Solar Energy 169 (2018) 335–342

Contents lists available at ScienceDirect

Solar Energy

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

Enhanced performance of TiO_2-based perovskite solar cells with Ru-doped TiO_2 electron transport layer

Shuo Wang[a], Bao Liu[a], Yu Zhu[a], Zirui Ma[a], Beibei Liu[a], Xu Miao[a], Ruixin Ma[a,c,*], Chengyan Wang[a,b,*]

[a] School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, PR China
[b] Beijing Key Laboratory of Rare and Precious Metals Green Recycling and Extraction, University of Science and Technology Beijing, Beijing 100083, PR China
[c] Beijing Key Laboratory of Special Melting and Preparation of High-End Metal Materials, Beijing 100083, PR China

ARTICLE INFO

Keywords:
Ru-doping TiO_2
Mesostructured perovskite solar cells
Optoelectronic properties
Resistivity

ABSTRACT

Perovskite solar cells (PSCs) as the most promising alternative to the Si solar cells have been developed rapidly in recent time. Superior electron mobility and conductivity of the compact layer material are necessary for high efficiency in perovskite solar cells by reducing excessive charge accumulation and guaranteeing effective electron injection at the compact layer/perovskite interface. In this study, Ru ions were introduced into traditional compact TiO_2 to improve the electron transporting layer (ETL) properties and conductivity performance. Ru^{4+} was discovered in the Ru:TiO_2 according to the result of XPS. The reduced trap-filled limit voltage (V_{TFL}) of the Ru:TiO_2 compact layers showed that trap density in the Ru:TiO_2 film was lower than that of the pristine TiO_2 film. The PSCs based on 1 mol% Ru:TiO_2 exhibited the suitable band gap, low resistivity and high carrier density, comparing with the undoped compact TiO_2, the charge transportation at the compact layer/mesoporous layer interface was enhanced with the incorporation of Ru, resulting in the reduction in hysteresis of the device. The power conversion efficiency (PCE) of the Ru-doped compact TiO_2 film based PSCs was improved from 14.83% to 18.35%.

1. Introduction

Recently, perovskite solar cells (PSCs) have been employed in a wide range of applications, specifically in photovoltaic applications, perovskite materials are direct band-gap semi-conductors with a serious of unique properties, such as fascinating optical absorption from the visible to the near infrared (NIR) region, long electron-hole diffusion lengths, long carrier life and high dielectric constant (Bai et al., 2017; Peng et al., 2017; Pintilie et al., 2017; Shi et al., 2017; Wang et al., 2017; Zhao and Zhu, 2016). The power conversion effcicency (PCE) of the PSCs has been rapidly increased from 3.8% (Kojima et al., 2009) to 22.1% (Yang et al., 2017). Typical sandwiched structure in PSCs includes TiO_2 electron transporting layer (ETL), light-harvesting active layer ($CH_3NH_3PbI_3$ crystal) and 2,2′,7,7′-Tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (Spiro-OMeTAD) hole transport material (HTM) (Bai et al., 2017).

For electron transporting layer, different metal oxides have been used as ETLs, such as TiO_2 (Huang et al., 2017a), ZnO (Dong et al., 2014; Mahmud et al., 2018; Ruankham et al., 2017; Zhang et al., 2017), SnO_2 (Huang et al., 2017b; Ren et al., 2017; Song et al., 2015), WO_x (Eze et al., 2017; Wang et al., 2016), In_2O_3 (Apostolopoulou et al., 2017), $BaTiO_3$ and $PbTiO_3$ (Pintilie et al., 2017). TiO_2 has been the dominant electron transporting material to extract and transport photogenerated electrons and prevent the contact between the FTO and the hole transport layer (HTM). However, the mobility of electrons in the TiO_2 is much lower than the mobility of electrons in the perovskite layer and the transport length of electrons in the mesoporous layer is much longer than that in the compact TiO_2 layer (Heo et al., 2015). Therefore, superior electron mobility and conductivity of the compact layer material are necessary for high performance perovskite solar cells by reducing excessive charge accumulation and guaranteeing effective electron injection at the compact layer/perovskite interface, which can be achieved by manipulating the composition (i.e. graphene:TiO_2 nanocomposites (Wang et al., 2014)) and doping metal ions. Recently, TiO_2 compact layers as well as mesoporous layers can be effectively enhanced by doping suitable metal ions, such as Y^{3+}, Zn^{2+}, Fe^{3+}, Mg^{2+}, Nb^{5+}, Ta^{5+} and Li^{+} (Chen et al., 2016; Gu et al., 2017; Huanping Zhou and Hsin-Sheng Duan, 2014; Liu et al., 2017; Lv et al., 2016; Ranjan et al., 2017; Wang et al., 2015) and have resulted in the improved electron transport properties of the TiO_2. Y-doped TiO_2

