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Broadband dye-sensitized upconverting nanocrystals enabled near-infrared planar perovskite solar cells

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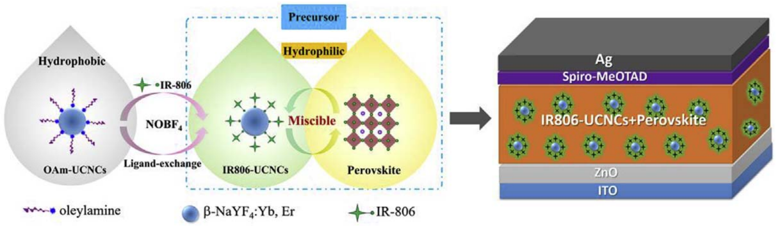
HIGHLIGHTS

- A well miscible IR806-UCNCs incorporated perovskite precursor is formed.
- NIR enabled IR806-UCNCs-incorporated planar perovskite solar cell is developed.
- Broadband upconversion of near-infrared into visible emission is achieved.
- Optoelectric conversion efficiency is improved from 13.52% to 17.49%.

GRAPHICAL ABSTRACT



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ABSTRACT

Extending the spectral absorption of perovskite solar cells (PSCs) from visible into near-infrared (NIR) range is a promising strategy to minimize non-absorption loss of solar photons and enhance the cell photovoltaic performance. Herein, we report on for the first time a viable strategy of incorporating IR806 dye-sensitized upconversion nanocrystals (IR806-UCNCs) into planar PSC for broadband upconversion of NIR light (800–1000 nm) into perovskite absorber-responsive visible emissions. A smart trick is firstly adopted to prepare hydrophilic IR806-UCNCs via a NOBF$_4$ assisted two-step ligand-exchange that allows incorporating with perovskite precursor for in-situ growth of upconverting planar perovskite film. Unlike typically reported upconverting nanoparticles with narrow NIR absorption, the as-prepared IR806-UCNCs are able to harvest NIR light broadly and then transfer the captured energy to the UCNCs for an efficient visible upconversion. The IR806-UCNCs-incorporated cell exhibits a power conversion efficiency of 17.49%, corresponding to 29% increment from that of the pristine cell (13.52%). This strategy provides a feasible way to enable the most efficient harvesting of NIR sunlight for solar cells and other optoelectric devices.

1. Introduction

Organolead trihalide perovskite materials (APbX$_3$, A = CH$_3$NH$_3$, NH=CHCH$_3$; X = Cl, Br, I) have attracted enormous interest in recent seven years owing to their several beneficial properties, such as low manufacturing cost, ambipolar charge transport, low exciton binding energy, long charge diffusion length, together with suitable bandgap as a light absorber with large absorption coefficient (10^4-10^5 cm^{-1}) [1–6]. Owing to these merits, perovskite solar cells (PSCs) have shown tremendous significance in the photovoltaic field and achieved a high power conversion efficiency (PCE) exceeding 22% [7]. A commonly used perovskite light absorber i.e. methylammonium lead iodide (MAPbI$_3$) has an optical bandgap of ~1.5 eV that allows absorbing the incident light with wavelengths ranging from 280 nm to 800 nm [8].

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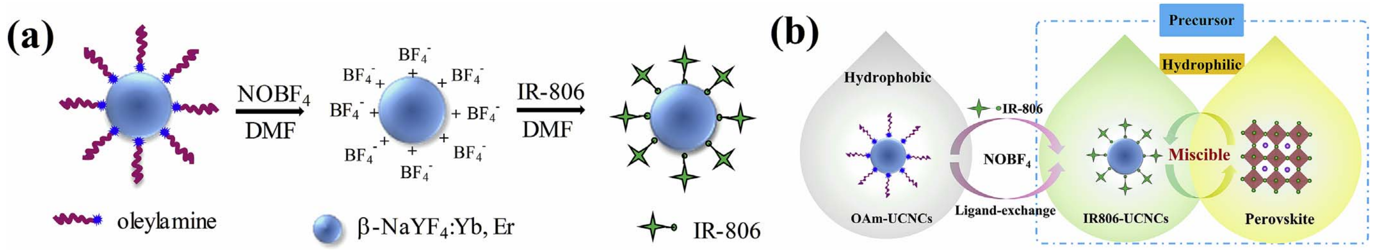

