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Topical Review

Lanthanide-doped upconversion materials: emerging applications for photovoltaics and photocatalysis

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Abstract

Photovoltaics and photocatalysis are two significant applications of clean and sustainable solar energy, albeit constrained by their inability to harvest the infrared spectrum of solar radiation. Lanthanide-doped materials are particularly promising in this regard, with tunable absorption in the infrared region and the ability to convert the long-wavelength excitation into shorter-wavelength light output through an upconversion process. In this review, we highlight the emerging applications of lanthanide-doped upconversion materials in the areas of photovoltaics and photocatalysis. We attempt to elucidate the fundamental physical principles that govern the energy conversion by the upconversion materials. In addition, we intend to draw attention to recent technologies in upconversion nanomaterials integrated with photovoltaic and photocatalytic devices. This review also provides a useful guide to materials synthesis and optoelectronic device fabrication based on lanthanide-doped upconversion materials.

Keywords: lanthanide, doping, upconversion, nanoparticle, luminescence, photocatalysis, solar cell

(Some figures may appear in colour only in the online journal)

1. Introduction

The rapid growth of energy consumption has accelerated the depletion of the Earth’s oil reserve. However, the costs of continuing on our current energy path are steep, as the combustion of fossil fuels results in damage to human health, the environment, and the economy. Worldwide concerns about such issues have significantly shaped current endeavors toward renewable and green energy resources. Photovoltaics and photocatalysis are two mainstream technologies that can meet sustainable development goals through unlimited access to clean solar energy [1, 2]. Photovoltaic cells (also called solar cells) are semiconductor devices that generate electrical power by converting solar radiation directly into electricity by the photovoltaic effect, as illustrated in figure 1(a). Photocatalysis is a chemical reaction between organic species and free radicals generated from photocatalysts upon irradiation with UV–visible or near-infrared (NIR) light. Figure 1(b) illustrates the basic operating principle of photocatalysis based on a semiconductor to generate free radicals (e.g. •OH and •O2).
The energy conversion efficiency of current photovoltaic cells is far from satisfactory as they only respond to a relatively small fraction of the solar photons with energy higher than the threshold bandgap ($E_g$) of the system. This clearly imposes fundamental limitations to the maximum achievable efficiency of solar cells. To boost the conversion efficiency, a nonlinear optical process, known as upconversion, involving lanthanide-doped nanocrystals or thin-film materials, has been recently explored. Lanthanides are the prime candidates to achieve efficient spectral conversion due to their rich energy-level structure that allows for facile photon management. They also have the ability to transform two (or more) sub-bandgap NIR photons into one usable above-bandgap photon, thereby minimizing non-absorption energy losses in photovoltaic devices.

The development of upconversion materials for photovoltaics can be dated back to 1996, when Gibart et al [5] reported the application of a 100 $\mu$m thick vitreoceramic layer co-doped with Er$^{3+}$ and Yb$^{3+}$ on the rear of a GaAs solar cell (figure 2). In the early 2000s, Trupke and Shalav at the University of New South Wales led the pioneering effort on developing the lanthanide-based solar upconverters from theory to practical working devices [6–8]. Another important development was reported by Demopoulos and co-workers, who firstly explored the upconversion effects through the choice of LaF$_3$:Yb/Er nanocrystals in dye-sensitized solar cells (DSSCs) following AM1.0 G filtered irradiation [9]. In 2011, Wang et al demonstrated the feasibility of using commercial LaF$_3$:Yb/Er upconversion phosphors in P3HT:PCBM organic solar cells [10].

Analogous to photovoltaics, photocatalytic systems having lanthanide-doped materials as spectral converters can operate on the same general principle but with enhanced performance. In 2005, Wang et al [11] developed the first visible photocatalyst, based on a combination of Er$_2$O$_3$ upconversion materials with TiO$_2$. To further tap into the potential of NIR light for enhanced photocatalytic reactions, in 2010 Qin et al [12] developed a NIR to UV upconversion system comprising TiO$_2$-coated YF$_3$:Yb/Tm nanoparticles as the photocatalyst. Another important breakthrough was accomplished by Shi et al [13], who reported on an intriguing photocatalyst through use of SrTiO$_3$:Er for visible-light-driven hydrogen production. More recently, Chen et al developed ZnO nanorod arrays, decorated with CdTe quantum dots and plasmon-enhanced NaYF$_4$:Yb/Er upconversion nanoparticles, for NIR-driven photoelectrochemical water splitting [14]. These groundbreaking studies have truly revolutionized our understanding of the upconversion principles underlying solar energy conversion processes.

This review aims to give a topical review of the current status of the field of lanthanide-doped upconversion materials, with a particular emphasis on their emerging applications in photovoltaics and photocatalysis. We intend to provide a set of criteria for future work by illustrating the most common designs of solar cells and photocatalysts involving upconversion materials. The success in achieving highly efficient energy conversion will certainly require the expertise of many disciplines, including inorganic synthesis, optoelectronics, catalysis, and materials science and engineering.

