## PCCP

## PAPER



View Article Online View Journal | View Issue

Cite this: Phys. Chem. Chem. Phys., 2014, 16, 9289

Received 19th March 2014, Accepted 2nd April 2014

DOI: 10.1039/c4cp01184h

www.rsc.org/pccp

## Introduction

Among the green energies, solar power is one of the most sustainable energies due to its abundance and renewability. At present, the best commercial solar cells based on single-crystal silicon have an efficiency of only 18%.<sup>1</sup> Such a low efficiency is caused by the spectrum mismatch between the solar spectrum and the response spectrum of silicon solar cells.<sup>2,3</sup> The solar spectrum spectral distribution covers from 300 nm to 2500 nm.<sup>4</sup> However, the available absorption band is around 500-1100 nm for the silicon solar cell.<sup>5,6</sup> For wavelengths shorter than 500 nm, the external quantum efficiency of silicon solar cells decreases significantly due to higher reflection and absorption by the antireflection coatings optimized for longer wavelength and due to increased emitter recombination caused by the high P-doping levels. Meanwhile, for wavelengths longer than 1100 nm, the excess energy is lost as heat to cause the excessive heating of conduction band electrons. Thus it can be seen that the current silicon solar cells only utilize a relatively small fraction of the solar spectrum. In order to increase the efficiency of silicon solar cells, the range of the available

# The energy transfer mechanism in $Pr^{3+}$ and $Yb^{3+}$ codoped $\beta$ -NaLuF<sub>4</sub> nanocrystals

Guotao Xiang,<sup>ab</sup> Jiahua Zhang,\*<sup>a</sup> Zhendong Hao,<sup>a</sup> Xia Zhang,<sup>a</sup> Guohui Pan,<sup>a</sup> Yongshi Luo,<sup>a</sup> Shaozhe Lü<sup>a</sup> and Haifeng Zhao<sup>a</sup>

The  $Pr^{3+}$  and  $Yb^{3+}$  codoped  $\beta$ -NaLuF<sub>4</sub> hexagonal nanoplates with a size of 250 nm × 110 nm were synthesized by a solvothermal process. X-Ray diffraction and scanning electron microscopy were used to characterize the crystal structure and morphology of the materials. The visible and near infrared spectra as well as the decay curves of  $Pr^{3+}$ :  ${}^{3}P_{0}$  level were used to demonstrate the energy transfer from  $Pr^{3+}$  ions to  $Yb^{3+}$  ions. The downconversion phenomenon has been observed under the direct excitation of the  ${}^{3}P_{2}$  level of  $Pr^{3+}$ . According to the analysis of the dependence of the initial transfer rate upon  $Yb^{3+}$  ion concentration, it indicates that the ET from  $Pr^{3+}$  ions to  $Yb^{3+}$  ions is only by a two-step ET process when the  $Yb^{3+}$  concentration is very low; however, with the increase of the  $Yb^{3+}$  concentration, a cooperative ET process occurs and gradually increases; when the  $Yb^{3+}$  ion concentration increases to 20 mol%, the ET from  $Pr^{3+}$  ions to  $Yb^{3+}$  ions occurs only by the cooperative ET process. When the doping concentration of  $Yb^{3+}$  ions reaches 20 mol% at a fixed concentration of  $Pr^{3+}$  ions (1 mol%), the theoretical quantum efficiency is 192.2%, close to the limit of 200%. The current research has great potential in improving the conversion efficiency of silicon solar cells.

> wavelength for silicon solar cells should be widened to reduce the spectral mismatch losses. Downconversion (DC) is considered as a promising method to solve the problem. Through the DC process, a high energy photon with a wavelength shorter than 500 nm can be divided into two or more low energy photons with the wavelength available for absorption of silicon solar cells.<sup>7</sup>

