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Geometrical concentration for enhanced up-conversion: A review of recent results in energy and biomedical applications

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ABSTRACT

Up-conversion is one of the promising approaches for energy and biomedical applications. To enable significant power conversion efficiencies, high irradiance is required. In solar energy applications, this irradiance translates to solar concentrations higher than one sun, unable to be obtained without geometrical or local-field concentration. For biomedical applications, enhanced sensitivity and imaging resolution are required, accompanied by low sample volumes. In this review, the performance of approaches with geometrical concentration on up-conversion processes is reviewed based on recently reported results. Compound parabolic concentrators in c-Si and β-$NaYF_4$: 25%Er^{3+} is to-date the most promising approach, with a device external quantum efficiency of 1.8% at incident irradiance of 240 W/m^2.

1. Introduction

Spectral conversion materials are able to absorb photons of a certain wavelength and changing it such that lower or higher energy photons are emitted. The mechanisms for achieving this can be conventional Stokes-shifted emission (also known as down-shifting), down-conversion (where ideally two photons are emitted for each absorbed photon), or anti-Stokes processes such as up-conversion, cooperative luminescence and two-photon absorption. Spectral conversion has seen remarkable research interest in multiple disciplines tied to wavelength conversion of light. That is from energy applications in solar cells [1], photocatalysis [2], artificial photosynthesis [3], plastics recycling [4], to biomedical applications in bioimaging and temperature sensing [5,6]. There have been significant advances in the development and understanding of the structure of new luminescent nanomaterials [7] as well as the spectral conversion mechanisms in novel materials [8,9].

There is, however, often the requirement of tailoring the luminescent properties of such systems, in order to enhance the performance of optical devices and enable widespread applications. Especially for nonlinear spectral conversion processes, such as up-conversion, it is important to optimise the intensity of the electric field for a higher quantum yield.

Highly local-field intensities can be achieved with plasmonic concentrators [10]. Plasmonic concentrators utilise metallic nanostructures to couple the incident electric field with the electrons of the nanostructure, leading to resonant oscillation at optical frequencies. Plasmon resonances are very sensitive to the size of the nanostructure. For visible to near-infrared spectral conversion, the wavelength is comparable to the size of mesoscopic nanostructures, *i.e.* 100–1000 nm. Therefore, plasmonic concentration increases the absorption and scattering cross section of the coupled ensemble [11,12], which may result in parasitic absorption and reduced sensitivity.

The focus of this review is on structures with size features larger than mesoscopic, which can achieve geometrical concentration in a less invasive manner. In this way, concentration of the electric field is obtained externally of the luminescent material system, therefore allowing for their independent development and optimisation. Geometrical concentration can be achieved with metallic or dielectric structures that rely on specular, diffuse or total internal reflection. An overview of the geometries reported in the literature is summarised in Fig. 1 and will be used as a guide throughout this review. Slanted (b) or spherical (c) metallic reflecting structures can replace the back reflector (a) commonly used in solar energy applications. Light transmitted by the spectral converter can then be concentrated by the back reflector. A luminescent concentrator (d) can in addition shift incident transmitted light to spectrally concentrate and utilise non-absorbed photons. Alternatively and depending on the application, dielectric tapered (e), compound parabolic (f), micro-lens arrays (g) or microspheres (h) can

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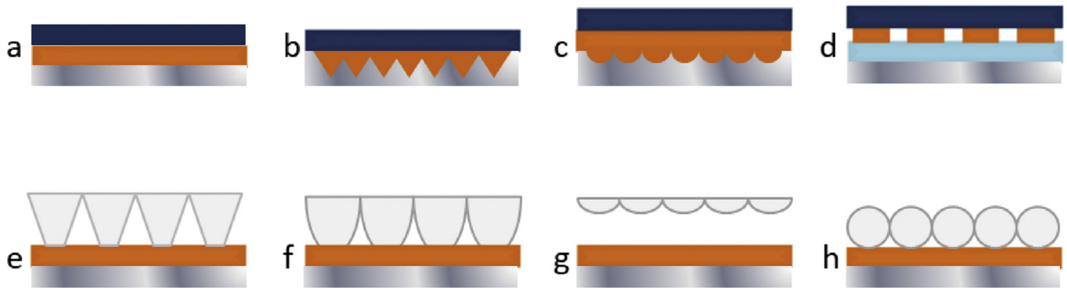

Fig. 1. Geometries for concentration with dielectric or metallic mesoscale structures in solar cells (dark blue) with spectral converters (orange). In (a) typical layered configurations without geometrical concentration a reflector can be replaced by (b) slanted or (c) spherical reflectors or complemented by (d) luminescent and spectral concentrators (blue). Dielectric concentrators in the form of (e) tapers, (f) compound parabolic concentrators, (g) micro-lens arrays or (h) microspheres can modify the electric field prior to its interaction with the spectral converter. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