2. Photon upconversion in lanthanide-doped materials

2.1. Principles

The fascinating luminescence of lanthanide-doped materials generally arises from electronic transitions within the [Xe]4f$^n$ configuration of the lanthanide dopants [3]. The main intra-4f electronic dipole transitions of lanthanide ions are forbidden by quantum mechanical selection rules. Nonetheless, the electronic transitions can be enabled by crystal-field-induced mixing of the f states with higher electronic configurations. Owing to the dipole-forbidden nature of the 4f–4f transition, these lanthanides exhibit very long decay times in the order of microseconds, which increase the probability of sequential excitations and excited state energy transfer of the lanthanide ions.

Downconversion is a Stokes emission process resulting from an excited lanthanide ion embedded in a host lattice as shown in figure 3(a). In a typical downconversion process, an optical active material absorbs incident irradiation and converts it to lower energy (longer wavelength) photons. Photon upconversion is an anti-Stokes emission process in which the sequential absorption of two or more photons leads to the emission of light at a shorter wavelength than the excitation wavelength. This process was first observed by Auzel in 1966 [15]. Two basic upconversion mechanisms involving lanthanides are excited-state absorption (ESA) and energy transfer upconversion (ETU), as illustrated in figure 3(b). Upconversion can only occur in materials with more than one metastable excited state, in which multiphonon relaxation processes are not predominant. In lanthanides, the electrons at 4f or 5f sublevels are shielded by the outer 5s, 5p, 5d orbitals and thus they do not strongly participate in the metal-ligand bonding. Consequently, the electron-phonon interaction is reduced and multiphonon relaxation processes are less competitive. Indeed, upconversion is an optical phenomenon most
commonly observed in materials containing lanthanide ions. Complementary to ESA and ETU processes, our group recently developed energy migration-mediated upconversion (EMU) involving four types of lanthanide ions and a core–shell structure (figure 3(b)) [16]. Through Gd sublattice-mediated energy migration, efficient tunable upconversion emissions in NaGdF$_4$:Tm/Yb@NaGdF$_4$:Ln core–shell nanoparticles were realized for a range of activators (Ln: Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$ and Sm$^{3+}$) that do not have long lived intermediary energy states.

2.2. Nanocrystals

Photon upconversion nanocrystals are inorganic nanomaterials that permit the generation of anti-Stokes emission upon excitation with a low-power diode laser (<10 W cm$^{-2}$). The generation of upconversion luminescence typically requires specific lanthanide activators, singly or multiply doped in crystalline host materials such as halides and oxides [17–20]. Ideal host materials need to have low lattice phonon energies required to minimize non-radiative losses and maximize the radiative emission. Fluorides usually exhibit low phonon energies ($\sim$350 cm$^{-1}$) and high chemical stability, and thus are regarded as the most promising host materials. Er$^{3+}$, Tm$^{3+}$ and Ho$^{3+}$ ions, featuring ladder-like arrangement energy levels, are frequently doped as activators into the fluoride host lattices to generate upconversion emission under a single NIR wavelength excitation. The amount of the activator needs to be maintained at relatively low level (usually less than 2 mol%) to minimize cross-relaxation energy loss. In most cases, the activator is often co-doped together with Yb$^{3+}$ sensitizer to enhance the upconversion efficiency because of its large absorption cross section at 980 nm.


Figure 3. Schematic illustration of downconversion (DC) and upconversion (UC) processes capable of converting $\lambda_1$ energy photon input into $\lambda_2$ energy photon output. Mechanisms of (a) DC process and (b) UC process: ESA, ETU, and EMU.
such as thermal decomposition, high-temperature coprecipitation, hydro(solvo)thermal synthesis, sol-gel procedure, cation exchange and ionic liquid-based synthesis have been utilized to synthesize upconversion nanocrystals with well-defined size, morphology, absorption and emission profile, carrier lifetime, and surface property [21–29].

Our group recently demonstrated the epitaxial growth of an optically inert NaYF₄ layer around a lanthanide-doped NaGdF₄@NaGdF₄ core–shell nanoparticle for effectively preventing surface quenching of excitation energy [30]. Through Gd sublattice-mediated energy migration, the NaYF₄ shell-coating strategy provides tunable upconversion emissions from a variety of activators doped at low concentrations (figure 4). In 2012, Zou et al. [31] demonstrated a remarkable 3300-fold enhancement in the upconversion luminescence of NaYF₄:Yb/Er nanoparticles that are coupled with a cyanine dye (IR-806) to trap photons with energies across a broad range of wavelengths (740–850 nm). The discovery of dye-sensitized upconversion is very important as for the first time, it provides the upconversion emission from lanthanide activators under a broadband and low-power excitation (2 mW).

Another notable finding was reported by Qiu’s group [32], who demonstrated for the first time the polarized energy transfer upconversion at a single particle level from lanthanide-doped fluoride nanorods. Using a 980 nm linearly polarized laser, the authors observed interesting luminescent phenomena such as sharp energy level split, singlet-to-triplet transitions, and multiple discrete luminescence intensity periodic variation with polarization direction.

