



The role of phosphor nanoparticles in high efficiency organic solar cells



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ABSTRACT

Phosphor materials can be applied to enhance the energy conversion efficiency of a solar cell. Such materials convert low-energy transmitted photons to higher-energy photons that can be absorbed by the cell, substantially decreasing the spectral mismatch between the cell and the solar spectrum. In this paper, the efficiency of organic solar cells (OSCs) was improved by incorporating phosphor nanoparticles as dual functionality into TiO₂ cathode buffer layer. The dependence of devices performance on doping concentration of NaYF₄:Yb³⁺,Er³⁺ nanoparticles was investigated. A high power conversion efficiency of 6.83% was achieved, which mainly attributes to the increase of short-circuit density. The absorption spectrum indicates that light-harvesting of doped films is higher than undoped film, which originates from scattering effect and NIR spectrum sensitization of phosphor nanoparticles. The measurement of electron-only devices shows that electron transport property of doped devices was apparently improved. Impedance spectroscopy reveals that the diffusion coefficient and carrier mobility were greatly enhanced. This study demonstrates that phosphor nanoparticles doping is useful for fabricating high performance OSCs.

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1. Introduction

With the emergence of the energy crisis, the development of new energy sources is urgent. In numerous possibilities, solar cells have prompted significant interest as a promising technology for renewable energy due to their potential advantages such as no-pollution, permanency and low consumption. Silicon solar cells have been put into commercial application for a few decades, but the high material cost is a main force that restrict their widespread application. Compared with their inorganic counterparts, organic solar cells (OSCs) have been the hot research topic in recent years owing to their advantages of low fabrication cost, flexibility, large-area and lightweight [1–6]. In the past few years, power conversion efficiency (PCE) of polymer-based solar cells has been rapidly improved to about 10% [7–9]. There are still some distance for the performance in terms of PCE and operational stability to approach to the key 10–10 targets (10% efficiency and 10 years of stability) [10,11]. In order to improve the efficiency of the devices, researchers have made a lot of laboratory research efforts. The device structure of OSCs is relatively mature, hence we could do some work of material design and modification to enhance device performance. TiO₂ possessing a good property of the electron

transmission, is usually employed as electron transport layer and much improvement about it are carried out. Xiong et al. used TiO₂ nanoparticles (NPs) as cathode buffer layer to improve the efficiency and stability of inverted OSCs [12]. In addition, some functional materials were doped into TiO₂ buffer layer, such as metal NPs and some rare earth ions [13–20].

NaYF₄:Yb³⁺,Er³⁺ NPs had been doped into active layer of solar cell and demonstrated a good effect for the performance improvement of OSCs especially the enhancement of short-circuit current density (J_{sc}) [21–25]. It could convert two or more low energy photons into one higher energy photon, which is a luminescence process named up-conversion (UC) effect. About 52% of the total solar energy flux is in IR and NIR range, so it is essential to further exploit the IR and NIR spectra fighting for a better enhancement of OSCs efficiency. Integration of UC effect in solar cells is a smart concept to utilize the solar spectra of NIR region, which will enhance the response of solar cells in NIR region. At the same time, the additive of NPs could also effectively improve charge transport property [26,27]. In this study, NaYF₄:Yb³⁺,Er³⁺ NPs synthesized by a facile approach were incorporated into TiO₂ cathode buffer layer. The synthesis of TiO₂ solution was described in some reference [28,29]. The active layer materials are determined as poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT) and [6,6]-phenyl C₇₁-butyric acid methyl ester (PC₇₁BM), which is one of the most popular composites used in OSCs as well as MoO₃

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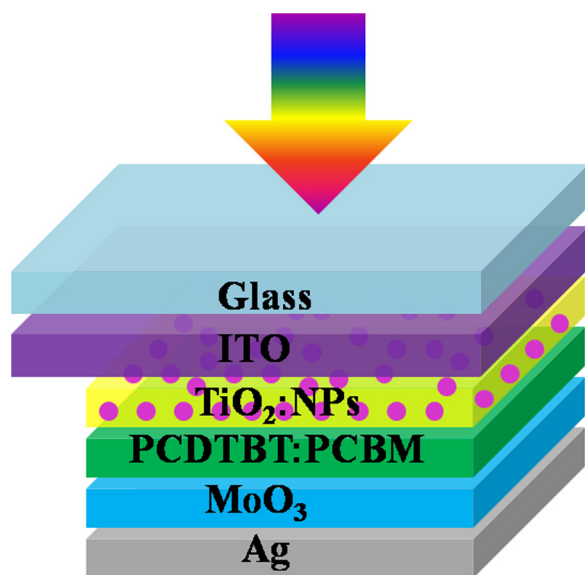


Fig. 1. The device structure of the inverted polymer solar cells.