> Recently, trivalent rare earth ion doped fluoride DC nanoparticles have attracted more and more attention. DC has been realized with  $\mathrm{Er^{3^+/Yb^{3^+}}, \mathrm{Pr^{3^+/Yb^{3^+}}, \mathrm{Ce^{3^+/Yb^{3^+}}, \mathrm{Tb^{3^+/Yb^{3^+}}}}$  and  $\mathrm{Ho^{3^+/}}$ Yb<sup>3+</sup> couples to convert visible photons into near-infrared (NIR) photons.<sup>8-12</sup> It is interesting that Yb<sup>3+</sup> is chosen as an acceptor in almost all of the DC couples. This is because the Yb<sup>3+</sup> ion has an only excited state approximately 10 000 cm<sup>-1</sup> just above the band edge of crystalline silicon. Nowadays, the luminescence properties of Pr<sup>3+</sup> doped phosphors are of considerable interest because of its special energy configuration and the energy match between  $\mathrm{Pr^{3^+}}$  and Yb<sup>3+</sup>. Zhang *et al.* have reported the excellent DC luminescence properties of  $\beta$ -NaYF<sub>4</sub>:  $\mathrm{Pr^{3^+}}, \mathrm{Yb^{3^+}}$  microcrystal with a maximum quantum efficiency of 181.6%.<sup>13</sup>

> β-NaLuF<sub>4</sub> is an efficient UC host material with the same crystalline phase as β-NaYF<sub>4</sub>. Recently, Qin *et al.* have found that β-NaLuF<sub>4</sub> is an excellent host for phosphors with efficient UC luminescence properties.<sup>14</sup> But beyond that, it also shows good performance in DC, as reported for the bright green emitting β-NaLuF<sub>4</sub>: Tb<sup>3+</sup>, β-NaLuF<sub>4</sub>: Ce<sup>3+</sup>/Tb<sup>3+</sup> and NIR emitting β-NaLuF<sub>4</sub>: Er<sup>3+</sup>, Yb<sup>3+</sup> with high quantum efficiency.<sup>15,16</sup>

<sup>&</sup>lt;sup>a</sup> State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, Jilin, China. E-mail: zhangjh@ciomp.ac.cn; Fax: +86-431-8617-6317; Tel: +86-431-8617-6317

<sup>&</sup>lt;sup>b</sup> Graduate School of Chinese Academy of Sciences, Beijing, 100039, China

#### Paper

In the current work, we present the efficient NIR DC in  $\beta$ -NaLuF<sub>4</sub>: Pr<sup>3+</sup>/Yb<sup>3+</sup> nanocrystals (NCs) which, as far as we know, have not been reported before. The dependences of Yb<sup>3+</sup> concentration on the visible and NIR emission spectra, decay time, and energy transfer (ET) efficiency have been investigated in detail. The mechanism of the DC process has been discussed. Results show that  $\beta$ -NaLuF<sub>4</sub> NCs are excellent hosts for DC and promising materials for application in solar cells.

## Experimental

#### Chemicals

NaOH, NH<sub>4</sub>F, HCl, methanol and ethanol were obtained from Beijing Chemical Reagent Company. Hexane was obtained from Tianjin Guangfu Chemical Reagent Company. Lanthanide (Ln) oxides of SpecPure grade (Yb<sub>2</sub>O<sub>3</sub>, Pr<sub>6</sub>O<sub>11</sub>, Lu<sub>2</sub>O<sub>3</sub>, 99.99%), were purchased from Yangkou state-run rare earth company. 1-Octadecene (ODE, 90%) and oleic acid (OA, 90%) were supplied by Alfa Aesar. All of the chemical reagents were used as received without further purification. LnCl<sub>3</sub> was prepared by dissolving the corresponding lanthanide oxides in hydrochloric acid at an elevated temperature followed by evaporating the water under vacuum conditions.

