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β-$NaYF_4:Yb^{3+}$, $Tm^{3+}@TiO_2$ core-shell nanoparticles incorporated into the mesoporous layer for high efficiency perovskite solar cells

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ABSTRACT

β-$NaYF_4:Yb^{3+}$, Tm^{3+} @ TiO_2 core-shell upconversion nanoparticles (UCNPs) were synthesized and incorporated into the TiO_2 mesoporous layer of perovskite solar cells (PSCs). Changes of the upconversion spectra of the UCNPs suggest the existence of the electron injection from $NaYF_4:Yb^{3+}$, Tm^{3+} to the conduction band (CB) of TiO_2 through the $NaYF_4:Yb^{3+}$, Tm^{3+}/TiO_2 nano-heterojunctions. The core-shell UCNPs that incorporated into the TiO_2 mesoporous layer not only act as the upconversion centers to use the NIR light but also serve as the light scatter centers to enhance the light harvesting. When using mesoporous layer containing the core-shell UCNPs in PSCs, the efficiency of the best devices is 16.27%, which is about 16.38% higher than that of the devices without core-shell UCNPs (13.98%). The significant enhancement in the performance of the PSCs is attributed to light scattering, NIR light upconversion and electron injection from the UCNPs to the CB of TiO_2.

1. Introduction

The new generation solar cells have drawn more attention because of the deterioration of the environment and the exhausting of the energy. Organometal halide perovskite ($CH_3NH_3PbX_3$, X = Cl, Br, I) is considered to be an attractive new solar cell material due to its unique optical and electronic properties [1–3]. Perovskite solar cells (PSCs) have increasingly improved their power conversion efficiency (PCE), from less than 4% in 2009 to over 21.6% in 2016 [4,5]. To date, there have been numerous attempts to improve the PCE of the PSCs, for example, by tuning the properties of interfaces [6,7], controlling the crystallization of perovskite active layers [8,9], engineering the chemical composition of perovskite and introducing additives to perovskite [10,11]. Note that the perovskite has a bandgap of about 1.5 eV and absorbs only a small fraction of incident photons in the visible range (up to 800 nm), though the standard spectrum of AM 1.5 G sunlight ranges from 280 nm to 2500 nm [12]. Up to date, most of the solar cells focused on the 48% visible light of the solar spectrum. The near-infrared (NIR) and ultraviolet (UV) light of the incident sunlight is wasted in the form of thermalization and non-absorption photons. Considering the fact NIR sunlight accounts for about 44% of the total solar spectrum, more researches have been aimed at utilizing NIR sunlight for high efficiency PSCs [13–15]. Employment of the upconversion materials to convert the NIR photons to higher energy photons that can be absorbed by the perovskite active layers will generate extra photocurrent in solar cells, offering a potential means of overcoming the Shockley-Queisser efficiency limit of a single-junction solar cell [16].

Among many kinds of upconversion luminescence materials, lanthanide-doped fluoride upconversion nanoparticles (UCNPs) are well known as the most efficient upconversion phosphor used in solar cells because of their long luminescence lifetimes and optical stability [12]. $NaYF_4$, $NaGdF_4$ and YF_3 are typical upconversion host crystals [17–19], in which Yb^{3+} ions are doped as NIR sensitizers and Ho^{3+}, Er^{3+}, and Tm^{3+} ions are co-doped as visible photon emitters [20,21]. Monodisperse β-$NaYF_4:Yb^{3+}$, Er^{3+} UCNPs modified by a designed double-hydrophilic diblock copolymer act as the mesoporous electrode instead of conventional TiO_2 mesoporous materials in PSCs, and lead to a high efficiency of 17.8% [15]. Hexagonal β-$NaYF_4:Yb^{3+}$, Er^{3+} Nanoprism and β-$NaYF_4:Yb^{3+}$, $Tm^{3+}@NaYF_4$ core-shell UCNPs mixed with diluted TiO_2 were incorporated into the PSCs as an upconverting mesoporous layer for NIR sunlight harvesting [13,14]. In all the above-mentioned researches (as summarized in Table S1), enhancement of PSC performance is

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merely attributed to the additional photocurrent generation via the conversion of NIR light to visible light by upconversion materials.

TiO_2 has been widely used in solar cells for its physical chemical stability, high semiconductor activity and non-poisonous [22–24]. In PSCs, the TiO_2 mesoporous layer not only plays as a scaffold providing mechanical support to the perovskite layer but also acts as an electron transporter [5]. Enlarging the contact area between the TiO_2 layer and the perovskite layer can facilitate the collection of the photo-generated electrons. In addition, it reported that NIR light can be effectively utilized through direct electron injection from the UCNPs to the conductive band (CB) TiO_2 via shared interface, because some energy levels of rare earth ions are well-matched to the CB of TiO_2 [25]. It was confirmed that hetero-junction interface of the UCNPs/TiO_2 heterostructure not only induces direct electron-injection from YbF_3-Ho to TiO_2 by utilizing NIR light, but also further improves the existing merits of TiO_2 through facilitating the interfacial photoinduced charge separation, which can give further improvement of dye-sensitized solar cells [26,27]. However, few reports have discussed the effect of implementation of the UCNPs/TiO_2 nano-heterojunction in mesoporous electrode of PSCs.

In this work, for better development of materials and understanding of devices, β-$NaYF_4$:Yb^{3+}, Tm^{3+} @ TiO_2 core-shell UCNPs were synthesized and introduced into the TiO_2 mesoporous layer of PSCs for the first time. The morphology, structure, and optical properties of the core-shell UCNPs were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), UV—Vis—NIR spectra and photoluminescence (PL) spectra. Photoelectric performance of PSCs with different core-shell UCNPs was investigated by measurements of photocurrent density-voltage (J-V) curves, electrochemical impedance spectroscopy (EIS) and incident photon-to-current conversion efficiency (IPCE). The role of the β-$NaYF_4$:Yb^{3+}, Tm^{3+} @ TiO_2 core-shell UCNPs on the performance of PSCs was discussed in detail.

