and thermodynamic properties to be evaluated. Also could permit to summarize and compare different results about similar solar cells designs with various **DC** materials. In the next section, we briefly discuss the difference between **DC** and a very similar process use in solar cells: downshifting.

2.2. Downconversion and downshifting

In the first section of this work we commented about two different manners to obtain spectral modification: **DC** and **UC**. Then we focus on the conversion of photons with high energy into two photons with a lower energy through **DC**. This process is also known as quantum cutting **QC**. There is another similar mechanism called downshifting **DS** whereby a conventional photoluminescence process converts a high energy photon into another with lower energy. Downshifting can be considered as a subcategory of downconversion and although both processes are similar, their quantum efficiencies differ. In **DS** process the quantum efficiency is lower than unity and losses due to thermalization are not mitigated [53]. However, losses due to surface recombination can be diminished increasing the efficiency of solar cells. In **DC** another main difference is that the converter emits two photons of low energy for each absorbed high energy photon, while **DS** layers emit maximum one low energy photon for each absorbed one. A schematic representation of **DS** and **DC** process is presented in Fig. 2. Once a photon is absorbed, by a sequential emission, two photons with lower energy are obtained in **DC**, if the wavelength is equivalent to the associated with the solar cell bandgap, then the material can be used to boost its efficiency. A similar process occurs in **DS** but as mentioned

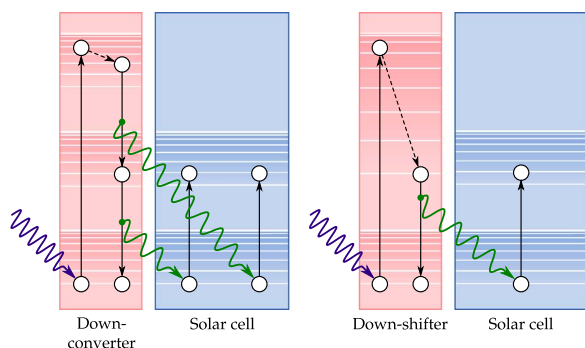


Fig. 2. Energy diagram that shows schematically different behaviors among a down-conversion and a downshifting material used to harvest the efficiency in a solar cell.

before just one photon can be retrieved for each absorbed one.

The use of a **DS** layer to improve the performance of solar cells has been first explored by Hovel et al. [54] since then **DS** materials have been studied both theoretically [14] and experimentally [55]. Conventional materials considered for **DS** layers in solar cells are polymers such as polymethylmethacrylate (**PMMA**) doped with luminescent organic dyes, quantum dots and organometallic complexes [56]. An increase in the efficiency has been shown in different solar cells as crystalline silicon [53,56], CdTe [57,58], solar cells based on thin films of CdTe/CdS [59] and organic dye-sensitized [60], among others. Another interesting fact is that in **DC** and **DS** the intensity of the shifted photon emission scales linearly on the incident intensity [61]. Therefore both schemes can be benefited with the inclusion of a concentrator system on the top layer of a solar cell. **DC** systems present better possibilities to ameliorate solar cells performance than a **DS** scheme since they have fewer losses due to thermalization and their quantum efficiency is equal or bigger than unity. Consequently, over the past few years, significant efforts were made to obtain an appropriate material for **DC**, which implies at least an additional step to split a high energy photon into two lower energy photons. Thus means a very careful design and synthesis of the material is needed.

3. Materials and methods

Much of the early work related with **DC** for solar cell applications was focused on lanthanide ions due to their optical properties. Recently, nanomaterials have been studied as an option as down-converters. Most common materials and best suitable methods of synthesis for lanthanides, nanophosphors and another kind of nanomaterials are presented below.

3.1. Lanthanide ions as downconversion materials

Lanthanides ions are extensively utilized for **DC** applications due to its optical properties. Typical materials used are lanthanide phosphors doping a host material [6–8,62]. An advantage of using this kind of materials in solar cells applications is the many years of study in semiconductors systems as hosts for lanthanide ions such as crystalline silicon, SiGe, germanium, gallium arsenide and other III–V hosts [8,16,63]. An additional benefit is the vast amount of methods that allow to synthesized lanthanides in different host matrices.

Lanthanide phosphors were conventionally prepared through solid-state reaction process [8,64]. The solid-solid reaction is the widest approach due to its simplicity; raw solid powders with the desired phosphors are mixed then heating above their melting points and finally cooling down under different atmospheres until incorporate the ion into the host. Fluorides and oxides based **DC** phosphors are often prepared by this method [29]. Solution based-chemical synthesis as hydrothermal [65,66] sol-gel [8,67] and co-precipitation,[68,69] are also useful methods to obtained this kind of materials. In particular,

the hydrothermal method offers the possibility of homogeneity control and phase purity [65,66]. In a typical sol–gel process, the precursors undergo a series of hydrolysis and polycondensation reactions to form a colloid. Then the sol-gel solution can be deposited by spraying, dipping or spinning. Heat treatments can pyrolyze the remaining organic or inorganic compounds and form amorphous or crystalline films. Co-precipitation methods are related to the precipitation of a solute that occurs when a vapor is supersaturated or when a melt is supercooled.

Other common fabrication methods are spray pyrolysis,[70], spin coating [71], sputtering [72], laser ablation [73,74] and plasma-enhanced chemical vapor deposition **PECVD** [75,76] and combustion synthesis [77,78]. Spray pyrolysis is a versatile and effective technique to deposit metal oxide films, which contain lanthanides. The spray pyrolysis solution mostly contains nitrates or chlorides with the desired lanthanide. The spray developed by an ultrasonic nebulizer is directed towards the substrate by a carrier gas of humid air. After deposition, the films are usually annealed in a variety of ambient, including air, nitrogen, argon and forming gas. The quality and properties of the films depend on parameters such as spray rate, substrate temperature, ambient atmosphere and droplet size. Particularly, the substrate temperature used for depositing a thin-film phosphor is the main parameter, which can control the morphology and crystallinity of the film.

Spray pyrolysis offers a cheap and easy way to fabricate thin films on a large scale, which does not require vacuum. While sputtering is a process whereby particles are ejected from a solid target material due to the bombardment of the target by energetic particles. Ejected atoms from the target travel to a substrate and can be deposited as a film. This process can lead, during prolonged ion or plasma bombardment of material, to significant erosion of materials, and can thus be harmful. Concerning laser ablation deposition; this technique is based on the ablation of a target through a laser irradiation that generates plasma. In general a vacuum chamber is needed. The quality of thin films is affected by growth conditions such as background gas pressure, laser energy density, repetition frequency, grow temperature and target substrate. In **PECVD** chemical reactions are induced through a plasma usually generated by radio frequency or direct current discharge. By controlling the plasma and reaction parameters good quality films, from vapor containing the chemical species used as precursors in the reaction, can be obtained. While combustion synthesis.

To maximize benefits obtained through **DC**, the host material, and lanthanide ions must be carefully chosen accordingly with the type and design of the solar cell. Host materials must exhibit high transmittance, photostability, excitation energy, absorption strength, chemical and thermal stability and low scattering [6,8,16,79]. The formation of defects and traps within the host material results in energy being absorbed inside the host instead of being transferred to the activator ion [6,8]. Therefore a highly crystalline host is recommended. Main criteria to choose the appropriate lanthanide ion are high emission lifetime and good chemical and electrical stability [8].

To select best candidates for host and type of lanthanide to adequate for a specific design of solar cell a good characterization of synthesized materials is indispensable. In general, optical spectroscopic techniques are routinely used to identify the aforementioned properties, which can be related to absorption, and emission processes that better suit **PV** applications. The absorption and emission spectra provide information, not just about the main features of luminescence such as quantum yields, radiative lifetimes and sensitization efficiency but also referring to the interaction of the lanthanides with the host [80]. For a given transition, by knowing the number of absorbent species N and the absorption spectra, it is possible to obtain the transition probability coefficient. The effective section absorption is related to Einstein' coefficients. To identify the energy-level structure known as Dieke diagram, the widest spectroscopy technique utilized is emission spectroscopy. Other useful spectroscopies are Raman e

Infrared (**IR**). Both help to determine chemical aspects in a host-lanthanide system. Through Raman spectroscopy, different important properties for solar cell technology such as crystallographic orientation, mechanical stress, doping, composition, phase, and phonons behavior can be measured with high accuracy [81]. Also, Raman spectroscopy is a useful complementary tool to characterize structural properties such as crystal orientation and symmetry of the molecules among others. About structural characterization common techniques to know the final structure of the crystal host are X-ray diffraction and microscopy techniques.

Concerning the use of lanthanides in solar cells a good experimental demonstration involved a system of a Tb^{3+} - Yb^{3+} couple in $(\text{Y},\text{Yb})\text{PO}_4:\text{Tb}^{3+}$ [58]. Here, **DC** was achieved through cooperative energy transfer from Tb^{3+} to two Yb^{3+} ions. Experimental work based on **DC** in Tb^{3+} - Yb^{3+} are reported in $\text{GdAl}_3(\text{BO}_3)_4$ [82], GdBO_3 [83], Y_2O_3 [84], CaF_2 nanocrystals [85,86] and lanthanum borogermanate glass [87]. Good quantum yields desirables for **PV** applications have been obtained with Gd III [88] and Eu III [89]. Common **DC** lanthanides materials are Pr^{3+} - Yb^{3+} codoped KY_3F crystals [90], $\text{Nd}:\text{SrTiO}$ thin films [91] and $\text{LiGdF}_4:\text{Eu}^{3+}$ and $\text{LiGdF}_4:\text{Er}^{3+}$, Tb^{3+} [92] among others [6,8]. An inconvenience of using a **DC** with lanthanides on the top of a solar cell is that this layer often is highly reflective which causes radiative losses. This can be avoided by an antireflective coating design to reflect the downconverted emission back into the solar cell [6].

3.2. Nanomaterials as novel downconversion materials

Materials at nanoscale change dramatically its chemical and optical properties with respect to the same material as bulk. Recently, research efforts have been focused on the use of nanomaterials as effective downconverters for **PV**. Here we present some of the most common nanomaterials studied.

As mentioned before nanophosphors are recently used as an innovative option for **DC** materials to improve efficiency in solar cells. A typical nanophosphor consists in a crystalline host material with a nanometric size and a dopant added at low concentration. Synthesis methods to create nanophosphors can be either chemical or physical [40,93,94]. Physical methods commonly utilized are sputtering, molecular beam epitaxy, ionized cluster beam, liquid metal ion source, consolidation, gas aggregation of monomers and laser ablation. Chemical approaches are precipitation in the presence of capping agents, sol-gel reaction, auto combustion and reaction in microemulsions. Characterization techniques used for nanophosphors are analogous to the ones mentioned for lanthanides ions. Some strong points in using nanophosphors materials in solar cells are the enhancement of optical properties due to quantum confinement effects and the possibility of obtaining uniform films. Film's uniformity improvement is related to the fact that nanophosphors can be coated more times than bulk phosphors. To take advantage of the luminescent properties of these nanocompounds size particle must be around 3–5 nm [94]. As the local environment is determinant to the optical response of nanophosphors precise size control in the nanocrystal host is a primary goal in synthesis methods. Typical size control techniques are arrested precipitation in chemical precipitation methods, soft chemistry routes with optimized molar ratios in sol-gel, ultrasonic assisted strategy, etc [94]. In 2016 Fukushima et al. presented a strong size control of Y_2O_3 nanophosphors by using homogeneous precipitation method with excessive urea [95].