#### Preparation of β-NaLuF<sub>4</sub> NCs

All of the doping ratios of Ln<sup>3+</sup> are molar in our experiments. In a typical procedure for the synthesis of  $\beta$ -NaLuF<sub>4</sub>: 1% Pr<sup>3+</sup>/x%  $Yb^{3+}$  (x = 0, 1, 5, 10, 20), 1 mmol RECl<sub>3</sub> were added to a 100 mL three-neck round-bottom flask containing ODE (15 mL) and OA (6 mL). The solution was magnetically stirred and heated to 140 °C for 30 min to form the lanthanide oleate complexes and remove residual water and oxygen. The temperature was then cooled to 50 °C with a gentle flow of argon gas through the reaction flask. Meanwhile, a solution of NH<sub>4</sub>F (4 mmol) and NaOH (2.5 mmol) dissolved in methanol (10 mL) was added to the flask and the resulting mixture was stirred for 30 min to evaporate methanol from the reaction mixture. The temperature was then increased to 300 °C in an argon atmosphere for 90 min and then naturally cooled to room temperature. The resultant solid state products were precipitated by the addition of ethanol, collected by centrifugation, washed with ethanol three times, and finally redispersed in cyclohexane.

#### Characterization

Powder X-ray diffraction (XRD) data were collected using Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å) on a Bruker D8 advance diffractometer equipped with a linear position-sensitive detector (PSD-50 m, M. Braun), operating at 40 kV and 40 mA with a step size of  $0.01^{\circ}$  ( $2\theta$ ) in the range of  $10^{\circ}$ – $70^{\circ}$ . The morphology was investigated using field emission scanning electron microscopy (SEM) (Hitachi S-4800). The excitation and emission spectra were measured using a FLS920 spectrometer (Edinburgh Instruments, U.K.). In fluorescence lifetime measurements, an optical parametric oscillator (OPO) was used as an excitation

source, and the signals were detected using a Tektronix digital oscilloscope (TDS 3052). The lifetimes were calculated by integrating the area under the corresponding lifetime curves with the normalized initial intensity.

### Results and discussion

The crystal structures and the phase purity of the as-prepared products were examined by XRD, as shown in Fig. 1(a). The positions and relative intensity of the diffraction peaks for  $\beta$ -NaLuF<sub>4</sub>: 1% Pr<sup>3+</sup>/x% Yb<sup>3+</sup> (x = 0, 1, 5, 10, 20) can be indexed well to the standard cards of the  $\beta$ -NaLuF<sub>4</sub> (JCPDS 27-0726). No second phase is detected in all XRD patterns, demonstrating that Pr<sup>3+</sup> and Yb<sup>3+</sup> substitutions for Lu<sup>3+</sup> sites have no effect on the phase structure of the  $\beta$ -NaLuF<sub>4</sub> host. SEM was used to evaluate the morphology of the prepared NCs. Fig. 1(b–f) shows the SEM images of  $\beta$ -NaLuF<sub>4</sub>: 1% Pr<sup>3+</sup>/x% Yb<sup>3+</sup> NCs. The samples doped with different concentrations of Yb<sup>3+</sup> ions exhibit the same morphology, displaying uniform hexagonal nanoplates with a size of 250 nm  $\times$  110 nm.

In order to investigate the DC properties of  $Pr^{3+}$  and  $Yb^{3+}$  codoped  $\beta$ -NaLuF<sub>4</sub> NCs, the excitation and emission spectra of the samples, which are the direct evidence of  $Pr^{3+} \rightarrow Yb^{3+}$  ET, were measured and are shown in Fig. 2 and 3, respectively. For monitoring  $Pr^{3+}:{}^{3}P_{0} \rightarrow {}^{3}H_{6}$  at 608 nm, the excitation spectrum consists of three bands centered at 443 nm, 467 nm and 482 nm, which are assigned to  $Pr^{3+}:{}^{3}H_{4} \rightarrow {}^{3}P_{2}$ ,  ${}^{3}H_{4} \rightarrow {}^{3}P_{1}$ ,  ${}^{1}I_{6}$  and  ${}^{3}H_{4} \rightarrow {}^{3}P_{0}$ , respectively. While, the three excitation bands of  $Pr^{3+}$  ions are also observed by monitoring  $Yb^{3+}:{}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$ .



**Fig. 1** (a) The standard XRD data of  $\beta$ -NaLuF<sub>4</sub> (JCPDS 27-0726) and the XRD patterns of the samples doped with different concentrations of Yb<sup>3+</sup>. The SEM images of  $\beta$ -NaLuF<sub>4</sub>: 1% Pr<sup>3+</sup>/x% Yb<sup>3+</sup> NCs: (b) x = 0, (c) x = 1, (d) x = 5, (e) x = 10 and (f) x = 20.



