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Dual functions of $\text{YF}_3\text{:Eu}^{3+}$ for improving photovoltaic performance of dye-sensitized solar cells

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In order to enhance the photovoltaic performance of dye-sensitized solar cell (DSSC), a novel design is demonstrated by introducing rare-earth compound europium ion doped yttrium fluoride ($\text{YF}_3\text{:Eu}^{3+}$) in TiO_2 film in the DSSC. As a conversion luminescence medium, $\text{YF}_3\text{:Eu}^{3+}$ transfers ultraviolet light to visible light via down-conversion, and increases incident harvest and photocurrent of DSSC. As a p-type dopant, Eu^{3+} elevates the Fermi level of TiO_2 film and thus heightens photovoltage of the DSSC. The conversion luminescence and p-type doping effect are demonstrated by photoluminescence spectra and Mott-Schottky plots. When the ratio of $\text{YF}_3\text{:Eu}^{3+}/\text{TiO}_2$ in the doping layer is optimized as 5 wt.%, the light-to-electric energy conversion efficiency of the DSSC reaches 7.74%, which is increased by 32% compared to that of the DSSC without $\text{YF}_3\text{:Eu}^{3+}$ doping. Double functions of doped rare-earth compound provide a new route for enhancing the photovoltaic performance of solar cells.

Solar energy has been considered as a green and renewable alternative energy source to traditional fossil fuels¹. Since the prototype of a dye-sensitized solar cell (DSSC) was reported in 1991 by Grätzel², it has aroused intensive interest and become one of hotspots in solar energy field because of its ease of fabrication and cost-effectiveness compared with silicon-based photovoltaic devices^{3,4}. Recently, some important progresses are achieved^{5–10}. However, the efficiencies of the DSSCs are lower than that of Si solar cells, which restrict DSSC's potential application. An effective method for enhancing the efficiency is broadening the absorption range of the DSSC. Consequently, many metal complexes dyes have been synthesized. But even the best of these (N-719, N-749, YD2-o-C8) only absorb visible light in the wavelength range of 400–800 nm^{3,4}, and most of the solar ultraviolet and infrared irradiations are not utilized. Recently, the researches on the energy relay dyes (ERDs) via Forster resonant to broaden the absorption domain and thus increase the photocurrent have been done^{11,12}. Another alternative route for widening absorption range is the conversion luminescence by doping rare-earth compounds. On the other hand, rare-earth ions are +3 value cations, when they are doped into TiO_2 semiconductor, a p-type doping effect occurs^{13,14}, which results in the elevation of Fermi level of the photoanode, and turns to the enhancement of the photovoltage of the DSSC. The introduction of doped rare-earth compound not only increases the photocurrent via conversion luminescence, but also improves the photovoltage by p-type doping effect, this double functions is very significant for enhancing the photovoltaic performance of the DSSC. Unfortunately, little significant research on conversion luminescence and/or p-type doping effect by rare-earth ions in the DSSC has been attempted^{15–17}.

Results

Phase analysis of $\text{YF}_3\text{:Eu}^{3+}$. The $\text{YF}_3\text{:Eu}^{3+}$ was prepared by hydrothermal method¹⁸. The X-ray diffraction (XRD) pattern of prepared $\text{YF}_3\text{:Eu}^{3+}$ is shown in Fig. 1. All diffraction peaks of the prepared sample are readily indexed as orthorhombic phase of YF_3 and are consistent with the standard pattern (JCPDS 74-0911). This indicates the formation of the orthorhombic phase of YF_3 . Furthermore, no EuF_3 phases are observed, this is because that in the preparation Y_2O_3 and Eu_2O_3 are completely dissolved and mixed (see method section), Eu^{3+} amount in YF_3 mixed solution is small (2.0 mol.%) as well as Y^{3+} and Eu^{3+} ions have similar electronic structures (s^2p^6) and radii (0.90 Å and 0.95 Å), therefore, Eu^{3+} ions occupy the lattice sites of Y^{3+} ions.

Figure 1 | XRD patterns of $\text{YF}_3:\text{Eu}^{3+}$.

