



Letter

Broadband dye-sensitized upconversion: A promising new platform for future solar upconverter design



A B S T R A C T

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During the past decade, lanthanide-doped upconversion luminescent nanoparticles, which are capable of generating shorter-wavelength photons under infrared light excitation, have attracted worldwide attention due to their promising applications in biomedical imaging, solar cells, and display technologies. However, such applications are still harmed by the low photoluminescence quantum yield and narrow excitation bandwidth of upconversion nanoparticles, which can be attributed to the small absorption cross-sections arising from formally forbidden 4f–4f transitions of the dopants (e.g., Yb³⁺, Er³⁺, Ho³⁺ ions). Just recently, a novel class of upconversion nanomaterials with an organic near-infrared dye as sensitizer of lanthanide dopants was developed, which allows for broadband, low-power near-infrared excitation and high overall luminescence quantum yield, making them highly promising as spectral converter for applications in solar cells.

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Frequency conversion has long been a topic of great interest. The use of lanthanide ions to convert photons to desired wavelengths already finds a wide range of commercial applications, including fluorescent lamps, lasers, white light-emitting diodes, and displays [1]. Lanthanide ions possess rich energy levels arising from the 4fⁿ configurations, and the electronic transitions with these energy levels can give rise to various emissions with wavelengths covering the ultraviolet, visible, and infrared. Photon upconversion represents an important class of lanthanide luminescence. It is a very interesting nonlinear optical phenomenon, which enables to turn low-energy laser stimulation into higher-energy luminescent emissions. Since its discovery in 1960s, photon upconversion has been extensively studied in lanthanide-doped bulk materials [2]. Recently, intense research efforts have been putted into lanthanide-doped upconversion nanomaterials, due to their promising applications in biological imaging and solar cells [3–6].

At present, efficiently harvesting solar energy for photovoltaics remains very challenging. The standard AM 1.5G solar spectrum consists of photons with wide spectral wavelengths from 280 to 2500 nm, but current solar cells only harness a relatively small portion of the incident sunlight (Fig. 1). This is attributed to the fact that only photons with energy higher than the bandgap of active materials can be absorbed, while the sub-bandgap photons are totally wasted. Conversion of the incoming sub-bandgap sunlight into above-bandgap light by using an upconversion layer is demonstrated to be an effective way to substantially reduce non-absorption energy losses. Recently, Trupke et al. showed that the limiting efficiency of a solar cell, coupled with an upconverter layer, would exceed the Shockley–Queisser limit [7]. An amazing feature

of using this approach is that upconverting layers can be readily applicable to existing solar technologies with few modification because the upconverters and solar cells can be optimized independently [8]. In principle, an ideal upconverter for enhancing solar cell efficiency must meet the following requirements: (i) it has broadband excitation range longer than the maximum absorption wavelength of active materials; (ii) its emission range is shorter than bandgap of active materials and, moreover, locates in the spectra regions where solar cells have their maximum spectral response; (iii) it shows good response under low-power excitation (in the range of 10–100 Wm⁻²); and (iv) it has high upconversion efficiency.

Despite the great potential of upconversion nanoparticles for photovoltaic applications, further considerable efforts are still required to optimize upconversion luminescence properties. The main challenge lies in the intrinsic low efficiency of upconversion luminescence [9,10], which has seriously hampered their practical use in photovoltaic applications [11]. Generally, upconversion nanoparticles consist of a host material (e.g., NaYF₄ and NaGdF₄) and lanthanide dopants (typically, Yb³⁺/Ho³⁺, Yb³⁺/Er³⁺, or Yb³⁺/Tm³⁺ couples) [12]. Yb³⁺ ions are usually doped to function as sensitizer ions, which absorb the 980-nm laser irradiation and then successively transfer their excitation energy to nearby co-doping activators (Ho³⁺, Er³⁺, Tm³⁺, etc.), finally creating upconversion emissions with wavelengths ranging from ultraviolet, visible to near-infrared regions. In addition, single trivalent lanthanide ions, like Er³⁺ and Ho³⁺, also can show upconversion luminescence under infrared laser excitations (about 1530 nm for Er³⁺ and 1170 nm for Ho³⁺) [13,14]. However, the Yb³⁺, Er³⁺, and Ho³⁺ ions

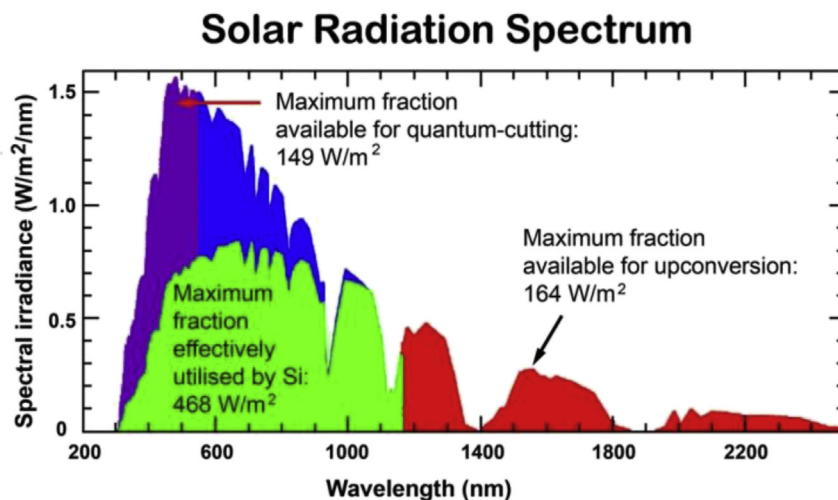


Fig. 1. AM 1.5G spectrum showing the fraction (highlighted in green) absorbed by a typical silicon-based solar cell and the spectral regions that can be utilized through quantum-cutting and upconversion processes (highlighted in purple and red, respectively) [4]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

