



Enhanced short-circuit current density of perovskite solar cells using Zn-doped TiO₂ as electron transport layer

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ABSTRACT

In present work, we focused on the improvement of short-circuit current density (J_{sc}) by using zinc-doped TiO₂ (Zn-doped TiO₂) as electron transport layer. Various Zn-doped TiO₂ compact layers with different doping concentrations are prepared by sol-gel method followed thermal treatment, and they were then used to fabricate perovskite solar cell. Effects of zinc (Zn) on the power conversion efficiency (PCE), absorption behavior, crystal structure, electrical conductivity, and surface morphology are systematically elucidated. Charge carrier dynamics between perovskite active layer and titanium dioxide (TiO₂) compact layer is discussed too. When the dopant concentration is less than 5.0 mol%, the absorption behavior, electrical conductivity and charge separation efficiency increase with Zn doping concentration. In contrast, when the Zn dopant is 7.0 mol%, it results in the decay of these properties mentioned. According to the optimized processing of perovskite solar cells, the J_{sc} is increased from 18.5 to 22.3 mA/cm² so as to the PCE is significantly improved from 11.3% to 14.0%.

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1. Introduction

Perovskite solar cells have attracted a great interest recently due to their potential application in developing low-cost, solution processable, large-area and mechanically flexible photovoltaic devices. In addition, perovskite solar cells show high power conversion efficiency (PCE), and the PCE have rapidly increased from 3.1% to 22.1% in only six years [1]. Many perovskite-type materials are usually used as the active layer for light harvesting because of their strong and broad light absorption characteristics in the visible range [2–7]. When it absorbs light energy larger than their bandgap, excitons are generated then they are immediately diffused and separated into electrons and holes. The electrons and the holes are injected to the electron transport layer and hole transport layer from perovskite layer respectively under the internal field built by n-i-p junction. If the charge carriers generated in the perovskite are not effectively transferred to the proper transport layers, they will be directly

recombined, accumulated in the perovskite or interface, and the charge transport will be reduced [8–10].

For perovskite solar cells, many metal oxides, such as aluminum oxide (Al₂O₃) [11], zinc oxide (ZnO) [12], zirconium oxide (ZrO₂) [13], tin oxide (SnO₂) [7] and titanium dioxide (TiO₂) [14–18], have been applied to the electron transport layer for improving the PCE. Among these metal oxides, TiO₂ is a good candidate due to the chemical stability, low-cost, and high charge transport ability [19–21]. Moreover, the conduction band of TiO₂ is lower than the conduction band of perovskite active layer, so the electron can be effectively transported from perovskite active layer to TiO₂ compact layer [22]. However, there is a need to increase the conductivity of TiO₂ for efficient electron transport. Metal ion dopants in TiO₂ is a good subject to improve photocurrent and electron-hole recombination for perovskite solar cells. Niobium-doped TiO₂ (Nb-doped TiO₂) nanorod was adopted to enhance the charge transport for perovskite solar cells because it provides better conductivity and interface contact [23]. Yttrium-doped TiO₂ (Y-doped TiO₂) compact layer was used as the electron transport layer for n-i-p structure perovskite solar cell [24]. Magnesium-doped TiO₂ (Mg-doped TiO₂) compact layer exhibits higher photocurrent than pristine TiO₂ compact layer due to the improved band alignment between TiO₂ and perovskite [25]. Lithium-treated TiO₂ (Li-treated TiO₂) nanoparticle was inserted at the electron transport layer of perovskite solar cells, because lithium-treated

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TiO₂ had more favorable charge injection and better conductivity than pristine TiO₂ [26].

Zinc-doped TiO₂ (Zn-doped TiO₂) has drawn attention due to the low-cost of zinc (Zn) precursor and high electrical conductivity (i.e., low internal electrical resistance). It is indicated that Zn dopant is able to modify TiO₂ electronic structure [27–30]. Wang et al. added many metal precursors, including Y, Zr, molybdenum (Mo), and Zn compounds to interact with TiO₂ nanocrystals [31]. The results show that the Zn-doped TiO₂ exhibited the highest conductivity. Thus, the Zn dopant is expected to improve carrier transport and subsequently enhance the short-circuit current density (J_{sc}) of solar cell. Herein, we use Zn-doped TiO₂ compact layer as electron transport layer with different doping concentrations. Various n-i-p structure perovskite solar cells were fabricated. We also studied the crystal structure, absorption behavior, electrical conductivity and surface morphology of various Zn-doped TiO₂ compact layers. Furthermore, the correlation between the charge carrier dynamics and Zn doping concentration for various Zn-doped TiO₂ compact layers is explored by time-resolved photoluminescence (TRPL) measurements. The photovoltaic performances of perovskite solar cells with various Zn-doped TiO₂ compact layer as electron transport layer are reported. The results address the issues of improving the electron compact layer and thus helping the further design of highly efficient perovskite solar cells.