More recently, Jin and co-workers revealed that fiber-optic sensors can display sensitivities several orders of magnitude greater than those of existing fluorescent techniques using NaYF₄:Yb/Tm upconversion nanocrystals [33]. They found that the integrated emission intensity increases with Tm³⁺ concentration up to 8 mol% without noticeable saturation for a pump power of 2.5 × 10⁶ W cm⁻², resulting in a 70-fold emission enhancement. The same group also demonstrated the possibility of generating a library of distinct time-domain codes using NaYF₄:Yb/Tm nanocrystals [34]. The ability to precisely control luminescence lifetimes of the upconversion nanocrystals by lanthanide doping provides new opportunities for optical multiplexing in medical research and data security. Another important development was explored by Yu and co-workers, who reported the first demonstration of amplified spontaneous emission and stimulated emission from NaYbF₄:Yb/Er@NaYF₄ core–shell nanocrystals via two- and three-photon upconversion processes [35]. Their study revealed that the microwaviness supports lasing emission for lanthanide-doped nanocrystals through the formation of whispering gallery modes.

2.3. Thin films

The development of optoelectronic devices is largely dependent on advances in thin-film deposition technology. Techniques employed to achieve the deposition of lanthanide-doped upconversion thin films can be broadly classified into chemical vapor deposition and physical vapor deposition, including sputtering [36, 37], pulsed-laser deposition (PLD) [38–42], molecular beam epitaxy (MBE) [43, 44], sol-gel procedure [45–47], thermal evaporation [48], and atomic layer deposition (ALD) [49]. Luminescent materials based on thin films have several advantages over conventional nanocrystals in optoelectronic applications such as excellent thermal stability and outstanding adhesion to solid substrates.

PLD, long known as the tool of choice for the growth of optical materials with a complex stoichiometry, has recently gained increased attention for preparing high-quality lanthanide-doped thin film materials because of its ease of use. The technique of PLD is illustrated in figure 5. A short and high-power (typically ~300 mJ) laser pulse first leads to a rapid removal of material from a solid target housed in an ultrahigh vacuum chamber. The ablated species then form an energetic plasma plume, which then condenses onto a substrate. An example of the principle of using PLD was recently demonstrated by Bubb et al. [40], who reported the epitaxial growth of single-crystalline LaEr(MoO₄)₂ thin films. Upon excitation at 980 nm, the as-grown LaEr(MoO₄)₂ thin films emitted light in the visible region as a result of the 4f–4f transitions of Er³⁺ (figures 6(a) and (b)). Hao et al have found a way to modulate upconversion emission using an electric field applied to thin films composed of BaTiO₃:Yb/Er (figure 6(c)) [41]. The researchers observed a 2.7-fold enhancement in the green emission band. As the applied voltage increases, the green-to-red intensity ratios were significantly boosted (figure 6(d)).

Another important technique for depositing thin films of upconversion single crystals is MBE, where the deposition rate (typically less than 3000 nm per hour) is precisely controlled to allow the films to grow epitaxially. In 1997, Satoshi
3. Enhancing conversion efficiency in photovoltaics

3.1. Fundamental considerations

The conversion efficiency ($\eta$) of a solar cell is a quantitative expression of the balance between the input of solar energy and the measurable energy output in watts [50]. The $\eta$ is calculated as the ratio between the generated maximum power ($P_m$) and the incident power ($P_i$). The incident power is equal to the irradiance of AM1.5 spectrum at 25 °C, calculated from the spectral power density $P(\lambda)$ and normalized to 1000 W m$^{-2}$. In principle, there are two loss mechanisms that contribute to the low energy conversion efficiency of today’s solar cells. The first mechanism is the thermalization energy loss in the form of heat dissipation through crystal lattice vibration. The second loss mechanism is ascribed to the non-absorption of photons carrying less energy than the bandgap of the material under investigation. Critically, in the case of crystalline Si (c-Si) solar cells, the transmission loss amounts to about 20% of the incident solar energy [51].

Photon upconversion, realized through the use of ladder-like energy levels in lanthanide-doped materials, provides an attractive approach to converting two or more non-absorbed NIR photons into a usable visible photon, potentially enabling the breaking of the Shockley–Queisser efficiency limit for a single junction cell. As illustrated in figure 7, the photons with energy higher than the bandgap of the solar cell can be absorbed, while sub-bandgap photons are transmitted through the device. When an energy upconverter is placed at the back of the solar cell, the transmitted photons can be absorbed by the upconverter. It should be noted that the design of an upconverter in combination with a reflector layer can further boost the energy conversion efficiency of the device. A proof-of-principle demonstration by Trupke et al [8] in 2002 showed that the theoretical efficiency limit of a solar cell can reach as high as 63.2% and 47.6% for concentrated and non-concentrated sunlight, respectively. The strategy focusing on the use of upconversion materials for photovoltaics has recently applied to a wide range of solar cells, including those based on Si, GaAs, and dye sensitized materials.

