Electrochimica Acta 245 (2017) 839–845

Contents lists available at ScienceDirect

Electrochimica Acta

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

Enhanced Photovoltaic Performance of Perovskite Solar Cells Based on Er-Yb Co-doped TiO_2 Nanorod Arrays

Xiaoli Wang[a], Zhenlong Zhang[a,**], Jianqiang Qin[a], Wenjia Shi[a], Yuefeng Liu[a], Huiping Gao[a], Yanli Mao[a,b,*]

[a] School of Physics and Electronics, Henan University, Kaifeng 475004, China
[b] Institute for Computational Materials Science, Henan University, Kaifeng 475004, China

ARTICLE INFO

Article history:
Received 10 April 2017
Received in revised form 31 May 2017
Accepted 5 June 2017
Available online 6 June 2017

Keywords:
Er-Yb co-doped TiO2
Nanorod arrays
Upconversion
Perovskite solar cell

ABSTRACT

In the present study, Er and Yb co-doped TiO_2 (Er-Yb:TiO_2) nanorod arrays were grown with a hydrothermal method, and perovskite solar cells were fabricated using them as an electron transfer material. The photovoltaic performance of the solar cells based on Er-Yb:TiO_2 was enhanced compared with that of solar cells based on un-doped TiO_2. The power conversion efficiency of the solar cells on Er-Yb:TiO_2 increased to 13.4%, which is 20.8% higher than that of the solar cells based on un-doped TiO_2. The experimental results indicate that the larger open circuit voltage could be due to the larger conduction band difference between Er-Yb:TiO_2 and perovskite material. The enlarged short circuit current could be attributed to the faster electron transfer, reduced recombination, and the upconversion of Er-Yb:TiO_2 NRs.

1. Introduction

Recently, perovskite solar cells (PSCs) have been paid more attentions due to its low cost, long charge diffusion length, and high efficiency [1–4]. In 2009, Tsutomu Miyasaka et al. applied perovskte material to solar cells for the first time and obtained the power conversion efficiency (PCE) of 3.8% [5]. In the past few years, the PCE of perovskite solar cells has reached 22.1% [6]. However, the perovskite solar cells only absorbs a small portion of incident light in the visible range [7,8], and a large portion of incident light energy is lost due to non-absorption of near infrared (NIR) light. This hampers the further improvement of power conversion efficiency for PSCs.

One of the methods to solve this problem is to expand the absorption light range using upconversion materials, which can transfer NIR to visible light. There have been some reports on the application of upconversion materials to dye sensitized solar cells (DSSCs) [9–11]. There are a few reports on the application of upconversion materials to perovskite solar cells, in which the upconversion materials applied in these reports are all based on $NaYF_4$ [8,12]. Until now, there are few reports on the application of TiO_2 based upconversion materials to perovskite solar cells.

In the present study, we synthesized Er and Yb co-doped TiO_2 (Er-Yb:TiO_2) nanorod arrays with an hydrothermal method, and fabricated perovskite solar cells using them as an electron transfer layer. The power conversion efficiency of solar cells based on Er-Yb:TiO_2 presents an enhancement of 20.8% compared with that of the solar cells based on un-doped TiO_2.

2. Experimental

2.1. Materials

Methylammonium Iodide (CH_3NH_3I), Lead (II) Chloride ($PbCl_2$), and 2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene(Spiro-OMeTAD) were purchased from Xi'an Polymer Light Technology Corp. (China). Titanium tetrachloride ($TiCl_4$), Titanium butoxide, Erbium trinitrate pentahydrate ($Er(NO_3)_3{\cdot}5H_2O$), Ytterbium nitrate pentahydrate ($Yb(NO_3)_3{\cdot}5H_2O$), N,N-Dimethylformamide (DMF), Chlorobenzene, 4-tert-Butylpyridine, lithiumbis(trifluoromethanesulfonyl)imide (Li-TFSI), and Acetonitrile were purchased from Shanghai Aladdin biochemical Polytron Technologies Inc. (Chian).