Nanophosphors for **DC** approach have been implemented into inorganic/organic solar cells such as an SmPO_4 **NPs** doped $\text{TiO}_2/\text{P3HT}$ bulk heterojunction (**BHJ**). These cells showed an efficiency increase of 3% on the undoped cell [96], commercial silicon solar cells through the deposition of Eu^{2+} -doped barium silicate ($\text{Ba}_2\text{SiO}_4:\text{Eu}^{2+}$) [97] and dye-sensitized solar cells [98,99], among others. An alternative use of nanophosphors in solar cells is to help to reduce the excess of energy offset between the conduction band and acceptor

energy levels [100].

Nanocrystal quantum dots promise the same advantages as phosphors for **DC** [101]. Other assets are a narrow emission band and the possibility of tuning the optical absorption and emission by varying its size. By using these properties it is possible in an idoneous case through a combination of quantum dots (**QDs**) right sizes to cover an extensive amount of solar spectrum allowing a solar cell efficiency increase. Common used semiconductor **QDs** in solar cells include: CdS , CdSe , CdTe , CuInS_2 , CuS , PbS , PbSe , InP , InAs , Ag_2S , Bi_2S_3 , Sb_2S_3 [102] and combinations of $\text{CuInS}_2/\text{ZnS}$ core shells [103]. **QDs** were also utilized in multiple exciton generation approaches to increase solar cells efficiency [104]. Characteristic synthesis methods of **QDs** are chemical procedures as the reduction of noble metal ions by ethanol under hydrothermal or atmospheric conditions at temperatures ranging between 20 and 200 °C [105], electrochemical oxidation and pyrolysis or physical synthesis such as laser ablation, microwave irradiation, hot injection [106], and chemical bath deposition [78], etc. Size control in **QDs** is a priority due that is intimately related to its optical behavior. Characterization methods previously discussed are also applied for **QDs**. For instance, spectroscopic techniques are the most commonly employed to know better **QDs** emission properties.

In a carefully prepared giant **QDs** system, light absorption mainly occurs in the shell but emission happens within the core increasing the performance of optical desired effects [107]. Even though this nanomaterial is proposed to be used with white-light devices, it could also be useful for solar cells applications.

Carbon nanostructures materials play a central role in the pursuit of new sustainable energy technologies and are also promising for **DC**. Recently, graphene **QDs** were explored as an option for **DC** in commercial solar cells [108]. Complex nanostructures such as hybrid nanostructures for example colloidal ZnS nanoparticles/ Si -nanotips showed promising potential for efficient solar spectrum utilization in crystalline silicon solar cells [109]. Here ZnS **QDs** serve as **DC** material for **UV** and as antireflection coating as well.

In the last years, perovskites have attracted the scientific attention due to its excellent performance as a base material in solar cells [110,111]. In 2014, Ahmed et al. found spontaneous parametric downconversion phosphorescence in a near and mid-infrared zone for a perovskite bound to lanthanide and others ions $\text{La}_7\text{Sr}_{0.3}\text{M}_{0.1}\text{Fe}_{0.9}\text{O}_3$ [112]. This optical behavior opened the possibility to explore perovskites as a **DC** material. Recent work of Want et al. propose a new kind of **QD** based on inorganic perovskites [113]. These materials exhibited optical features as low-threshold and ultrastable stimulated emission was demonstrated under atmospheric conditions. These features are favorable for implementations in solar cells as downconverters. About standard perovskites used in solar cells, a major inconvenience is their low stability under humidity conditions. However, a promising advance to improve stability in lead halide perovskite solar cells was presented by Jingbi You et al. in 2015 [114]. Through employing an all-solution-processed metal oxide the research group was able to maintain 90% of the perovskite performance after 60 days in air at room temperature [114]. This result raised the possibility of using perovskites in commercial solar cell applications. Solar cells based in perovskites could also benefit from the utilization of a **DC** layer.

A resume of some of the principal synthesis methods used to fabricate downconverters is presented in the Table 1.

There is a wide research work in nanomaterials as a source of **DC** to enhance solar cells efficiency. Here we presented some selected materials showing the most promising. In all the cases size control is the predominant parameter to suit the optical response that better match the considered solar cell design. The challenge in synthesis methods is to provide the best control of the nanomaterial size and geometry. An excellent discussion about nanostructures architectures for solar cells can be found in [130].

Table 1
Common methods used for the fabrication of downconverters materials.

Synthesis Method	Advantages	Disadvantages	Examples of downconverters
Co-precipitation (Permit to obtain materials from a solution by –precipitation then at appropriate temperatures a final powder of the desired substance is obtained)	Simple experimental requirements Permit control of particle size	Poor shape control Low accurate stoichiometric phase	KCaGd(PO ₄) ₂ :Ce ³⁺ ,Yb ³⁺ [68], YF ₃ :Pr ³⁺ , Yb ³⁺ [115], Tb ³⁺ ,Yb ³⁺ codoped Y ₂ O ₃ [84], Hexagonal NaYF ₄ :15%Tb ³⁺ , 10% Yb ³⁺ nanoparticles [116]
Chemical bath deposition (Thin films are obtained by the immersion of substrates in solutions with ions of interest, particularly metal ions).	Simple experimental requirements Control of the films thickness Low cost implementations	Lack of reproducibility with respect to other chemical methods	CdO Nanotips [78], deposition method of quantum dots onto solar cells surfaces [117].
Chemical Vapor deposition (CVD) (By a chemical reaction from the precursors present in the vapor phase the material of interest is generated.)	High purity Relatively high deposition rates,	High temperatures requirement The precursors used must be volatile at near-room temperatures	ZnO:Er ³⁺ /Yb ³⁺ , Tm, Yb co-doped [118], Graphene quantum dots [119].
Combustion synthesis (Materials are synthesized by highly exothermic redox chemical reactions promote at high temperatures)	Yields high purity products Use of relatively simple equipment	Requires high temperatures	GdAl ₃ (BO ₃) ₄ :RE ³⁺ ,Yb ³⁺ (RE=Pr, Tb and Tm) [82], TbAG:Ce ³⁺ ,Yb ³⁺ [120],
Hydrothermal (High temperature-high pressure aqueous solutions, vapors, and/or fluids react with solid material).	Good control of size and shape It is possible to obtain crystallized powders	Difficult to control the process, Problems of reliability and reproducibility.	Eu ³⁺ -doped Y(OH) ₃ nanotubes [121], Eu ³⁺ -Doped NaGdF ₄ Nanocrystal [122]
Laser Deposition (In this method a focused laser beam impinges a target of a material of interest that can be deposited in a substrate)	Simple experimental implementation High purity It is possible to fabricated a wide number of materials	Requires laser equipment which sometimes is expensive Problems of reliability and reproducibility.	Metal-Ion Codoped Y ₃ Al ₅ O ₁₂ [74], Na _{0.5} R _{0.5} MoO ₄ :Ln ³⁺ (R ³⁺ =La, Gd), (Ln ³⁺ =Eu, Tb, Dy, Yb/Er) thin phosphor films [123]. Zn/ZnO core/shell nanoparticles [124]
Sol Gel (This method is based on inorganic polymerization reactions. It includes four steps: hydrolysis, polycondensation, drying, and thermal decomposition.)	Excellent composition control It is possible to obtained ultrafine porous powders. Homogeneity of product, strong promise for employment industrially on a large scale, use of matrix. It uses relatively low temperatures	The cost of the precursors may be expensive Depends strongly on the local environment fluctuations	70SiO ₂ –30HfO ₂ glass ceramic planar waveguides co-activated by Tb ³⁺ /Yb ³⁺ ions [125]
Solid State Method (Materials are fabricated trough mixtures of adequate precursors in an appropriate stoichiometry relation heated at high temperatures)	This method permit to synthesized a large number of compounds	Poor shape control Usually high temperatures are required	Tb ³⁺ ,Yb ³⁺ codoped transparent glass ceramics containing CaF ₂ [85], KCaGd(PO ₄) ₂ :Eu ³⁺ [89]
Sputtering (Form the bombardment of a target by a generated plasma . The atoms from the target then travel through the plasma and form a layer on the substrate.)	Large surface area deposition Good reproducibility	It is possible to promote surface damage in the substrate used. A vacuum chamber is indispensable increasing the cost in this method	Cerium co-doped tantalum (V) oxide (Ta ₂ O ₅ : Eu, Ce) thin films [72], SiN x: Tb ³⁺ -Yb ³⁺ [126],
PECVD (The chemical vapor deposition technique uses a plasma to improve the yield and performance of the synthesis)	Less temperature dependent Good mechanical properties of the film fabricated.	In some cases toxic precursors are needed High cost equipment Plasma could damages the films fabricated	Polymorphous silicon thin films (pm-Si) [75], Silicon-Rich-Nitride Thin Films [127]
Spray Pyrolysis (The traditional multisource CVD process can be converted to a single-source deposition process by spraying a solution onto a surface with an adequate temperature)	simple and low-cost method Suitable for large scale deposition	Size of droplets of initial solution are not the same which can lead to inhomogeneity in the material.	Thulium and ytterbium-doped titanium oxide thin films [128], Yb-doped ZnO thin films [129]

4. Solar cells devices with downconversion approaches

4.1. DC in semiconductor-based solar cells

Semiconductors-based solar cells *have been* demonstrated to be an *excellent option for PV* commercial systems. The most common materials utilized in this type of solar cells includes mono and polycrystalline silicon, amorphous silicon and III–Vs, II–VIs and I–III–VI₂s compounds [131,132]. Theoretical work predicted that is possible to achieve a conversion efficiency of 38.6% in a silicon-based

solar cell by using an ideal **DC** layer. For semiconductor solar cells with absorption peaks in the infrared zone such as silicon or GaAs a **DC** material with **NIR** downconversion is suggested [24]. Usually, in experimental implementations, a thin layer containing the **DC** material is placed on top of the solar cell [133]. In Fig. 3, a representation of this scheme is shown.

Since the pioneering work reported by Trupke and Richards in 2002, different materials such as oxides doped with lanthanide ions [134,135], silicon nanoparticles [136–138] and quantum dots [103,139–141], among others have been explored as **DC** layers for

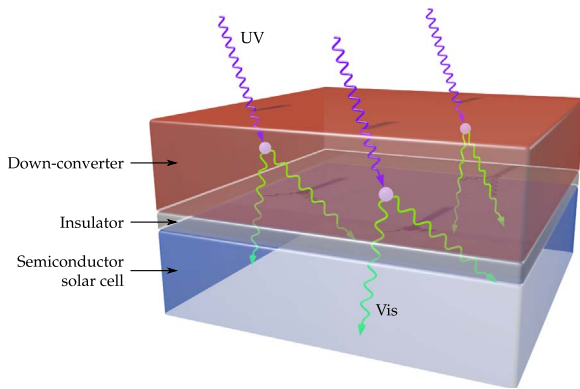


Fig. 3. Representation of a common arrangement of a DC layer in semiconductors based solar cells. The DC layer is placed on the top to optimize the wavelength of the impinging photons into the cell.

semiconductor-based solar cells. In lanthanide ions case, an inconvenient to overcome is the mismatch between the absorption of the ions and the semiconductor bandgap. Such mismatch could affect the solar cell efficiency drastically. As a strategy to solve this, Xiaojie Wu et al. proposed the use of a semiconductor as ZnSe to increase the absorption of the solar resource. In their work a heterostructure composed of $\text{Y}_2\text{O}_3: [(\text{Tb}^{3+}\text{-Yb}^{3+}), \text{Li}^+]$ and ZnSe exhibit NIR emission that approaches the maximal spectral response (~ 1000 nm) of a silicon device showing that the idea is viable [142].

