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Short communication

Enhancing photoelectrical performance of dye-sensitized solar cell by doping with europium-doped yttria rare-earth oxide

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ABSTRACT

The doped rare-earth oxide europium-doped yttria (Y_2O_3:Eu^{3+}) is introduced into the TiO_2 film electrode in a dye-sensitized solar cell. As a luminescence medium, Y_2O_3:Eu^{3+} improves the light harvesting via a conversion luminescence process and increases the photocurrent, as a p-type dopant, Y_2O_3:Eu^{3+} elevates the energy level of the oxide film and increases the photovoltage. When the TiO_2 electrode is doped by 3 wt.% Y_2O_3:Eu^{3+}, the cell light-to-electric conversion efficiency is improved by a factor of 1.14 compared to that of a cell without Y_2O_3:Eu^{3+} doping.

1. Introduction

Considerable efforts have been devoted to the dye-sensitized solar cell (DSSC) since the first prototype was reported by Gratzel and O'Regan in 1991 [1]. While great progress on the DSSC has occurred over the past decade [2–4], however, how to enhance its efficiency is still a crucial problem. In general, the cell consists of a porous nanocrystalline TiO_2 film sensitized by a dye for absorbing incident light, a redox electrolyte, and a platinized counter electrode to catalyze the redox couple regeneration reaction [2]. To improve the harvest of incident light, thus increase the photocurrent of the DSSC, many dyes have been synthesized, however, even the best of these (N-719, see below; N-749) only absorb visible light in the wavelength range 300–800 nm [2], so most of the solar ultraviolet irradiation is not utilized. If the ultraviolet irradiation can be transferred to visible light by conversion luminescence, and is reabsorbed by the dye in the DSSC, more solar irradiation may be utilized, the DSSC photocurrent will be effectively enhanced. On the other hand, the DSSC photovoltage depends on the energy level of the electron in the oxide film [2,3]. If the energy level can be heightened by p-type doping, the DSSC photovoltage will be increased. However, little significant research on conversion luminescence and/or p-type doping in the DSSC has been attempted.

Rare-earth-doped compounds as luminescent media have been the subject of extensive research and have wide applications [5]. Among these, europium-doped yttrium oxide (Y_2O_3:Eu^{3+}) is a typical example and is considered to be one of the best red luminescent media with good luminescent properties, high stability, high melting point (2400 °C), and high thermal conductivity [6]. Here, Y_2O_3:Eu^{3+}, as a luminescence medium and p-type dopant is introduced into the DSSC to improve its photocurrent, photovoltage and solar conversion efficiency.

2. Experimental

2.1. Materials

Chemical reagents including tetrabutyl titanate, isopropanol, polyethylene glycol 20000, 4-tert-butylpyridine (TBP), oxalic acid, hydrochloric acid, OP emulsification agent (Triton X-100), iodine, lithium iodide, europium oxide, yttrium oxide were analytic purity from Shanghai Chemical Agent Ltd., Shanghai, China. The organic solvent was distilled before use. The sensitized dye N-719 [$RuL_2(NCS)_2$, L = 4,4′-dicarboxylate-2,2′-bipyridine] was from SOLARONIX SA (Aubonne, Switzerland).

2.2. Preparation of Y_2O_3:Eu^{3+} powder

Y_2O_3 and Eu_2O_3 with a mass ratio of 95:5 were dissolved in a 6 mol L^{-1} HCl solution, then 15 wt.% oxalic acid ($H_2C_2O_4$) solution was added, and the mixture was allowed to react for 3 h, which resulted in the co-deposition of oxalate salts $Y_2(C_2O_4)_3$ and $Eu_2(C_2O_4)_3$. The deposit was calcined at 870 °C for 2.5 h to produce Y_2O_3:Eu^{3+} powder.

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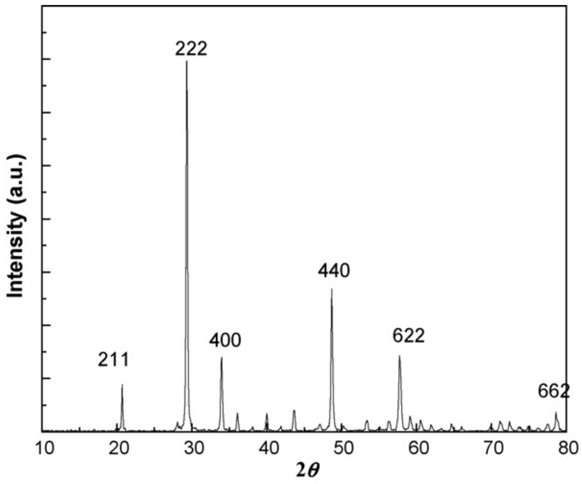

Fig. 1. XRD patterns of Y_2O_3:Eu^{3+} powder.

