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Enhanced light harvesting of dye-sensitized solar cells with up/down conversion materials

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ABSTRACT

Rare-earth doped ZnO up/down-conversion materials were prepared and introduced into photoelectrodes to enhance the photovoltaic efficiency of dye-sensitized solar cells. In this paper, we achieved a optimal efficiency of 5.13% with the incorporation of ZnO:Eu^{3+},Tb^{3+} and ZnO:Er^{3+}, Yb^{3+}, which is about 70% higher than that of dye-sensitized solar cells based on pure TiO_2. This is probably due to the enhancement of light harvesting via converting ultraviolet and near infrared radiation to visible emission by downconversion and upconversion luminescence process, respectively. In addition, the ZnO:Eu^{3+},Tb^{3+} film acted as a blocking layer inhibit the charge recombination, suppressing the dark current for DSSCs. Results indicate that the ZnO:Eu^{3+},Tb^{3+}/TiO_2:ZnO:Er^{3+}, Yb^{3+} double composite layers can obviously improve the efficiency of dye-sensitized solar cells, and the combine of the up and down conversion materials is an effective method to extend the response both to ultraviolet and near-infrared radiation in dye-sensitized solar cells.

1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted extensive attention as one of the promising alternatives for silicon solar cells [1,2]. High power conversion efficiency of 15% for a solid-state dye-sensitized solar cell (DSSC) has been achieved by using $CH_3NH_3PbI_3$ as a dye sensitizer and a hole transport material (HTM) consisting of organic materials in place of electrolyte [3]. However, DSSCs have a maximum absorption in visible light of solar spectrum, which confines the enhancement of power conversion efficiency [4]. Lots of research efforts have been focused on extending light absorption to enhance the conversion efficiency[5–7]. The development of photoanode for DSSCs is critical because the light harvesting in DSSCs is dependent on the absorption spectrum of dye-loaded photoanode [4,8].

As is well known that rare earth ions have been studied to be used in fiber lasers, plasma displays, solar cells and bio-imaging probes due to the advantage of optical properties for their intra 4f transitions [9–11]. Hexagonal wurtzite ZnO as one of the excellent host materials for the doping of the rare earth has been widely reported because of its unique properties, such as wide band gap (3.37 eV), large exciton binding energy (60 meV), chemical stability, high electron mobility, low cost of production, and it has a wide range of applications in solar cells, UV photodetectors, photocatalysis, filed emission display, light-emitting diodes, etc [12,13]. Rare earth ions doped up/down conversion materials is an available approach to compensate for the non-absorbable wavelength region of DSSCs via converting near-infrared and ultraviolet radiation to visible emission [8,14,15].

Upconversion (UC), is a luminescence process where absorb two or more low energy infrared photons and then convert them to a high energy visible photon. Among the lanthanide ions in upconversion process, Er^{3+}-Yb^{3+} codoped materials is the most commonly used [16]. As example, M. A. Hernández-Rodríguez et al. achieved upconversion emission spectra of Er^{3+}-Yb^{3+} codoped fluoroindate glasses under infrared excitation at 1480 nm and applied the samples in Si solar cell to obtain a optimal photocurrent [17].

Downconversion (DC), lanthanide ions based nanoparticles convert the UV-blue part of solar spectrum into visible light, which have been widely used and reported [18,19]. In 2011, H. Hafez et al. prepared Sm^{3+} and Eu^{3+} doped TiO_2 nanoparticles as photoelectrode by the sol-gel method, and high efficiencies of 5.81% and 5.16% for Sm^{3+} and Eu^{3+} were obtained respectively via improving the response to UV radiation in DSSCs [20].