As mentioned before among different semiconductor systems utilized for solar cells, crystalline silicon **c-Si** is the most prevalent. Silicon solar cells have been extensively studied and currently is a mature technology. Due to that **c-Si** based solar cells are natural candidates to test the viability of using DC layers as a possibility to improve their efficiency. Suggested conditions to achieve this improvement are excitation at wavelengths between 350 and 550 nm, emission in a range from 350 and 1100 nm, low excitation intensity, quantum efficiency larger than the unity and low absorption in the regions of the spectrum that will not be down-converted [16,63]. Because silicon-based solar cells are the most prevalent in commercial applications most of the research work, which involves the implementation of a DC layer, is focus in this kind of cells. In 2012, Chin-Lung et al. were able to increase in more than 2% (from 15.2% to 17.2%) the conversion efficiency of a screen-printed monocrystalline silicon solar cells (**SPMSSCs**) by using a layer of Eu^{3+} -doped $\text{Y}(\text{OH})_3$ nanotubes [143]. Another successful example is a commercial silicon solar cell with a $\text{Pr}^{3+}\text{-Yb}^{3+}$ co-doped with **ZBLA** (family of glasses with a composition of $\text{ZrF}_4\text{-BaF}_2\text{-LaF}_3\text{-AlF}_3\text{-NaF}$) as downconverters [144]. Silicon nanoparticles also can help to improve the charge separation inside the polycrystalline solar cell. Recently, Chowdhury et al. deposited silicon nanoparticles (**Si NPs**) of 2.85 nm by spin coating onto a $\text{aSi:H} (\text{n}^+)/\text{a-Si:H} (\text{i})/\text{c-Si} (\text{p})$ HIT solar cell layer stack [138]. They measured a **Jsc** increase from 2.33% to 5.16% due to the presence of **Si NPs**. In 2014, Gardelis and Nassiopoulou reported an increase of up to 37.5% in conversion efficiency of a Si-based solar cell after deposition of light-emitting $\text{CuInS}_2/\text{ZnS}$ core-shell quantum dots on the active area of the cell [103]. They attributed this improvement to the combined effect of downconversion and the anti-reflecting property of the dots.

Previously, we commented the recent use of graphene quantum dots (**GQDs**) as downconverters, in 2016 Meng-Lin Tsai et al. increased the efficiency in an n-type Si heterojunction solar cell obtaining 16.55% [108]. The explanation about high efficiency was achieved for this kind of solar cells is twofold: DC effect and augmentation in the photons absorbed in the depletion region, which allows an effective carrier separation. They report that the short circuit current and the fill factor are increased from 35.31 to 37.47 mA cm^{-2} and 70.29–72.51%, respectively.

Also in 2016 a promising composite material: $\text{Tm}^{3+}/\text{Yb}^{3+}$ codoped

with tellurite glasses showed the conversion of ultraviolet (240–400 nm) and blue (450–490 nm) photons into NIR ones (920–1100 nm) [145]. This optical response matches the optimal spectral response of silicon (Si) solar cells. However, in the pursuit of an adequate downconverter, the stability under high radiation and atmospheric conditions must also take into account. Lanthanide ceramic hosts such as oxyfluoride glass ceramics (**GCs**) attracted attention due to their transparency, mechanical and chemical stability necessary to implement PV commercial systems. Yiping Tai et al. propose an $\text{Er}^{3+}/\text{Yb}^{3+}$ co-doped **GCs** containing DC layers of CaF_2 nanocrystals to be applied in silicon commercial solar cells [146].

GaAs based solar cells exhibit high conversion efficiencies, in fact, they have replaced silicon cells for satellite applications. The main problem with **GaAs** solar cells is the losses due to the reflectivity of their surfaces. A modification of the surface is made to prevent these losses by using nanostructures or surface indentation (roughness creation). Arrays of nanotips and nanopillars are commonly considered for these purposes. Surface modification and an appropriate DC layer also can considerably improve the performance of a **GaAs** cell. As a case of study, we consider the work of Chien-Chung et al. whereby combining a dual-layer of **CdS QDs** on a hybrid **GaAs** solar cell an increase from 28.25% to 29.04%, in the overall power conversion efficiency was obtained. The dual layer was placed on top of the solar cell working as an antireflection layer and DC material [147]. In general, **QDs** are used as downconverters in **GaAs**-based solar cells. Some examples are layers of crystalline silicon nanopillar arrays and **QDs** of **CdS** and **ZnS** nanoparticles/Si nanotips [109] and **QDs** of **CdS** and **CdSe/ZnS** core-shell in colloidal solutions deposited on the top layer of a GaAs cell [148]. For **QD** materials could be considered as an adequate downconverter, two experimental challenges must be taken into account: First, the chosen deposition technique can affect the final efficiency of the cell, and second its low stability in air and at high-temperature conditions. Other semiconductor-based solar cells explored with a lanthanide DC layer are germanium and silicon germanium solar cells [16,62].

As we have discussed, there are different strategies for using a DC layer in a semiconductor-based solar cell. Here we presented the most representatives and in all cases by optimizing the downconverter concentration and deposition an increase in the conversion efficiency was found. However, the real cost of implementation of this kind of solar cells is still unknown mainly due to the lack of research work related to its time evolution in ambient conditions. Other common solar cells are dye-sensitized solar cells in the next subsection principal characteristics of this kind of cells including DC materials are discussed.

4.2. DC in dye-sensitized solar cells

Dye-sensitized solar cells are a good alternative to conventional semiconductor-based solar cells due to its low cost and their relative ease fabrication process. In **DSSCs** two conductive glass electrodes are employed, usually coated with fluorine-doped tin oxide (**FTO**) or indium tin oxide (**ITO**). One electrode is the anode, also called working electrode (**WE**), which is mainly screen printed with TiO_2 or ZnO and sensitized with a dye, which absorbs photons in the visible region. Other electrode is the cathode, or counter electrode (**CE**), which is covered with a thin platinum film (serves as catalysis). Between the two electrodes is the electrolyte, generally an organic solvent with a redox system [149]. Fig. 4 shows the two possible configurations for using DC materials in **DSSCs**. Either the downconverter can be integrated with the acceptor and the dye inside the cell (left) or an additional layer containing the downconverter can be placed in the front of the anode (right). One advantage of using an external layer is that also can prevent degradation of the dye within **DSSCs** due to the UV radiation.

Among the compounds used as sensitizers, Ru-complexes such as N3 and N719 have been widely employed. However, their main

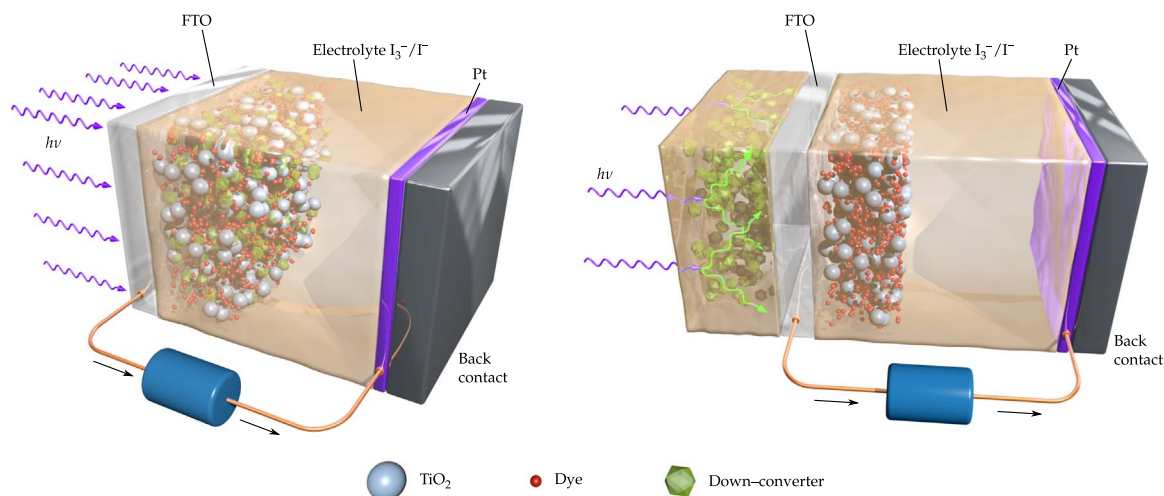


Fig. 4. Use of DC layers in DSSCs. (Right) a DSSC with a downconverter material inside the cell. (Left) another possible configuration is to locate a layer which contains the downconverter on top of the cell. One advantage of using a external layer is that can prevent degradation within DSSCs.

absorption peaks occur in the region between 290 and 700 nm preventing the use of about 50% of the sunlight bandwidth. [122]. Despite this problem, it is possible to improve the efficiency of DSSCs using a DC layer [98,122]. This DC layer has two purposes, on the one hand, it allows using energy in the UV range owing to its conversion to visible light and on the other hand to improve stability on DSSCs because it prevents thermal degradation of the dye or electrolyte caused by UV energy.

Lanthanide ions inside oxide hosts (e., TiO_2) are suitable candidates for DC in DSSCs. TiO_2 presents various advantages as photoanode substrate in DSSCs., it is a stable metal oxide that exhibits a mesoporous surface desirable for dye absorption, and it has good charge transport capability. Moreover, nanostructured TiO_2 such as nanowires [150], nanotubes and nanoparticles aggregates [151] permit to achieve large surface area useful to improve the solar cell performance. Recently, lanthanide ions as Eu^{3+} , Sm^{3+} [49], LiGdF_4 : Eu (LGF) [152], $\text{Ca}_3\text{La}_3(1-x)\text{Eu}_{3x}(\text{BO}_3)_5$ ($\text{CLBO}_{:3x}\text{Eu}^{3+}$) [153] among others on TiO_2 films have been studied as photoanodes. The DSSCs increased their efficiencies in all cases. A successful example is a solar cell with a photoanode of TiO_2 doped with $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}$ proposed by Guang Zhu et al. which presented an efficiency of 7.91% which is higher than an efficiency of 6.97% of a solar cell without the DC layer [154].

Other typical oxides utilized in DSSCs such as SiO_2 , ZnO , SrTiO_3 and Nb_2O_5 doped with phosphors for a DC approach were explored lately [155]. In 2014, Mi Ja Lim et al. [156] studied the possibility of using DC and UC materials (double composite layer) on TiO_2 . The DC material was $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ while the UC material was $\text{Gd}_2\text{O}_3:\text{Er}^{3+}/\text{Yb}^{3+}$. These DSSCs had an efficiency of 8.88%, about 21% higher than the solar cell without the inclusion of the double composite layer (7.36%).

Efficiency amelioration by the addition of a DC layer in DSSCs is promising, however, there are still issues to overcome as UV light absorption increase and outdoor stability improvement for commercial applications. Some strategies to improve performance on DSSCs are the use of nanomaterials as quantum dots or plasmonics systems such as metal nanoparticles to augment the absorption of lanthanide ions species [98,155]. Recently, Nikhil Chander et al. demonstrated that by using a nanophosphor $\text{YVO}_4:\text{Eu}^{3+}$ on a TiO_2 photoanode it is possible to improve the absorption and outdoor stability of a DSSCs [157]. Other kind of solar cells also studied with DC are commented in the next subsection.

4.3. Others solar cells with DC approach

Most scientific research about solar cells with an additional DC

material is related to semiconductor-based solar cells and DSSCs. However, in recent years some third generation solar cells have also been explored in this context.

Hybrid cells consisting typically of an inorganic semiconductor material and an organic conjugated polymer have been proposed as an alternative to traditional solar cells due to its low-cost production. Principal advantages and key issues can be found in Xia Fan et al. work [158]. Recently, a SmPO_4 nanophosphor was utilized as downconverter in a hybrid solar cell of $\text{TiO}_2/\text{P3HT}$ bulk heterojunction [159]. This solar cell exhibits an increase in power conversion efficiency of 3% on the one without the use of the nanophosphor. Here, the inclusion of the SmPO_4 nanophosphor also helps to tailor the energy level alignment of the acceptor TiO_2 .