2.3. Preparation of film electrodes of DSSC

A TiO_2 colloid was prepared according to the methods previously used [7–9]. The Y_2O_3:Eu^{3+} powder was dispersed in the TiO_2 colloid to form a $TiO_2 + Y_2O_3$:Eu^{3+} colloid. A TiO_2 film with a thickness of 12 μm was prepared by coating the TiO_2 colloid on the FTO plate using a doctor blade technique, then the TiO_2–Y_2O_3:Eu^{3+} layer with thickness of 4 μm was coated on the TiO_2 film by the same method. After sintering at 450 °C for 30 min and soaking in dye N-719 solution for 24 h, a dye-sensitized film electrode ($TiO_2 + Y_2O_3$:Eu^{3+}) was obtained. For comparison, a dye-sensitized TiO_2 film electrode without Y_2O_3:Eu^{3+} also was made. The thickness of the oxide films for the DSSCs with and without Y_2O_3:Eu^{3+} were both 16 μm. The DSSC with and without Y_2O_3:Eu^{3+} containing layer were assembled using the same methods as described previously [7–9].

2.4. Measurement of sample properties

The powder X-ray diffraction (XRD) patterns were recorded by a X-ray diffractometer (BRUKER D8, Karlsruhr, Germany) using Cu Kα radiation (λ = 1.5405 Å). The average particle sizes of the nanocrystals were calculated using the Scherrer equation [10].

$$D = \frac{K\lambda}{\beta \cos\theta} \qquad (1)$$

The UV–vis diffuse reflection spectrum of sample was measured with a UV–Vis 2550 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). The photoluminescence spectra were obtained using a fluorescence spectrometer (F-4500, excitation wavelength 254 nm, Hitachi, Ltd., Hitachi City, Japan).

2.5. Measurement of photoelectric performance of DSSC

The photovoltaic tests of DSSCs were carried out by measuring the *I–V* character curves under a simulated solar light irradiation of 100 mW cm^{-2} from a 100 W Xe lamp (XQ-500W, Shanghai Photoelectricity Device Company, Shanghai City, China). The fill factor (*FF*) and the light-to-electric energy conversion efficiency (η) of DSSC were calculated according to the following equations [11]:

$$\eta(\%) = \frac{V_{\max} \times J_{\max}}{P_{\text{in}}} \times 100\% = \frac{V_{OC} \times J_{SC} \times FF}{P_{\text{in}}} \times 100\% \qquad (2)$$

$$FF = \frac{V_{\max} \times J_{\max}}{V_{OC} \times J_{SC}} \qquad (3)$$

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

The spectral response (200–300 nm) for each DSSC was determined by measuring the wavelength dependence of the incident photon-to-current conversion efficiency (IPCE) using a light from a Xe lamp through a monochromator (USB 2.0, Newport Corporation, Mountain View, CA, USA) and focusing onto the cell. The IPCE is calculated according to the following equation [12]:

$$\text{IPCE}\ (\lambda) = \frac{12,400 \times J_{SC}\ (\text{mA cm}^{-2})}{\lambda\ (\text{nm}) \times P_{\text{in}}\ (\text{mW cm}^{-2})} \qquad (4)$$

3. Results and discussions

3.1. Y_2O_3:Eu^{3+} powder

Fig. 1 shows the XRD patterns of Y_2O_3:Eu^{3+} powder. According to the standard pattern of Y_2O_3 (JCPDS 25-1011), each diffraction peak in Fig. 1 can be ascribed to the body-centred cubic phase of Y_2O_3. As a luminescent material, it is said that the body-centred cubic phase is the most effective [13]. From Fig. 1, no Eu_2O_3 phase is observed, which is due to Eu^{3+} ions occupying the lattice sites of Y^{3+} ions, and no single Eu_2O_3 phase exists. Similar observations were made by Masuda and Pol [6,14]. According to the Scherrer equation [10] and the XRD in Fig. 1, the particle size of Y_2O_3:Eu^{3+} is calculated to be 52 nm. This nanometer crystal size favors [5] the photoluminescence of Y_2O_3:Eu^{3+}.