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In this current work, we use ZnO as matrix material due to its stable chemical properties, high electron mobility, easy fabrication procedures, and by doping rare earth in ZnO can realize a high photoluminescence of rare earth ion [21]. And we first applied a multifunctional ZnO:Eu^{3+},Tb^{3+}/TiO_2:ZnO:Er^{3+}, Yb^{3+} double composite layers to construct photo anode of DSSCs to enhance the efficiency of solar cells by improving the light harvesting for DSSCs. The ZnO:Eu^{3+},Tb^{3+} film has a wide UV to blue light absorption and its highly efficient green emission matches the main absorption region of the commonly used dye N719. Also, ZnO:Eu^{3+},Tb^{3+} film was prepared on Fluorine doped tin oxide (FTO) substrates as a blocking layer can inhibit the charge recombination between photoelectrode and I_3^-, therefore, the dark current will be suppressed efficiently for DSSCs [22]. In addition, Er^{3+}, Yb^{3+} codoped ZnO nanoparticles have the solar cell responsed to near infrared radiation, thus the light harvesting efficiency will be improved. By the utilizing of DC and UC materials, the efficiency of DSSCs can be enhanced via converting ultraviolet and near-infrared radiation to visible emission [14,20].

2. Experimental

2.1. Preparation of ZnO:Eu^{3+},Tb^{3+} films

ZnO:2 mol% Eu^{3+}, 2 mol% Tb^{3+} films were prepared on FTO glass substrates by a sol-gel method described by Che [23]. Typically, 0.01 mol $Zn(OOCCH_3)_2{\cdot}2H_2O$ and 0.01 mol monoethanol amine were dissolved in 2-methoxyethanol under stirring at 60 °C until a transparent solution was obtained. And then $Eu(NO_3)_3{\cdot}6H_2O$, $Tb(NO_3)_3{\cdot}6H_2O$ were added into the above solution at room temperature with constant stirring for 1 h to form transparent sols.

2.2. Synthesis of ZnO:Er^{3+}, Yb^{3+} nanoparticles

0.5 mol% Er^{3+}, 2 mol% Yb^{3+} and 2 mol% Li^+ doped ZnO nanoparticles denoted by ZnO:Er^{3+}, Yb^{3+} in DSSC were synthesized by the method according to the reference [24]. $Zn(OOCCH_3)_2{\cdot}2H_2O$, $Er(NO_3)_3{\cdot}6H_2O$, $Yb(NO_3)_3{\cdot}6H_2O$, and $LiNO_3$ were dissolved in 60 ml deionization water under vigorous stirring at 80 °C, then citric acid was added in the transparent solution to form the mole ratio of (Zn^{2+} + Er^{3+} + Yb^{3+} + Li^+) to citric acid is 1:3. The ammonium hydroxide was gradually added to the above solution until pH of the solution is about 7, and the solution turned to be black solid after drying in air at 120 °C for 10 h. Finally, the white ZnO doped with Er^{3+},Yb^{3+}, and Li^+ powder was obtained by calcining in furnace at 800 °C for 2 h.

2.3. DSSCs fabrication

The photoanode pastes were prepared according to the method mentioned in our previous report [25]. To prepare the ZnO:Eu^{3+}, Tb^{3+}/TiO_2:ZnO:Er^{3+}, Yb^{3+} composite film electrodes, firstly, the obtained sols were spin-coated onto the cleaned FTO surface at 2000 rpm for 20 s for six times, followed by drying at 100 °C for 10 minutes, and the final FTO/ZnO:Eu^{3+},Tb^{3+} films were annealed at 450 °C for 1 h. Secondly, 10 mg of ZnO:Er^{3+}, Yb^{3+} was added in the TiO_2 pastes. After stirring for 24 hours at room temperature, the mixed pastes TiO_2:ZnO:Er^{3+}, Yb^{3+} were fabricated on FTO and FTO covered by ZnO:Eu^{3+},Tb^{3+} thin film using the doctor blade method. And then, the ZnO:Eu^{3+},Tb^{3+}/TiO_2:ZnO:Er^{3+}, Yb^{3+} composite layers were annealed in air at 450 °C for 30 min. In order to absorb the dye, the photoelectrodes were immersed into a ethanol solution of 0.36 mM N719 ruthenium dye for 24 h at room temperature, finally washed with ethanol to remove the nonchemisorbed dye and dried in air. Pt counter electrode was prepared by spin-coating method, followed by annealing at 450 °C for 30 minutes [26]. Subsequently, fix the sensitized photoelectrode and Pt counter electrode together using a hot-melt film spacer. Finally, a dye sensitized solar cell was assembled by injecting electrolyte (OPV-MPN-I) into the space between the electrodes. The structure of the DC/UC-doped dye sensitized solar cells is described in Fig. 1.