Scheme 1. (a) Schematic preparation of hydrophilic IR806-UCNCs via a two-step ligand-exchange process. (b) Proposed scheme for forming a well miscible IR806-sensitized-UCNCs-incorporated perovskite precursor.

This means that approximately 50% of the total solar energy flux in the infrared is missing in the form of thermalization and non-absorption photons. Thus, improved use of low-energy near-infrared (NIR) solar photons below the absorption threshold of perovskite remains a significant challenge for high-efficiency PSC devices.

A viable approach to reduce such non-absorption photon loss is the employment of upconversion nanocrystals (UCNCs) to absorb the low-energy NIR solar photons, allowing the conversion and re-emission of absorbable high-energy photons to generate extra photocurrent in solar cells [9]. Such a photon upconversion strategy has been extensively studied in Si [10,11], inorganic thin-film [12], polymer [13,14], and dye-sensitized solar cells [15,16]. Inorganic rare-earth-doped upconversion materials i.e. ytterbium and erbium co-doped beta-phase sodium yttrium fluoride (β-$NaYF_4$:Yb, Er), serve as the most efficient upconversion phosphor for bright green photoluminescence and is predicted to be able to theoretically increase the PCE from 20% to 25% of a typical Si solar cell under concentrated solar power [11]. Although the NIR response has been demonstrated in a compelling way, the enhancement in cell efficiency contributed by upconversion solar cells is still limited. The main limitation of β-$NaYF_4$:Yb, Er lies in its inherently weak and narrowband absorption (spectral window is only 10–20 nm at around 980 nm or 785 nm) that is associated with the instinct *4f*-*4f* electronic transitions of the doped rare earth ions (Yb^{3+}/Er^{3+}) [17]. As we well know, organic infrared dye shows a broad NIR spectral absorption i.e. ~10 times larger than that of β-$NaYF_4$:Yb, Er. The use of NIR dye to sensitize β-$NaYF_4$:Yb, Er can enhance the upconversion luminescence of the doped rare earth ions, in which dye molecules (Note that the first singlet excited state is 12500 cm^{-1} [18,19]) function as antennas to absorb incident light and simultaneously transfer their excitation energy to the upcoverting rare earth ions (Note that the $^2F_{5/2}$ energy level of Yb^{3+} is 10250 cm^{-1} [18], and the $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$ energy level of Er^{3+} is 19157 cm^{-1}, 18282 cm^{-1}, 15337 cm^{-1} [20], respectively.) in the UCNCs via Förster-type energy transfer (FRET), and consequently increasing and broadening spectral absorption [21].