Another scheme developed to take advantage of DC in photovoltaics is by luminescent solar concentrators (LSCs). Here, a highly transparent glass plate or a transparent polymer sheet with a luminescent species is used. The luminescence of the particle is randomly emitted and is guided to the solar cell trough total internal reflection [6]. LSCs present many advantages such as that heat generated can be well dissipated into the collector plate area. Direct and diffuse light are collected improving the performance of the PV device as well [6,62]. Nonetheless, a drawback of this scheme is that part of the emission is lost at the surfaces. As luminescent species, organic dyes, lanthanides ions as well as some nanoparticles are employed. Examples of conventional dyes used can be found in [160].

An inconvenience in using dyes is their poor stability under solar irradiation as well as their significant re-absorption losses. Theoretical models proposed to maximize the efficiency by optimizing the light output in LSCs, which is a function of various properties including fluorescent dye concentration, collector dimensions, and matrix quality are found in [6,161]. By using this idea van Sark predicted efficiencies of up to 9.1% with an InGaP cell or 14.5% with a Cu (In,Ga)Se₂ cell [162]. The use of luminescent materials also as spectral converters is appealing since many of those present downshifting or downconversion too. Nanophosphors and quantum dots, for example, PbS or CdSe nanoparticles, are also explored as downshifting materials for LSCs. The same type of materials can be utilized to the downconversion effect as long as the synthesis conditions permit obtaining good photoluminescent properties and quantum efficiency larger than unity. Lately, quantum dots were used to enhance the effectiveness of LSCs through downconversion [108,163]. QDs with CdSe cores and ZnS shells have been probed in an LSCs exhibiting less photo-degradation rate [164]. In particular, lead sulfide quantum dots generated nearly the double of the output current than standard quantum dots or organic dyes as rhodamine B in the same kind of LSCs [165].

On the other hand, organic photovoltaic (OPV) solar cells consist of donor and acceptor semiconducting organic materials sandwiched between two electrodes. OPV has several advantages including flexibility, light weight and relatively low cost in large area production. As well as the other solar cells, OPV cells also present the possibility to increase their efficiencies through downconversion. In the last few years, nanophosphors have been used as downconverter materials to improve the performance in OPV. NaYF₄:Yb³⁺ and Er³⁺ nanophosphors into the TiO₂ (cathode) proved to be effective to increase the short circuit current in a PCDTBT:PC₇₁BM heterojunction solar [166]. The PCDTBT:PC₇₁BM or Poly[N-9'-hepta-decanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3' benzothiadiazole):[6,6]-phenyl C₇₁-butyric acid methyl ester, is a common active layer in OPV. A Jsc augmentation from 12.86 to 14.75 mA cm⁻² leads to a high efficiency of 6.83%. In 2015, a bi-functional layer of Eu³⁺-doped ZnO was proposed for downconversion purposes in a P3HT:PC₆₁BM (Poly(3-hexylthiophene) and [6,6]-phenyl C₆₁ butyric acid methyl ester) bulk heterojunction solar cell [167]. The bilayer also served as an electron transporting layer. An increase in the short circuit current density from 8.94 to 9.11 mA cm⁻² was obtained. Due to this result, the authors suggested that this bilayer can be employed in other types of organic solar cells.

In a similar scheme, a solar cell based on PTB7:[70]PCBM (Polythieno[3,4-b]thiophene-benzodithiophene: [6,6]-phenyl C₇₁-butyric acid methyl ester) bulk heterojunction has been benefited with the use of silicon nanocrystals (Si-nc) and harvesting up to 24% photocurrent enhancement under concentrated sunlight [168]. In this hybrid solar cell, the Si-nc is incorporated into a PEDOT:PSS thin film that must be treated to modify hydrophobic characteristics of the surface which can impact the performance and stability of the Si-nc negatively.

To conclude this section in the Table 2, different types of solar cells studied in the context of downconversion are presented.

Here, some solar cells explored with downconversion materials have been presented. Currently, research is focused in study better ways to profit optical properties of downconverters as well as in improving the stability in ambient conditions for commercial applications.

5. Perspectives and challenges

Due to its effectiveness PV is currently an excellent option to provide energy resources minimizing the environmental impact. In 2016, Louwen et al. analyzed the environmental impact of the production of PV systems over time. They have concluded that for every doubling of installed photovoltaic capacity, energy use decreases by 13% and 12% and greenhouse gas footprints by 17% and 24%, for poly and monocrystalline based solar cells, respectively [176]. The extensively research to improve the efficiency of different solar cells could raise these values. Regarding the use of downconverters in solar cells to boost the efficiency in PV some factors must be taken into account for commercial implementations such as the availability of downconverters, the deposition methods that allow covering a large surface area as well as the stability in ambient conditions.

Lanthanides are the most common materials used as downconverters. To exhibit a good performance in the majority of the cases a sensitizer which allows the adequate absorption of UV-Vis part of the solar spectra is a need. If the required amount of sensitizer is high a quenching of the emission can occur affecting the overall efficiency of a solar cell. Due to that to have more competitive solar cells research work oriented to improve and optimize sensitizers is necessary.

Lanthanides present an unequal disposition for extraction that represents a vulnerability for large scale fabrication. The world mining of these elements is dominated by China, India, United States, Russia, Australia, Commonwealth of Independent States, Brazil, Canada, and the Republic of South Africa [177]. For large scale production commercial routes that ensure its disposition are required.

Table 2
Solar cells which present an increase in its efficiencies by the use of downconverter materials.

Type of Solar cell	Downconverter used	Excitation (nm)	Emission (nm)	Increase of the efficiency η (%)
c-Si [169]	Cds (QDs)	365	330–550	A 33% with respect to the cell without the Cds (QDs)
c-Si [170]	Poly(lauryl methacrylate) (PLMA) thin film doped with Mn: ZnSe quantum dots (QDs)	300–450	550–750	5.96%, about 1.04% was due to the PL conversion. The rest is related with antireflective properties.
Mono-Si [78]	CGO nanotips (NTs)	512	695	14%
Commercial Silicon and Gallium Phosphide (GaP) [171]	Tellurite glasses doped with Tb ³⁺ and Yb ³⁺	355 and 482	500 to 700	7% with respect to a Silicon commercial cell with undoped glass.
DSSCs [98]	ZnO:Eu ³⁺ , Tb ³⁺ /TiO ₂ /ZnO:Er ³⁺ , Yb ³⁺ composite thin films	316, 396	491, 549, 581 and 611.	GaP solar cell, efficiency enhancement of 1.1% with respect the GaP solar cell. From 3.01 to 5.13
DSSCs [172]	ZnO:Er ³⁺ , Dy ³⁺	338 and 394	The material also present UC 394, 458, 483, 575, 593 and 611,	
DSSCs [173]	SrAl ₂ O ₄ :Eu ²⁺ , Dy ³⁺	250 to 400	450–600	The efficiency achieved is about 4.48%, that means 212% and 245% higher than with pure TiO ₂ and about 91.4% and 105% higher than with TiO ₂ /graphene (G) structure, respectively
Hybrid organic/ inorganic solar cell [168]	Si-ncs/PEDOT:PSS	> below ~450	above ~680	13% 6.69 to 7.80 (2 suns)
Hybrid solar cell [174]	graphene quantum dots (GQDs)	373	451	62.85 to 63.87
Organic solar cell [175]	A UV-curing epoxy glue, containing an anthracene derivative used as luminescent layer	300–400	500–700	1.57 to 1.79

Even though this inconveniences the good results of efficiency in the studies at laboratory scale with commercial solar cells made lanthanides attractive options for future commercial applications [16,63].

As mentioned before nanomaterials have attracted the attention of many research efforts in **PV** in the late years. A benefit of nanomaterials is that can help to reduce considerably the material usage that could decrease the final cost. Promising nanomaterials used for **DC** such as quantum dots can be solution-processed which facilitates the production at big scale [178]. Even though the use of nanomaterials is very promising there are serious challenges to be addressed as the control of the interplay between the environment and the solar cell, the complexity of *obtaining* uniformity in deposition at large scales and that large surface areas in nanostructures increase charge-carrier recombination, among others [179].

Besides the characteristics and performance of materials, to implement downconversion in commercial **PV** the methods and procedures related to the fabrication must assure a competitive price, low variability of critical process and process-induced defects, long-term reliability and sustainable manufacturing [180]. The necessity of adding an additional material or layer implies an increase in the total cost that depends on the kind of material as well as the deposition method. Then there is a compromise among the perks of growing efficiency and the extra cost of production. Future efforts must be devoted to making solar cells with **DC** competitive in price and reliable in long term ambient conditions. To evaluate best candidates a benchmark of solar cell efficiency measurements are necessary.

6. Conclusions

Many challenges remain to solve in photovoltaic systems before solar energy can be considered as a primary source of energy worldwide. In the pursuit of **PV** systems performance improvement, different approaches have been taken into consideration such as an intermediate-band, multijunction cells, the use of concentration of sunlight, multiple exciton generation, hot-carriers and spectral modification thought downconversion or/and upconversion. Among different options, downconversion is an appealing way to harvest the efficiency in solar cells because it permits to optimize the solar spectrum usage.

As a rule of thumb, an electrical isolated thin layer that contains the material responsible of **DC** is placed on top of the solar cell however in few cases can be located on the rear surface in a bifacial solar cell. The top thin layer can be of different chemical nature. In general, **DC** can be achieved by using host lattice states or ions to obtain quantum efficiencies larger than unity. For instance, schemes using single or, double ions are possible. In the latter case, the excited ion can relax from the higher energy state into the lower energy state by transferring its energy to the second ion. After the energy transfer, both ions can emit a photon to reach the ground state. Lanthanide ions are largely used for **DC**. From the theoretical point of view many attempts to explain different **DC** physical process have been realized since the forties till recently. These models range classical physics to quantum electrodynamics. Moreover, models describing the impact of **DC** in solar cells have already been worked out. The models take into account different mechanisms that are important to explain efficiency enhancements. Mechanisms such as the cooperative energy transfer which has been included in some models through the use of Monte Carlo methods. Some of these models consider the interaction of the energy donor ion with its nearest neighbors, providing a more realistic analysis. Moreover in some models when an analogous photosynthetic reaction mechanism is included the theoretical net photo-generated current in a **PV** increases by 35%. There are several research works about thermodynamic, optical and electronic properties of **DC** materials and solar cells arrays with **DC** layers. An adequate analysis of all the available information through 'high-throughput' (**HT**) method that

uses an intelligent data mining scheme is suggested to find optimal conditions for practical implementations.

Besides the lanthanides embedded in different hosts such as oxides, emerging materials at nanoscale provide new options with several advantages: quantum dots, nanophosphors, graphene quantum dots, silicon nanoparticles among others have proved its effectiveness by improving the final efficiency in different solar cells. *Synthesis methods of the various materials discussed above* can be broadly divided into two groups: *physical and chemical methods*. *The selection of the appropriate material and the more convenient synthesis method depend on the optical match between the solar cell bandgap and the optical spectral response of the downconverter*. Stability criteria must also be taken into account.

Recently, a vast number of research articles have been devoted to nanomaterials due to the ease of tailoring its optical response by changing their geometries and sizes. Promising materials are giant nanophosphors, graphene quantum dots, and nanosized perovskites. A drawback to overcome is achieving optimal deposition of these nanomaterials on solar cells; in some cases, a homogeneous deposition is fundamental as in the case of quantum dots to prevent self-assembly. Semiconductor-based solar cells in particular silicon-based solar cells have been the most normal cells used to study the **DC** approach. Dyes sensitized and hybrid solar cells, as well as luminescent solar concentrators (**LSCs**), have been explored showing that in these types of solar cells the use of downconverters is an excellent option to increase the final solar cell efficiency.