---

[*] Corresponding authors at: School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, PR China.
E-mail addresses: maruixin@ustb.edu.cn (R. Ma), chywang@yeah.net (C. Wang).

https://doi.org/10.1016/j.solener.2018.05.005
Received 23 March 2018; Received in revised form 29 April 2018; Accepted 1 May 2018

(Huanping Zhou and Hsin-Sheng Duan, 2014) was utilized as an effective compact layer in a planar PSC device with a PCE of 19.3% (without a mask). Gu et al. incorporated Fe^{3+} into TiO_2 to improve the conductivity of TiO_2 compact layers compared with the pristine TiO_2 and boosting the photovoltaic performance of PSCs (Gu et al., 2017).

Ruthenium (Ru)-doped TiO_2 has been widly used in electrocatalytic (Chen and Chen, 2005) and photocatalytic (Chu et al., 2005) to enhanced the catalytic performance rather than enhancing its photoelectricity properties for applications in PSCs. Among various ions used for doping in TiO_2, Ruthenium (Ru) appears as a good choice as the Ru^{4+} ion has an ionic radius of 0.062 nm which is comparable to Ti^{4+} (0.061 nm). Hence Ti^{4+} can be substituted by Ru^{4+} in the TiO_2 framework without strain or secondary phases. Xu et al. incorporated Ru into TiO_2 via a one-step spray pyrolysis method to improve the conductivity of TiO_2 compact layers compared with the pristine TiO_2 and boosting the photovoltaic performance of planar PSCs (Xu et al., 2018). In this report, Ru-TiO_2 compact layers were successfully fabricated and used as ETLs for mesoporous perovskite solar cells. The Ru-TiO_2 precursor solution can be obtained easily through mixing the $RuCl_3$ solution with TiO_2 compact solution in appropriate proportion, including 0 mol%, 0.5 mol%, 1 mol%, 2 mol% and 5 mol%. The XPS spectra showed that the Ru^{3+} was oxidized into Ru^{4+} and incorporated into TiO_2 successfully after annealing. The carrier density and conductivity were enhanced significantly compared with the pure TiO_2 compact layer. Consequently, we obtained an efficiency of 18.35% for 1 mol% Ru^{4+}-TiO_2-based solar cells. The results reported in this work demonstrated that the performance of PSCs can be enhanced by directly doping TiO_2 compact layers with Ru ions.

2. Experimental

2.1. Materials

PbI_2 (99.99%), CH_3NH_3I (99.99%), anhydrous chlorobenzene (≥99.0%), anhydrous dimethylformamide (DMF) and anhydrous dimethylsulfoxide (DMSO), titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol) and Spiro-OMeTAD (2,29,7,79-tetrakis (N,N-di-p-methoxyphenylamine)-9,9-spirobifluoren-e, ≥99.0%) were purchased from Sigma-Aldrich. $RuCl_3 \cdot 5H_2O$ (98.5%), 4-*tert*-Butylpyridine (t-BP), and Li-bis- (trifluoromethanesulfonyl)imide (Li-TFSI) were purchased from Aladdin reagent. Titanium dioxide nanoparticles (particle size of 30 nm) were provided by Dyesol All. Solvents were used without any further purification.

2.2. Fabrication of solar cell devices

FTO layers on glass substrates, with a sheet resistance of 8 Ω/□ (Pilkington), were patterned by etching with the Zn powder and 2 M HCl followed by cleaning with soap and then were cleaned with alkaline detergent, acetone, absolute ethanol and deionized water for 15 min, The cleaned substrates were UV-ozone treated for 15 min, respectively, before they were used for spin-coating. The TiO_2 compact layers were prepared by dissolving titanium diisopropoxide bis(acetylacetonate) solution in ethanol in a 1:10 vol ratio with mixing $RuCl_3$ in titanium precursor solution in 0.5, 1.0, 2.0, and 5.0 mol% for the doped films. The TiO_2 compact films (undoped and doped) were obtained by spin-coating of precursor solution on the UV-ozone treated substrates at 3000 rpm for 30 s by annealing at 150 °C for 5 min and then sintered in air at 500 °C for 30 min resulting in 50 nm compact layers. Mesoporous TiO_2 layer (mass ratio 1:7) was spin-coated at 4000 rpm for 30 s and then annealed in air at 500 °C for 30 min and cooled down to room temperature. $MAPbI_3$ precursor solution was prepared by mixing 159 mg CH_3NH_3I, 462 mg PbI_2 in anhydrous DMF: DMSO (9:1, v/v), then filtered with 0.22 µm nylon filter to obtain a clear solution. The $MAPbI_3$ precursor solution was spin-coated on the TiO_2 coated substrates at 3000 rpm for 30 s and 200 µl chlorobenzene was slowly dripped on the surface of the film 10 s after the beginning of spin-coating. Perovskite layer was annealed at 100 °C for 20 min resulting in a thickness of 300 nm. 72.3 mg Spiro-OMeTAD, 28.8 µl 4-*tert*-butylpyridine and 17.5 µl of Li-bis(trifluoromethanesulfonyl)imide solution (520 mg/ml in acetonitrile) were dissolved in 1 ml chlorobenzene to form Spiro-OMeTAD solution, Spiro-OMeTAD layer was formed sequentially by spin-coating Spiro-OMeTAD solution at 3000 rpm for 30 s having a thickness of 200 nm. Finally, Au electrode was deposited using thermal evaporation at a constant evaporation rate of 0.1 nm/s. Except for the fabrication of TiO_2 layer, the whole process is carried out in glove-box under Ar condition at home temperature.