To date, there exists limited reports concerning upconverting PSCs, in which UCNCs such as β-$NaYF_4$:Yb, Er, $mCu_{2-x}S@SiO_2@Er_2O_3$, Er-Yb:TiO_2, $LiYF_4$:Yb, Er and β-$NaYF_4$:Yb, Tm@$NaYF_4$ integrated with mesoporous TiO_2 electron transport layer [22–26] or barely used as mesoporous scaffold [27], followed by perovskite filtration. In contrast to complex UCNCs-mesoporous structured PSCs, integration of UCNCs within planar-heterojunction structured PSCs represents a facile approach by simplifying the device architecture. To incorporate UCNCs into ultra-thin perovskite layer of planar PSCs, the crucial challenge is to obtain a miscible UCNCs included perovskite precursor solution in commonly-used polar and hydrophilic solvents. Generally, the surfaces of UCNCs are capped with long-chain alkyl ligands such as oleic acid or oleylamine (OAm), to control the dispersibility and stability of UCNCs in nonpolar and hydrophobic solvents [28]. However, the capped organic ligand creates an insulating barrier around each UCNC, which impairs the miscibility of UCNCs and hydrophilic perovskite precursor solution. Such UCNCs immiscible perovskite precursor leads to insufficient interfacial contact between UCNCs and perovskite in film, which is unfavorable for energy transfer from UCNCs to perovskite light-absorber [29,30]. To solve these issues, a ligand-exchange strategy was developed to replace the originally capped long-chain alkyl ligands with specifically designed species, enabling phase transfer of UCNCs from a nonpolar solvent (e.g. n-hexane) to various polar media (e.g. N,N-dimethylformamide (DMF)) without affecting the UCNC size and shape [31]. In this context, it is expected that NIR dye sensitized-UCNCs can be incorporated within the ultra-thin perovskite layer by means of such ligand-exchange strategy, for the purpose of broadband upconversion of NIR light for PSCs. However, up to date, this NIR dye sensitized-UCNCs-incorporated planar PSCs has yet to be reported.

Herein, we for the first time report a facile route to incorporating IR806 dye (see chemical structure in Fig. S1) -sensitized upconversion crystals (IR806-UCNCs) into planar PSC for broadband upconversion of NIR light (800–1000 nm) into perovskite absorber-responsive visible emissions. A two-step ligand-exchange approach is used to synthesize hydrophilic IR806-β-$NaYF_4$:Yb, Er. Typically, nitrosonium tetrafluoroborate ($NOBF_4$) is employed to replace the originally capped OAm ligands on the surface of UCNCs and hence stabilize BF_4^--capped β-$NaYF_4$:Yb, Er in DMF, followed by anchoring IR806 to the surface of β-$NaYF_4$:Yb, Er (see Scheme 1a) to form a well miscible IR806-UCNCs-incorporated perovskite precursor in DMF (see Scheme 1b). The IR806-UCNCs-incorporated perovskite film is capable of harvesting NIR light in a range of 800–1000 nm and transferring its excitation energy to the Yb^{3+}/Er^{3+} ions to generate strong upconversion emission that can be absorbed by the perovskite in PSCs. As a consequence, an overall PCE of 17.49% under standard air mass 1.5 global sunlight (AM 1.5G) and an impressively high NIR-PCE of 0.382% under NIR irradiation ($\lambda > 780$ nm) are achieved by IR806-UCNCs-incorporated cell. Such a high NIR-PCE surpasses the previous record value for UCNCs-incorporated PSCs [27].

2. Experimental

2.1. Materials

All chemicals were used without further purification. Er_2O_3 (99.99%), Yb_2O_3 (99.99%), Y_2O_3 (99.99%) and Na_2CO_3 (99.99%) trifluoroacetic acid (CF_3COOH, 99.5%), oleylamine (OAm, C18: 80–90%), n-hexane (98%), were purchased from Aladdin. $NOBF_4$ (95%) and PbI_2 (99.9985%) were purchased from Alfa Aesar. The CH_3NH_3I (> 99%) and 2,29,7,70-tetrakis-(N,N-di-*p*-methoxyphenyl-amine)-9,99- spirobifluorene (Spiro-MeOTAD) (> 99%) were obtained from Dyesol. Lithium bis(trifluoromethanesulfonyl) imide (Li-TFSI, 99.95%), acetonirtile (99.8%), 4-*tert*-butylpyridine (TBP, 96%) were purchased from Sigma-Aldrich. All other organic solvents were obtained as analytical grade from J & K Chemical Ltd. with storage in seal bottle with molecular sieves.

2.2. Synthesis of β-$NaYF_4$:Yb, Er UCNCs

β-$NaYF_4$:Yb, Er UCNCs were synthesized according to the method reported in the literature [32]. Typically, CF_3COONa, $Y(CF_3COO)_3$, Yb $(CF_3COO)_3$, and $Er(CF_3COO)_3$ were synthesized by dissolving Na_2CO_3,