Photoluminescence properties of $\text{YF}_3:\text{Eu}^{3+}$. The excitation spectrum of $\text{YF}_3:\text{Eu}^{3+}$ (emission at 592 nm) is shown in Fig. 2a. The excitation spectrum of $\text{YF}_3:\text{Eu}^{3+}$ consists of a number of line peaks in the range of 318–475 nm, and a main peak appears at 393 nm. The typical line peaks located at 318, 361, 383, 393 and 464 nm are related to the 4f electronic transitions of Eu^{3+} ions: ${}^7\text{F}_0 \rightarrow {}^5\text{H}_6$, ${}^7\text{F}_0 \rightarrow {}^5\text{D}_4$, ${}^7\text{F}_0 \rightarrow {}^5\text{G}_2$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ and ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$, respectively, which are accorded with the literatures^{18–20}. These results indicate that the Eu^{3+} ions can be excited with ultraviolet light either indirectly through the YF_3 host lattice or directly through absorption by Eu^{3+} ions themselves.

Fig. 2b shows the emission spectrum of $\text{YF}_3:\text{Eu}^{3+}$ under 393 nm excitation, consisting of line peaks mainly locate at 592, 612, 650 and 701 nm, corresponding to the transitions of Eu^{3+} ions: ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j = 1, 2, 3, 4$)^{21–23}. These luminescence bands are located in the absorption range of the N-719 dye. Combining the excitation and emission spectra, the ultraviolet irradiation can be absorbed by the N-719 dye in the DSSC via down-conversion luminescence, which widens the light absorption range of the DSSC.

Electrochemical analysis for $\text{YF}_3:\text{Eu}^{3+}$ doped TiO_2 film. The influence of $\text{YF}_3:\text{Eu}^{3+}$ on the energy level of TiO_2 is assessed through Mott-Schottky electrochemical analysis^{24,25}. Fig. 3a shows Mott-Schottky plots ($1/C^2$ vs. V) of the TiO_2 film with different amount of $\text{YF}_3:\text{Eu}^{3+}$, from which the flat-band potential (V_{FB}) can be obtained (Table 1). It can observe a negative shift in the flat-band potential with the increase of $\text{YF}_3:\text{Eu}^{3+}$ percentage from the -0.44 V for pure TiO_2 film to -0.83 V for the film doped with $\text{YF}_3:\text{Eu}^{3+}$ of 7 wt%. According to the doping principle, pristine TiO_2 is a n-type semiconductor^{13,14}, the introduction of +3 value metal ions into +4 value metal oxide (TiO_2) will cause a p-type doping effect (similar to that +3 value ions doped in Si semiconductor). Eu^{3+} ion is +3 value rare-earth ion, so Eu^{3+} ion doping is a p-type doping, which leads to the negative shift in the flat-band potential with the increase of $\text{YF}_3:\text{Eu}^{3+}$ percentage in the TiO_2 film. It is notable that the doping does not change TiO_2 semiconductor type, but it changes the Fermi level and the flat-band potential of the TiO_2 .

The potentiodynamic parameters of the $\text{YF}_3:\text{Eu}^{3+}/\text{TiO}_2$ films were measured by electrochemical method^{24,25}. Fig. 3b shows the

Figure 2 | Excitation (a) and emission (b) spectra of $\text{YF}_3:\text{Eu}^{3+}$.

Figure 3 | Mott-Schottky plots (a) and current-potential curves (b) of $\text{YF}_3:\text{Eu}^{3+}/\text{TiO}_2$ systems.

current-potential curves of $\text{YF}_3:\text{Eu}^{3+}/\text{TiO}_2$. For all samples, with the increase of the applied potential, the photocurrent densities firstly increase, and then gradually tend to a saturation value. On the other hand, the photocurrent densities for the $\text{YF}_3:\text{Eu}^{3+}/\text{TiO}_2$ are all larger than that for TiO_2 alone. As shown in Fig. 3b and Table 1, the saturated current density for TiO_2 alone is about $10.12 \mu\text{A}\cdot\text{cm}^{-2}$, and the saturated photocurrent densities for all $\text{YF}_3:\text{Eu}^{3+}/\text{TiO}_2$ are larger than this.