3.2. Dye-sensitized solar cells

Dye-sensitized solar cells (DSSCs) are a new class of efficient photoelectrochemical systems, relying on a semiconductor thin film configured between a photo-sensitized anode and an electrolyte [52]. The emergence of the DSSC has led to next-generation photovoltaics that are color-tunable, transparent, low cost, and flexible. For effective utilization of the solar spectrum, one must consider maximizing the range of energy bands absorbable by the DSSCs. Despite considerable research efforts, the improvement in the efficiency of state-of-the-art DSSCs remains a challenging matter, largely due to the lack of suitable photosensitizers with absorption bands located in the NIR region.

The integration of an upconverter layer into DSSCs may provide a solution. In 2010, Demopoulos and co-workers [9] firstly proposed a multiple-layer structure for enhancing the NIR sunlight harvesting in a conventional DSSC. In their design, LaF$_3$:Yb/Er phosphors were combined with TiO$_2$ materials as the upconverter layer to synthesize a triple-layer working electrode. When irradiated at 980 nm (2.5 W), an open-circuit voltage of 0.40 V and a short-circuit current of 0.036 mA were obtained. However, the researchers measured a lowered overall efficiency of the DSSCs, likely due to charge carrier recombination at the interface of the triple-layer
Shortly after this groundbreaking study, Demopoulos and co-workers further developed a new DSSC configuration comprising highly uniform NaYF₄:Er/Yb hexagonal nanoplatelets as an external, bifunctional layer [53]. This arrangement could allow light absorption and reflection to be performed concurrently, thus having advantages in terms of simplified fabrication and enhanced light harvesting. However, both the reflected and upconverted light by the nanophosphors can be absorbed by the electrolyte and the counter electrode used in the external upconversion layer configuration.

In 2013, Liang et al [54] reported a nearly 30% efficiency enhancement in DSSCs using core–shell–shell NaYF₄:Yb/Er@SiO₂@TiO₂ microplates sandwiched between a counter electrode and a transparent TiO₂ layer in order to take full advantage of the scattering and upconverting functions of the microplates (figure 8(a)). In a parallel investigation, a rear-reflector structure that combines NIR-light-harvesting NaGdF₄:Yb/Er/Fe upconversion nanoparticles and light-reflecting silver particles was exploited by Ramasamy et al in an effort to improve the performance of the DSSCs (figure 8(b)) [55]. Interestingly, they found that doping of Fe³⁺ ions modified the local crystal field around the Er³⁺ ions, leading to emission enhancement in the NaGdF₄:Yb/Er/Fe nanoparticles. An additional 3-fold improvement of the emission intensity was achieved by combining silver particles with the upconversion phosphors, which was predominantly attributed to surface plasmon coupling and large scattering effects of the silver particles.

Another promising system for enhanced light harvesting and conversion was reported by Miao et al, who observed...
super-intense upconverted white emission of Yb2O3 poly-crystalline powders upon 980 nm excitation [56]. They found that the luminescence intensity of Yb2O3 was more than one order stronger than that of well-known β-NaYF4:Yb/Er nanoparticles, and Yb2O3 phosphors. By arranging the upconversion layer on the front side of DSSCs, the authors observed a much better performance from Yb2O3-coupled devices when compared to β-NaYF4:Yb/Er-coupled counterparts (figures 8(c) and (d)). Other upconversion materials, including Y3Al5O12:Er/Yb transparent ceramics [57], NaYF4:Er/Yb-graphene composites [58] and TiO2−xF2:Er/Yb powder [59], have also been utilized to stretch the absorption of the DSSCs into the NIR region.

### 3.3. Si-based solar cells

In principle, c-Si-based solar cells work best with excitation in the 900–1100 nm range. Therefore, the most desirable upconverters for c-Si solar cells are those capable of converting an excitation wavelength of above 1100 nm into an emission at a shorter wavelength centered around 1000 nm. Nanostructured materials doped with Er3+ or Ho3+ are particularly suitable upconverters for c-Si solar cells due to their strong absorption in the NIR region (1480–1580 nm and 1150–1225 nm for Er3+ and Ho3+, respectively) and good match of their emission bands (980 nm and 910 nm corresponding to 4I11/2 → 4I15/2 transition of Er3+ and 3F4 → 3I8 transition of Ho3+, respectively) with the absorption of the solar cells.

Shalav et al at the University of New South Wales led the pioneering effort to examine the feasibility of using NaYF4:Er (20 mol%) phosphors as the upconverters in a bifacial c-Si solar cell [7]. In their work, reflective white paint was applied to the rear side of the upconversion layer. A peak external quantum efficiency of 2.5% was obtained for the solar cell under excitation by a 1523 nm laser source with 5.1 mW. In 2007, Richards et al [60] improved the quantum conversion efficiency to 3.4% using a NaYF4:Er-modified c-Si solar cell on excitation at 1523 nm (power density: 2.4 W cm−2). The generation of photocurrent in a commercial c-Si solar cell was achieved by Hernández-Rodríguez et al in 2013 [61]. In their study, fluorindate glasses co-doped with Yb3+ and Er3+ ions were placed on top of the cell, and the incident light is perpendicular to the solar cell and the glass sample (see figure 9(a)). They found that the EQE increases with the power of the source and depends strongly on the concentration of optically active ions in the host material. With an excitation power of 37 mW at 1480 nm, the researchers achieved an EQE of ~0.4% for the Yb3+/Er3+ co-doped sample as shown in figure 9(b).