2. Experiment

Fig. 1 shows the schematic illustration of the fabrication of TiO_2 mesoporous film with $NaYF_4$:Yb^{3+}, Tm^{3+}@TiO_2 core-shell UCNPs (a-e) and the schematic configuration of the final PSC device (f).

2.1. Synthesis of β-$NaYF_4$:Yb^{3+}, Tm^{3+} upconversion nanoparticles

Monodispersed β-$NaYF_4$:Yb^{3+}, Tm^{3+} UCNPs were synthesized using a modified solvothermal method [28]. Typically, an aqueous solution of 0.795 mL YCl_3 (1 M), 0.2 mL $YbCl_3$ (1 M) and 0.05 mL $TmCl_3$ (0.1 M) (all the rare-earth chlorides concentration 99.99%, Aladdin) was mixed with 6 mL oleic acid (OA, AR, Aladdin) and 15 mL 1-octadecene (ODE, AR, Aladdin) under persistently stirring in a 50 mL three-necked flask. Next, the mixture was heated to 160 °C to form a transparent golden yellow solution, and then cooled down to 60 °C. Afterwards, 10 mL methanol (AR, Sinopharm Chemical) stock solution that contain 0.1 g NaOH (AR, Sinopharm Chemical) and 0.148 g NH_4F (AR, Sinopharm Chemical) were added drop by drop in the flask and the solution become turbid yellow. The turbid solution was stirred at 60 °C for 20 min to guarantee all the fluorides have reacted. After that, the reaction temperature was increased to 80 °C for 20 min for thoroughly evaporate methanol, and then increased to 290 °C and maintained for 1.5 h in the flowing of the nitrogen air. After then, the mixture was cooled down rapidly to room temperature. The final product was collected by centrifugation and washed with ethanol/cyclohexane (AR, Sinopharm Chemical) several times to remove possible remnants.

2.2. Synthesis of β-$NaYF_4$:Yb^{3+}, Tm^{3+}@ TiO_2 core-shell UCNPs

β-$NaYF_4$:Yb^{3+}, Tm^{3+}@TiO_2 core-shell UCNPs were prepared according to the synthetic protocol of Li and co-workers [29]. Firstly, the surface of β-$NaYF_4$:Yb^{3+}, Tm^{3+} nanocrystals were modified by cetyltrimethyl ammonium bromide (CTAB, 90% Aladdin). Briefly, the prepared β-$NaYF_4$:Yb^{3+}, Tm^{3+} nanocrystals were dispersed in 10 mL cyclohexane to form a β-$NaYF_4$:Yb^{3+}, Tm^{3+}/cyclohexane stock solution with a concentration of 0.1 M. Then 1 mL β-$NaYF_4$:Yb^{3+}, Tm^{3+}/cyclohexane stock solution and 0.05 g CTAB were added into 20 mL ultrapure water in a flask under vigorous stirring. After sufficiently stir, cyclohexane was evaporated in a water-bath (set at 80 °C) to fully form a transparent solution. Then, the transparent solution was washed with water twice, the products of β-$NaYF_4$:Yb^{3+}, Tm^{3+}/CTAB NPs were dispersed in 10 mL isopropanol. Secondly, core-shell β-$NaYF_4$:Yb^{3+}, Tm^{3+} @TiO_2 NPs were synthesized by directly coating a TiO_2 layer on the surface of β-$NaYF_4$:Yb^{3+}, Tm^{3+}/CTAB NPs. Briefly, a 10 mL β-$NaYF_4$:Yb^{3+},

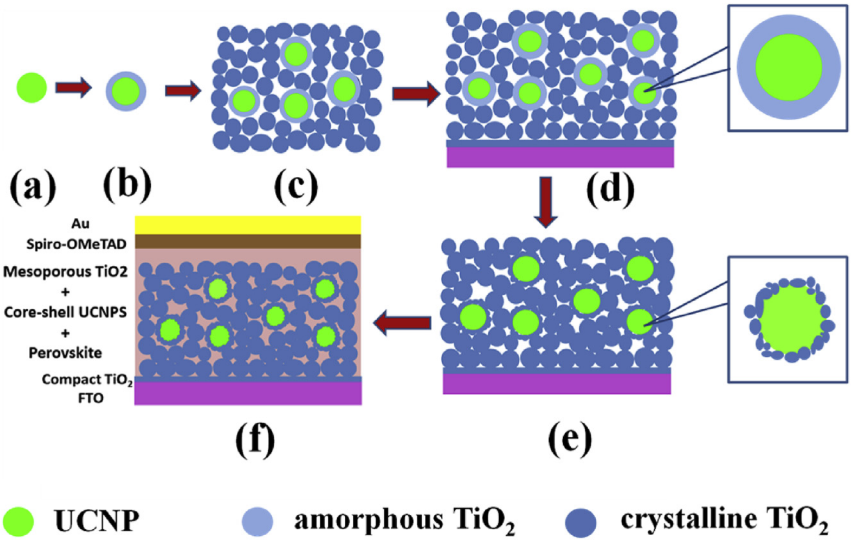

Fig. 1. (a—e) Schematic illustration of the fabrication of TiO_2 mesoporous film with $NaYF_4$:Yb^{3+}, Tm^{3+}@TiO_2 core-shell upconversion nanoparticles (UCNPs) and (f) schematic configuration of the final perovskite solar cell (PSC) device.