** Corresponding author at: School of Physics and Electronics, Henan University, Kaifeng 475004, China.
* Corresponding author.
E-mail addresses: zzl@henu.edu.cn (Z. Zhang), ylmao@henu.edu.cn (Y. Mao).

http://dx.doi.org/10.1016/j.electacta.2017.06.032
0013-4686/

2.2. Growth of TiO_2 nanorods arrays

Patterned FTO-coated glass substrate was cleaned by sonication for 20 mins in detergent, acetone, 2-propanol, and ethanol, respectively. Oxygen plasma was subsequently used to treat the substrate for 20 min. A compact layer of TiO_2 was formed on FTO by treating the substrate in a 0.2 M aqueous solution of $TiCl_4$ at 70 °C for 30 mins. TiO_2 nanorods (NRs) were grown on the compact layer by a hydrothermal method [13]. In brief, 20 mL of 37% hydrochloric acid and 20 mL of deionized water were mixed. Subsequently 0.7 mL of titanium(IV) n-butoxide was added and stirred for 30 min. In the next step, nothing was added to the solution for the growth of un-doped TiO_2, a certain amount of $Er(NO_3)_3{\cdot}5H_2O$, (Er/Ti, nominal atomic ratio, 1%) was added for the growth of Er doped TiO_2 (Er-TiO_2), and pre-calculated amount of $Er(NO_3)_3{\cdot}5H_2O$ (Er/Ti, nominal atomic ratio, 13%) and $Yb(NO_3)_3{\cdot}5H_2O$ (Yb/Ti, nominal atomic ratio, 0.5%, 1%, 3%, and 5%) were added for the growth of Er-Yb co-doped TiO_2 (Er-Yb:TiO_2). The mixed solution and a compact layer coated FTO substrate was sealed in a stainless steel autoclave. The sealed autoclave was placed inside the oven preheated to 170 °C for several hours. After cooling to room temperature, the TiO_2 nanorods film was rinsed with ethanol and deionized water, and annealed at 500 °C for 60 min.

2.3. Solar cell fabrication

The perovskite precursor solution was prepared by dissolving CH_3NH_3I and $PbCl_2$ in anhydrous DMF at a molar ratio of 3:1 at 60 °C. The perovskite precursor solution was spin-coated on the annealed TiO_2 film at 2000 rpm for 45 s in an argon-filled glove box. The sample was dried on a hotplate at 110 °C for 60 min. The hole-transporter layer was deposited by spincoating a solution of spiro-MeOTAD at 2000 rpm for 45 s. The spiro-MeOTAD solution was prepared by dissolving 72.3 mg of spiro-MeOTAD in 1 ml of chlorobenzene, to which 28.8 μl of 4-tert-butylpyridine and 17.5 μl of Li-TFSI solution (520 mg Li-TFSI in 1 ml acetonitrile) were added. Finally, a 80 nm gold layer was thermally evaporated on top of the device.

2.4. Characterization

X-ray diffraction (XRD) patterns were recorded on a DX-2700 diffractometer. Photocurrent-voltage (*I–V*) measurements were performed using a Keithley 2440 Sourcemeter under AM 1.5 G illumination from a Newport Oriel Solar Simulator with an intensity of 100 mW/cm^2. The active area was 0.1 cm^2 determined by a shadow mask. The incident photon to current conversion efficiency (IPCE) was determined using a Qtest Station 500ADX (America). Morphologies and microstructures were observed with a scanning electron microscope (SEM, JEM-7001F, JEOL). UV–vis absorption spectra were collected on a UV–vis spectrophotometer (Varian Cary 5000). Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements were acquired with a FLS 980 E fluorometer (Edinburgh Photonics), with an excitation source of 515 nm diode laser. The electrochemical impedance spectroscopy (EIS) was performed under a forward bias of 0.6 V under 1 sun illumination conditions with an electrochemical workstation (CHI660e, Shanghai CHI Co., Ltd.) with the frequency range from 1 Hz to 300 kHz. The magnitude of the alternative signal was 10 mV.