Amorphous silicon (α-Si:H) has a rather large bandgap of 1.7 eV, and its photovoltaic devices thus have higher transmission loss than c-Si solar cells. The application of NaYF4:Yb/Er phosphors in α-Si solar cells was first reported by Wild et al [62, 63], with a maximum current enhancement of 6.2 μA following illumination at 980 nm (28 mW). This was followed by Chen et al [64], who applied a layer of β-NaYF4:Er (10%) microprism coating on the back of a thin film α-Si:H solar cell and investigated its response to sub-band gap NIR excitation (figures 9(c) and (d)). Photocurrents of 0.3 μA and 0.01 μA were obtained for the thin film device illuminated by 980 nm and 1560 nm lasers, respectively. Interestingly, when irradiated with 980 nm (60 mW) and 1560 nm (100 mW) lasers simultaneously, the photocurrent of the device improved to 0.54 μA, indicating that co-excitation with dual wavelengths accessible to upconversion materials is an effective method to enhance the conversion efficiency of photovoltaic devices.

In 2012, Li et al reported flexible α-Si:H solar cells made of NaYF4:Yb/Er/Gd (18/2/30%) nanorods and Au nanoparticles [65]. On 980 nm excitation, the authors found that the flexible cell with the upconverters showed a 72-fold
improvement in photocurrent (1.16 mA) and an EQE of 0.14% following an excitation of 1100 mW. More recently, Wild et al demonstrated enhanced optical response of $\alpha$-Si:H solar cells for sub-bandgap light under broadband light excitation by utilizing commercially available Gd$_2$O$_2$S:Yb/Er microprisms. (d) Log–log plots of short circuit current as a function of excitation power. Reproduced with permission from [61, 64]. Copyright 2012, 2013 Elsevier.

Table 1. Selected photovoltaic devices containing lanthanide-doped upconversion materials.

<table>
<thead>
<tr>
<th>Solar cell type</th>
<th>Materials</th>
<th>Excitation/Power or power density</th>
<th>Efficiency (Enhancement)</th>
<th>Year [Ref]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>Vitroceramic:Yb/Er</td>
<td>Ti-Sapphire IR laser/1 W</td>
<td>2.5% (Enhancement)</td>
<td>1996 [5]</td>
</tr>
<tr>
<td>Organic</td>
<td>NaYF$_4$:Yb/Er</td>
<td>980 nm laser/146 mW</td>
<td>0.0062% (29.1%)</td>
<td>2012 [68]</td>
</tr>
<tr>
<td>DSSC</td>
<td>LaF$_3$:Yb/Er</td>
<td>AM 1.0 solar illumination/100 mW cm$^{-2}$</td>
<td>2.66% (Enhancement)</td>
<td>2010 [9]</td>
</tr>
<tr>
<td>DSSC</td>
<td>NaYF$_4$:Yb/Er–graphene</td>
<td>AM 1.5 solar irradiation/100 mW cm$^{-2}$</td>
<td>2.84% (~4.4%)</td>
<td>2012 [58]</td>
</tr>
<tr>
<td>DSSC</td>
<td>NaYF$_4$:Yb/Er@SiO$_2$</td>
<td>AM 1.5 solar irradiation/100 mW cm$^{-2}$</td>
<td>8.65% (10.9%)</td>
<td>2013 [71]</td>
</tr>
<tr>
<td>DSSC</td>
<td>TiO$_2$–F$_2$:Yb/Er</td>
<td>AM 1.5 solar irradiation/100 mW cm$^{-2}$</td>
<td>7.08% (31%)</td>
<td>2013 [59]</td>
</tr>
<tr>
<td>DSSC</td>
<td>NaYF$_4$:Yb/Er</td>
<td>AM 1.5 solar irradiation/100 mW cm$^{-2}$</td>
<td>4.32 (23.1%)</td>
<td>2013 [72]</td>
</tr>
<tr>
<td>DSSC</td>
<td>NaGdF$_3$:Yb/Er/Fe</td>
<td>AM 1.5 solar irradiation/100 mW cm$^{-2}$</td>
<td>7.04% (21.3%)</td>
<td>2014 [55]</td>
</tr>
<tr>
<td>DSSC</td>
<td>NaYF$_4$:Yb/Er@SiO$_2$</td>
<td>AM 1.5 solar irradiation/100 mW cm$^{-2}$</td>
<td>6.34% (6%)</td>
<td>2014 [73]</td>
</tr>
<tr>
<td>c-Si</td>
<td>NaYF$_4$:Er</td>
<td>1523 nm laser/5.1 mW</td>
<td>2.5% (Enhancement)</td>
<td>2005 [7]</td>
</tr>
<tr>
<td>c-Si</td>
<td>NaYF$_4$:Er</td>
<td>1523 nm laser/6 mW</td>
<td>3.4% (Enhancement)</td>
<td>2007 [60]</td>
</tr>
<tr>
<td>c-Si</td>
<td>Fluoroindate glass:Yb/Er</td>
<td>1480 nm/37 mW</td>
<td>0.4% (Enhancement)</td>
<td>2013 [61]</td>
</tr>
<tr>
<td>$\alpha$-Si</td>
<td>$\beta$-NaYF$_4$:Yb/Er</td>
<td>980 nm/28 mW</td>
<td>0.03% (Enhancement)</td>
<td>2010 [63]</td>
</tr>
<tr>
<td>$\alpha$-Si</td>
<td>NaYF$_4$:Yb/Er/Gd</td>
<td>980 nm/11 W</td>
<td>0.14% (Enhancement)</td>
<td>2012 [65]</td>
</tr>
</tbody>
</table>