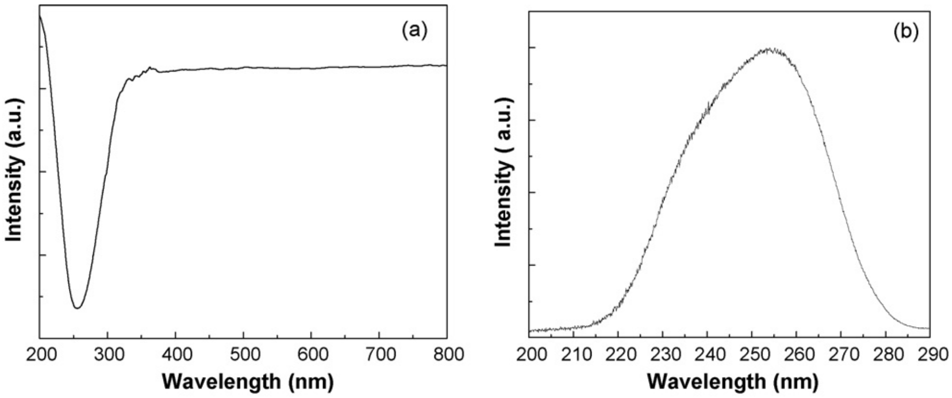

Fig. 2. UV–vis diffuse reflection spectrum (a) and excitation spectrum (b) of Y_2O_3:Eu^{3+}.

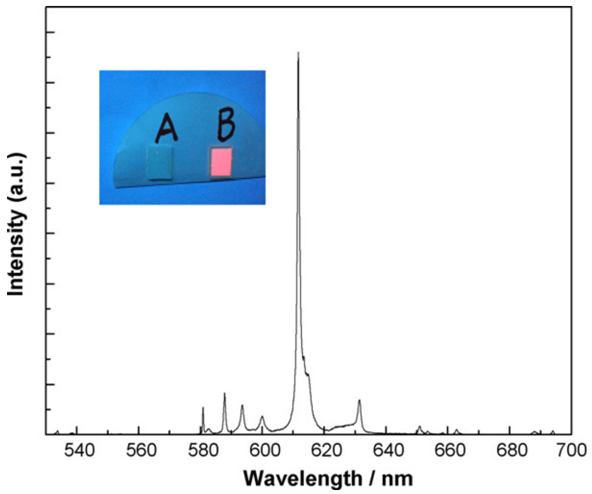

Fig. 3. Emission spectrum of Y_2O_3:Eu^{3+} excited at 254 nm.

3.2. The properties of Y_2O_3:Eu^{3+} powder

Fig. 2 shows the UV–vis diffuse reflection spectrum and the excitation spectrum of Y_2O_3:Eu^{3+}. An ultraviolet absorption band with a wavelength range of 230–320 nm and a centre peak at 254 nm, which is assigned [5,15] to the charge-transfer band (CTB) of Eu^{3+}. The CTB of Y_2O_3:Eu^{3+} corresponds to the electronic transition from the 2p orbit of O^{2-} to the 4f orbit of Eu^{3+}. The ultraviolet absorption band implies that ultraviolet irradiation from the sun can be absorbed by Y_2O_3:Eu^{3+}.

Fig. 3 shows the emission spectrum of the Y_2O_3:Eu^{3+} powder excited at 254 nm. The inset A and B are the photographs of TiO_2 and Y_2O_3:Eu^{3+} film under ultraviolet irradiation, respectively. It can be seen that Y_2O_3:Eu^{3+} possess an obvious luminescence function. One intense emission peak at 612 nm is observed, which is due to the fact that the electron of Eu^{3+} is excited to a higher energy state, whereupon radiationless transition occur until the electron resides at the $^5D_0$ energy level in 4f shell. A radiative transition then occurs to the ^7F_J levels ($^5D_0 \rightarrow {}^7F_2$) [10,16,17]. The luminescence at 612 nm is just within the absorption wavelength range of sensitizing dye N-719. Combining excitation with emission spectra, the ultraviolet irradiation from the sun can be reabsorbed by the dye N-719 via the conversion luminescence of Y_2O_3:Eu^{3+} and the solar light harvest of DSSC may thus be increased.

Table 1
Influence of Y_2O_3:Eu^{3+} on photoelectric parameters of DSSCs.

Y_2O_3:Eu^{3+} (%)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	η (%)
0 wt.%	13.04	0.715	0.615	5.74
1 wt.%	13.31	0.734	0.621	6.07
2 wt.%	13.59	0.759	0.624	6.44
3 wt.%	13.26	0.788	0.623	6.52
4 wt.%	12.35	0.799	0.611	6.03
5 wt.%	10.41	0.817	0.643	5.47

3.3. Photoelectric performance of DSSCs

From Fig. 4a, the IPCE for the DSSC with Eu^{3+} doping is higher than that without Eu^{3+} doping in ultraviolet range with a wavelength of 200–280 nm (They both have similar IPCE spectra in visible range). Obviously, this is due to the conversion luminescence of Eu^{3+} ion from ultraviolet light to visible light and reabsorption by dye N-719 in the DSSC.