2.4. Characterization

The structure of the rare earth doped ZnO was investigated by X-ray diffraction (XRD, D8-Advance, Bruker). The photoluminescence (PL) was characterized using the 7-FRSpec fluorescent spectrometer made by Sofn using a Xe lamp as the excitation source. The absorption spectra of N719 dye was measured by a UV-vis-NIR spectrophotometer (TU-1901, Purkinje). The morphology of anode films were examined with field emission scanning electron microscope (FE-SEM, Quanta FEG250). The photocurrent response to time was measured by cycles of light switching on and off under a Xe lamp as the light source. The I-V characteristics of the DSSCs were measured with an Aglient B2901A source/meter under a Xe lamp. The irradiation areas of the working electrode were about 0.16 cm^2. All of these measurements were carried out at room temperature.

3. Results and discussion

The XRD is used to characterize the crystal structures of ZnO:Eu^{3+},Tb^{3+} and ZnO:Er^{3+}, Yb^{3+},Li^+. Fig. 2(a) and (b) show the XRD patterns of 2 mol% Eu^{3+}, 2 mol% Tb^{3+} co-doped ZnO and 0.5 mol% Er^{3+}, 2 mol% Yb^{3+}, 2 mol% Li^+ doped ZnO, respectively. For the samples, the diffraction peaks correspond to hexagonal wurtzite ZnO crystal structure with Joint Committee on Powder Diffraction Standards (JCPDS) no. 36-1451 and no extra peaks due to other oxide phases are observed in the XRD patterns, indicating that rare earth ions might have been incorporated into ZnO lattice sites of Zn^{2+}. In addition, the sharp diffraction peaks suggest that the prepared samples are highly crystalline.

Fig. 3 shows the absorption spectra of N719, the spectrum of solar radiation, the room temperature photoluminescence emission and excitation spectra of ZnO:Eu^{3+},Tb^{3+} and ZnO:Er^{3+},Yb^{3+},Li^+. From the Fig. 3(b), the excitation peaks of ZnO:Eu^{3+},Tb^{3+} at 316 nm, 396 nm correspond to the transition $^7F_5$-$^5D_0$ of Tb^{3+} and the transition $^7F_0$-$^5L_6$ of Eu^{3+}. Also, the emission spectra of ZnO:Eu^{3+}, Tb^{3+} and ZnO:Er^{3+},Yb^{3+},Li^+ are shown in Fig. 3(d) and (e). The emission peaks 491 nm, 549 nm and 581 nm due to transition $^5D_4$-$^7F_6$,$^5D_4$-$^7F_5$ and $^5D_4$-$^7F_4$ of Tb^{3+} are observed [13]. Besides, the emission 611 nm which is from the transition from $^5D_0$-$^7F_2$ of Eu^{3+} is also obtained [27]. Here, Fig. 3(e). shows the UC luminescence spectra of ZnO doped with Er^{3+}, Yb^{3+} and Li^+ under excitation by 980 nm laser, and the emission peaks centered at 489 nm, 527 nm, 549 nm and 667 nm corresponding to the transition $^4F_{7/2}$-$^4I_{15/2}$, $^2H_{11/2}$-$^4I_{15/2}$, $^4S_{3/2}$-$^4I_{15/2}$ and $^4F_{9/2}$-$^4I_{15/2}$, respectively [28]. From the

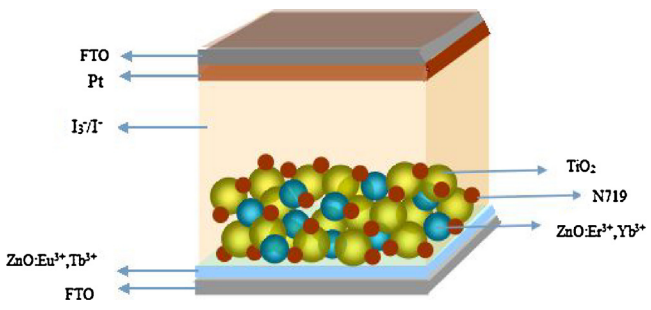

Fig. 1. The structure of DSSCs.