Fig. 2 Excitation spectra of  $Pr^{3+:3}P_0 \rightarrow {}^{3}H_6$  emission (608 nm, black line) and  $Yb^{3+:2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  emission (985 nm, red line) in  $\beta$ -NaLuF<sub>4</sub>: 1%  $Pr^{3+}/5\%$  Yb<sup>3+</sup> NCs.



Fig. 3 Visible and NIR emission spectra of the samples doped with various concentrations of  $Yb^{3+}$  under 443 nm excitation.

infrared emissions at 985 nm, which indicates the presence of ET from  $Pr^{3+}$  to  $Yb^{3+}$ .

The emission spectra covering the visible and near infrared spectral range for samples with a fixed  $Pr^{3+}$  concentration at 1 mol% and various concentrations of  $Yb^{3+}$  are presented under 443 nm excitation corresponding to  $Pr^{3+}:{}^{3}H_{4} \rightarrow {}^{3}P_{2}$  transition. For the range from 600 nm to 650 nm, the spectra exhibit two emissions peaked around 608 nm and 640 nm, which are assigned to the  ${}^{3}P_{0} \rightarrow {}^{3}H_{6}$  transition and  ${}^{3}P_{0} \rightarrow {}^{3}F_{2}$  transition of  $Pr^{3+}$ , respectively. In the NIR region, a strong emission band around 985 nm is observed for the  $Pr^{3+}$  and  $Yb^{3+}$  codoped samples, which is assigned to  $Yb^{3+}:^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition. The phenomenon of NIR emission of  $Yb^{3+}$  under the direct excitation of the  ${}^{3}P_{2}$  level of  $Pr^{3+}$  is another evidence for ET from  $Pr^{3+}$  to  $Yb^{3+}$ .

It is noticed that the intensity of the  ${}^{3}P_{0} \rightarrow {}^{3}H_{6}$  transition and  ${}^{3}P_{0} \rightarrow {}^{3}F_{2}$  transition of  $Pr^{3+}$  is reduced with the increased Yb<sup>3+</sup> ion concentration. In the meantime, the intensity of the NIR



Fig. 4 Schematic energy level diagram of  $Pr^{3+}$  and  $Yb^{3+}$  with the involved ET process.

emission of Yb<sup>3+</sup> is firstly increased and then decreased when the Yb<sup>3+</sup> concentration over 5%. It is also a proof of ET from Pr<sup>3+</sup> to Yb<sup>3+</sup>. Additionally, the obvious decrease of the NIR emission intensity when the Yb<sup>3+</sup> concentration reaches 10 mol% is due to the concentration quenching. In the present material, 5 mol% represents the optimal Yb<sup>3+</sup> doped concentration.

To understand the DC mechanism more clearly, the schematic energy level diagram with the involved ET process is depicted in Fig. 4. Upon excitation by 443 nm wavelength, the Pr3+ ion in the ground state  ${}^{3}H_{4}$  is excited to the  ${}^{3}P_{2}$  level. From the  ${}^{3}P_{2}$ level the ion relaxes to the  ${}^{3}P_{0}$  level by nonradiative relaxation processes induced by the narrow energy gap between the  ${}^{3}P_{2}$  and  ${}^{3}P_{0}$  multiplets. The  $Pr^{3+}:{}^{3}H_{4} \rightarrow {}^{3}P_{0}$  transition is located at approximately twice the energy of the Yb<sup>3+</sup>:  ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition and the  $Pr^{3+} : {}^{3}H_{4} \rightarrow {}^{1}G_{4}$  transition is located at approximately the same position of the energy of the  $Yb^{3+}:^2F_{5/2} \rightarrow {}^2F_{7/2}$  transition. In addition, Yb<sup>3+</sup> has no other levels up to the UV region. Thus, the ET from the  $Pr^{3+}$  ion in the  ${}^{3}P_{0}$  level to  $Yb^{3+}$  ions has two possible routes: (1) two-step ET, as shown in Fig. 4(a): the first ET step involves the transfer of energy of the Pr<sup>3+</sup> ion in the <sup>3</sup>P<sub>0</sub> level to one  $Yb^{3+}$  ion through cross relaxation  $[{}^{3}P_{0} (Pr^{3+}) + {}^{2}F_{7/2} (Yb^{3+}) \rightarrow {}^{1}G_{4-}$  $(Pr^{3+}) + {}^{2}F_{5/2} (Yb^{3+})]$ ; next, the second ET step involves the deexcitation of the Pr<sup>3+</sup> ion in the <sup>1</sup>G<sub>4</sub> level to the ground state which then transfers its energy to another  $Yb^{3+}$  ion  $[{}^{1}G_{4}(Pr^{3+}) + {}^{2}F_{7/2}(Yb^{3+})$ →  ${}^{3}H_{4}(Pr^{3+}) + {}^{2}F_{5/2}(Yb^{3+})]$ . (2) Cooperative ET, as shown in Fig. 4(b): the  $Pr^{3+}$  ion in the  ${}^{3}P_{0}$  level transfers its energy to two  $Yb^{3+}$  ions simultaneously and then the Yb<sup>3+</sup> ions are excited to the  ${}^{2}F_{5/2}$  level.