2.3. Characterization

The field emission scanning electron microscope (FESEM) images were obtained on a ZEISS SUPRA55. Energy dispersive spectrometry (EDS, Thermo-NS7, manufacturer) was used to determine the elemental composition. X-ray diffraction (XRD) patterns were collected with a SmartLab from Rigaku at 40 Kv and 150 mA by using Cu-Ka radiation ($\lambda = 0.15405$ nm). The valence states of the constituent elements were identified by high resolution X-ray photoelectron spectroscopy (XPS) using Mg Kα and $h\nu = 1253.6$ eV. AFM figures were measured using 300HV scanning force microscope (SEIKO). The photovoltaic performance of PSCs was recorded using a Keithley 4200 source meter with a delay time of 100 ms under one-sun AM 1.5G (100 mW/cm^2) illumination with a solar light simulator (Newport Oriel Sol3A Class AAA, 64023A Simulator), which was calibrated using a NREL standard Si solar cell. The error range of the sun simulator is 1000 ± 3 W/m^2. Hall effect measurement was performed with four contacts van der Pauw method (ECOPIA H S-2000). Hall Effect measurements were conducted with a magnetic field intensity of 0.5 T and current 0.1 mA under dark testing environment. EIS measurements were conducted by an electrochemical workstation (CHI660d) (1 MHz–100 Hz) and the fitting software was Zview software. The UV–vis light absorption measurement was performed by using an ultraviolet–visible (UV–vis) spectrophotometer (Shimadzu UV-3101 PC). The external quantum efficiency (EQE) measurements were obtained on a Keithley 2000 multimeter as a function of the wavelength from 350 to 800 nm on the basis of a Spectral Products DK240 monochromator. The active area of the cell is 0.1 cm^2. All samples were measured in air (25 °C).

3. Results and discussion

As shown in Fig. 1(a), the mesoporous-structured perovskite solar cells, consisting of FTO/Ru-TiO2 (or pristine TiO_2)/mesoporous-TiO2/MAPbI3/Spiro-OMeTAD/Au were fabricated. Fig. 1(b) showed the cross-sectional SEM image of the device. The thickness of each layer has been optimized (~50 nm for TiO_2 compact layer, ~200 nm for perovskite film, ~200 nm Spiro-OMeTAD and ~80 nm Au). In Fig. 1(c), the top view SEM image of the perovskite film showed full surface coverage without any hole, which guarantees good light absorption. Fewer traps and defects are produced so that carrier recombination is suppressed, which is favorable to photovoltaic performance of PSCs (Li et al., 2016).

Fig. 2(a) shows the XRD patterns of pristine TiO_2 and Ru-TiO_2 films having different amount of Ru. It is obvious that the anatase phase is retained in all the samples irrespective of the increase of Ru concentration. No peak for elemental Ru or RuO_2 could be detected in the XRD plots, suggesting that Ru is doped successfully in the crystal lattice of anatase TiO_2. The diffraction peaks of pristine TiO_2 at $2\theta = 25.3°$, 37.6°, 48.1°, 53.9° and 54.5° correspond to (1 0 1), (0 0 4), (2 0 0) and (2 1 1) planes of pure anatase form (JCPDS 21-1272) except FTO peaks. Due to the lower effective mass of electrons in the anatase phase, anatase TiO_2 showed higher electrical conductivity as compared to the rutile and brookite phase and hence is the desirable phase (Ranjan et al., 2017). However, there is also peak broadening with the increase