Journal of Power Sources 249 (2014) 72–78

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Performance enhancement in dye-sensitized solar cells by utilization of a bifunctional layer consisting of core–shell β-$NaYF_4$:Er^{3+}/Yb^{3+}@SiO_2 submicron hexagonal prisms

Kaimo Guo, Meiya Li*, Xiaoli Fang, Mengdai Luoshan, Lihua Bai, Xingzhong Zhao

School of Physics and Technology, and the Key Laboratory of Artificial Micro/Nano Structures of Ministry of Education, Wuhan University, Wuhan 430072, PR China

HIGHLIGHTS

- Synthesis of highly uniform β-$NaYF_4$:Er^{3+}/Yb^{3+}@SiO_2 core–shell hexagonal nano-prisms.
- Fabrication of DSSCs with β-$NaYF_4$:Er^{3+}/Yb^{3+}@SiO_2 as a bifunctional material.
- Enhanced light scattering and up-conversion were obtained in β-$NaYF_4$:Er^{3+}/Yb^{3+}@SiO_2.
- The properties of the DSSC with 15 wt % β-$NaYF_4$:Er^{3+}/Yb^{3+}@SiO_2 were greatly improved.
- Improvement is attributed to light scattering and up-conversion of β-$NaYF_4$:Er^{3+}/Yb^{3+}.

ARTICLE INFO

Article history:
Received 11 August 2013
Received in revised form
1 October 2013
Accepted 17 October 2013
Available online 25 October 2013

Keywords:
Silicon dioxide coated sodium yttrium fluoride core–shell structure
Light scattering
Up-conversion
DSSCs
Short-circuit current
Photoelectric conversion efficiency

ABSTRACT

Highly uniform, monodisperse β-$NaYF_4$:Yb^{3+}/Er^{3+}(NYFYE) up-conversion phosphor submicron hexagonal prisms coated with a SiO_2 layer are synthesized via a hydrothermal route, forming a core–shell NYFYE@SiO_2 crystallites. These crystallites are incorporated into TiO_2 nanocrystalline porous film to act as a bifunctional layer and form a composite photoanode employed in dye-sensitized solar cells (DSSCs). The influences of different amount of the NYFYE@SiO_2 on the performance of the composite photoanodes and DSSCs are investigated. Studies indicate that by adding NYFYE@SiO_2 the light scattering, absorption and near-infrared light harvesting of the composite photoanode are significantly increased, resulting in the great enhancement in the short-circuit current density (J_{sc}) and photoelectric conversion efficiency (η) of the DSSCs. The optimal properties with an J_{sc} of 14.91 mA cm^{-2} and η of 7.28% are obtained in a DSSC with NYFYE@SiO_2 content of 15 wt %, increasing significantly by 14% and 29%, respectively, in comparison with those of the DSSC with pure TiO_2 photoanode. This significant enhancement in the performance of the DSSCs can be attributed to the enhanced light absorption due to the enhanced light scattering and near-infrared up-conversion of the NYFYE@SiO_2 bifunctional layer in the photoanode of the DSSCs.

1. Introduction

Exploitation and utilization of renewable energy has recently been proposed as a main solution for fossil fuel crisis and global warming. Among the candidates for the renewable energy so far, solar cell is a good choice. Dye-sensitized solar cells (DSSCs),first demonstrated by Oregan and Grätzel in 1991 [1], has been regarded as the most promising solar cells in the renewable energy field due to its relatively high photoelectric conversion efficiency, potentially low cost and simple fabrication methodology [2–5].Typically, a standard DSSC comprises a photoanode of dye-sensitized porous nanocrystalline TiO_2 film, a Pt-coated conductive glass as counter electrode and an electrolyte solution with a redox couple iodide/triiodide (I^-/I_3^-) between the electrodes. In order to improve the photoelectric conversion efficiency of DSSCs, various techniques, such as controlling TiO_2 photoanode into various nanostructural morphologies [6–8], dopants [9–11], new synthesized redox shuttles [12,13] and dyes capable of effectively absorbing visible and near-infrared light [14], have been explored. The dye adsorbed onto the surface of the porous TiO_2