To judge the process of the ET from  $Pr^{3+}$  ions to  $Yb^{3+}$  ions, we analyzed the dependence of the initial transfer rate upon  $Yb^{3+}$  ion concentration. For the first step of the two-step ET process, the  $Pr^{3+}$  ion in the  ${}^{3}P_{0}$  level transfers its energy to only one  $Yb^{3+}$  ion. Thus the transfer rate from a donor  $(Pr^{3+})$  at site 0 to an acceptor  $(Yb^{3+})$  at site *i* in the surroundings  $(i \neq 0)$  can be written as

$$X_{0i} = x f(R_{0i}) X_0.$$
(1)

Here *x* is the concentration of the acceptor and thus the probability of an acceptor at site *i* is *x*;  $f(R_{0i})$  is a function of the distance,  $R_{0i}$  is the distance from the donor at site 0 to the acceptor at site *i*;  $X_0$  is the radiative decay rate of the <sup>3</sup>P<sub>0</sub> state of Pr<sup>3+</sup> in β-NaLuF<sub>4</sub>. Consequently, for all Yb<sup>3+</sup> neighbors at distances  $R_{0i}$ , the initial transfer rate can be taken as

$$\langle X_0 \rangle_{\rm CR} = X \sum_i f(R_{0i}) X_0. \tag{2}$$

This leads to

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$$\langle X_0 \rangle_{\rm CR} \propto x.$$
 (3)

For the cooperative ET, the donor transfers its energy simultaneously to two acceptors adjacent to itself at site *i* and j(i < j) respectively. Refer to eqn (1), then the transfer rate from the donor to a pair (i, j) of acceptors is

$$X_0(i,j) = x^2 f(R_{0i}) f(R_{0j}) X_0^2.$$
(4)

For all the pairs (i, j) of acceptors, the initial transfer rate is

$$\langle X_0 \rangle_{\text{COOP}} = x^2 \sum_{i < j} f(R_{0i}) f(R_{0j}) X_0^2.$$
(5)

This leads to

$$\langle X_0 \rangle_{\text{COOP}} \propto x^2.$$
 (6)

So it can be concluded that eqn (3) approximately fits for the two-step ET process and eqn (6) approximately fits for the cooperative ET process.

At present, we need to get the values of the initial transfer rate. Fig. 5 shows the decay curves of  $Pr^{3+}$ :  ${}^{3}P_{0}$  level in the initial period of 8  $\mu$ s. The initial transfer rates were obtained by the slopes of the curves from the maximum intensity to 70% of the maximum intensity. To be specific, the initial transfer rates equal the slopes of the curves of  $Pr^{3+}$  and  $Yb^{3+}$  codoped samples minus the slope of the curve of  $Pr^{3+}$  singly doped sample. In this way, we obtained the  $Yb^{3+}$  ion concentration dependence of the initial transfer rates and plotted in a double logarithmic