Photovoltaic performance of DSSCs. To study the effect of ultraviolet irradiation on the DSSC, we used a filter stop (ZWB3) to remove the light with wavelength larger than 420 nm. Fig. 4a shows the photovoltaic character curves of the DSSC with and without $\text{YF}_3:\text{Eu}^{3+}$ doing under an ultraviolet irradiation of $24 \text{ mW}\cdot\text{cm}^{-2}$. The DSSC without $\text{YF}_3:\text{Eu}^{3+}$ shows the following photovoltaic parameters: short circuit current density (J_{SC}) = $1.192 \text{ mA}\cdot\text{cm}^{-2}$, open circuit voltage (V_{OC}) = 0.584 V, fill factor (FF) = 0.536 and light-to-electric energy conversion efficiency (η) = 0.373%. However, the DSSC containing $\text{YF}_3:\text{Eu}^{3+}$ displays enhanced photovoltaic parameters: J_{SC} = $1.406 \text{ mA}\cdot\text{cm}^{-2}$, V_{OC} = 0.691 V, FF = 0.573 and η = 0.557%. This enhancement indicates that ultraviolet light can be effectively converted to visible light by $\text{YF}_3:\text{Eu}^{3+}$, and the more incident light are harvested, therefore, the efficiency of the DSSC is improved.

The photocurrent-voltage curves of the DSSCs with and without $\text{YF}_3:\text{Eu}^{3+}$ doping under a simulated solar light irradiation of $100 \text{ mW}\cdot\text{cm}^{-2}$ were measured and shown in Fig. 4b, and the photovoltaic parameters are listed in Table 2. Obviously, with the increase of $\text{YF}_3:\text{Eu}^{3+}$ amount in the DSSC, V_{OC} values increase, J_{SC} values first increase and then decrease. When the amount of $\text{YF}_3:\text{Eu}^{3+}$ is 5 wt.% in the doping layer, the DSSC achieves a maximum efficiency of 7.741%. The increase in J_{SC} when the doping amount is less than 5 wt.% can be attributed to the down-conversion luminescence of Eu^{3+} from ultraviolet light to visible light. Moreover, the changes of TiO_2 energy level by doping rare-earth ions improve the carrier transport at the interface of TiO_2/Dye , which further improves the J_{SC} . However, when the amount of $\text{YF}_3:\text{Eu}^{3+}$ is beyond

5 wt.% in the doping layer, more grain, phase and domain interfaces are produced in the doping layer. These interfaces can capture photo-generated electrons and holes, hinder the charge carrier transportation, leading to a decrease in photocurrent^{26,27}. This is why J_{SC} increases and then decreases with the increment of $\text{YF}_3:\text{Eu}^{3+}$ amount in the doping layer of the DSSC.

On the other hand, as shown in Fig. 4b and Table 2, the V_{OC} values increase with the increase of $\text{YF}_3:\text{Eu}^{3+}$ contents. When the amount of $\text{YF}_3:\text{Eu}^{3+}$ is 7 wt.% in the doping layer, the DSSC obtains a V_{OC} value of 0.800 V, increasing 10% compared to the DSSC without $\text{YF}_3:\text{Eu}^{3+}$ doping. According to DSSC operation principle³⁴, the V_{OC} corresponds to the energy difference between the electronic Fermi level of TiO_2 film and the redox potential of the electrolyte ($V_{\text{OC}} = E_{\text{F}(\text{TiO}_2)} - E_{\text{redox}}$). When Eu^{3+} or Y^{3+} ions are doped and substituted for the Ti^{4+} ion lattice sites in TiO_2 , it will give a p-type doping effect, similar to that M^{3+} ions doped in Si crystal for Si solar cells, which results in the elevation of the Fermi level of TiO_2 electrode (more negative vs vacuum) and the increase of V_{OC} values²⁸.

As shown in Table 2, when the ratio of $\text{YF}_3:\text{Eu}^{3+}/\text{TiO}_2$ is 5 wt.% in the doping layer, the light-to-electric energy conversion efficiency of the DSSC reaches 7.741%, increasing by 32% compared to the DSSC without the rare-earth ions doping. The enhanced degree of photovoltaic performance of the DSSC by doping rare-earth fluoride is higher than that by doping rare-earth oxide^{15–17}.

