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# **Preparation of Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> downconversion luminescent material** and its application in dye-sensitized solar cells

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 $Gd_2O_3:Eu^{3+}$  downconversion luminescent powder was prepared using the homogeneous precipitation method. Its optical properties were analyzed and it was introduced into a dye-sensitized solar cell (DSSC). As a luminescence medium,  $Gd_2O_3:Eu^{3+}$  improved light harvesting via conversion luminescence and increased the photocurrent of the DSSC. As a p-type dopant insulating rare earth oxides form an energy barrier, and the  $Gd_2O_3:Eu^{3+}$  elevated the energy level of the oxide film and increased the photovoltage. The photoelectric conversion efficiency for a DSSC with  $Gd_2O_3:Eu^{3+}$  doping (6:100) reached 7.01%, which was 17.4% higher than the photoelectrical conversion efficiency of a DSSC without  $Gd_2O_3:Eu^{3+}$  doping.

dye-sensitized solar cell, downconversion, rare-earth oxide, luminescent material, p-type doping

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Considerable effort has been devoted to the dye-sensitized solar cell (DSSC) since the first prototype was reported by O'Regan et al. [1] and Gratzel [2]. There has been great progress in development of the DSSC over the past decade, because of its low cost, simple preparation, and conversion efficiency which has reached 11% [3]. In general, the sensitizer of the DSSC contains mainly N3 and N719 dyes [1-6], and the DSSC consists of a porous nanocrystalline TiO<sub>2</sub> film sensitized by a dye for absorbing incident light. However, even the best of these dyes (N719) absorbs only visible light in the wavelength range 300-800 nm, while the standard air-mass (AM1.5) terrestrial spectrum covers the wavelength region from UV to IR (200-2500 nm). Downconversion materials are a viable option for reducing the spectral mismatch losses. Trupke et al. [7] have suggested that the dye molecules in a DSSC could avoid the absorption of high-energy photons in a conventional semiconductor solar cell with infinite bands, by directing the

high-energy part of the solar spectrum toward a downconverter with suitable low-pass mirrors. However, few studies have been carried out on the use of conversion luminescence in the DSSC. Our group [8] has reported work in which  $Y_2O_3$ :Eu<sup>3+</sup> nanophosphor was prepared by the co-precipitation method. As a luminescence medium  $Y_2O_3$ :Eu<sup>3+</sup> improved light harvesting via a conversion luminescence process and increased the photocurrent. As a p-type dopant,  $Y_2O_3$ :Eu<sup>3+</sup> elevated the energy level of the oxide film and increased the photovoltage.

In the present study,  $Gd_2O_3:Eu^{3+}$  nanophosphor was prepared by the homogeneous precipitation method [9,10]. Since  $Gd_2O_3$  is isostructural with  $Y_2O_3$ ,  $Gd_2O_3:Eu^{3+}$  can be used as a phosphor and is comparable to  $Y_2O_3:Eu^{3+}$ .  $Gd_2O_3:Eu^{3+}$  has been reported to be a more effective phosphor than  $Y_2O_3:Eu^{3+}$  for particular applications such as an X-ray scintillator, because  $Gd_2O_3$  has higher density and light efficiency [11]. In addition, the synthesis of  $Gd_2O_3:Eu^{3+}$  phosphor with higher photoluminescence (PL) intensity than commercially available  $Y_2O_3:Eu^{3+}$  has been

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reported [12,13]. In the present study,  $Gd_2O_3:Eu^{3+}$  as a luminescence medium and p-type dopant was introduced into the DSSC to improve photocurrent, photovoltage and solar conversion efficiency.

## 1 Experimental

### 1.1 Materials

Tetrabutyl titanate, absolute ethyl alcohol, glacial acetic acid, polyethylene glycol 20000, 4-tert-butylpyridine (TBP), nitric acid, OP emulsification agent (Triton X-100), iodine, lithium iodide, urea and ammonium hydroxide were analytical grade materials supplied by Shanghai Chemical Agent Ltd., Shanghai, China. Gadolinium oxide and europium oxide with purity 99.99% and 99.999% respectively, were supplied by Shanghai Yuelong Non-Ferrous Metals Limited, Shanghai, China. The sensitized dye N-719 (RuL2(NCS)2, L=4,4'-dicarboxylate-2,2'-bipyridine) was from SOLARO-NIX SA (Aubonne, Switzerland).