Fig. 6 Plot (log-log) of the initial transfer rate *versus* the Yb<sup>3+</sup> concentration in  $\beta$ -NaLuF<sub>4</sub>: 1% Pr<sup>3+</sup>/x% Yb<sup>3+</sup> NCs.

diagram, as shown in Fig. 6. When the concentration of Yb<sup>3+</sup> ions changes from 1 mol% to 10 mol%, the slope  $n_1$  value is 1.3, indicating that the two-step ET process and the cooperative ET process coexist simultaneously but the two-step ET process is dominant. When the concentration of Yb<sup>3+</sup> ions increases to 20 mol%, the slope  $n_2$  value is 2, indicating that the ET from Pr<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the cooperative ET process. On the basis of above data and analysis, we propose that the ET from Pr<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the two-step ET process when the Yb<sup>3+</sup> concentration is very low; however, with the increase of the Yb<sup>3+</sup> concentration, the cooperative ET process occurs and gradually increases; when the Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the State of Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the two-step ET process occurs and gradually increases; when the Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the State of Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the State of Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the State of Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the state of Yb<sup>3+</sup> ions is only by the two-step ET process occurs and gradually increases; when the Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the State of Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions to Yb<sup>3+</sup> ions is only by the cooperative ET process.

Fig. 7 shows the decay curves of  $Pr^{3+}:^{3}P_{0}$  level in β-NaLuF<sub>4</sub>: 1%  $Pr^{3+}/x$ %  $Yb^{3+}$  (x = 0, 1, 5, 10, 20) NCs. With increasing  $Yb^{3+}$  concentration, the decay of the  ${}^{3}P_{0}$  level of  $Pr^{3+}$  rapidly speeds up, which can be explained by the existence of extra decay



Fig. 5 Decay curves of  $Pr^{3+}$ :<sup>3</sup> $P_0$  level in the initial period of 8  $\mu$ s in  $\beta$ -NaLuF<sub>4</sub>: 1%  $Pr^{3+}/x$ % Yb<sup>3+</sup> NCs under 482 nm excitation.



**Fig. 7** Decay curves of  $Pr^{3+,3}P_0$  level in  $\beta$ -NaLuF<sub>4</sub>: 1%  $Pr^{3+}/x$ %  $Yb^{3+}$  NCs ( $\lambda_{EX}$  = 482 nm,  $\lambda_{EM}$  = 608 nm). Inset, decay time and  $\eta_{ETE}$  as functions of  $Yb^{3+}$  concentration.

pathways due to the Yb<sup>3+</sup> doping: ET from the <sup>3</sup>P<sub>0</sub> level of Pr<sup>3+</sup> to the <sup>2</sup>F<sub>5/2</sub> level of Yb<sup>3+</sup> accelerates the decay rate of the <sup>3</sup>P<sub>0</sub> level of Pr<sup>3+</sup>. All decay curves exhibit nonexponential characteristics. For the Pr<sup>3+</sup> singly doped sample, it is due to cross relaxation between Pr<sup>3+</sup> ions. For the Pr<sup>3+</sup> and Yb<sup>3+</sup> codoped samples, it is attributed to the variation in distribution of Yb<sup>3+</sup> ions around the Pr<sup>3+</sup> ion, leading to a variety of ET rates.

The decay time  $\tau$  is calculated by

$$\tau = \int_0^t \frac{I(t)}{I(0)} \mathrm{d}t,\tag{7}$$

where I(t) is the luminescence intensity as a function of time t and I(0) represents the initial intensity at t = 0. The energy transfer efficiency ( $\eta_{\text{ETE}}$ ) and theoretical quantum efficiency ( $\eta_{\text{TQE}}$ ) can be determined from decay curves. The  $\eta_{\text{ETE}}$  is defined as the ratio of  $\text{Pr}^{3+}$  depopulated by ET to  $\text{Yb}^{3+}$  over the total number of the  $\text{Pr}^{3+}$  excited. By dividing the integrated intensity of the decay curve of  $\text{Pr}^{3+}$  and the  $\text{Yb}^{3+}$  codoped sample by that of the  $\text{Pr}^{3+}$  single doped one, the  $\eta_{\text{ETE}}$  is obtained as a function of  $\text{Yb}^{3+}$  concentration