The **PV** systems should maintain their initial efficiency over a lifetime of at least 20 years and it must, therefore, not be only mechanically stable, but also resistant to degradation caused by exposure to the environment. Few works are dedicated to this subject. To succeed in the implementation of **DC** optimized solar cells in commercial systems more work must be addressed to improve their stability and robustness in ambient conditions.

Acknowledgements

M.B. de la Mora wants to thank the financial support through the project PAPIIT IG10045. O. Amelines-Sarria acknowledges financial support from SEP-PRODEP project UNICACH-PTC-078. Eduardo Lugo would like to thank the Magnetophotonic materials SEP-PRODEP grant. Carlos Hernández thank the fellowship of CONACyT postdoctoral grant. Authors want to thank Victor Duarte Alaniz from Department of Physical Chemistry from Institute of Chemistry UNAM for the artwork and graphics presented in this review. Authors want to thank Jesús Capistrán for useful discussions about solar cells efficiency. The authors want to dedicate this work to the memory of Professor B. M. Monroy.

References

- [1] F. Dincer, The analysis on photovoltaic electricity generation status, potential and policies of the leading countries in solar energy, *Renew. Sustain. Energy Rev.* 15 (2011) 713–720.
- [2] G. Masson, A snapshot of global PV (1992–2014), in: M. Brunisholz (Ed.) IEA-PVS Reporting Countries, EPIA, Becquerel Institute (BE), RTS Corporation (JP), 2014, pp. 1–16.
- [3] S.v.A., Global Solar PV Capacity to Reach Nearly 500 GW in 2019, IHS Says, in: IHS Technology, 2015.
- [4] R. Liu, Steady growth for the world operator terminal market from 2016 to 2019 after a slowdown in 2015, in: IHS Technology, 2016.
- [5] W. Shockley, H.J. Queisser, Detailed balance limit of efficiency of p-n junction solar cells, *J. Appl. Phys.* 32 (1961) 510–519.
- [6] J.-C.G. Bünzli, A.-S. Chauvin, Chapter 261 – lanthanides in solar energy conversion, in: G.B. Jean-Claude, K.P. Vitalij (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Elsevier, 2014, pp. 169–281.
- [7] N.J. Ekins-Daukes, Routes to High Efficiency Photovoltaic Power Conversion, in: *IEEE*, 2013, pp. 13–16.
- [8] Q.Y. Zhang, X.Y. Huang, Recent progress in quantum cutting phosphors, *Prog. Mater. Sci.* 55 (2010) 353–427.
- [9] J. Zhou, Q. Liu, W. Feng, Y. Sun, F. Li, Upconversion luminescent materials:

- advances and applications, *Chem. Rev.* 115 (2015) 395–465.
- [10] D.L. Dexter, Possibility of luminescent quantum yields greater than unity, *Phys. Rev.* 108 (1957) 630–633.
- [11] R.H. Bartram, A. Lempicki, Luminescence and optical spectroscopy of condensed matter electron multiplication in scintillators and phosphors, *J. Lumin.* 72 (1997) 734–736.
- [12] D. Timmerman, I. Izeddin, P. Stallinga, I.N. Yassievich, T. Gregorkiewicz, Space-separated quantum cutting with silicon nanocrystals for photovoltaic applications, *Nat. Photon* 2 (2008) 105–109.
- [13] C. Ronda, Luminescent materials with quantum efficiency larger than 1, status and prospects, *J. Lumin.* 100 (2002) 301–305.
- [14] B.S. Richards, Luminescent layers for enhanced silicon solar cell performance: down-conversion, *Sol. Energy Mater. Sol. Cells* 90 (2006) 1189–1207.
- [15] B.S. Richards, Enhancing the performance of silicon solar cells via the application of passive luminescence conversion layers, *Sol. Energy Mater. Sol. Cells* 90 (2006) 2329–2337.
- [16] X. Huang, S. Han, W. Huang, X. Liu, Enhancing solar cell efficiency: the search for luminescent materials as spectral converters, *Chem. Soc. Rev.* 42 (2013) 173–201.
- [17] T. Förster, *Zwischenmolekulare Energiewanderung und Fluoreszenz (Intermolecular energy migration and fluorescence)*, *Annalen der Physik (in German)*, 437, 1948, pp. 55–75.
- [18] D.L. Dexter, A theory of sensitized luminescence in solids, *J. Chem. Phys.* 21 (1953) 836–850.
- [19] H. Kuhn, Classical aspects of energy transfer in molecular systems, *J. Chem. Phys.* 53 (1970) 101–108.
- [20] D.L. Andrews, A unified theory of radiative and radiationless molecular energy transfer, *Chem. Phys.* 135 (1989) 195–201.
- [21] J.S. Avery, Resonance energy transfer and spontaneous photon emission, *Proc. Phys. Soc.* 88 (1966) 1.
- [22] L. Gomberoff, E.A. Power, The resonance transfer of excitation, *Proc. Phys. Soc.* 88 (1966) 281.
- [23] D.L. Andrews, R.D. Jenkins, A quantum electrodynamic theory of three-center energy transfer for upconversion and downconversion in rare earth doped materials, *J. Chem. Phys.* 114 (2001) 1089–1100.
- [24] T. Trupke, M.A. Green, P. Würfel, Improving solar cell efficiencies by down-conversion of high-energy photons, *J. Appl. Phys.* 92 (2002).
- [25] V. Badescu, A. De Vos, Influence of some design parameters on the efficiency of solar cells with down-conversion and down shifting of high-energy photons, *J. Appl. Phys.* 102 (2007) 073102.
- [26] B. Viorrel, V. Alexis De, B. Alina Mihaela, S. Aleksandra, Improved model for solar cells with down-conversion and down-shifting of high-energy photons, *J. Phys. D: Appl. Phys.* 40 (2007) 341.
- [27] F.T. Rabouw, A. Meijerink, Modeling the cooperative energy transfer dynamics of quantum cutting for solar cells, *J. Phys. Chem. C* 119 (2015) 2364–2370.
- [28] F.T. Rabouw, S.A. den Hartog, T. Senden, A. Meijerink, Photonic effects on the Förster resonance energy transfer efficiency, *Nat. Commun.* 5 (2014).
- [29] D. Serrano, Quantum Cutting Processes in Rare-Earth Doped Fluorides for Photovoltaic applications, Université de Caen Basse-Normandie, 2012.
- [30] J.-M. Meijer, L. Aarts, B.M. van der Ende, T.J.H. Vlught, A. Meijerink, Downconversion for solar cells in YF₃:Nd³⁺, Yb³⁺, *Phys. Rev. B* 81 (2010) 035107.
- [31] Q. Duan, F. Qin, Z. Zhang, W. Cao, Quantum cutting mechanism in NaYF₄:Tb³⁺, Yb³⁺, *Opt. Lett.* 37 (2012) 521–523.
- [32] L. Zhou, P.A. Tanner, L. Ning, W. Zhou, H. Liang, L. Zheng, Spectral properties and energy transfer between Ce³⁺ and Yb³⁺ in the Ca₃Sc₂Si₃O₁₂ host: is it an electron transfer mechanism?, *J. Phys. Chem. A* (2016).
- [33] D.C. Yu, F.T. Rabouw, W.Q. Boon, T. Kieboom, S. Ye, Q.Y. Zhang, A. Meijerink, Insights into the energy transfer mechanism in Ce³⁺–Yb³⁺ codoped YAG phosphors, *Phys. Rev. B* 90 (2014) 165126.
- [34] M. Inokuti, F. Hirayama, Influence of energy transfer by the exchange mechanism on donor luminescence, *J. Chem. Phys.* 43 (1965) 1978–1989.
- [35] M. Yokota, O. Tanimoto, Effects of diffusion on energy transfer by resonance, *J. Phys. Soc. Jpn.* 22 (1967) 779–784.
- [36] L. Yang, M. Yamashita, T. Akai, Green and red high-silica luminous glass suitable for near- ultraviolet excitation, *Opt. Express* 17 (2009) 6688–6695.
- [37] P. Solarz, W. Ryba-Romanowski, Energy transfer processes in K₅Li₂GdF₁₀:Eu,Pr, *Radiat. Meas.* 42 (2007) 759–762.
- [38] P. Villanueva-Delgado, K.W. Krämer, R. Valiente, Simulating energy transfer and upconversion in β-NaYF₄: Yb³⁺, Tm³⁺, *J. Phys. Chem. C* 119 (2015) 23648–23657.