## **1.2** Preparation of Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphor

Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphor was prepared using the homogeneous precipitation technique by the following procedure [9,10]. Appropriate amounts of Gd<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub> were dissolved in dilute HNO<sub>3</sub> solution. The HNO<sub>3</sub> soluatin was made from a 1:1 (v/v) mixture of deionized water and 60%–65% HNO<sub>3</sub> solution. After heating and evaporating the excess water and HNO<sub>3</sub> until nitrate crystals emerged, the required amount of water was added to form 0.05 mol/L  $Gd(NO_3)_3$  and 0.05 mol/L  $Eu(NO_3)_3$  aqueous solutions. The required volumes of the Gd(NO<sub>3</sub>)<sub>3</sub> and Eu(NO<sub>3</sub>)<sub>3</sub> soluations were then mixed to give a solution with the mole ratio Gd(NO<sub>3</sub>)<sub>3</sub>:Eu(NO<sub>3</sub>)<sub>3</sub>=100:6. Excess 0.2 mol/L urea solution was mixed with the Gd(NO<sub>3</sub>)<sub>3</sub>/Eu(NO<sub>3</sub>)<sub>3</sub> solution, and sufficient aqueous ammonium hydroxide was added to adjust the pH to 8-9. The resulting solution was heated in a water bath at 90°C, and refluxed for 5 h after a precipitate started to form. The reaction mixture was then guenched in ice water, the precipitated precursor powder was washed with water and ethyl alcohol to eliminate residual salts. The powder was vacuum dried at 80°C for 24 h, then calcined at 800°C for 2 h, for subsequent use as a nanophosphor.

#### 1.3 Preparation of film electrodes of DSSC

A TiO<sub>2</sub> colloid was prepared according to the method developed by our group [14–17]. Varying amounts of  $Gd_2O_3:Eu^{3+}$  nanophosphor were dispersed in TiO<sub>2</sub> sol, ultrasonicated and stirred for 30 min, then hydrothermally treated to form a TiO<sub>2</sub>+Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> colloid. A film with thickness about 12 µm was prepared by coating TiO<sub>2</sub> colloid on an fluorine doped tin oxide coated glass (FTO) using a doctor blade and sintering at 450°C for 30 min, then a

TiO<sub>2</sub>+Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> layer with thickness of about 4  $\mu$ m was coated on the TiO<sub>2</sub> film by the same method. After sintering at 450°C for 30 min and soaking in N-719 dye solution for 24 h, a dye sensitized film electrode (TiO<sub>2</sub>+Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>) was obtained. For comparison, a dye-sensitized TiO<sub>2</sub> film electrode without Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> was also made. The thickness of the oxide films for the DSSC with and without Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> were about 16  $\mu$ m. DSSCs with and without the Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> bearing layer were assembled using the methods described previously [17].

#### 1.4 Characterization and measurements

Powder X-ray diffraction (XRD) patterns were recorded with an X-ray diffractometer (Bruker D8, Karlsruhr, Germany) using Cu K $\alpha$  radiation ( $\lambda = 1.5405$  Å). Micrographs were recorded using a field emission scanning electron microscope (SEM, S-4800, Hitachi, Japan). Photoluminescence spectra were obtained using a fluorescence spectrometer (FLS920, with excitation wavelength 263 nm, Edinburgh Instruments, UK). Photovoltaic tests of DSSCs were carried out by measuring the *I–V* characteristic curves under simulated solar light irradiation of 100 mW/cm<sup>2</sup> from a 100 W Xe lamp (XQ-500W, Shanghai Photoelectricity Device Company, Shanghai, China).

