Application of doped rare-earth oxide TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) in dye-sensitized solar cells

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Abstract. Tm$^{3+}$ and Yb$^{3+}$ are codoped into TiO$_2$ film in a dye-sensitized solar cell (DSSC). The emission and excitation spectra of TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) power shows that the rare-earth ions possess up-conversion luminescence function, which results in harvesting more incident light and increasing photocurrent for the DSSC. On the other hand, owing to the p-type doping effect by Tm$^{3+}$ and Yb$^{3+}$, the photovoltage of the DSSC is enhanced. Under a simulated solar light irradiation of 100 mW·cm$^{-2}$, a DSSC containing Tm$^{3+}$/Yb$^{3+}$ achieves a conversion efficiency of 7.05%, which is increased by 10.0% compared with a DSSC lacking Tm$^{3+}$/Yb$^{3+}$.

1. Introduction

Considerable effort has been devoted to the development of dye-sensitized solar cells (DSSCs) since its first prototype was reported by Gratzel and O'Regan in 1991 [1], however, how to enhance its efficiency still is a crucial problem. To improve incident light harvest, and thus increase the photocurrent of the DSSC, many dyes have been synthesized, however, even the best of these (N-719, N-749) only absorb visible light in the wavelength range 300-800 nm [2,3], so most of the solar infrared irradiations are not utilized. If the infrared irradiations can be transferred to visible light via upconversion luminescence by rare-earth compounds, and are 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 photoanode [2,3]. Rare-earth ions are positive trivalent cations, when they are doped in semiconductor TiO$_2$, a p-type doping effect occur [4,5], which results in the elevation of electron energy level of the photoanode, and turn to the enhancement of the photovoltage of the DSSC. However, little significant research on conversion luminescence and/or p-type doping by rare-earth ions in the DSSC has been attempted [6-8]. Here, Tm$^{3+}$ and Yb$^{3+}$, as luminescence medium and p-type dopant, are introduced into the DSSC, it is expected that the photocurrent, photovoltage and solar conversion efficiency of the DSSC can be improved.

2. Experimental part

2.1. Materials
Yb$_2$O$_3$, Tm$_2$O$_3$ and other reagents were analytical grade (99.99%) and purchased from Shanghai Chemical Agent Ltd. China. Ti(OC$_4$H$_9$)$_4$ was purchased from Fluka. The sensitized dye N-719 was purchased from SOLARONIX SA. The above reagents were used without further purification. Conducting glass plate (FTO glass, sheet resistance 8 Ω·cm$^{-2}$) purchased from Hartford Glass Co., was cut into 2 × 1.5 cm$^2$ sheets, and was used as a substrate to precipitate a TiO$_2$ porous film.

2.2. Preparation of TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) power

TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) powder was prepared by the following processes: 0.056 g Tm$_2$O$_3$ and 0.58 g Yb$_2$O$_3$ were dissolved in a HNO$_3$ solution at 100 °C, 10 mL Ti(OC$_4$H$_9$)$_4$ was added into 150 ml distilled water under vigorously stirring. Then the above two solutions were mixed and the pH value of the mixed solution was adjusted at 2 by adding acetic acid and nitric acid solution. After peptizing at 80 °C for 12 h, the mixture was transferred to an autoclave and hydrothermally treated at 200 °C for 12 h to form a white suspension. The resultant white solid product was dried in a vacuum oven at 60 °C for 12 h. After the solid product was annealed at 800 °C for 2.5 h, a TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) powder was obtained.

