Dual functions of YF₃:Eu³⁺ 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 (YF₃:Eu³⁺) in TiO₂ film in the DSSC. As a conversion luminescence medium, YF₃:Eu³⁺ transfers ultraviolet light to visible light via down-conversion, and increases incident harvest and photocurrent of DSSC. As a p-type dopant, Eu³⁺ elevates the Fermi level of TiO₂ 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 YF₃:Eu³⁺/TiO₂ 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 YF₃:Eu³⁺ 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 fuels. 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, 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, they are doped into TiO₂ 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 YF₃:Eu³⁺. The YF₃:Eu³⁺ was prepared by hydrothermal method.¹⁶ The X-ray diffraction (XRD) pattern of prepared YF₃:Eu³⁺ is shown in Fig. 1. All diffraction peaks of the prepared sample are readily indexed as orthorhombic phase of YF₃ and are consistent with the standard pattern (JCPDS 74-0911). This indicates the formation of the orthorhombic phase of YF₃. Furthermore, no EuF₃ phases are observed, this is because that in the preparation Y₂O₃ and Eu₂O₃ are completely dissolved and mixed (see method section), Eu³⁺ amount in YF₃ mixed solution is small (2.0 mol.%) as well as Y³⁺ and Eu³⁺ ions have similar electronic structures (s²p⁶) and radii (0.90 Å and 0.95 Å), therefore, Eu³⁺ ions occupy the lattice sites of Y³⁺ ions.
Photoluminescence properties of YF$_3$Eu$^{3+}$. The excitation spectrum of YF$_3$Eu$^{3+}$ (emission at 592 nm) is shown in Fig. 2a. The excitation spectrum of YF$_3$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: $^7$F$_0$ $\rightarrow$ $^1$H$_6$, $^7$F$_0$ $\rightarrow$ $^1$D$_4$, $^7$F$_0$ $\rightarrow$ $^1$G$_2$, $^7$F$_0$ $\rightarrow$ $^1$L$_6$ and $^7$F$_0$ $\rightarrow$ $^1$D$_2$, respectively, which are accorded with the literatures$^{19-20}$. 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 YF$_3$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: $^3$D$_0$ $\rightarrow$ $^7$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 YF$_3$Eu$^{3+}$ doped TiO$_2$ film. The influence of YF$_3$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 YF$_3$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 YF$_3$Eu$^{3+}$ percentage from the $-0.44$ V for pure TiO$_2$ film to $-0.83$ V for the film doped with YF$_3$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 YF$_3$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 YF$_3$Eu$^{3+}$/TiO$_2$ films were measured by electrochemical method$^{24,25}$. Fig. 3b shows the
current-potential curves of YF$_3$Eu$^{3+}$/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 YF$_3$Eu$^{3+}$/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 mA·cm$^{-2}$, and the saturated photocurrent densities for all YF$_3$Eu$^{3+}$/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 YF$_3$Eu$^{3+}$ doing under an ultraviolet irradiation of 24 mW·cm$^{-2}$. The DSSC without YF$_3$Eu$^{3+}$ shows the following photovoltaic parameters: short circuit current density ($J_{SC}$) = 1.192 mA·cm$^{-2}$, open circuit voltage ($V_{OC}$) = 0.584 V, fill factor (FF) = 0.536 and light-to-electric energy conversion efficiency ($\eta$) = 0.373%.

However, the DSSC containing YF$_3$Eu$^{3+}$ displays enhanced photovoltaic parameters: $J_{SC}$ = 1.406 mA·cm$^{-2}$, $V_{OC}$ = 0.691 V, FF = 0.573 and $\eta$ = 0.557%. This enhancement indicates that ultraviolet light can be effectively converted to visible light by YF$_3$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 YF$_3$Eu$^{3+}$ doping under a simulated solar light irradiation of 100 mW·cm$^{-2}$ were measured and shown in Fig. 4b, and the photovoltaic parameters are listed in Table 2. Obviously, with the increase of YF$_3$Eu$^{3+}$ amount in the DSSC, $V_{OC}$ values increase, $J_{SC}$ values first increase and then decrease. When the amount of YF$_3$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 YF$_3$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 photogenerated electrons and holes, hinder the charge carrier transportation, leading to a decrease in photocurrent$^{28,29}$. This is why $J_{SC}$ increases and then decreases with the increment of YF$_3$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 YF$_3$Eu$^{3+}$ contents. When the amount of YF$_3$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 YF$_3$Eu$^{3+}$ doping. According to DSSC operation principle$^{30,31}$, the $V_{OC}$ corresponds to the energy difference between the electronic Fermi level of TiO$_2$ film and the redox potential of the electrolyte ($V_{OC} = E_{TiO2} - E_{redox}$). 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 $V_{OC}$ values$^{28}$. As shown in Table 2, when the ratio of YF$_3$Eu$^{3+}$/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$^{32-37}$.