- [39] P. Ramasamy, P. Manivasakan, J. Kim, Upconversion nanophosphors for solar cell applications, *RSC Adv.* 4 (2014) 34873–34895.
- [40] G. Chen, C. Yang, P.N. Prasad, Nanophotonics and nanochemistry: controlling the excitation dynamics for frequency up- and down-conversion in lanthanide-doped nanoparticles, *Acc. Chem. Res.* 46 (2013) 1474–1486.
- [41] X. Zhang, Z. Zhao, X. Zhang, D.B. Cordes, B. Weeks, B. Qiu, K. Madanan, D. Sardar, J. Chaudhuri, Magnetic and optical properties of NaGdF₄:Nd³⁺, Yb³⁺, Tm³⁺ nanocrystals with upconversion/downconversion luminescence from visible to the near-infrared second window, *Nano Res.* 8 (2015) 636–648.
- [42] P.P. Pal, J. Manam, Structural and photoluminescence studies of Eu³⁺ doped zinc oxide nanorods prepared by precipitation method, *J. Rare Earths* 31 (2013) 37–43.
- [43] B.R. Judd, Optical absorption intensities of rare-earth ions, *Phys. Rev.* 127 (1962) 750–761.
- [44] G.S. Ofelt, Intensities of crystal spectra of rare-earth ions, *J. Chem. Phys.* 37 (1962) 511–520.
- [45] M. Saraf, P. Kumar, G. Kedawat, J. Dwivedi, S.A. Vithayathil, N. Jaiswal, B.A. Kaiparettu, B.K. Gupta, Probing highly luminescent europium-doped lanthanum orthophosphate nanorods for strategic applications, *Inorg. Chem.* 54 (2015) 2616–2625.
- [46] W. Luo, J. Liao, R. Li, X. Chen, Determination of Judd-Ofelt intensity parameters from the excitation spectra for rare-earth doped luminescent materials, *Phys. Chem. Chem. Phys.* 12 (2010) 3276–3282.
- [47] Z.R. Abrams, A. Niv, X. Zhang, Solar energy enhancement using down-converting particles: a rigorous approach, *J. Appl. Phys.* 109 (2011).
- [48] W. Ruppel, P. Würfel, Upper limit for the conversion of solar energy, *IEEE Trans. Electron Devices* 27 (1980) 877–882.
- [49] H. Hafez, M. Saif, M.S.A. Abdel-Mottaleb, Down-converting lanthanide doped TiO₂ photoelectrodes for efficiency enhancement of dye-sensitized solar cells, *J. Power Sources* 196 (2011) 5792–5796.
- [50] O.M. ten Kate, M. de Jong, H.T. Hintzen, E. van der Kolk, Efficiency enhancement calculations of state-of-the-art solar cells by luminescent layers with spectral shifting, quantum cutting, and quantum tripling function, *J. Appl. Phys.* 114 (2013) 084502.
- [51] F.H. Alharbi, S. Kais, Theoretical limits of photovoltaics efficiency and possible improvements by intuitive approaches learned from photosynthesis and quantum coherence, *Renew. Sustain. Energy Rev.* 43 (2015) 1073–1089.
- [52] S. Curtarolo, G.L.W. Hart, M.B. Nardelli, N. Mingo, S. Sanvito, O. Levy, The high-throughput highway to computational materials design, *Nat. Mater.* 12 (2013) 191–201.
- [53] H. Ahmed, S.J. McCormack, J. Doran, External quantum efficiency improvement with luminescent downshifting layers: experimental and modelling, *Int. J. Spectrosc.* 2016 (2016) 7.
- [54] H.J. Hovel, R.T. Hodgson, J.M. Woodall, The effect of fluorescent wavelength shifting on solar cell spectral response, *Sol. Energy Mater.* 2 (1979) 19–29.
- [55] U. Mehmood, S.-u. Rahman, K. Harrabi, I.A. Hussein, B.V.S. Reddy, Recent advances in dye sensitized solar cells, *Adv. Mater. Sci. Eng.* 2014 (2014) 12.
- [56] D. Alonso-Álvarez, D. Ross, E. Klampaftis, K.R. McIntosh, S. Jia, P. Storiz, T. Stolz, B.S. Richards, Luminescent down-shifting experiment and modelling with multiple photovoltaic technologies, *Prog. Photovolt.: Res. Appl.* 23 (2015) 479–497.
- [57] D. Alonso-Álvarez, D. Ross, B.S. Richards, Luminescent down-shifting for CdTe solar cells: a review of dyes and simulation of performance, in: *Proceedings of the 38th IEEE Photovoltaic Specialists Conference (PVSC)*, IEEE, 2012, pp. 000009–000014.
- [58] B.M. van der Ende, L. Aarts, A. Meijerink, Lanthanide ions as spectral converters for solar cells, *Phys. Chem. Chem. Phys.* 11 (2009) 11081–11095.
- [59] S. Kalytchuk, S. Gupta, O. Zhovtiuk, A. Vaneski, S.V. Kershaw, H. Fu, Z. Fan, E.C.H. Kwok, C.-F. Wang, W.Y. Teoh, A.L. Rogach, Semiconductor nanocrystals as luminescent down-shifting layers to enhance the efficiency of thin-film CdTe/Cds and crystalline Si solar cells, *J. Phys. Chem. C* 118 (2014) 16393–16400.
- [60] G. Griffini, F. Bella, F. Nisic, C. Dragonetti, D. Roberto, M. Levi, R. Bongiovanni, S. Turri, Multifunctional luminescent down-shifting fluoropolymer coatings: a straightforward strategy to improve the uv-light harvesting ability and long-term outdoor stability of organic dye-sensitized solar cells, *Adv. Energy Mater.* 5 (2015) (n/a-n/a).
- [61] L. Tsakalagos, Nanostructures for photovoltaics, *Mater. Sci. Eng.: R: Rep.* 62 (2008) 175–189.
- [62] X. Chen, S. Li, G.J. Salamo, Y. Li, L. He, G. Yang, Y. Gao, Q. Liu, Sensitized intense near-infrared downconversion quantum cutting three-photon luminescence phenomena of the Tm³⁺ ion activator in Tm₃+Bi₃+YNbO₄ powder phosphor, *Opt. Express* 23 (2015) A51–A61.
- [63] C. Strumpel, C. McCann, G. Beaucarne, V. Arkhipov, A. Slaoui, V. Svrcek, C. del Canizo, I. Tobias, Modifying the solar spectrum to enhance silicon solar cell efficiency – an overview of available materials, *Sol. Energy Mater. Sol. Cells* 91 (2007).
- [64] L.A. Sloan, D.J. Procter, Lanthanide reagents in solid phase synthesis, *Chem. Soc. Rev.* 35 (2006) 1221–1229.
- [65] C. Li, J. Yang, P. Yang, H. Lian, J. Lin, Hydrothermal synthesis of lanthanide fluorides LnF₃ (Ln=La to Lu) nano-/microcrystals with multiform structures and morphologies, *Chem. Mater.* 20 (2008) 4317–4326.
- [66] J. Oliva, O. Meza, L.A. Diaz-Torres, P. Salas, E. De la Rosa, A. Martinez, C. Angeles-Chavez, Effect of solvent on the up- and downconversion emissions of Y₂O₃:Yb³⁺–Er³⁺ nanofibers synthesized by a hydrothermal method, *J. Opt. Soc. Am. B* 28 (2011) 649–657.
- [67] M. Yu, J. Lin, Z. Wang, J. Fu, S. Wang, H.J. Zhang, Y.C. Han, Fabrication, patterning, and optical properties of nanocrystalline YVO₄:A (A=Eu³⁺, Dy³⁺, Sm³⁺, Er³⁺) phosphor films via sol–gel soft lithography, *Chem. Mater.* 14 (2002) 2224–2231.
- [68] L. Zhao, L. Han, Y. Wang, Efficient near-infrared down-conversion in KCaGd(PO₄)₂:Ce³⁺,Yb³⁺, *Opt. Mater. Express* 4 (2014) 1456–1464.
- [69] A. Kozłowska, M. Nakielska, D. Podnieśiński, H. Węglarz, A. Wajler, Z. Librant, T. Łukasiewicz, A. Małg, Comparison of spectroscopic properties of neodymium-doped aluminium garnet (Nd:YAG) ceramics obtained by reactive sintering of Al₂O₃, Y₂O₃ and Nd₂O₃ and by synthesis of nanocrystalline Nd:YAG powders, in, 2011pp. 79341B-79341B-79346.
- [70] C.D. Hernández-Pérez, M. García-Hipólito, M.A. Álvarez-Pérez, O. Álvarez-Fregoso, F. Ramos-Brito, C. Falcony, Luminescent characteristics of praseodymium-doped zinc aluminate powders, *Phys. Status Solidi (a)* 207 (2010) 417–422.
- [71] K. Binnemans, Lanthanide-based luminescent hybrid materials, *Chem. Rev.* 109 (2009) 4283–4374.
- [72] K. Miura, T. Suzuki, O. Hanaizumi, Photoluminescence properties of europium