Mott-Schottky analysis was carried out using standard electrochemical impedance spectroscopy at 1000 Hz in acetonitrile solution of containing 0.1 mol/L lithium perchlorate, 10 mmol/L lithium iodide and 1 mmol/L iodine, by scanning the potential from the positive to the negative direction in steps of 5 mV/s at room temperature. The TiO<sub>2</sub> thin film on FTO glass was the photoanode, the cathode was Pt foil, and a silver/silver chloride (Ag/AgCl) microelec-trodes was used as reference electrode.

## 2 Results and discussion

# 2.1 Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphor

Figure 1 shows a typical XRD pattern of  $Gd_2O_3$ :Eu<sup>3+</sup> phosphor calcined at 800°C in air. It is basically consistent with the standard X-ray diffraction card JCPDS 12-0797 without any impurity peaks, indicating  $Gd_2O_3$  with pure cubic structure. An SEM image of the powders is shown in Figure 2, and reveals that the particle size was 30–60 nm.

## 2.2 The properties of Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphor

Excitation spectra and emission spectra of  $Gd_2O_3:Eu^{3+}$ nanophosphor are shown in Figures 3 and 4. The spectral properties are typical of the well-known  $Gd_2O_3:Eu^{3+}$ [18–20]. The excitation spectrum was obtained by monitoring the emission of the  $Eu^{3+} {}^5D_0 \rightarrow {}^7F_2$  transition at 611 nm. It can be seen clearly that the excitation spectrum (Figure 3) consists of a broad band with a maximum at 256 nm due to

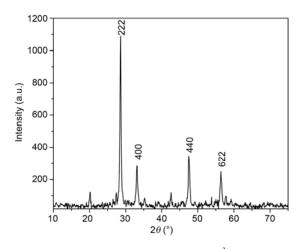


Figure 1 XRD pattern of the prepared  $Gd_2O_3$ :Eu<sup>3+</sup> nanophosphor.

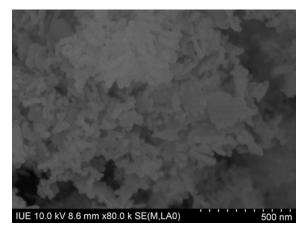
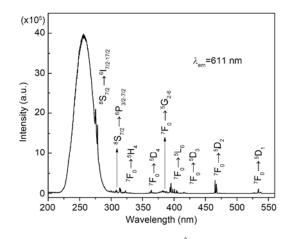


Figure 2 The SEM picture of  $Gd_2O_3$ : Eu<sup>3+</sup> nanophosphor.

the charge-transfer band (CTB) between  $O^{2-}$  and  $Eu^{3+}$ . The sharp peaks at 308 nm and the weak shoulder at 275 nm superimposed on the CTB of Eu<sup>3+</sup> can be attributed to the Gd<sub>2</sub>O<sub>3</sub> host excitation band, the <sup>8</sup>S-<sup>6</sup>P, and <sup>8</sup>S-<sup>6</sup>I transition lines of Gd<sup>3+</sup>, respectively [21]. The presence of the Gd<sub>2</sub>O<sub>3</sub> host band and Gd<sup>3+</sup> excitation lines in the excitation spectrum of Eu<sup>3+</sup> indicates that there is energy transfer from the Gd<sub>2</sub>O<sub>3</sub> host and Gd<sup>3+</sup> to Eu<sup>3+</sup>. In the longer wavelength region, the f-f transition lines of  $Eu^{3+}$  (assigned in Figure 3) can be observed with very weak intensity compared with the  $Eu^{3+}-O^{2-}CTB$ . Upon excitation into the CTB of  $Eu^{3+}$  at 263 nm, the resulting emission spectrum is composed of  ${}^{5}D_{0,1,2} \rightarrow {}^{7}F_{J}$  (J=0, 1, 2, 3, 4) transition lines of Eu<sup>3+</sup>, with the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  hypersensitive transition (611 nm) being the most prominent group (Figure 4). All of the other emission peaks at 534 ( ${}^{5}D_{1} \rightarrow {}^{7}F_{1}$ ), 580 ( ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ ), 588, 593, 599 ( ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ ), 651 ( ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$ ), and 708 nm ( ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ ) are assigned in Figure 4. The presence of emission lines from higher excited states of  $Eu^{3+}$  (<sup>5</sup>D<sub>1</sub>, <sup>5</sup>D<sub>2</sub>) is attributed to the low vibration energy of the Gd–O band (545 cm<sup>-1</sup>). Multiphonon relaxation by Gd-O vibration is not able to completely bridge the gaps