Note: Efficiency is defined as the overall light-to-electrical energy conversion efficiency of the solar cells coupled with upconversion materials. Enhancement refers to the improvement in efficiency when compared to the reference cell without the upconversion materials.

3.4. Other material-based solar cells

Apart from DSSCs and Si-based solar cells, the integration of upconversion materials with other types of solar cells has also been reported, including organic solar cells and GaAs solar cells (table 1). Wang et al in 2011 demonstrated for the first
time the feasibility of photon upconversion in P3HT:PCBM organic solar cells by LaF3:Yb/Er phosphors [10]. In their work, a photocurrent density of \( \sim 16.5 \mu \text{A cm}^{-2} \) was obtained on 975 nm excitation (power density: 25 mW cm\(^{-2}\)). In a follow-up study, they examined the organic solar cell modified with semiconducting MoO3:Yb/Er phosphors [67]. The MoO3:Yb/Er phosphors served as a buffer layer in the solar cell to enable both hole extraction and upconversion capabilities. Upon AM1.5 solar illumination, the researchers obtained less than 1% of the short-circuit current attributable to the upconversion effect.

In 2012, Wu et al [68] reported the effects of NaYF4:Yb/Er upconversion nanoparticles on NIR laser-driven polymer solar cells, as illustrated in figure 10(a). The authors observed noticeable enhancements in the photocurrent and efficiency of the solar cells following laser illumination at 980 nm with a power of 146 mW. However, the use of upconversion nanoparticles did not improve the efficiency of the device under illumination with simulated AM1.5 solar irradiation (figures 10(b) and (c)). They suspected that a large portion of the incoming photons was scattered or blocked by the NaYF4:Yb/Er thin film, resulting in decreased performance of the device. Another notable work was reported by Chu and co-workers in 2012 [69], who validated the tantalizing benefit of the upconversion materials by adhering a 300 \( \mu \text{m} \)-thick layer of \( \text{Y}_6\text{W}_2\text{O}_{15}:\text{Er/Yb} \) phosphors to the rear of a thin film GaAs solar cell. They obtained a maximum output power of 0.339 \( \mu \text{W} \) when illuminated with a 973 nm laser at 145.65 W cm\(^{-2}\).

In 2013, Su et al demonstrated an interesting approach for fabricating a hetero-nanostructured photo-anode that comprises NaYF4:Yb/Er@NaYF4 core–shell nanoparticles for enhanced NIR light harvesting [70]. The core–shell approach enables the achievement of spatial confinement of lanthanide activators in the core, thus minimizing surface quenching of upconversion luminescence by solvent molecules. The photo-anode contains an inverse opal featuring a TiO2 framework filled with quantum dot-modified upconversion nanoparticles. The quantum dots are able to absorb the photons emitted by the upconversion nanoparticles and convert them to electrons. The TiO2 opal creates a continuous electron conducting pathway and provides a large interfacial

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Figure 10. (a) Schematic diagram of an organic solar cell based on NaYF4:Yb/Er phosphors. (Inset) TEM image of the NaYF4:Yb/Er nanocrystals used. (b), (c) I–V characteristics of the as-fabricated organic solar cells recorded under illumination with a 980 nm laser at a power of 146 mW and with simulated solar light (AM1.5 G) at 100 mW cm\(^{-2}\), respectively. Reproduced with permission from [68]. Copyright 2012 Elsevier.
surface area for supporting the upconversion nanoparticles and the quantum dots. As a result, the researchers obtained a much higher electrical current than the control experiment performed on a device without the upconversion nanoparticles.