Table 1
Photovoltaic parameters of the solar cells based on TiO_2 NRs.

Sample	V_{oc} (V)	I_{sc} (mA/cm^2)	FF	PCE (%)
un-doped TiO_2	0.80 ± 0.04	20.4 ± 0.3	0.63 ± 0.03	10.3 ± 0.6
13% Er:TiO_2	0.83 ± 0.03	21.3 ± 0.3	0.64 ± 0.02	11.5 ± 0.6
13% Er-6% Yb-TiO_2	0.87 ± 0.04	21.7 ± 0.4	0.66 ± 0.02	12.9 ± 0.5

3. Results and discussion

We prepared un-doped TiO_2 and Er doped TiO_2 (Er:TiO_2) nanorod arrays, and fabricated perovskite solar cells using them as electron transfer layer. I–V measurements were carried out by reverse scan (RS) and forward scan (FS). The photovoltaic parameters, such as short circuit current (I_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) of the solar cells were calculated by the average of RS and FS for each device. The average photovoltaic parameters were obtained from an average of values from 10 pieces of devices. The dependence of PCE on the Er doping content is shown in Fig. 1A. The PCE of solar cells first increases, and then decreases with the increase of doping content, which reaches the maximum at Er doping content of 13% (Er/Ti, atomic ratio). We synthesized Er and Yb co-doped TiO_2 (Er-Yb:TiO_2) NRs with a constant doping content of Er (13%, Er/Ti, atomic ratio) and varied doping content of Yb. Fig. 1B shows the PCE dependence on doping content of Yb. It indicates that the PCE of the solar cells is the maximum at the Yb doping content of 6% (Yb/Ti, atomic ratio). The detailed photovoltaic parameters of solar cells based on un-doped TiO_2, 13% Er:TiO_2, and 13% Er-6%Yb:TiO_2 NRs are listed in Table 1. The photovoltaic parameters of solar cells based on 13% Er-6%Yb:TiO_2 NRs are enhanced compared with those of solar cells based on un-doped TiO_2. The PCE of the solar cells based on 13% Er-6% Yb:TiO_2 is 20.8% higher than that of solar cells

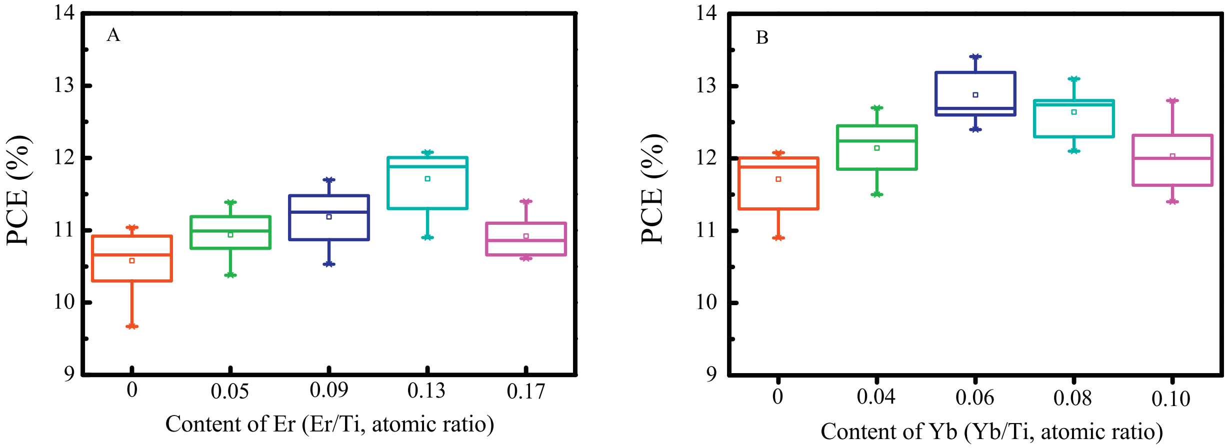

Fig. 1. Dependence of PCE on the doping content of (A) Er, and (B) Yb.