---

* Corresponding author.
E-mail address: myli@whu.edu.cn (M. Li).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.10.067

film of DSSCs plays an important role in harvesting sunlight. Upon light irradiation, the dye is promoted into an electronically excited state by absorbing photon and produce photo-stimulated electrons, and this electrons can transfer into the conduction band of the TiO_2 film. Thus, the light-harvesting efficiency (LHE) of the dye and the quantity of the photo-stimulated electrons would determine the efficiency of DSSCs to a great extent [15]. And enhancing the LHE of dye would be an effective way to increase the photoelectric conversion efficiency of DSSCs. However, the Ru dyes (N_3 and its derivatives), currently the most common used dyes in DSSCs, usually absorb light only up to about 700 nm due to their relatively large optical bandgap ($Eg = \sim 1.8$ eV) [16], which means that approximately 50% energy of the solar spectrum in near-infrared (NIR) region is not utilized [16,17]. Consequently, the photoelectric conversion efficiency of DSSCs, to great extent, is limited by this spectral mismatch losses. Accordingly, extending the spectral response range of the photoanode to the NIR region is greatly expected to increase the photoelectric conversion efficiency of DSSCs.

Up-conversion (UC), first proposed in 1959 [18], refers to a nonlinear optical process in which an UC material can convert NIR light (>900 nm) to visible light (≤700 nm) by absorbing NIR low-energy photons and then emitting visible high-energy photons (anti-Stokes type emission). UC materials have recently received considerable attention due to their wide applications in biomedical imaging [19,20],semiconductor quantum dots and organic dyes [21], photovoltaic applications [22,23] and flat-panel displays monitors [24]. Among the investigated UC materials so far, the hexagonal phase(β-) of $NaYF_4$ host lattice doped with lanthanide combinations of Yb^{3+}/Er^{3+} has the highest UC efficiency [25]. This β-$NaYF_4$:Yb^{3+}/Er^{3+} (named as NYFYE) can generate strong green emission after absorbing NIR light [26]. Recently, studies on enhancing the photoelectric conversion efficiency of DSSCs via incorporating with such UC materials has been conducted [27,28]. For the purpose of matching well with nanocrystalline TiO_2 and light scattering demand, the crystallite size of the UC material used in the photoanode of DSSCs should be submicron or smaller. However, compared with bulk UC material, small UC crystallites show a classical drawback, namely poor luminescent efficiency. For example, in the case of lanthanide-based UC nano-crystallite, the presence of surface defects and ligands with high-energy vibrational modes such as OH or NH_2 groups can lead to the quenching of the excited lanthanide states by multiphonon relaxation processes (namely energy losses) [29,30]. In addition, the surface defects and ligands of the UC nano-crystallite in TiO_2 photoanode film would act as an electron trapping center and lead to charge recombination at the surface, which is the major limitation for their application in DSSCs [27]. Fortunately, coating UC nano-crystallite with an insulating layer to form a core–shell architecture helps to overcome this problem to some extent [28]. Therefore, by using the insulating SiO_2 as a coating layer to solve the above mentioned problem and prepare the core(NYFYE)-shell(SiO_2) structure (NYFYE@SiO_2) crystallites and apply them in DSSCs, greatly enhancing the photoelectric conversion efficiency of DSSCs might be expected. However, such study has rarely been reported.

In this paper, we report the preparation of highly uniform and monodisperse core–shell structural NYFYE@SiO_2 crystallites by hydrothermal method. Different amounts of NYFYE@SiO_2 were incorporated into TiO_2 nanocrystalline films to form the composite photoanodes and then the DSSCs, as shown schematically in Fig. 1. The influence and mechanism of such NYFYE@SiO_2 crystallites on the performance of the photoanodes and the DSSCs were investigated.

