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Enhancement of dye sensitized solar cell efficiency through introducing concurrent upconversion/downconversion core/shell nanoparticles as spectral converters

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ABSTRACT

Extending the spectral absorption of dye-sensitized solar cells from the visible into near-infrared and ultra-violet range enables the minimization of non-absorption loss of solar photons. Here, we report a viable strategy to implement simultaneously near-infrared upconversion and ultra-violet down-conversion for dye-sensitized solar cells through constructing a type of upconversion-core/downconversion-shell-structured nanoparticles. For the first time, $NaYF_4$:20%Yb,2%Er@$NaYF_4$:7%Eu core/shell nanoparticles are applied to TiO_2 photoanode for fabricating near-infrared/ultra-violet-enabled dye-sensitized solar cell devices. The incorporation of designed nanoparticles into TiO_2 photoanode of dye-sensitized solar cells achieves high efficiency of 7.664% under one sun illumination, increasing the power conversion efficiency by about 13.95%. We confirm that the enhancement of overall efficiency includes 4.82% upconversion contribution, 7.58% downconversion function and 1.55% scattering effect. Our strategy opens the path for further broadening the solar spectral use to improve the performance of photovoltaic devices.

1. Introduction

In recent decades, extensive efforts have been devoted to the development of new photovoltaic devices or enhancement of the photoelectric conversion efficiency of existing solar cells in order to alleviate energy pressures arising from the excessive consumption of fossil fuels. Among these various photovoltaic technologies, Dye-sensitized solar cells (DSSCs) have been regarded as highly promising next-generation devices, which have the potential advantages of their low cost, ease of processing and relatively high power conversion efficiencies (PCEs) [1,2]. The maximum DSSCs conversion efficiency can theoretically reach ~30% [3]. However, the current conversion efficiency record is still limited to ~12% [4–7]. This problem is principally arose from the inability to absorb and utilize extra photons involving near-infrared (NIR) or ultra violet (UV) lights that constitute almost half of the radiant energy from the sun [8–13].

One strategy that increases the conversion efficiency of DSSC devices is to convert photons with energies below the bandgap of photovoltaic devices into visible photons (<750 nm) that lie in the absorption region of the N719 dye [14–18]. To date, various host materials doped with Yb^{3+}/Er^{3+} ion pairs (*e.g.*,Y_2O_3:Yb^{3+}/Er^{3+} [19], LaF_3:Yb^{3+}/Er^{3+} [20] and $NaYF_4$:Yb^{3+}/Er^{3+} [21]) have been applied as spectral converters in DSSC in an effort to preferably harvest the NIR solar photons. In particular, uniform β-$NaYF_4$:Yb^{3+}/Er^{3+} have been demonstrated to possess higher upconversion (UC) efficiency due to the low phonon energy of $NaYF_4$ matrix [21]. Despite the unique NIR harvesting and converting properties, the inevitable surface defects and ligands of such nanomaterials is a major drawback as it leads to severe electron recombination.

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Consequently, the efficiency enhancement from UC contribution is merely about 1% over the overall DSSC efficiency, which is lower than that induced by scattering effect of UC particles. In order to address this issue, the core/shell-structured UC materials have been developed with the aim of decreasing the surface defects. The introduced core/shell nanostructures has been proven as effective route for improving NIR photons absorption, while maintaining good electron transport through TiO_2 photoanode film [20,22–24]. For instance, Zhang et al. incorporated a novel $NaYF_4$:Yb^{3+}/Er^{3+}/TiO_2 core/shell nanoparticle into TiO_2 photoanode, which can effectively overcome the electron trapping by suppressing the surface defects [20]. Liang et al. showed that the insulating SiO_2 layer in designed β-$NaYF_4$:Yb^{3+}/Er^{3+}@SiO_2@TiO_2 submicroprisms can minimize the electron trapping caused by $NaYF_4$:Yb^{3+}/Er^{3+} nanocrystals, increasing the UC contribution to 2.17% in enhancement efficiency [22]. The $Na_xGdF_yO_z$:Yb/Er@TiO_2 UC/semiconductor core/shell nanoparticles were also utilized as NIR photons converter for DSSCs, achieving efficiently light trapping through harvesting of NIR solar photons and light scattering [23]. Note that, the inert $NaYF_4$ shell was also used as shield layer onto $NaYF_4$:Yb^{3+}/Er^{3+} core for directly mitigating the electron-trapping problem [24]. Subsequently, our group has introduced a new dye-sensitized $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Nd core/shell nanoparticles for DSSCs with improved NIR harvesting performance [25]. These promising studies highlight the value of employing well-preformed core/shell-structured UC converters to efficiently harvest NIR photons for DSSC devices. However, all of the mentioned converters only harvest NIR light, it is lack of expanding the UV harvesting for the use in DSSCs. Recently, an improvement of solar cell UV-respond has also been reported through using rare-earth doped fluorides materials to modify tin oxide compact layer [26–28]. It has been demonstrated that the rare-earth modified tin oxide strategy not only facilitates enhancement of infrared response, but also efficiently mitigates dye degradation and photoelectron recombination. Along this line, the Al_2O_3:Eu^{3+}-TiO_2:Er^{3+},Yb^{3+} composite further confirms its excellent capacity to convert UV and NIR radiation for solar cells [29]. Yet, concurrent and efficient upconversion and downconversion (DC) processes in the same nanoparticles incorporated in the photoanode for DSSCs remain unexplored.