Table 1

Device performance, including open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE), dependent on the different doping concentration of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
A	0.87 ± 0.01	12.86 ± 0.02	49.16 ± 0.12	5.50 ± 0.12
B	0.87 ± 0.02	14.49 ± 0.01	50.13 ± 0.31	6.32 ± 0.14
C	0.87 ± 0.01	14.75 ± 0.03	53.64 ± 0.21	6.83 ± 0.04
D	0.87 ± 0.02	14.01 ± 0.04	50.74 ± 0.20	6.20 ± 0.11
E	0.87 ± 0.01	13.59 ± 0.01	49.80 ± 0.17	5.88 ± 0.13

was chosen as hole transport material. The $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs in TiO_2 cathode buffer layer could contribute to enhance the light trapping of active layer thereby improve the efficiency of OSCs in theory, so exploring the feasibility of this solution and researching the role of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs playing in our devices are instant.

2. Experimental

For the preparation of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs, the initial chemicals, including $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$, NaOH , NH_4F , 1-octadecene (ODE) and oleic acid (OA) were used without further purification. In a typical procedure for the synthesis of

$\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$, 1 mmol $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$ ($\text{RE} = \text{Y}, \text{Yb}, \text{Er}$) was added to a 100 mL three-neck round-bottom flask containing a certain amount of ODE and OA. The solution was magnetically stirred and heated to 150°C for 30 min to remove residual water and oxygen. Then, the temperature was cooled down to room temperature with a gentle flow of argon gas through the reaction flask. Meanwhile, a solution of NH_4F and NaOH dissolved in methanol was added, and then the temperature was increased to 50°C . After methanol was evaporated, the reaction mixture was heated to 300°C in an argon atmosphere, kept for 60 min and then naturally cooled to room temperature. The resultant products were precipitated by the addition of ethanol, collected by centrifugation, washed with ethanol three times, and finally redispersed in methylbenzene for further experiments.

The device structure was indium tin oxide (ITO)/nano-crystal titanium dioxide: $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}/\text{PCDTBT}:\text{PC}_{71}\text{BM}/\text{molybdenum oxide} (\text{MoO}_3)/\text{silver} (\text{Ag})$, which is shown in Fig. 1. Detailed process of devices preparation just likes the previous description [30,31]. TiO_2 doping with different concentration of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs was spin-cast on top of the pre-cleaned ITO substrate at 3000 rpm for 18 s then annealed at 450°C for 2 h in the muffle furnace and cooled by nature. The TiO_2 films with and without $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ doping were measured by spectroscopic ellipsometry, and the thicknesses are all about 25 nm. The OSCs with 0, 0.04 mmol mL^{-1} , 0.05 mmol mL^{-1} , 0.067 mmol mL^{-1} , and 0.1 mmol mL^{-1} $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ are named as Device A, Device B, Device C, Device D and Device E, respectively. The $\text{PCDTBT}:\text{PC}_{71}\text{BM}$ (1:4 by weight) active layer was prepared by spin-coating with 1,2-dichlorobenzene (DCB) solution at 2000 rpm. Subsequently, the devices were completed by thermal evaporation of MoO_3 and Ag electrode with the thickness of 10 nm and 100 nm, respectively. The current density–voltage (J – V) characteristics were measured with a computer-programmed Keithley 2400 source/meter under AM 1.5G solar illuminations with an Oriel 300 W solar simulator intensity of $\sim 100 \text{ mW cm}^{-2}$ in air without encapsulation. The incident photon-to-current efficiency (IPCE) was measured with Crowntech QTest Station 1000 AD. The light absorption spectra were measured by means of ultraviolet/visible spectrometer (UV 1700, Shimadzu). The impedance was analyzed by a Precision Impedance Analyzer 6500B Series of Wayne Kerr Electronics.

3. Results and discussion

The cells parameters including short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and PCE are deduced from the J – V characteristics and summarized in Table 1, and all values are typically average of 50 devices. Fig. 2(a) presents J – V

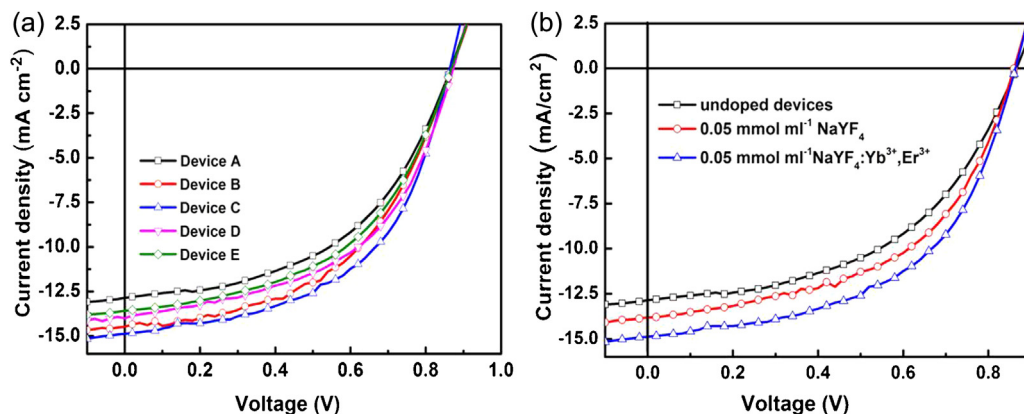


Fig. 2. (a) J – V characteristics of devices doping with various concentrations of $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs at 100 mW cm^{-2} , (b) J – V comparison of cells with only $\text{PCDTBT}:\text{PC}_{71}\text{BM}$, NaYF_4 NPs doping, and $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$ NPs doping.

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