Discussion

Different from other researches, in which spectral converters by rare-earth compound were installed on the front or the back²⁹, we introduced doped rare-earth compound ($\text{YF}_3:\text{Eu}^{3+}$) in the TiO_2 photoanode (doping layer) of DSSC, which resulted in more effective conversion luminescence and p-type doping effect. As a conversion luminescence medium, $\text{YF}_3:\text{Eu}^{3+}$ broadens ultraviolet light harvest via down-conversion luminescence and increases photocurrent; As a p-type dopant, Eu^{3+} ions elevate the Fermi level of the TiO_2 film and thus heightens the photovoltage. When the doping amount is 5 wt.% in the doping layer, the light-to-electric energy conversion efficiency of the DSSC reaches 7.74%, which is increased by 32% compared to

Table 1 | Flat-band potential (V_{FB}) and saturated current density (I_{SAT}) for $\text{YF}_3:\text{Eu}^{3+}/\text{TiO}_2$ systems

RE/ TiO_2 (wt.%)	0 wt%	1 wt%	3 wt%	4 wt%	5 wt%	6 wt%	7 wt%
* V_{FB} (V vs. SCE)	−0.44	−0.61	−0.68	−0.74	−0.77	−0.79	−0.83
** I_{SAT} ($\mu\text{A}\cdot\text{cm}^{-2}$)	10.12	12.26	12.65	14.65	15.52	11.30	10.76

*obtained from the Fig. 3a.
 **obtained from the Fig. 3b.

Figure 4 | J–V curves of DSSC with and without $\text{YF}_3:\text{Eu}^{3+}$ doping (5 wt.%) under an ultraviolet light irradiation of $24 \text{ mW} \cdot \text{cm}^{-2}$ (a) and J–V curves of the DSSC with different amount of $\text{YF}_3:\text{Eu}^{3+}$ doping under a simulated solar light irradiation of 100 mW cm^{-2} (b).

that of the DSSC without $\text{YF}_3:\text{Eu}^{3+}$. The present results demonstrate the feasibility of the conversion luminescence and p-type doping effect by doped rare-earth compound in the DSSC and provide a novel route for enhancing the photovoltaic performance of solar cells.

Methods

Materials. Chemical reagents including tetrabutyl titanate, polyethylene glycol (molecular weight of 20000), 4-tert-butylpyridine (TBP), oxalic acid, nitric acid, OP emulsifying agent (Triton X-100), iodine, lithium iodide, tetramethyl ammonium iodine, acetonitrile, isopropanol, yttrium oxide, europium oxide, hydrochloric acid, hydrofluoric acid, ammonium hydrogen fluoride are analytic purity from Shanghai Chemical Agent Ltd., Shanghai, China. The sensitized dye N-719 [$\text{RuL}_2(\text{NCS})_2$, $\text{L} = 4,4'$ -dicarboxylate-2,2'-bipyridine] was from Solaronix SA, (Aubonne, Switzerland).

Preparation of $\text{YF}_3:\text{Eu}^{3+}$. $\text{YF}_3:\text{Eu}^{3+}$ powder was prepared by hydrothermal method according to the following procedures¹⁸. Firstly, Y_2O_3 (0.100 mol) and Eu_2O_3 (0.002 mol) were mixed and homogenized thoroughly. Then, hydrochloric acid was added into the mixture under heating and stirring. After being completely dissolved, the mixture was quickly transferred into a Teflon-lined stainless-steel autoclave, then, NH_4HF_2 (0.500 mol) was added into the autoclave under stirring. Afterwards, appropriate de-ionized water was added until the filled degree reached 75–80% of the total container volume. Then, pH value of the mixed solution was adjusted to 4.5 using hydrofluoric acid. The obtained solution was hydrothermally treated at 200°C for 4 days. After being naturally cooled to room temperature, the obtained product was centrifuged, washed until the pH value of the system equalled to 7, and then dried in air at ambient temperature. Thus, $\text{YF}_3:\text{Eu}^{3+}$ powder was obtained.

Preparation of film electrodes and fabrication of DSSC. The TiO_2 colloid was prepared as reported previously^{17,30,31}. Then, the $\text{YF}_3:\text{Eu}^{3+}$ powder was dispersed into the TiO_2 colloid by ultrasonically vibrating for 90 min and hydrothermally treating at 200°C for 24 h to form a $(\text{TiO}_2 + \text{YF}_3:\text{Eu}^{3+})$ colloid. A TiO_2 film with a thickness of about 12 μm was prepared by coating the TiO_2 colloid on the FTO plate. Then, sintered at 450°C for 30 min. Afterwards, the doping layer of $(\text{TiO}_2 + \text{YF}_3:\text{Eu}^{3+})$ with a thickness of about 4 μm was coated on the TiO_2 film in the same way. Then, the film was soaked in dye N-719 for 24 h to form a dye-sensitized film electrode. For comparison, a dye-sensitized TiO_2 film electrode without $\text{YF}_3:\text{Eu}^{3+}$ was made, the film thicknesses was about 16 μm , which was the same as the film with $\text{YF}_3:\text{Eu}^{3+}$ doping.