$$\eta_{\text{ETE},x\%\text{Yb}} = 1 - \frac{\tau_{x\%\text{Yb}}}{\tau_0},\tag{8}$$

where  $\tau_{x\%Yb}$  represents the decay time of  $Pr^{3+}:^{3}P_{0}$  level with various concentrations of Yb<sup>3+</sup>. For the samples doped with  $x \mod Yb^{3+}$  ions (x = 1, 5, 10), the ET from  $Pr^{3+}$  ions to Yb<sup>3+</sup> ions occurs in two ways (the two-step ET process and the cooperative ET process) and the proportion of the two processes cannot be obtained, so the theoretical quantum efficiency cannot be calculated. However, for the sample doped with 20 mol% Yb<sup>3+</sup> ions, the ET from  $Pr^{3+}$  ions to Yb<sup>3+</sup> ions occurs only by the cooperative ET process. That is to say, in the sample doped with 20 mol% Yb<sup>3+</sup> ions, two infrared photons (around 985 nm) are emitted by Yb<sup>3+</sup> ions per absorbed one blue photon (around 482 nm) by Pr<sup>3+</sup> ions in theory. The  $\eta_{TQE}$  of this sample, defined as the ratio of the number of photons emitted to the number of photons that are absorbed, can be obtained as

$$\eta_{\text{TQE},x\%\text{Yb}} = \eta_{\text{Pr}} (1 - \eta_{\text{ETE},x\%\text{Yb}}) + 2\eta_{\text{Yb}} (\eta_{\text{ETE},x\%\text{Yb}}),$$
(9)

where  $\eta_{Pr}$  and  $\eta_{Yb}$  represent the quantum efficiencies of  $Pr^{3+}$ and  $Yb^{3+}$  ions, respectively.<sup>17</sup> They are set to 1, assuming that all excited ions decay radiatively.<sup>18</sup> This assumption leads to an upper limit of the quantum efficiency. The  $\tau$  and  $\eta_{ETE}$  are listed in the inset of Fig. 7 according to the formulas mentioned above. With the increase of  $Yb^{3+}$  concentration from 1% to 20%, the  $\eta_{ETE}$  increases obviously from 16.4% to 92.2%. For the  $\beta$ -NaLuF<sub>4</sub>: 1%  $Pr^{3+}/20\%$   $Yb^{3+}$  NCs,  $\eta_{TQE}$  reaches 192.2%, close to the limit of 200%.

## Conclusions

In summary, we conclude that an efficient NIR DC in  $\beta$ -NaLuF<sub>4</sub>: Pr<sup>3+</sup>/Yb<sup>3+</sup> NC has been demonstrated and the mechanism of the DC process has been investigated carefully. On the basis of the analysis of the dependence of the initial transfer rate upon Yb<sup>3+</sup> ion concentration, we propose that the ET from  $Pr^{3+}$  ions to  $Yb^{3+}$  ions occurs only by the two-step ET process when the  $Yb^{3+}$  concentration is very low; however, with the increase of the  $Yb^{3+}$  concentration, the cooperative ET process occurs and gradually increases; when the  $Yb^{3+}$  ion concentration increases to 20 mol%, the ET from  $Pr^{3+}$  ions to  $Yb^{3+}$  ions occurs only by the cooperative ET process. For the  $\beta$ -NaLuF<sub>4</sub>: 1%  $Pr^{3+}/20\%$   $Yb^{3+}$  NCs, the theoretical quantum efficiency ( $\eta_{TQE}$ ) reaches 192.2%, close to the limit of 200%. The current experiment results indicate that  $\beta$ -NaLuF<sub>4</sub>:  $Pr^{3+}/Yb^{3+}$  NCs are promising DC materials for application in solar cells.

## Acknowledgements

This work is financially supported by the National Natural Science Foundation of China (51172226, 61275055, 11274007, 11174278) and the Natural Science Foundation of Jilin province (201205024, 20140101169JC).

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