- and cerium co-doped tantalum-oxide thin films prepared using co-sputtering method, *J. Mater. Sci. Chem. Eng.* 3 (2015) 30–34.
- [73] V.S. Aart Schoonderbeek, Oliver Haupt, Uwe Stute, Laser processing of thin films for photovoltaic applications, *LMN-J. Laser Micro/Nanoeng.* 5 (2010) 248–255.
- [74] M.K. Lau, J. Hao, Broadband near-infrared quantum cutting in metal-ion codoped Y3Al5O12 thin films grown by pulsed-laser deposition for solar cell application, *J. Nanomater.* 2013 (2013) 6.
- [75] A. Remolina, B.M. Monroy, M.F. García-Sánchez, A. Ponce, M. Bizarro, J.C. Alonso, A. Ortiz, G. Santana, Polymorphous silicon thin films obtained by plasma-enhanced chemical vapor deposition using dichlorosilane as silicon precursor, *Nanotechnology* 20 (2009) 245604.
- [76] L.V. Mercaldo, P.D. Veneri, E. Esposito, E. Massera, I. Usatii, C. Privato, PECVD in-situ growth of silicon quantum dots in silicon nitride from silane and nitrogen, *Mater. Sci. Eng.: B* 159–160 (2009) 77–79.
- [77] J. Intrater, A review of synthesis and application of lanthanide-doped materials, *Ceramic Transactions*, vol. 67, Edited by B. Potter and A. Bruce To obtain contact: American Ceramic Society 735 Ceramic Place Westerville, OH 43081, Materials and Manufacturing Processes, 13, 1998, pp. 324–324.
- [78] W. Feng, J. Liu, X. Yu, Efficiency enhancement of mono-Si solar cell with CdO nanopip antireflection and down-conversion layer, *RSC Adv.* 4 (2014) 51683–51687.
- [79] E. Klampaftis, D. Ross, K.R. McIntosh, B.S. Richards, Enhancing the performance of solar cells via luminescent down-shifting of the incident spectrum: a review, *Sol. Energy Mater. Sol. Cells* 93 (2009) 1182–1194.
- [80] J.-C.G. Bünzli, S.V. Eliseeva, Basics of lanthanide photophysics, in: P. Hänninen, H. Härmä (Eds.), *Lanthanide Luminescence: Photophysical, Analytical and Biological Aspects*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2011, pp. 1–45.
- [81] A.B. George Sarau, R. Lewandowska, S. Christiansen, From Micro- to Macro-Raman Spectroscopy: Solar Silicon for a Case Study, *Advanced Aspects of Spectroscopy*, In Tech, 2012.
- [82] Q.Y. Zhang, G.F. Yang, Z.H. Jiang, Cooperative downconversion in GdAl3(BO3)4:RE3+,Yb3+ (RE=Pr, Tb, and Tm), *Appl. Phys. Lett.* 91 (2007) 951903.
- [83] Z. Li, Y. Zeng, H. Qian, R. Long, Y. Xiong, Facile synthesis of GdBO3 spindle assemblies and microdisks as versatile host matrices for lanthanide doping, *CrystrEngComm* 14 (2012) 3959–3964.
- [84] Y. Jun-Lin, Z. Xiao-Yan, Z. Jing-Tai, Z. Zhi-Jun, C. Hao-Hong, Y. Xin-Xin, Energy transfer mechanisms in Tb3+, Yb3+ codoped Y2O3 downconversion phosphor, *J. Phys. D: Appl. Phys.* 41 (2008) 105406.
- [85] S. Ye, B. Zhu, J. Chen, J. Luo, J.R. Qiu, Infrared quantum cutting in Tb3+,Yb3+ codoped transparent glass ceramics containing CaF2 nanocrystals, *Appl. Phys. Lett.* 92 (2008) 141112.
- [86] L. van Pietersom, M.F. Reid, A. Meijerink, Reappearance of fine structure as a probe of lifetime broadening mechanisms in the 4f N → 4f N-15d excitation spectra of Tb3+, Er3+, and Tm3+ in CaF2 and LiYF4, *Phys. Rev. Lett.* 88 (2003) (067405-067401-067405-067404).
- [87] X. Liu, S. Ye, Y. Qiao, G. Dong, B. Zhu, D. Chen, G. Lakshminarayana, J. Qiu, Cooperative downconversion and near-infrared luminescence of Tb3+-Yb3+ codoped lanthanum borogermanate glasses, *Appl. Phys. B* 96 (2009) 51–55.
- [88] R.T. Wegh, H. Donker, K.D. Oskam, A. Meijerink, Visible quantum cutting in LiGdF4:Eu3+ through downconversion, *Science* 283 (1999) 663–666.
- [89] C. Yen-Chi, H. Woan-Yu, C. Teng-Ming, Enhancing the performance of photovoltaic cells by using down-converting KCaGd(PO4)2:Eu3+ phosphors, *J. Rare Earths* 29 (2011) 907–910.
- [90] Y. Xu, X. Zhang, S. Dai, B. Fan, H. Ma, J.-I. Adam, J. Ren, G. Chen, Efficient near-infrared down-conversion in Pr3+-Yb3+ codoped glasses and glass ceramics containing LaF3 nanocrystals, *J. Phys. Chem. C* 115 (2011) 13056–13062.
- [91] T. Fix, H. Rinnert, M.G. Blamire, A. Slaoui, J.L. MacManus-Driscoll, Nd:SrTiO3 thin films as photon downshifting layers for photovoltaics, *Sol. Energy Mater. Sol. Cells* 102 (2012) 71–74.
- [92] R.T. Wegh, H. Donker, E.V.D. van Loef, K.D. Oskam, A. Meijerink, Quantum cutting through downconversion in rare-earth compounds, *J. Lumin.* 87–89 (2000) 1017–1019.
- [93] C. Caron, D. Boudreau, A.M. Ritchey, Luminescent properties of europium-doped (H3O)Y3F10[middle dot]xH2O nanocrystals, *J. Mater. Chem. C* 3 (2015) 9955–9963.
- [94] H. Chandler, Development of nanophosphors—a review, *Mater. Sci. Eng.: R: Rep.* 49 (2005) 113–155.
- [95] S. Fukushima, T. Furukawa, H. Nioka, M. Ichimiya, T. Sannomiya, J. Miyake, M. Ashida, T. Araki, M. Hashimoto, Synthesis of Y2O3 nanophosphors by homogeneous precipitation method using excessive urea for cathodoluminescence and upconversion luminescence bioimaging, *Opt. Mater. Express* 6 (2016) 831–843.
- [96] Q.H. Li, Y.B. Yuan, T.H. Wei, Y. Li, Z.H. Chen, X. Jin, Y.C. Qin, W.F. Sun, The origin of efficiency enhancement of inorganic/organic hybrid solar cells by robust samarium phosphate nanophosphors, *Sol. Energy Mater. Sol. Cells* 130 (2014) 426–434.
- [97] J.Y. Chen, C.K. Huang, W.B. Hung, K.W. Sun, T.M. Chen, Efficiency improvement of Si solar cells using metal-enhanced nanophosphor fluorescence, *Sol. Energy Mater. Sol. Cells* 120 (Part A) (2014) 168–174.
- [98] N. Yao, J. Huang, K. Fu, X. Deng, M. Ding, M. Shao, X. Xu, Enhanced light harvesting of dye-sensitized solar cells with up/down conversion materials, *Electrochim. Acta* 154 (2015) 273–277.
- [99] M. Ye, X. Wen, M. Wang, J. Iocozzia, N. Zhang, C. Lin, Z. Lin, Recent advances in dye-sensitized solar cells: from photoanodes, sensitizers and electrolytes to counter electrodes, *Mater. Today* 18 (2015) 155–162.
- [100] X. Jin, Q. Li, Y. Li, Z. Chen, T.-H. Wei, X. He, W. Sun, Energy level control: toward an efficient hot electron transport, *Sci. Rep.* 4 (2014) 5983.
- [101] J. Kundu, Y. Ghosh, A.M. Dennis, H. Htoon, J.A. Hollingsworth, Giant nanocrystal quantum dots: stable down-conversion phosphors that exploit a large Stokes shift and efficient shell-to-core energy relaxation, *Nano Lett.* 12 (2012) 3031–3037.
- [102] L. Etgar, Semiconductor nanocrystals as light harvesters in solar cells, *Materials* 6 (2013) 445.
- [103] S. Gardelis, A.G. Nassiopoulou, Evidence of significant down-conversion in a Si-based solar cell using CuInS2/ZnS core shell quantum dots, *Appl. Phys. Lett.* 104 (2014) 183902.
- [104] G. Conibeer, Applications of Si nanocrystals in photovoltaic solar cells, *Silicon Nanocrystals: fundamentals, synthesis and applications*, pp. 555–582.
- [105] X. Wang, J. Zhuang, Q. Peng, Y. Li, A general strategy for nanocrystal synthesis, *Nature* 437 (2005) 121–124.
- [106] J. Duan, H. Zhang, Q. Tang, B. He, L. Yu, Recent advances in critical materials for quantum dot-sensitized solar cells: a review, *J. Mater. Chem. A* 3 (2015) 17497–17510.
- [107] B.N. Pal, Y. Ghosh, S. Brovelli, R. Laocharoensuk, V.I. Klimov, J.A. Hollingsworth, H. Htoon, ‘Giant’ CdSe/CdS core/shell nanocrystal quantum dots as efficient electroluminescent materials: strong influence of shell thickness on light-emitting diode performance, *Nano Lett.* 12 (2012) 331–336.
- [108] M.-L. Tsai, W.-C. Tu, L. Tang, T.-C. Wei, W.-R. Wei, S.P. Lau, L.-J. Chen, J.-H. He, Efficiency enhancement of silicon heterojunction solar cells via photon management using graphene quantum dot as downconverters, *Nano Lett.* 16 (2016) 309–313.
- [109] C.-Y. Huang, D.-Y. Wang, C.-H. Wang, Y.-T. Chen, Y.-T. Wang, Y.-T. Jiang, Y.-J. Yang, C.-C. Chen, Y.-F. Chen, Efficient light harvesting by photon down-conversion and light trapping in hybrid ZnS nanoparticles/Si nanopip solar cells, *ACS Nano* 4 (2010) 5849–5854.
- [110] J. Fan, B. Jia, M. Gu, Perovskite-based low-cost and high-efficiency hybrid halide solar cells, *Photonics Res.* 2 (2014) 111–120.
- [111] M. Yang, Y. Zhou, Y. Zeng, C.-S. Jiang, N.P. Padture, K. Zhu, Square-centimeter solution-processed planar CH3NH3PbI3 perovskite solar cells with efficiency exceeding 15%, *Adv. Mater.* 27 (2015) 6363–6370.
- [112] M.A. Ahmed, R.M. Khafagy, O. El-sayed, Laser-induced down-conversion and infrared phosphorescence emissivity of novel ligand-free perovskite nanomaterials, *J. Mol. Struct.* 1062 (2014) 133–140.
- [113] Y. Wang, X. Li, J. Song, L. Xiao, H. Zeng, H. Sun, All-inorganic colloidal perovskite quantum dots: a new class of lasing materials with favorable characteristics, *Adv. Mater.* 27 (2015) 7101–7108.
- [114] J. You, L. Meng, T.-B. Song, T.-F. Guo, Y. Yang, W.-H. Chang, Z. Hong, H. Chen, H. Zhou, Q. Chen, Y. Liu, N. De Marco, Y. Yang, Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers, *Nat. Nanotechnol.* 11 (2016) 75–81.
- [115] L. Aarts, B. v.d. Ende, M.F. Reid, A. Meijerink, Downconversion for Solar Cells in YF3:Pr3+, Yb3+, *Spectrosc. Lett.* 43 (2010) 373–381.
- [116] B. Zheng, L. Lin, S. Xu, Z. Wang, Z. Feng, Z. Zheng, Efficient near-infrared downconversion and energy transfer mechanism in Tb4+-Yb3+ co-doped NaYF4 nanoparticles, *Opt. Mater. Express* 6 (2016) 2769–2775.
- [117] A. Martínez, I. Zarazua-Macias, D. Esparza, A. Cerdan, T. Lopez-Luke, E. De la Rosa, Quantum Dots Solar Cells of CdS Deposited by Chemical Bath Method, in: *Latin America Optics and Photonics Conference*, Optical Society of America, Cancun, 2014, pp. LTh4A.37.
- [118] R. Elleuch, R. Salhi, J.-L. Deschanvres, R. Maalej, Antireflective downconversion ZnO:Er3+,Yb3+ thin film for Si solar cell applications, *J. Appl. Phys.* 117 (2015) 055301.
- [119] S. Bak, D. Kim, H. Lee, Graphene quantum dots and their possible energy applications: a review, *Curr. Appl. Phys.* 16 (2016) 1192–1201.
- [120] N.D. Meshram, P.J. Yadav, A.A. Pathak, C.P. Joshi, S.V. Moharil, Near infrared emission of TbAG:Ce3+,Yb3+ phosphor for solar cell applications, *AIP Conf. Proc.*, 1728, 2016, 020201.
- [121] C.-L. Cheng, J.-Y. Yang, Hydrothermal synthesis of Eu3+-doped Y(OH)3 nanotubes as downconversion materials for efficiency enhancement of screen-printed monocrystalline silicon solar cells, *IEEE Electron Device Lett.* 33 (2012) 697–699.
- [122] J. Shen, Z. Li, R. Cheng, Q. Luo, Y. Luo, Y. Chen, X. Chen, Z. Sun, S. Huang, Eu3+-doped NaGdF4 nanocrystal down-converting layer for efficient dye-sensitized solar cells, *ACS Appl. Mater. Interfaces* 6 (2014) 17454–17462.
- [123] R. Krishnan, J. Thirumalai, Synthesis and up/down conversion luminescence properties of Na0.5R0.5MoO4:Ln3+ (R3+=La, Gd), (Ln3+=Eu, Tb, Dy, Yb/Er) thin phosphor films grown by pulsed laser deposition technique, *RSC Adv.* 4 (2014) 64258–64266.
- [124] S.C. Singh, R.K. Swarnkar, R. Gopal, Zn/ZnO core/shell nanoparticles synthesized by laser ablation in aqueous environment: optical and structural characterizations, *Bull. Mater. Sci.* 33 (2010) 21–26.
- [125] G.A. Goget, D. Ristic, B. Dieudonné, E. Moser, S. Varas, S. Berneschi, M. Ivanda, A. Montell, C.A. Duverger, G.C. Righini, B. Boulard, M. Ferrari, Rare-earth-activated glasses for solar energy conversion, in: *Proceedings of the 13th International Conference on Transparent Optical Networks*, 2011, pp. 1–4.
- [126] L. Dumont, J. Cardin, P. Benzo, M. Carrada, C. Labbé, A.L. Richard, D.C. Ingram, W.M. Jadwisieniczak, F. Gourbilleau, SiNx:Tb3+-Yb3+, an efficient down-conversion layer compatible with a silicon solar cell process, *Solar Energy Mater. Sol. Cells* 145 (2) (2016) 84–92.
- [127] A. Kumar, W.R. Taube, R. Sarvanan, P.B. Agarwal, P. Kothari, D. Kumar, Plasma enhanced chemical vapor deposited (Pecvd) silicon rich nitride thin films for improving silicon solar cells efficiency, *Int. J. Sci. Eng. Technol.* 1 (2012)