The DSSC was assembled by injecting the electrolyte (0.6 M tetra butyl ammonium iodide, 0.1 M iodine, 0.1 M lithium iodide, 0.5 M 4-tert-butyl-pyridine (TBP) in

acetonitrile) into the aperture between the dye-sensitized TiO_2 film electrode and a platinum counter electrode. The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte solution from leaking^{17,30,31}.

Measurement and characterization. The phase purity and crystal structure of $\text{YF}_3:\text{Eu}^{3+}$ powders were analyzed with the powder X-ray diffraction (XRD) measurements. The XRD patterns were recorded by an X-ray diffractometer (BRUKERD8, Karlsruhe, Germany) using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The 2θ angle of the XRD spectra was recorded at a scanning rate of 3° min^{-1} .

The excitation and emission spectra were measured using a spectrophotometer (FLS920, Edinburgh, UK), in which a xenon lamp and a photomultiplier tube (R955, Hamamatsu) were equipped as excitation source and the detector of fluorescence, respectively.

Electrochemical experiments were conducted on an electrochemical cell filled with an electrolyte solution contained 0.01 M LiClO_4 , 10 mM LiI and 1 mM I_2 in acetonitrile solvent, where a Pt counter electrode, a saturated calomel reference electrode (SCE) and a working electrode were immersed. The capacitance-voltage (C-V) curves^{24,25} and potentiodynamic current-applied potential (I-V) curves^{32,33} were measured by using an Electrochemical Workstation (CHI660C, Shanghai Chenhua Device Company, China). The data of C-V were used for evaluating the flat band potential according to Mott-Schottky equation (Eq. 1)^{24,25}, which relates the capacity to the potential difference between the surface and the bulk of a semiconductor ΔV :

$$C^{-2} = \frac{2}{\epsilon_0 \epsilon N_i} (Z_i \Delta V - \frac{kT}{e}) \quad (1)$$

In the above equation, ϵ is the dielectric constant of the material, ϵ_0 is the permittivity of the vacuum, e is the element charge, N_i is the concentration of donors in n-type and acceptors in p-type semiconductor, Z_i is +1 for donors and −1 for acceptors.

The photovoltaic parameters of the DSSC were characterized by measuring the J-V character curves under a simulated solar light irradiation of $100 \text{ mW} \cdot \text{cm}^{-2}$ from a 100 W Xe lamp (XQ-500 W, Shanghai Photoelectricity Device Company, Shanghai City, China). The fill factor (FF) and light-to-electric energy conversion efficiency (η) of the cell were calculated according to the following equations³:

$$FF = \frac{V_{\text{max}} \times J_{\text{max}}}{V_{\text{OC}} \times J_{\text{SC}}} \quad (2)$$

$$\eta = \frac{V_{\text{max}} \times J_{\text{max}}}{P_{\text{in}}} \times 100\% = \frac{V_{\text{OC}} \times J_{\text{SC}} \times FF}{P_{\text{in}}} \times 100\% \quad (3)$$

where J_{SC} is the short-circuit current density ($\text{mA} \cdot \text{cm}^{-2}$), V_{OC} is the open-circuit voltage (V), P_{in} is the incident light power, and J_{max} ($\text{mA} \cdot \text{cm}^{-2}$) and V_{max} (V) are the current density and voltage in the J-V curves at the point of maximum power output, respectively.

Table 2 | Effect of $\text{YF}_3:\text{Eu}^{3+}$ on photovoltaic properties of the DSSCs

RE/ TiO_2 (in doping layer, wt.%)	J_{SC} (mAcm^{-2})	V_{OC} (V)	FF	η (%)
0	13.329	0.727	0.603	5.841
1	13.433	0.734	0.652	6.428
3	13.899	0.743	0.659	6.806
4	14.508	0.760	0.671	7.393
5	14.894	0.787	0.661	7.741
6	10.657	0.791	0.674	5.685
7	9.579	0.800	0.690	5.291

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Author contributions

J.Wu designed the device and experiments, J.Wang, Y.X. and G.Y. carried out most experiments. J.Wu wrote the manuscript, and all authors J.Wu, J.Wang, J.L., Y.X., G.Y., M.H., Z.L., Y.H., L.F., S.Y. & T.S. discussed the results and contributed to revisions.

Additional information

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