2.3. Preparation of film electrodes and DSSCs

A TiO$_2$ colloid was prepared according to the methods previously used [9-11]. The TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) powder was dispersed in the TiO$_2$ colloid to form a TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) colloid. The TiO$_2$ colloid was spread on the FTO glass plate by using a doctor-blading technique. The process was done for two times to form a thick TiO$_2$ film (about 10 µm). The TiO$_2$ film was sintered at 300 °C in air for 30 min. Then the TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) layer with a thickness of 5 µm was spread onto the TiO$_2$ film by the same method. After sintering at 450 °C for 30 min and soaking in a 3×10$^{-3}$ M ethanol solution of N719 for 24 h to absorb the dye adequately, a dye-sensitized rare-earth-doped TiO$_2$ film electrode was obtained. For comparison, a dye-sensitized TiO$_2$ film electrode without the rare-earth-doping (RE$_2$O$_3$) also was prepared. The thicknesses of the TiO$_2$ film electrodes with and without RE$_2$O$_3$ were both 15 µm.

A DSSC was assembled by injection of an electrolyte [9-11] into the aperture between the TiO$_2$ film electrode (anode electrode) and a platinized conducting glass electrode (cathode electrode). The two electrodes were clipped together and a cyanoacrylate adhesive was used as sealant to prevent the electrolyte solution from leaking.

2.4. Measurement and characterization

The powder XRD pattern was recorded with a X-ray diffractometer (BRUKER D8 advance, Germany) using Cu Kα radiation ($\lambda = 1.5405$ Å). The excitation and emission spectra were recorded with a spectrophotometer (FSP920, EDINBUERGH Instruments, Britain) equipped with a diode laser with wavelength 980 nm as excitation source. The photovoltaic test of DSSC was carried out by measuring the I–V characteristic curves under a white light irradiation from a 100 W Xe arc lamp (XQ-500W, Shanghai Photoelectricity Device Company, China) in ambient atmosphere.

![Figure 1. XRD patterns of TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) powder.](image-url)
3. Results and discussion

3.1. XRD
Figure 1 shows the XRD patterns of TiO$_2$: (Tm$^{3+}$, Yb$^{3+}$) powder. The primary components in the powder are Tm$_2$Ti$_2$O$_7$ and Yb$_2$Ti$_2$O$_7$ pyrochlore phases (marked p), and TiO$_2$ rutile phase (marked r). According to the XRD and the Scherrer formula, the particle size of the powder is calculated to be 30 nm, this nanometer crystal size favors the light collection and photoluminescence of the powder.

3.2. The excitation and emission spectra of TiO$_2$: (Tm$^{3+}$, Yb$^{3+}$)
Figure 2a shows the excitation spectrum of TiO$_2$: (Tm$^{3+}$, Yb$^{3+}$). The curve shows a strong and broad excitation band in the wavelength range of 950-1000 nm. The band centered at 980 nm can be identified as the characteristic transition of Yb$^{3+}$ ion from the ground multiplet $^2$F$_{7/2}$ to the excited multiplet $^2$F$_{5/2}$ [13,14]. This infrared excitation band with emission wavelength at 475 nm indicates that the infrared irradiation from the sun can be transferred to the visible light by TiO$_2$: (Tm$^{3+}$, Yb$^{3+}$).

The emission spectrum of TiO$_2$: (Tm$^{3+}$, Yb$^{3+}$) excited with a 980-nm diode laser operating at 100 mW is shown in Figure 2b. From the Figure 2b, an up-conversion luminescence is observed, the emission band centered at 475, 647 and 685 nm are corresponded to electronic transitions for Tm$^{3+}$ ion: $^1$G$_4$ → $^3$H$_6$, $^1$G$_4$ → $^3$F$_4$, $^3$F$_3$ → $^3$H$_6$, respectively [13,14]. The luminescence emission bands for TiO$_2$: (Tm$^{3+}$, Yb$^{3+}$) at 475, 647 and 685 nm is just the absorption wavelength range of the dye N-719 in the DSSC. Combining the excitation with emission spectra of TiO$_2$: (Tm$^{3+}$, Yb$^{3+}$), the infrared irradiation from the sun can be reabsorbed by the dye N-719 in the DSSC via an up-conversion luminescence of TiO$_2$: (Tm$^{3+}$, Yb$^{3+}$) and the solar light harvest of DSSC can be improved.