Herein, we report the application of a novel $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Eu^{3+} core/shell nanoparticle for the improvement of NIR and UV lights harvesting in DSSC devices. This architecture of $NaYF_4$:Yb^{3+}/Er^{3+} core and $NaYF_4$:Eu^{3+} shell domain are able to absorb simultaneously NIR and UV photons and efficiently reemit visible lights, which matches the main absorption range of the commonly used N719 dye. DSSCs treated by the optimized core/shell nanoparticles reach a PCE of 7.664% under AM 1.5G, higher than that of regular DSSC (6.726%), leading to a 13.95% improvement over the overall DSSC efficiency.

2. Results and discussion

Fig. 1 illustrates a schematic diagram for the application of $NaYF_4$:Yb^{3+}/Er^{3+}@$NaYF_4$:Eu^{3+} core/shell nanoparticles enabled the NIR/UV DSSC device by converting simultaneously low-energy NIR and high-energy UV photons into absorbable visible photons. The UC/DC core/shell nanoparticles are deposited onto the mesoporous TiO_2 layer for constructing the improved photoanode, and the configuration of a DSSC structure is shown in left part of Fig. 1. The light-absorbing N719 dye in regular DSSC devices possesses strong absorption with typically defined range of 450–700 nm (the right part of Fig. 1). The presence of Yb^{3+}/Er^{3+} ion pairs in the core can absorb 980 nm NIR photons beyond 700 nm. The embedment of Eu^{3+} ions in shell layer extends the spectrum respond of DSSC devices to the underutilized UV photons below 400 nm. Moreover, the absorbed solar photons can be converted to visible photons that match the absorption spectrum of the N719 dye. Along this line, the strategy will activate a synergistic effect in UC core and DC shell layers for improving DSSC efficiency [30,31].

Hexagonal-phase $NaYF_4$ is chosen as the host matrix for lanthanide ions because it is known to be one of the most efficient materials for UC and DC processes [32,33]. We firstly optimized the optical matching phenomenon between UC/DC emitting spectrum of various lanthanide ions and absorption of N719 dye. Yb^{3+}/Er^{3+} ion pair, effectively upconverting NIR photons to green ones (peaks at 540 nm), was demonstrated to be excellent UC emitter for the maximized absorption of N719 dye (Fig. S1, ESI). The DC process in Eu^{3+} ion has been verified to effectively extend N719 dye respond to 395 nm (Fig. S2, ESI) [34,35]. In order to enable concurrent and high-efficiency UC and DC processes within the same nanoparticles, a core/shell structure was constructed to separately bear UC and DC lanthanide ions in its different layers. We subsequently discuss two doping strategies involving the UC process in core and shell layer. Core/shell nanocrystals of $NaYF_4$:20%Yb,2%Er@$NaYF_4$:5% Eu and $NaYF_4$:5%Eu@$NaYF_4$:20%Yb,2%Er nanocrystals were synthesized through an adapted procedure from the literature [36]. Details of synthesis steps were described in the ESI. The transmission electron microscopy (TEM) results (Fig. 2a–d) show that the $NaYF_4$:20%Yb,2%Er (UC core), $NaYF_4$:20%Yb,2%Er@$NaYF_4$:5%Eu (UC@DC), $NaYF_4$:5%Eu (DC core) and $NaYF_4$: 5%Eu@$NaYF_4$:20% Yb,2%Er (DC@UC) are hexagonal and uniform, with a mean size of 37.4 ± 0.3, 44.5 ± 0.2, 38.1 ± 0.3 and 44.9 ± 0.2 nm, respectively. This implies that the shell layer has a thickness of ~3.5 nm for the core/shell nanoparticles. The X-ray diffraction (XRD) patterns confirm that the all core and core/shell nanoparticles are of hexagonal

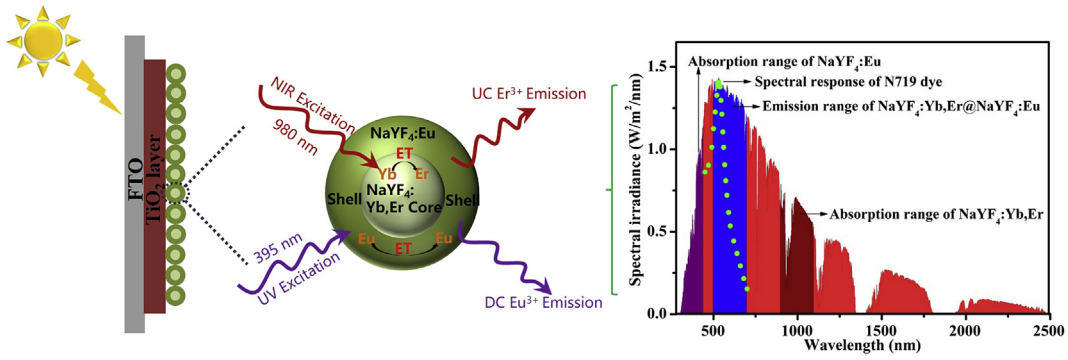

Fig. 1. Near-infrared and ultraviolet sunlight harvesting and then spectral conversion into visible range to activate N719 dye for the enhancement of a DSSC device.