From Table 1, J_{SC} increases with increase in the amount of Y_2O_3:Eu^{3+} until 2 wt.%, beyond which, J_{SC} decreases. The increase mainly comes from the conversion luminescence of Eu^{3+}, which results in that more incident light being harvested, thus increasing J_{SC}. This decrease is due to the fact that introduction of rare-earth oxides produces defects in the oxide film, which causes the recombination of photoinduced holes and electrons and the decrease of J_{SC} [18].

On the other hand, the V_{OC} increases with increase in the percentage of Y_2O_3:Eu^{3+}. When the amount of Y_2O_3:Eu^{3+} is 5 wt.%, the V_{OC} reaches 0.817 V, which is the highest value yet observed in a DSSC, indicating the significance of p-type doping. According to Gratzel [2,3], the V_{OC} corresponds to the difference between the energy level of the electrons in the oxide film and the redox potential of the electrolyte. When rare-earth ions are doped and substitute for the Ti^{4+} ion lattice sites in TiO_2, giving a p-type doping similar to that in Si semiconductors, the energy level of the oxide film is elevated, which leads to the increase of V_{OC}. Similar phenomena also were observed by Ko et al. [19]. They found that Al-doping of the TiO_2 electrode increased V_{OC}, while W-doping had the opposite effect (n-type doping).

The solar conversion efficiency for a DSSC with Y_2O_3:Eu^{3+} doping (3 wt.%) reached 6.52%, which is a factor of 1.14 compared to that of a DSSC without Y_2O_3:Eu^{3+} doping (Fig. 4b). Furthermore, by choosing a suitable doping ion and concentration as a p-type luminescence medium, it is possible to further increase the conversion efficiency of the DSSC.

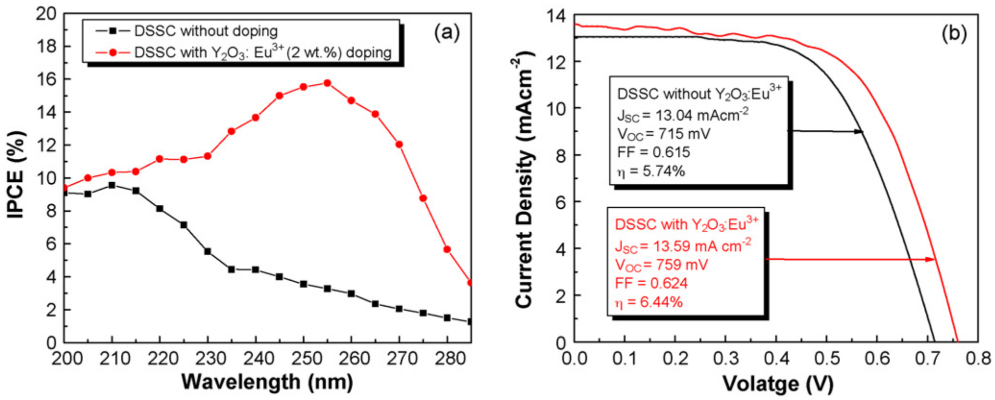

Fig. 4. (a) Photocurrent action spectra (IPCE) and (b) current–voltage curves of DSSCs with and without Y_2O_3:Eu^{3+} 2 wt.% in TiO_2 electrode.

4. Conclusions

In summary, the present results demonstrate the improvement in the photoelectric performance of DSSC by introducing Y_2O_3:Eu^{3+} into the TiO_2 electrode. As a luminescence medium, Y_2O_3:Eu^{3+} improves both the light harvest and the photocurrent, as p-type dopant, Y_2O_3:Eu^{3+} elevates both the energy level of oxide film and the photovoltage of DSSC. With 3 wt.% of Y_2O_3:Eu^{3+} dopant in the TiO_2 electrode, the light-to-electric conversion efficiency of the DSSC reaches 6.52% under a simulated solar light irradiation of 100 mW cm^{-2}, which is enhanced by a factor of 1.14 compared to that of the DSSC without Y_2O_3:Eu^{3+} doping. This finding demonstrates the feasibility of the conversion luminescence with p-type doping in a dye-sensitized solar cell and provides an effective way to improve the sunlight conversion efficiency for solar cells.

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