3.3. The photovoltaic performance of DSSCs
Under a simulated solar light irradiation of 100 mW·cm$^{-2}$, the photovoltaic parameters of DSSCs with different doped ratio of RE$_2$O$_3$/TiO$_2$ in TiO$_2$ electrodes were measured and shown in Table 1. With the increase of the amount of RE$_2$O$_3$ in the DSSC, $J_{SC}$ increases and then decreases. The increase in $J_{SC}$ with the amount of RE$_2$O$_3$ at low concentrations is due to the up-conversion luminescence of RE ions, which RE ions absorb infrared light and transfers to visible light, resulting in an increasing photocurrent in the DSSC. However, when Tm$^{3+}$ and Yb$^{3+}$ are doped in TiO$_2$, some crystal defects are produced, especially in the higher concentration of RE ions. The defects can capture photoinduced electrons and holes, leading to a decrease in photocurrent [15,16]. This explains why $J_{SC}$ increases and then decreases with the increase of the amount of RE$_2$O$_3$ in the DSSC.

On the other hand, the $V_{OC}$ increases with increase in the percentage of RE$_2$O$_3$. According to Gratzel [2,3], $V_{OC}$ corresponds to the difference between the Fermi level of the electrons in the oxide film and the redox potential of the electrolyte. When RE$^{3+}$ ions are doped in TiO$_2$ film and substituted...
for the Ti$^{4+}$ ion lattice sites, a p-type doping effect occurs, similarly to that trivalent positive ion doped in Si semiconductors, which results in the elevation of the energy level of oxide film and the increase of $V_{OC}$. Similar phenomena also was observed by Ko et al. [15]. They found that Al-doped TiO$_2$ electrode increased $V_{OC}$, and W-doped TiO$_2$ had an opposite effect (n-type doping). Although the explanation for phenomena by them is not based on p-type or n-type doping.

Comprising $J_{SC}$, $V_{OC}$, $FF$ and $\eta$, when the RE$_2$O$_3$ amount is 3.33 wt. % in the doping layer, the light-to-electric conversion efficiency of the DSSC reaches 7.05 %, which is enhanced by 10.0 % compared with the DSSC lacking of RE ions.

Table 1. The effects of TiO$_2$:(Tm$^{3+}$, Yb$^{3+}$) on the photovoltaic parameters of DSSCs

| RE$_2$O$_3$ (wt.% in doping layer) | $J_{SC}$ (mA·cm$^{-2}$) | $V_{OC}$ (mV) | $FF$ | $\eta$ (%) |
|-----------------------------------|--------------------------|---------------|------|-----------|
| 0.00                              | 15.40                    | 717           | 0.580| 6.41      |
| 1.67                              | 15.75                    | 721           | 0.575| 6.53      |
| 2.50                              | 16.03                    | 725           | 0.596| 6.93      |
| 3.00                              | 15.83                    | 731           | 0.601| 6.95      |
| 3.33                              | 15.52                    | 733           | 0.619| 7.05      |
| 3.57                              | 15.02                    | 741           | 0.614| 6.83      |
| 3.75                              | 14.11                    | 748           | 0.608| 6.42      |

4. Conclusion

In summary, we introduce Tm$^{3+}$ and Yb$^{3+}$ into the TiO$_2$ film in dye-sensitized solar cell (DSSC). As luminescence medium, Tm$^{3+}$/Yb$^{3+}$ improve the incident light harvest via an up-conversion luminescence process, transferring infrared light into visible light, enhancing the photocurrent of the DSSC. As p-type doping, the rare-earth ions elevate the Fermi level of the oxide film, heightening the photovoltage of the DSSC. Under a simulated solar light irradiation of 100 mW·cm$^{-2}$, the DSSC containing rare-earth ions achieves a light-to-electric energy conversion efficiency of 7.05 %, which is enhanced by 10.0 % compared with the DSSC lacking the rare-earth ions. The present findings demonstrate the feasibility of the conversion luminescence and p-type doping in DSSC and provide an effective way to improve their solar conversion efficiency.

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