**Figure 3** The excitation spectra of  $Gd_2O_3$ :Eu<sup>3+</sup> nanophosphor.

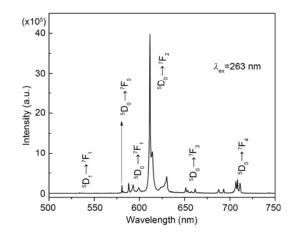
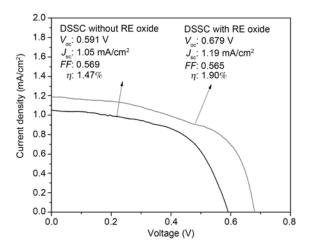


Figure 4 The emission spectra of  $Gd_2O_3$ : Eu<sup>3+</sup> nanophosphor.

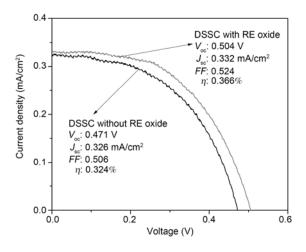
between the higher energy levels  $({}^{5}D_{1}, {}^{5}D_{2})$  and the  ${}^{5}D_{0}$  level of Eu<sup>3+</sup>, resulting in the emission from these levels [21].

#### 2.3 Photoelectric performance of DSSC

To investigate the effect of ultraviolet irradiation, we used a filter (ZWB3) that only the light with wavelength less than 420 nm could pass through. Figures 5 and 6 show the photocurrent-voltage curves of DSSCs and the solar cells with no dye, and with and without  $Gd_2O_3$ :Eu<sup>3+</sup> in TiO<sub>2</sub> the electrode under the ultraviolet irradiation of 24 mW/cm<sup>2</sup>. Figure 5 shows that the DSSC lacking the rare-earth ions as dopent had the following photovoltaic parameters: short-circuit current density  $(J_{sc})=1.05 \text{ mA/cm}^2$ , open-circuit voltage (Voc)=0.591 V, fill factor (FF)=0.569 and light-to-electric energy conversion efficiency  $(\eta)=1.47\%$ . The DSSC containing the rare-earth ions as dopent displayed the enhanced photovoltaic parameters:  $J_{\rm SC}$ =1.19 mA/cm<sup>2</sup>,  $V_{\rm OC}$ =0.679 V, FF=0.565 and  $\eta$ =1.90%. Figure 6 indicates that with no dye in the solar cells, the cells lacking the rare-earth ions as dopent had the photovol



**Figure 5** Current-Voltage curves of DSSCs under ultraviolet irradiation (24 mW/cm<sup>2</sup>).

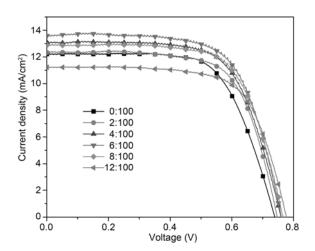


**Figure 6** Current-Voltage curves of the solar cells when no dye under ultraviolet irradiation (24 mW/cm<sup>2</sup>).

taic parameters:  $J_{SC}$ =0.326 mA/cm<sup>2</sup>,  $V_{OC}$ =0.471 V, *FF*=0.506 and  $\eta$ =0.324%. The solar cells containing the rare-earth ions as dopent displayed the enhanced photovoltaic parameters:  $J_{SC}$ =0.332 mA/cm<sup>2</sup>,  $V_{OC}$ =0.504 V, *FF*=0.524 and  $\eta$ =0.366%. The enhancement indicates that the rare-earth ions dopent converts ultraviolet light to visible light which the N-719 dye can absorb effectively, increasing the harvested sunlight and improving the efficiency of the DSSC.