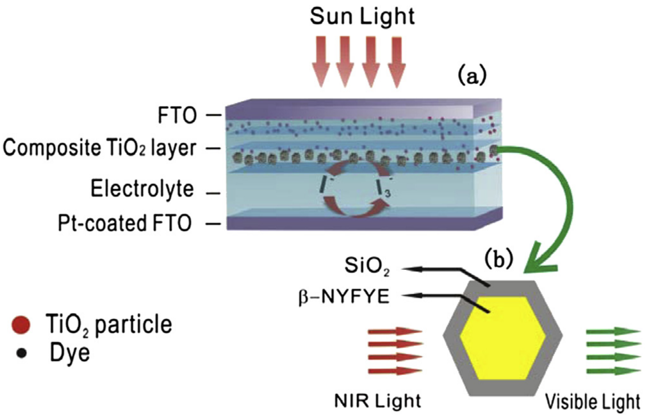

Fig. 1. (a) Schematic structure of the DSSCs incorporated with core–shell NYFYE@SiO_2 in TiO_2 film. (b) Cross section of an NYFYE@SiO_2 hexagonal prism and the schematic of the UC process.

2. Experimental section

2.1. Materials

NaF, $Y(NO_3)_3\cdot 6H_2O$, $Yb(NO_3)_3\cdot 6H_2O$ and $Er(NO_3)_3\cdot 6H_2O$ were purchased from Wuhan Chemical Corporation (China). The ethanol (EtOH, 95%), Triton-X100, acetylacetone, Poly (ethylene glycol) (PEG, MW = 20,000), Tetraethylorthosilicate (TEOS, 99.9%), ammonia (28–30 wt % NH_3 in water), nitric acid (HNO_3, 65% ~ 68%), polyvinylpyrrolidone (PVP, $M_w = 55$ k in terms of monomeric units) (>99.5%) and propylene carbonate (PC) were obtained from Sinopharm Chemical Reagent Corporation (China). The Ru dye and cis-di(thiocyanato)-bis(2,2′-bipyridyl-4,4′-dicarboxylate) ruthenium(II) (N719) were purchased from Solaronix (Switzerland). The Iodine (I_2, 99.8%) was acquired from Beijing Yili Chemicals (China). Lithium iodide (LiI, 99%) and 4-tert-butylpyridine (TBP) were purchased from Acros (China). The fluorine-doped SnO_2 conductive glasses (FTO, sheet resistance 10–15 $\Omega\ sq^{-1}$, Asahi Glass, Japan) were used as the substrate for the preparation of mesoporous nanocrystalline TiO_2 film. All water used in the fabrication was deionized (18.2 MΩ, milli-Q pore).

2.2. Synthesis of NYFYE@SiO_2 core–shell structure

NYFYE@SiO_2 submicron hexagonal prisms with highly uniformity and monodispersity were grown by a modified hydrothermal reduction technique [31]. Typically, a DI-water solution (20 ml) in beaker containing $Y(NO_3)_3\cdot 6H_2O$, $Yb(NO_3)_3\cdot 6H_2O$ and $Er(NO_3)_3\cdot 6H_2O$ (ion molar ratio, Y/Yb/Er = 78:20:2) were first prepared and stirred magnetically for 20 min; Then an aqueous solution of sodium citrate (40 ml) was added into the above solution, keeping for continuous stirring for 1 h. Subsequently, an aqueous solution (82 ml) of NaF (2.1 g) was added to the above solution and stirred for another 40 min. Finally, the pH value of the solution was adjusted to 3.5. Then the solution was transferred into two Teflon-lined autoclaves (100 ml for each) and heated at 200 °C for 4 h to obtain the submicron hexagonal prisms. This as-prepared NYFYE solution was then centrifuged at 6000 rpm for 5 min for three times and dried at 80 °C for 3 h to remove excess sodium citrate and obtain the white precipitates (NYFYE submicron hexagonal prisms). The white precipitates were then re-dispersed into EtOH solution and then coated with silica to form NYFYE@SiO_2 core–shell structure by the modified Stober method [32]. The as-prepared NYFYE@SiO_2 white powders were then collected by centrifugation and then dried at 80 °C for 3 h for further usage.