- 111–116.
- [128] S. Forissier, H. Roussel, P. Chaudouet, A. Pereira, J.-L. Deschanvres, B. Moine, Thulium and ytterbium-doped titanium oxide thin films deposited by ultrasonic spray pyrolysis, *J. Therm. Spray Technol.* 21 (2012) 1263–1268.
- [129] I. Soumahoro, G. Scherber, A. Douayar, S. Colis, M. Abd-Lefdil, N. Hassanain, A. Berrada, D. Muller, A. Slaoui, H. Rinnert, A. Dinia, Structural, optical, and electrical properties of Yb-doped ZnO thin films prepared by spray pyrolysis method, *J. Appl. Phys.* 109 (2011) 033708.
- [130] P.V. Kamat, Meeting the clean energy demand: nanostructure architectures for solar energy conversion, *J. Phys. Chem. C* 111 (2007) 2834–2860.
- [131] V. Avrutin, N. Izyumskaya, H. Morkoç, Semiconductor solar cells: recent progress in terrestrial applications, *Superlattices Microstruct.* 49 (2011) 337–364.
- [132] K. Tanabe, A review of ultrahigh efficiency III-V semiconductor compound solar cells: multijunction tandem, lower dimensional, photonic up/down conversion and plasmonic nanometallic structures, *Energies* 2 (2009) 504.
- [133] D. Verma, T.O. Saetre, O.-M. Midtgard, Review on up/down conversion materials for solar cell application, in.
- [134] Y. Tai, G. Zheng, H. Wang, J. Bai, Broadband down-conversion based near infrared quantum cutting in Eu²⁺–Yb³⁺ co-doped SrAl₂O₄ for crystalline silicon solar cells, *J. Solid State Chem.* 226 (2015) 250–254.
- [135] G. Gao, L. Wondraczek, Near-infrared down-conversion in Mn²⁺–Yb³⁺ co-doped Zn₂GeO₄, *J. Mater. Chem. C* 1 (2013) 1952–1958.
- [136] M. Stupca, M. Alsalhi, T. Al Saud, A. Almuhanna, M.H. Nayfeh, Enhancement of polycrystalline silicon solar cells using ultrathin films of silicon nanoparticle, *Appl Phys. Lett.* 91 (2007).
- [137] J. Carrillo-López, J.A. Luna-López, I. Vivaldo-De la Cruz, M. Aceves-Mijares, A. Morales-Sánchez, G. García-Salgado, UV enhancement of silicon solar cells using thin SRO films, *Sol. Energy Mater. Sol. Cells* 100 (2012) 39–42.
- [138] F.I. Chowdhury, A. Alnuaimi, K. Islam, A. Nayfeh, Efficiency enhancement in thin-film c-Si HIT solar cells using luminescent 2.85 nm silicon nanoparticles, in: *Proceedings of the IEEE 40th Photovoltaic Specialist Conference (PVSC)*, 2014, pp. 2209–2213.
- [139] Y. Ahn, J. Kim, S. Shin, S. Ganorkar, Y.-H. Kim, Y.-T. Kim, S.-I. Kim, Efficiency enhancement of GaAs solar cell using luminescent down-shifting layer consisting of (CdSe)ZnS quantum dots with calculation and experiment, *J. Sol. Energy Eng.* 137 (2014) (021011-021011).
- [140] H.C. Chen, C.C. Lin, H.V. Han, K.J. Chen, Y.L. Tsai, Y.A. Chang, M.H. Shih, H.C. Kuo, P.C. Yu, Enhancement of power conversion efficiency in GaAs solar cells with dual-layer quantum dots using flexible PDMS film, *Sol. Energy Mater. Sol. Cells* 104 (2012).
- [141] X. Pi, Q. Li, D. Li, D. Yang, Spin-coating silicon-quantum-dot ink to improve solar cell efficiency, *Sol. Energy Mater. Sol. Cells* 95 (2011) 2941–2945.
- [142] X. Wu, F. Meng, Z. Zhang, Y. Yu, X. Liu, J. Meng, Broadband down-conversion for silicon solar cell by ZnSe/phosphor heterostructure, *Opt. Express* 22 (2014) A735–A741.
- [143] C.L. Cheng, J.Y. Yang, Hydrothermal synthesis of Eu³⁺-doped Y(OH)₃ nanotubes as downconversion materials for efficiency enhancement of screen-printed monocrystalline silicon solar cells, *IEEE Electron Device Lett.* 33 (2012) 697–699.
- [144] J. Merigeon, O. Maalej, B. Boulard, A. Stanculescu, L. Leontie, D. Mardare, M. Girtan, Studies on Pr³⁺–Yb³⁺ codoped ZBLA as rare earth down convertor glasses for solar cells encapsulation, *Opt. Mater.* 48 (2015) 243–246.
- [145] X. Zhou, J. Shen, Y. Wang, Z. Feng, R. Wang, L. Li, S. Jiang, X. Luo, An efficient dual-mode solar spectral modification for c-Si solar cells in Tm³⁺/Yb³⁺ codoped tellurite glasses, *J. Am. Ceram. Soc.* 99 (2016) 2300–2305.
- [146] Y. Tai, H. Wang, H. Wang, J. Bai, Near-infrared down-conversion in Er³⁺–Yb³⁺ co-doped transparent nanostructured glass ceramics for crystalline silicon solar cells, *RSC Adv.* 6 (2016) 4085–4089.
- [147] C.-C. Chung, B.T. Tran, H.-V. Han, Y.-T. Ho, H.-W. Yu, K.-L. Lin, H.-Q. Nguyen, P. Yu, H.-C. Kuo, E.Y. Chang, The effect of CdS QDs structure on the InGaP/GaAs/Ge triple junction solar cell efficiency, *Electron. Mater.* 10 (2014) 457–460.
- [148] H.-V. Han, C.-C. Lin, Y.-L. Tsai, H.-C. Chen, K.-J. Chen, Y.-L. Yeh, W.-Y. Lin, H.-C. Kuo, P. Yu, A highly efficient hybrid GaAs solar cell based on colloidal-quantum-dot-sensitization, *Sci. Rep.* 4 (2014) 5734.
- [149] M. Grätzel, Dye-sensitized solar cells, *J. Photochem. Photobiol. C: Photochem. Rev.* 4 (2003) 145–153.
- [150] D. Maheswari, D. Sreenivasan, Review of TiO₂ nanowires in dye sensitized solar cell, *Appl. Sol. Energy* 51 (2015) 112–116.
- [151] B. Marie-Isabelle, Nano-TiO₂ for dye-sensitized solar cells, *Recent Pat. Nanotechnol.* 6 (2012) 10–15.
- [152] H.-J. Kim, Song, J.S. Kim, S. S. Efficiency enhancement of solar cell by down-conversion effect of Eu³⁺ doped LiGdF₄, *J. Korean Phys. Soc.* 45 (2004) 609–613.
- [153] W.B. Dai, Y.F. Lei, P. Li, L.F. Xu, Enhancement of photovoltaic performance of TiO₂-based dye-sensitized solar cells by doping Ca₃La₃(1-x)Eu_{3x}(BO₃)₅, *J. Mater. Chem. A* 3 (2015) 4875–4883.
- [154] G. Zhu, X. Wang, H. Li, L. Pan, H. Sun, X. Liu, T. Lv, Z. Sun, Y3Al5O12:Ce phosphors as a scattering layer for high-efficiency dye sensitized solar cells, *Chem. Commun.* 48 (2012) 958–960.
- [155] N. Yao, J. Huang, K. Fu, X. Deng, M. Ding, X. Xu, Rare earth ion doped phosphors for dye-sensitized solar cells applications, *RSC Adv.* 6 (2016) 17546–17559.
- [156] M.J. Lim, Y.N. Ko, Y. Chan Kang, K.Y. Jung, Enhancement of light-harvesting efficiency of dye-sensitized solar cells via forming TiO₂ composite double layers with down/up converting phosphor dispersion, *RSC Adv.* 4 (2014) 10039–10042.
- [157] N. Chander, A.F. Khan, V.K. Komarala, Improved stability and enhanced efficiency of dye sensitized solar cells by using europium doped yttrium vanadate down-shifting nanophosphor, *RSC Adv.* 5 (2015) 66057–66066.
- [158] X. Fan, M. Zhang, X. Wang, F. Yang, X. Meng, Recent progress in organic-inorganic hybrid solar cells, *J. Mater. Chem. A* 1 (2013) 8694–8709.
- [159] Q. Li, Y. Yuan, T. Wei, Y. Li, Z. Chen, X. Jin, Y. Qin, W. Sun, The origin of efficiency enhancement of inorganic/organic hybrid solar Cells by robust samarium phosphate nanophosphors, *Sol. Energy Mater. Sol. Cells* 130 (2014) 426–434.
- [160] C.L. Liu, Baojun, Multiple dyes containing luminescent solar concentrators with enhanced absorption and efficiency, *J. Opt.* 17 (2015) 025901.
- [161] A.A. Earp, G.B. Smith, J. Franklin, P. Swift, Optimisation of a three-colour luminescent solar concentrator daylighting system, *Sol. Energy Mater. Sol. Cells* 84 (2004) 411–426.
- [162] A.M.a.R.E.I.S. W.G.J.H.M. van Sark, Solar spectrum conversion for photovoltaics using nanoparticles, third generation photovoltaics, in: V. Pthenakis (Ed.) *Third Generation Photovoltaics*, In Tech, 2012.
- [163] C. Wang, R. Winston, W. Zhang, D. Pelka, S. Carter, Optical enhancement for luminescent solar concentrators, in, 2010, pp. 77850D–77857.
- [164] Y. Zhao, G.A. Meek, B.G. Levine, R.R. Lunt, Near-infrared harvesting transparent luminescent solar concentrators, *Adv. Opt. Mater.* 2 (2014) 606–611.
- [165] C. Wang, G. Shcherbatyuk, R. Inman, D. Pelka, W. Zhang, Y. Rodriguez, S. Carter, R. Winston, S. Ghosh, Efficiency improvement by near infrared quantum dots for luminescent solar concentrators, in, 2010, pp. 77720G–77726.
- [166] C. Liu, X. Zhang, J. Li, Y. He, Z. Li, H. Li, W. Guo, W. Xie, The role of phosphor nanoparticles in high efficiency organic solar cells, *Synth. Met.* 204 (2015) 65–69.
- [167] W. Na, L. Qun, Q. Xvsheng, M. Chang-Qi, The preparation of a Eu³⁺-doped ZnO bi-functional layer and its application in organic photovoltaics, *Mater. Res. Express* 2 (2015) 125901.
- [168] V. Svrcak, T. Yamanari, D. Mariotti, S. Mitra, T. Velusamy, K. Matsubara, A silicon nanocrystal/polymer nanocomposite as a down-conversion layer in organic and hybrid solar cells, *Nanoscale* 7 (2015) 11566–11574.
- [169] C.-C. Lin, H.-C. Chen, H.-V. Han, Y.-L. Tsai, C.-H. Chang, M.-A. Tsai, H.-C. Kuo, P. Yu, Improved efficiency for nanopillar array of c-Si photovoltaic by down-conversion and anti-reflection of quantum dots, in, 2012, pp. 825609–825606.
- [170] D.-C. Cheng, H.-C. Hao, M. Zhang, W. Shi, M. Lu, Improving Si solar cell performance using Mn:ZnSe quantum dot-doped PLMA thin film, *Nanoscale Res. Lett.* 8 (2013) 1–5.
- [171] Ld.A. Florêncio, L.A. Gómez-Malagón, B.C. Lima, A.S.L. Gomes, J.A.M. Garcia, L.R.P. Kassab, Efficiency enhancement in solar cells using photon down-conversion in Tb/Yb-doped tellurite glass, *Sol. Energy Mater. Sol. Cells* 157 (2016) 468–475.
- [172] J.H.N. Yao, K. Fu, S. Liu, D. E. Y. Wang, Efficiency enhancement in dye-sensitized solar cells with down conversion material ZnO:Eu³⁺, Dy³⁺, *J. Power Sources* 267 (2014) 405–410.
- [173] W. He, T.S. Atabaev, H.K. Kim, Y.-H. Hwang, Enhanced sunlight harvesting of dye-sensitized solar cells assisted with long persistent phosphor materials, *J. Phys. Chem. C* 117 (2013) 17894–17900.
- [174] M.-L. Tsai, W.-R. Wei, L. Tang, H.-C. Chang, S.-H. Tai, P.-K. Yang, S.P. Lau, L.-J. Chen, J.-H. He, Si hybrid solar cells with 13% efficiency via concurrent improvement in optical and electrical properties by employing graphene quantum dots, *ACS Nano* 10 (2016) 815–821.
- [175] S. Engmann, M. Machalet, V. Turkovic, R. Röscher, E. Rädlein, G. Gobsch, H. Hoppe, Photon recycling across a ultraviolet-blocking layer by luminescence in polymer solar cells, *J. Appl. Phys.* 112 (2012) 034517.
- [176] A. Louwen, W.G.J.H.M. van Sark, A.P.C. Faaij, R.E.I. Schropp, Re-assessment of net energy production and greenhouse gas emissions avoidance after 40 years of photovoltaics development, *Nat. Commun.* 7 (2016) 13728.
- [177] A.V. Naumov, Review of the world market of rare-earth metals, *Russ. J. Non-Ferr. Met.* 49 (2008) 14–22.
- [178] O.E. Semonin, J.M. Luther, M.C. Beard, Quantum dots for next-generation photovoltaics, *Mater. Today* 15 (2012) 508–515.
- [179] M.C. Beard, J.M. Luther, A.J. Nozik, The promise and challenge of nanostructured solar cells, *Nat. Nanotechnol.* 9 (2014) 951–954.
- [180] R. Singh, G.F. Alapatt, A. Lakhtakia, Making solar cells a reality in every home: opportunities and challenges for photovoltaic device design, *IEEE J. Electron Devices Soc.* 1 (2013) 129–144.