2. Experimental details

2.1. Materials and sample preparation

The methylammonium iodide (CH₃NH₃I, MAI) was synthesized similar to literature [32,33]. 30.0 mL hydriodic acid (HI, 57.0 wt% aqueous solution) was added into the methylamine (CH₃NH₂, 33.0 wt% in ethanol) with continuous stirring at 0 °C for 2 h under argon gas. The yellow solution was obtained and then rotary evaporated at 55 °C for 2 h to get the white precipitate. The white precipitate was purified in recrystallization with ethanol and diethyl ether. Finally, the pure MAI powder was dried at 60 °C in a vacuum oven for 24 h. The perovskite precursor solution (i.e., CH₃NH₃PbI_{3-x}Cl_x) was prepared by mixing MAI powder and lead chloride (PbCl₂, 99.999%) at 39.0 wt% in 1.0 mL dimethylformamide (HCON(CH₃)₂, DMF, anhydrous, 99.8%). In contrast, the 2,2',7,7'-Tetrakis [N,N-di(4-methoxyphenyl)amino]–9,9'-spirobifluorene (spiro-OMeTAD) solution was synthesized according to the literature [34]. 104 mg of lithium-bis-(trifluoromethanesulfonyl)imide (Li-TFSI, 99.95%) was dissolved in 200.0 μL acetonitrile (CH₃CN, 99.5%). The spiro-OMeTAD solution was well prepared by dissolving 80 mg spiro-OMeTAD, 28.5 μL 4-tert-butylpyridine (tBP, 96%), and 17.5 μL Li-TFSI solution in 1.0 mL chlorobenzene (C₆H₅Cl, CB, 99.8%) with continuous stirring. For the synthesis of TiO₂ precursor solution, 375 μL of titanium isopropoxide (Ti(OCH(CH₃)₂)₄, TTIP, > 97%) was added to 2.5 mL of ethanol (C₂H₅OH, 99.5%). In a separate beaker, 35 μL of 2.0 M HCl solution was added to 2.5 mL of ethanol. It was then added to Ti precursor solution in continuous ice bath stirring. For Zn precursor solution, 26.4 mg of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, > 97%) was dissolved in 2.5 mL of ethanol until it was completely dissolved to form Zn precursor solution in vigorous stirring. Then, Zn precursor solution was added to Ti precursor solution with various stoichiometric ratio in continuous stirring for 2 h. All chemicals were purchased from commercial products without any purification.

2.2. Fabrication of the perovskite solar cells

The Zn-doped TiO₂ precursor solution was spin-coated on the FTO glass by 1000 rpm for 40 s and calcined at 550 °C for 30 min to

form a Zn-doped TiO₂ compact layer. The FTO glass (7 Ω, Ruilong) was cleaned sequentially with detergent, methanol and isopropanol. The perovskite precursor solution was spin-coated on the Zn-doped TiO₂ compact layer by 2000 rpm for 45 s. Subsequently, the spiro-OMeTAD solution was spin-coated over a perovskite layer at 4000 rpm for 30 s. Finally, gold electrode was thermally deposited on the device surface through a shadow mask with 0.09 cm² active area. The performance of every perovskite solar cell was evaluated statistically by 12 separated solar cells in average.

2.3. Characterization

The current density-voltage (J-V) characteristic of the device was recorded by the source meter (Keithley 2410). Solar-simulated AM 1.5 sunlight was generated using an irradiation (Newport-69920, 100 mW/cm²) calibrated with a silicon reference cell (Oriental P/N 91150V, VLSI standards) with KG-5 visible color filter. For the hysteresis measurement, the data is recorded under the reverse and forward bias in a 10 ms delay time. In forward bias, scanning has 5 s stabilization before illumination [35]. External quantum efficiency (EQE) was measured by IPCE spectrometer (EQE-R-3011, Enli Technology Co. Ltd). It was calibrated by a single-crystal silicon reference cell for each EQE measurements. Energy dispersive spectra (INCA Penta FET-x3, Oxford Instruments) was gathered in the field emission-SEM (JSM-7500 F, JEOL). The Zn-doped TiO₂ film was prepared for SEM/EDS measurement, and its film thickness is ~700 nm measured by alpha stepper (Dektak 6M Stylus Profilometer, Veeco). The accelerating voltage was set at 10 kV for Zn distinctive resolution of the prepared Zn-doped TiO₂ film. The detection time of each position were fixed at 200 s. X-ray photoelectron spectrometry (XPS, ULVAC-PHI Inc.) was used to analyze Zn doping concentration of various Zn-doped TiO₂ compact layers by using Al K_α radiation with a photoelectron 45° take off angle under high vacuum (~10⁻⁷ Torr). The surface morphology of various Zn-doped TiO₂ compact layers was observed by SEM (SNE-4500M, SEC) and AFM (Dimension-3100 Multimode, Digital Instruments) in tapping mode. UV–vis absorption spectra was measured by UV–vis spectrometer (V-630, Jasco). Synchrotron X-ray diffraction was performed by synchrotron X-ray spectroscopy (λ~1.025 Å) on beam line 13A1 of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The steady state photoluminescence (PL) spectra were obtained by pumping the samples with a continuous-wave diode laser (λ_{exc}=440 nm, PDLH-440-25, DongWoo Optron Co. Ltd.). The emission spectra were analyzed by a photomultiplier tube detector system (PDS-1, DongWoo Optron Co. Ltd.) and standard photon-counting electronics using a monochromator (Monora 150i, DongWoo Optron Co. Ltd.). TRPL spectroscopy was performed using a time-correlated single photon counting (WELLS-001 FX, DongWoo Optron Co. Ltd.) spectrometer. A pulse laser (λ_{exc}=440 nm) with an average power of 1 mW, operating at 312.5 MHz, with 2 μs duration was used for excitation.

3. Results and discussion

Various Zn-doped TiO₂ compact layers exhibit the anatase phase as shown in Fig. 1(a). For the pristine TiO₂ compact layer, all diffraction peaks can be perfectly indexed as the body-centered tetragonal structure of TiO₂ anatase phase, with unit cell parameters a=b=3.78 Å and c=9.52 Å [COD ID:720675]. The intensity of (101) crystal plane for anatase TiO₂ phase decreases as the Zn doping concentration increases. However, the intensity of (110) crystal plane for rutile TiO₂ phase becomes obvious when the Zn doping concentration is above 3.0 mol%. The structural defects

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