4. Enhancing photocatalytic performance through broadband absorption

Photocatalysis is an environmentally friendly solution for air or water contamination and soil pollution [74–78]. The photocatalysts in the form of nanoparticles can be dispersed as coatings to building materials for self-cleaning applications. The photocatalytic process is generally initiated by light irradiation of semiconducting materials with band gaps that match the wavelength of the light source. At present, TiO₂, [79, 80] ZnO [81], CdS [82] and Bi₂WO₆ [83] are commonly used photocatalysts for the degradation of organic pollutants. Principally, the photocatalytic activity depends on the ability of the catalyst to generate electron-hole pairs, thus producing hydroxyl radical and superoxide ions. When bound together with harmful pollutants, these highly reactive radicals can effectively oxidize the pollutants and break them down into carbon dioxide and water molecules [84–86].

The photocatalytic performance of a semiconductor material is mainly limited by its intrinsic optical properties as the occurrence of the photocatalytic reaction requires an excitation source with energy equal or greater than the band gap of the semiconductor. For example, titania (TiO₂) is the most frequently used photocatalyst due to its high stability and low cost, biocompatibility, and chemical inertness. However, TiO₂ with a bandgap of 3.2 eV can only be activated by UV light, a wavelength range which amounts to about 5% usable photons in the solar spectrum [87–89]. To get around this problem, many alternatives have been proposed over the past decade to amplify the photocatalytic activity of TiO₂, either by enhancing the separation of photogenerated charge carriers or making the use of visible radiation feasible. These methods include doping of TiO₂ host lattice with foreign atoms [90, 91], coupling of TiO₂ with organic dyes [92] or quantum dots [93–95], and utilization of upconversion phosphors [12, 96]. In particular, the combination of conventional semiconductor photocatalysts with upconversion phosphors has attracted a great deal of attention by virtue of their unique optical characteristics. By combining luminescent ions (such as Eu³⁺, Nd³⁺, Ho³⁺, Er³⁺, and Tm³⁺) with the photocatalysts to form composite materials, high-energy photons in the UV spectral region can be generated by upconverting two or more NIR photons, and subsequently transferred to the photocatalysts (figure 11) [16, 97].

4.1. Visible-light-active catalysts

For the design and synthesis of photoactive catalysts responsive to visible light, most of the research works have been focused on the use of Er³⁺-activated composite materials, as Er³⁺ can emit violet light following laser irradiation at a wide range of visible wavelengths (e.g. 450, 488, 542, 633, and 652 nm). In 2005, Wang et al combined a composite material of 40CdF₂:0.8Er₂O₃ with TiO₂ to form a hybrid photocatalyst [11]. The researchers observed five emission peaks by this material below 387 nm upon excitation at 488 nm. It is noteworthy that the upconverted emission can be completely absorbed by TiO₂. Their photocatalytic investigations demonstrated that nearly 33% of methylene orange molecules, used as a model organic pollutant, can be degraded within 20 h on 488 nm excitation in the presence of the photocatalyst. By comparison, commercial TiO₂ catalysts only exhibited a maximum degradation yield of 2% under the identical conditions. Since 2005, the use of TiO₂ photocatalysts coupled with upconversion phosphors has been envisaged as an effective approach for the degradation of inorganic and organic pollutants under visible light irradiation [98–100].

Doping by activators, such as Er³⁺ and Tm³⁺, into semiconductor materials of TiO₂, CdS, SrTiO₃, and Bi₂WO₆ presents a promising approach to preparing visible-light-driven catalysts for dye degradation and water splitting. As a proof-of-concept demonstration, Shi et al reported the use of Er³⁺-doped SrTiO₃ materials as effective photocatalysts for the generation of H₂ and O₂ molecules following excitation at a broad range of wavelengths [13]. They found that the extended responsive range of the materials from UV to the visible region after Er³⁺ doping was attributed to the generation of elevated excited states of Er³⁺ promoted by the upconversion process and the energy transfer from Er³⁺ to the SrTiO₃ host (figure 12). An interesting note is that Er³⁺-doped SrTiO₃ materials with B-site occupancy exhibit higher photocatalytic activity than those with A-site occupancy. Considering the narrow absorption cross section of lanthanide ions, one may consider enhancing the absorption of photocatalytic systems by further integrating them with organic dyes with tunable and high extinction coefficients.

4.2. NIR-light-active catalysts

To explore photoactivation of TiO₂ by NIR light, Yb³⁺/Tm³⁺ co-doped upconversion nanoparticles can be employed in combination with TiO₂ materials. When photoexcited at...
The design of unique nanostructures capable of facilitating the energy transfer between the light-upconverting component and the constituent semiconductor catalysts is beneficial to vastly increased photocatalytic efficiency. As the interfacial layer formed between the upconversion and semiconductor materials provide effective control over the current density of the photocatalytic system, the resulting heterojunction should be dense and thin. An innovative strategy was recently reported by Li et al. [106], who demonstrated the preparation of highly ordered mesoporous TiO₂ nanostructures in the presence of Yb³⁺ and Tm³⁺ ions. The as-prepared TiO₂ nanocrystals were utilized as effective photocatalysts for the degradation of rhodamine B. The mesoporous structure provided a large surface area (113 m² g⁻¹) where the solar energy can be adequately harvested to generate oxidative species needed for the redox reaction with pollutants. Another notable example was reported by Zhang et al. [107], who synthesized NaYF₄:Yb/Tm@TiO₂ core–shell microrods by a hydrothermal method. The anatase-phase TiO₂ shell was conformally coated onto the lanthanide-doped NaYF₄ microrods with controlled thickness. In the presence of these core–shell microrods, almost 90% of methylene blue molecules were degraded upon NIR irradiation for 12 h.