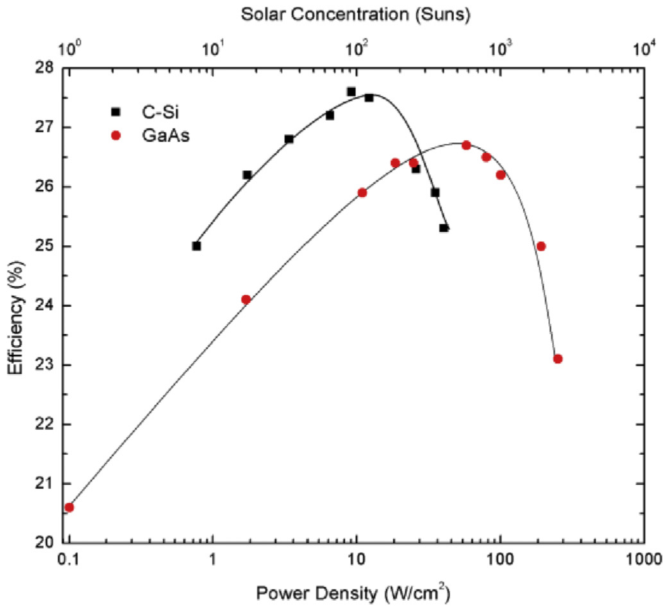

Fig. 2. Conversion efficiency of c-Si and GaAs solar cells at high solar concentration, with highest efficiency at approximately 100 suns and 1000 suns, respectively. The lines are drawn as guide to the eye. For c-Si the data are from Ref. [23] and for GaAs from Ref. [21].

concentrate incident light on the spectral converter. In this way, higher geometrical concentration can be achieved at the peak absorption of the spectral converter, due to the broadband transmission of dielectric concentrators.

This review is structured as follows: The requirements for different applications will be firstly introduced, followed by a presentation of methods for determining the spatial distribution of the electric field by geometrical means, and finally recent reports in energy and biomedical applications will be reviewed.

2. Requirements for geometrical concentration

Spectral conversion can enhance the energy conversion of solar cells. That is, either by down-shifting or down-conversion of one photon with energy higher than the band-gap, or by up-conversion of two or more photons with energy below the band-gap. Down-shifting and down-conversion involve the conversion of one photon; therefore their dependence on the excitation power is linear. For up-conversion, however, two photons are involved resulting in non-linear power-dependence, which makes it sensitive to irradiance and geometrical concentration. Molecular up-conversion *via* triplet-triplet annihilation (TTA-UC), was reported at irradiance as low as 10^2 W/m^2 [1]. However, in lanthanide up-conversion, excitation with irradiance levels in the range of 10^3–10^6 W/m^2 [1] are commonly used to investigate up-conversion materials under laser excitation.

In addition, the conversion efficiency of a solar cell is not linear with solar concentration. Solar concentration is commonly measured in suns, with 1 sun defined as 1000 W/m^2 integrated over the solar spectrum from 280 nm to 4000 nm [13]. Due to the mismatch between the spectral irradiance of lasers and solar simulators with the solar spectrum, spectral mismatch corrections [14] can be applied. In this way, the expected solar concentration can be calculated when considering the photoluminescence quantum efficiency or yield (PLQY) of up-conversion materials under broadband excitation.

Up-conversion solar cells, were first demonstrated by Gibart et al. with gallium arsenide (GaAs) cells [15] and with crystalline silicon (c-Si) cells by Shalav et al. [16]. Both demonstrations were based on a layered configuration shown in Fig. 1(a), where the semiconductor layer is followed by the up-converter absorbing photons below the band-gap of the semiconductor. Both c-Si and GaAs are the most mature single band-gap semiconductors to-date approaching the upper-bound for photovoltaic efficiency on earth [17]. These are also the most intensively investigated in concentrating solar cells with efficiency of 27.6 ± 1.2% at 92 suns and 29.3 ± 0.7% at 49 suns, for c-Si and GaAs, respectively [18].

For c-Si solar cells, the conversion efficiency reaches a maximum at approximately 100 suns [19]. Above this solar concentration, the density of injected carriers makes Auger recombination dominant, effectively reducing the carrier lifetime [20] with subsequent reduced efficiency as shown in Fig. 2. For GaAs solar cells, the highest reported efficiency to-date is reported at 49 suns [18], however as shown in Fig. 2, from 1 to 1000 suns the efficiency increases monotonically to 26.5% despite the high carrier density. Above this solar concentration, the efficiency drops due to increased series resistance in the emitter, base and contacts of the solar cell [21,22].

It is clear that the difference between the solar concentration on the solar cell and the up-converter is more than one order of magnitude. Therefore, an up-conversion solar cell with geometrical concentration of the sub-band-gap photons transmitted by the solar cell is a promising approach. The concentration can be achieved either through internal photon management in the material or externally. An equivalent solar concentration in this case can be defined as [24,25],

$$C_{exc} = \frac{\int_{\lambda_1}^{\lambda_2} P_{exc}(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} P_{AM1.5D}(\lambda) d\lambda} \tag{1}$$

where P_{exc} is the excitation irradiance, $P_{AM1.5D}$ the spectral irradiance of the air-mass 1.5 direct (AM1.5D) solar spectrum [13], between the integration limits λ_1 and λ_2 that correspond to the absorption band of the up-converter.

For a luminescent material, the primary figure of merit is the PLQY,