**Discussion**

Different from other researches, in which spectral converters by rare-earth compound were installed on the front or the back$^{29}$, we introduced doped rare-earth compound (YF$_3$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, YF$_3$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

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

| RE/TiO$_2$ (wt.% | 0 wt% | 1 wt% | 3 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 |
| $I_{SC}$ (mA·cm$^{-2}$) | 0.12 | 1.26 | 1.26 | 1.46 | 1.52 | 1.13 | 1.07 |

*obtained from the Fig. 3a
**obtained from the Fig. 3b
that of the DSSC without YF$_3$: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, OEP 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 [RuL$_2$(NCS)$_2$, L = 4,4' -dicarboxylate-2,2'-bipyridine] was from Solaronix SA., (Aubonne, Switzerland).

**Preparation of YF$_3$:Eu$^{3+}$.** YF$_3$:Eu$^{3+}$ powder was prepared by hydrothermal method according to the following procedures$^{17}$. Firstly, Y$_2$O$_3$ (0.100 mol) and Eu$_2$O$_3$ (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$_4$HF$_2$ (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, YF$_3$:Eu$^{3+}$ powder was obtained.

**Preparation of film electrodes and fabrication of DSSC.** The TiO$_2$ colloid was prepared as reported previously$^{15,30}$. Then, the YF$_3$: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 (TiO$_2$ + YF$_3$: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 (TiO$_2$ + YF$_3$:Eu$^{3+}$) was prepared as reported previously$^{17,30,31}$. Then, the YF$_3$:Eu$^{3+}$ powder was dispersed into a Tefton-lined stainless-steel autoclave, then, NH$_4$HF$_2$ (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, YF$_3$:Eu$^{3+}$ powder was obtained.

The TiO$_2$ film was sintered at 450°C for 30 min. After cooling down to room temperature, the TiO$_2$ film was sintered at 450°C for 30 min. The resulting film was then used to fabricate the DSSC. 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 (TiO$_2$ + YF$_3$:Eu$^{3+}$) was prepared as reported previously$^{17,30,31}$. Then, the YF$_3$:Eu$^{3+}$ powder was dispersed into a Tefton-lined stainless-steel autoclave, then, NH$_4$HF$_2$ (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, YF$_3$:Eu$^{3+}$ powder was obtained.

The DSSC was assembled by injecting the electrolyte (0.6 M tetra butyl ammonium perchlorate) 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$^{15,30,31}$.

**Measurement and characterization.** The phase purity and crystal structure of YF$_3$:Eu$^{3+}$ powders were analyzed with the powder X-ray diffraction (XRD) measurements. The XRD patterns were recorded by an X-ray diffractometer (BRUKER D8, Karlsruhe, Germany) using Cu-Kα radiation ($λ = 1.5405 Å$). 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 0.1 M LiClO$_4$, 10 mM LiI and 1 mM L$_2$ 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$^{15,32}$ and potentiodynamic current-applied potential (I-V) curves$^{15,32}$ were measured using an Electrochemical Workstation (CHI660C, Shanghai Chenhua Device Company, China). The data of C-V were used for evaluating the flat band voltage ($V_{FB}$), which is the potential difference between the surface and the bulk of a semiconductor $V_{FB}$.

$$V_{FB} = \frac{1}{2} \left( V_{OC} - |V_{JSC}| \right)$$

where $V_{OC}$ is the open-circuit voltage, $V_{JSC}$ is the short-circuit current density (mA cm$^{-2}$), $V_{JSC}$ is the short-circuit current density (mA cm$^{-2}$), and $P_{in}$ is the incident light power.

The photovoltaic parameters of the DSSC were characterized by measuring the $J$–$V$ characteristic curves under a simulated solar light irradiation of 100 mW 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 equations:

$$FF = \frac{V_{max} \times J_{max}}{V_{OC} \times J_{SC}}$$

$$η = \frac{V_{max} \times J_{max}}{P_{in}} \times 100\% = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}} \times 100\%$$

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

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