Alternatively, upconversion nanoparticles can be deposited directly on a semiconductor film to modulate the rate of photocatalytic reactions as in the case of the NaYF₄:Yb/Er–hematite film system reported by Liu and co-workers [105]. When excited at 980 nm with a diode laser, NaYF₄:Yb/Er nanoparticles, electrochemically deposited on a fluorine-doped tin oxide electrode, emitted at 550 and 670 nm. Subsequently, the upconverted visible photons were absorbed by the surrounding hematite film, leading to a better efficiency in water splitting than conventional hematite materials.

The preparation of photocatalytic systems with prolonged lifetimes of charge carriers for increased photocatalytic efficiency remains a daunting challenge. In most photocatalysts, photogenerated electrons and holes tend to quickly recombine to form electron-hole pairs, thus suppressing the catalytic reactivity of the photocatalysts. An intriguing solution to this problem is to consolidate graphene sheets with the catalytic structures. The graphene sheets are excellent conductors capable of facilitating electron transfer and stabilizing the photogenerated electrons and holes upon NIR light irradiation. In 2012, Ren et al. [108] demonstrated the degradation of methylene orange molecules by a three-component...
photocatalyst comprising a commercial P25 catalyst, reduced graphene-oxide sheets, NaYF4:Yb/Tm nanocrystals (figure 13). Approximately 30% of methylene orange molecules were decomposed after 10 min when irradiated with simulated sunlight (AM1.5 G) at 100 mW cm$^{-2}$; this compared with only 4% yield of the decomposition reaction using the P25 photocatalyst alone.

To inhibit the recombination of the photogenerated charge carriers, one may consider enhancing interfacial charge transfer through use of multi-component systems. For instance, Chen et al reported a highly efficient water-splitting system, based on a novel photocatalyst involving ZnO nanorod arrays, CdTe quantum dots, and Au nanoparticle-modified NaYF4:Yb/Er nanoparticles [14]. When irradiated at 980 nm, the upconverted visible photons emitted by the NaYF4:Yb/Er nanoparticles were absorbed by the CdTe quantum dots, resulting in the formation of electrons at the conduction band and holes at the valence band. The electrons at the excited states were then transferred to the conduction band of the ZnO nanorod, effectively preventing the recombination of the electrons and the holes. In addition, the authors argued that the modification of the NaYF4:Yb/Er nanoparticles with an optimal amount of Au nanoparticles increased upconversion emission intensity, enabling them to boost the photocurrent density in the photoelectrochemical reaction. The four-component system can provide a short-circuit photocurrent density of up to 0.036 mA cm$^{-2}$ with an applied voltage of 1.0 V, which presents an almost 40-fold improvement over photodevices made of pristine ZnO nanorods. On two parallel investigations, multi-component YAlO3:Er–ZnO–TiO2 and NaYF4:Yb/Tm@CdS@TiO2 materials were reported to show improved photocatalytic efficiencies in the degradation of acid red B and methylene blue, respectively [109, 110]. Taken together, these efforts suggest that synergistic material combinations can lead to unprecedented optical properties, which are hardly accessible by an individual constituent.

5. Outlook and perspective

The applications of lanthanide-doped upconversion materials for photovoltaics and photocatalysis are emerging fields with many possibilities and challenges that lay ahead. The upconversion materials have shown great promise in enhancing the optical response of photovoltaic devices and photocatalysts to a wide solar spectrum. Despite the benefit, efficient upconversion processes are generally restricted to Er$^{3+}$, Tm$^{3+}$, and Ho$^{3+}$ activators, characterized by ladder-like arranged energy levels. Furthermore, the upconversion materials respond well only to two narrow excitation bands, namely 800 and 980 nm. The realization of efficient upconversion also requires laser irradiation or concentrated sunlight, which clearly hinders the practical implementation of upconversion materials for solar energy harvesting and photocatalysis.

Recent efforts on the investigations of surface plasmon coupling, photonic crystal engineering, and energy clustering at sublattice levels have led to the development of promising approaches to boost upconversion efficiency [19, 111–114]. A long-term goal would involve developing upconversion nanocrystals that can be excited across a broad range of wavelengths [115–118]. Many transition metals, quantum dots, and organic dyes are known to have large absorption cross sections. In this respect, the coupling of highly light-sensitive materials with the upconversion nanocrystals to dramatically improve upconversion luminescence appears feasible. However, for these conjugated systems, the fundamental question of how the transfer of energy occurs between the upconversion nanocrystals and the sensitizers remains unresolved. Finding answers to this question certainly requires considerable, multidisciplinary efforts.
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