The data in Figure 7 and Table 1 show that  $J_{SC}$  increased with the Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>dopent level up to 6:100 (the mole ratio of gadolinium and titanium), beyond which  $J_{SC}$  decreased. The increase in  $J_{SC}$  comes mainly from the ultraviolet response of Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup> nanophosphor, which caused more to be harvested, thus increasing  $J_{SC}$  The decrease in  $J_{SC}$  at higher dopent levels is due to the fact that introduction of rare-earth oxides produced defects in the oxide film, which caused the recombination of photoinduced holes and electrons and hence decrease  $J_{SC}$  [22].

Figure 8 is a Mott-Schottky plot for the TiO<sub>2</sub> electrode



**Figure 7** Current-Voltage curves of DSSCs without and with different ratio of  $Gd_2O_3$ :Eu<sup>3+</sup> nanophosphor in TiO<sub>2</sub> electrode.

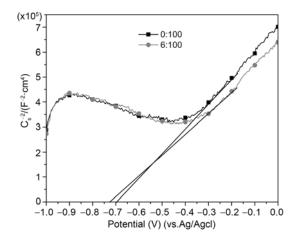


Figure 8 Mott-Schottky plots of  $TiO_2$  electrode with and without doped nanophosphor.

with and without doped nanophosphor. It is clear from Figure 8 that under the same conditions, the TiO<sub>2</sub> working electrode of TiO<sub>2</sub> had similar flatband potential with (-0.723 V) or without (-0.692 V) nanophosphor. Figure 8 also shows that the slope of the linear region of the Mott-Schottky curve desreased when the nanophosphor was doped, thus increasing its charge carriers density.

On the other hand, the  $V_{\rm OC}$  increased with increasing amount of Gd<sub>2</sub>O<sub>3</sub>:Eu<sup>3+</sup>. When the mole ratio of element gadolinium and titanium was 12:100,  $V_{\rm OC}$  reached 0.776 V, which is the highest value yet observed in a DSSC, indicating the significance of p-type doping. According to Gratzel [2],  $V_{\rm OC}$  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<sup>4+</sup> ion lattice sites in TiO<sub>2</sub>, 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  $V_{\rm oc}$ . Similar phenomena were observed by Ko et al.

Mole ratio $(N_{\text{Gd}}: N_{\text{Ti}})$	$J_{\rm sc}~({\rm mA/cm}^2)$	$V_{\rm oc}$ (V)	FF	$\eta$ (%)
0:100	12.30	0.739	0.657	5.97
2:100	12.47	0.747	0.677	6.31
4:100	13.18	0.759	0.667	6.68
6:100	13.79	0.76	0.669	7.01
8:100	12.93	0.766	0.685	6.78
12:100	11.25	0.776	0.687	5.99

[23] who found that Al-doping of the TiO<sub>2</sub> electrode increased  $V_{oc}$ , while W-doping had the opposite effect (n-type doping). Yang et al. [24,25] found that an energy barrier was formed when the TiO<sub>2</sub> electrode was modified with a rare earth ion layer of a certain thickness. The energy barrier efficiently suppressed charge recombination. As a result, the photovoltage and photoelectrical conversion efficiency were improved under optimal conditions.

The solar conversion efficiency for a DSSC with  $Gd_2O_3:Eu^{3+}$  (6:100) doped nanophosphor reached 7.01%, which is 17.4% higher than for a DSSC without  $Gd_2O_3:Eu^{3+}$  nanophosphor doping (Figure 7). 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.

## 3 Conclusion

In summary,  $Gd_2O_3:Eu^{3+}$  nanophosphor was introduced into a dye-sensitized solar cell. As a luminescence medium,  $Gd_2O_3:Eu^{3+}$  improved light harvesting via a conversion luminescence process and increased photocurrent. As a p-type dopant insulating rare earth oxides form an energy barrier, and the  $Gd_2O_3:Eu^{3+}$  elevated the energy level of the oxide film and increased the photovoltage. The solar conversion efficiency for a DSSC with  $Gd_2O_3:Eu^{3+}$  doping (6:100) reached 7.01%, which is 17.4% higher than for a DSSC without  $Gd_2O_3:Eu^{3+}$  nanophosphor doping.

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