exhibit a narrow absorption bandwidth and low absorption efficiency in the infrared region due to the parity forbidden $4f-4f$ transitions, which not only results in low upconversion efficiency, but also limits their practical applications in solar cells since only a small fraction of the solar spectral range can be harvested. The absorption cross-sections of Yb^{3+} (in the 950–1100 nm range), Er^{3+} (in the 1480–1580 nm range), and Ho^{3+} (in the 1150–1225 nm range) ions are about 10^{-20} , 10^{-21} , and 10^{-21} cm^2 , respectively [15]. Therefore, the existing solar cell systems may benefit much from upconversion technology, only if the excitation bandwidth and quantum yield of upconverter can be greatly increased.

Although many strategies have recently been explored to enhance the luminescence intensity of lanthanide-doped upconversion nanoparticles (such as host lattice modification, doping concentration optimization, core/shell nanostructure design and surface plasmon coupling) [15–17], the quantum yield of the most efficient upconversion nanoparticles (namely, $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$) still remains very low ($<10\%$) [18]. In order to enlarge the absorption of the sub-bandgap spectral range for solar upconverter systems, Chen et al. fabricated the $\text{NaGdF}_4:\text{Er}^{3+}@\text{NaGdF}_4:\text{Ho}^{3+}@\text{NaGdF}_4$ core-shell-shell upconversion nanoparticles with both the Er^{3+} and Ho^{3+} ions as infrared light harvester [19], while Qiu et al. recently proposed the strategy of simultaneous multi-wavelength infrared laser excitations for $\text{LaF}_3:\text{Er}^{3+}$ and $\text{LaF}_3:\text{Ho}^{3+}$ upconversion nanomaterials [20,21]. These investigations definitely have made great contribution to the community of searching upconversion nanomaterials for solar cell applications. However, the issue of narrowband excitation and low upconversion efficiency is still needed to be addressed. Consequently, considerable efforts should be made to develop a new class of upconversion nanomaterials that can efficiently produce upconversion luminescence under broadband, low power excitation.

In 2012, writing in *Nature Photonics*, Zou et al. firstly reported the very interesting phenomenon of broadband-excited photon upconversion [22]. In their pioneering study, Zou et al. introduced the concept of dye-sensitized photon upconversion, in which an organic infrared dye (IR-806) can be used as an antenna for 10 nm $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles to harvest broadband near-infrared photons (740–850 nm). In sharp contrast to Yb^{3+} sensitizers, organic dyes exhibit absorption cross-sections $\sim 1000-10000$ times as high, and over a much broader spectral

range [23]. Accordingly, Zou et al. found that the extinction coefficient of IR-806 dye at 806 nm is about 5×10^6 times higher than that of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles at 975 nm. As a result, the overall upconversion by the dye-sensitized nanoparticles was dramatically enhanced (by a factor of ~ 3300) due to the increased absorptivity and overall broadening of the absorption spectrum of the upconverter. The observed overall upconversion enhancement should be attributed to the increased absorption and the antenna effect (namely, Förster resonance energy transfer). Moreover, it was found that the monochromatic quantum yield of the IR-806 dye-modified 10 nm $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ nanoparticles under 800 nm excitation is 0.12% (power density is 450 Wcm^{-2}). Therefore, to achieve higher quantum efficiency from dye-sensitized upconversion nanoparticles, suitable combination of organic dyes and upconversion nanoparticles must be found.

Just recently, reporting in *Nano Letters*, Chen et al. demonstrated an efficient dye-sensitized photon upconversion with quantum yield as high as 4.8% (excitation wavelength: 800 nm; power density: 10 Wcm^{-2}) [24]. In the work of Chen et al., IR-808 dye was chosen as the antenna to absorb the near-infrared light between 700 and 850 nm, while 50 nm $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4:\text{Nd}^{3+}$ active-core/active-shell nanoparticles were selected to produce upconversion emissions (Fig. 2(a)). The core/shell nanostructured design can protect the lanthanide core from surface quenching and thus increase upconversion luminescence efficiency. The extinction coefficient of IR-808 dye is $12.7 \text{ l g}^{-1} \text{ cm}^{-1}$, which is about 3000 times higher than that of $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4:\text{Nd}^{3+}$ core/shell nanoparticles at 794 nm ($4.2 \times 10^{-3} \text{ l g}^{-1} \text{ cm}^{-1}$). Importantly, the emission spectrum of IR-808 dye overlaps strongly with the absorption peaks of Nd^{3+} in the shell and with that of the Yb^{3+} in the core of the $\text{NaYbF}_4:\text{Tm}^{3+}@\text{NaYF}_4:\text{Nd}^{3+}$ core/shell nanoparticles (Fig. 2(b)), providing the condition for efficient Förster resonance energy transfer from the IR-808 dye to Nd^{3+} and Yb^{3+} ions. Then, Chen et al. proposed the concept of energy-cascaded upconversion luminescence in dye-sensitized active-core/active-shell upconverting nanoparticles through multistep energy-transfer: (1) NIR-absorbing organic dyes transfer the excitation energy across the organic/inorganic interface to Nd^{3+} ions (type I ions, intermediate sensitizers) doped in the active-shell layer; (2) Nd^{3+} sensitizers in the shell transfer their excitation energy across the core/shell lattice interface to Yb^{3+} ions (type II ions, sensitizers) in the core layer; and (3) Yb^{3+} ions transfer the excitation energy to Tm^{3+} activators

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