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Mild solution-processed metal-doped TiO_2 compact layers for hysteresis-less and performance-enhanced perovskite solar cells

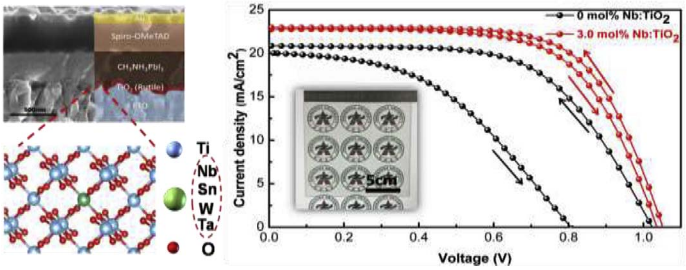
Chao Liang, Pengwei Li, Yiqiang Zhang*, Hao Gu, Qingbin Cai, Xiaotao Liu, Jiefei Wang, Hua Wen, Guosheng Shao

School of Materials Science and Engineering, State Centre for International Cooperation on Designer Low-Carbon and Environmental Material (SCICDLCEM), Zhengzhou University, Zhengzhou 450001, Henan, People's Republic of China

HIGHLIGHTS

- Metal-doped TiO_2 thin film can be grown below 70 °C.
- Doping process can be controlled effectively via a series of metal chloride precursors.
- PSC with metal-doped TiO_2 leads to a ~25% improved PCE of over 16%.

GRAPHICAL ABSTRACT



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ABSTRACT

TiO_2 is extensively used as electron-transporting material on perovskite solar cells (PSCs). However, traditional TiO_2 processing method needs high annealing temperature (> 450 °C) and pure TiO_2 suffers from low electrical mobility and poor conductivity. In this study, a general one-pot solution-processed method is devised to grow uniform crystallized metal-doped TiO_2 thin film as large as 15×15 cm^2. The doping process can be controlled effectively via a series of doping precursors from niobium (V), tin (IV), tantalum (V) to tungsten (VI) chloride. As far as we know, this is so far the lowest processing temperature for metal-doped TiO_2 compact layers, as low as 70 °C. The overall performance of PSCs employing the metal-doped TiO_2 layers is significantly improved in term of hysteresis effect, short circuit current, open-circuit voltage, fill factor, power conversion efficiency, and device stability. With the insertion of metal ions into TiO_2 lattice, the corresponding $CH_3NH_3PbI_3$ PSC leads to a ~25% improved PCE of over 16% under irradiance of 100 mW cm^{-2} AM1.5G sunlight, compared with control device. The results indicate that this mild solution-processed metal-doped TiO_2 is an effective industry-scale way for fabricating hysteresis-less and high-performance PSCs.

1. Introduction

Organometal halide PSCs have attracted plenty of attention as a hopeful alternative to traditional inorganic silicon-based photovoltaics, because of their intense broad-band absorption, long carrier transport distance, high charge carrier mobility, and low-cost solution fabrication [1–4]. Within a short period of 8 years, the PCE has been promoted from 3.8% to over 20% [5–7]. To date, TiO_2 has been extensively used as electron-transporting layer (ETL) on planar heterojunction PSCs [8–10]. This compact inorganic film is typically formed via high-temperature sintering (> 450 °C) to transform the amorphous oxide layer into a functional crystallinity [11]. But, high-temperature processing

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* Corresponding author.
E-mail address: yqzhang@zzu.edu.cn (Y. Zhang).

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may significantly increase the manufacturing cost and depletion of energy. Therefore, several new deposition strategies have been developed to obtain TiO_2 ETL at low temperature (< 200 °C), such as atomic layer deposition [12,13], nanocomposites of graphene/TiO_2 nanoparticles [14], and addition of titanium diisopropoxide bis(acetylacetonate) [15]. Recently, Aswani Yella et al. prepared rutile TiO_2 as an ETL through chemical deposition below 100 °C [16]. Similarly, our previous work had successfully demonstrated that TiO_2 ETL can be synthesized via sub-100 °C chemical bath deposition [17].

Meanwhile, it is widely recognized that the band structure and trap states of TiO_2 can be effectively modified via doping chemistry, deliberately inserting impurities into TiO_2 lattice [18]. In turn, properties of TiO_2 and performance of TiO_2-based devices can be tailored, such as the conduction band structure of TiO_2, device lifetime, charge transport and recombination. So far, aluminum [19], lithium [20], magnesium [21–24], niobium [25–30], yttrium [31,32] and zirconium [33] doping of TiO_2 have been employed in perovskite solar cells. All the doping methods developed follow the same strategy of mixing a dopant precursor with TiO_2 precursor solution. However, these doping methods suffer from the complexity of the preparation procedure, high-temperature manufacturing (400–500 °C), limited control of large-area spin-coating film quality, expensive Ti/dopant organometal precursor or subtle efficiency improvement, which prevent the doped TiO_2 film from application in large-scale industrial fabrication of PSCs on a series of substrates.

To address these issues, we developed a facile one-pot low-temperature solution doping method (LSDM) to grow uniform crystallized metal-doped TiO_2 onto the fluorine-doped tin oxide (FTO) substrate as large as 15×15 cm^2 at 70 °C. Taking Nb^{5+} as an example, niobium (V) chloride ($NbCl_5$) was dropwise added into titanium tetrachloride ($TiCl_4$) to form the precursor solution, and Nb-doped TiO_2 ETL was then epitaxially deposited onto FTO substrate via LSDM. With the addition of $NbCl_5$, the doped TiO_2 ETL was found to substantially increase the short circuit current (J_{sc}) from 20.87 mA/cm^2 to 22.90 mA/cm^2 and the fill factor (FF) from 60.09% to 66.96%, resulting in a ~25% improved PCE of 16.12% under irradiance of calibrated sunlight. In addition, owing to the effective Nb^{5+} passivation of interfacial traps and alleviation of the charge accumulation, the hysteresis behavior was drastically reduced. More importantly, other doping precursors, including tin (IV) chloride ($SnCl_4$), tantalum (V) chloride ($TaCl_5$), or tungsten (VI) hexachloride (WCl_6) can be successfully incorporated into TiO_2 lattice via this LSDM with enhanced device performances of open-circuit voltage (V_{oc}) (Ta dopant), J_{sc} (W or Sn dopant) and FF (Ta, W, or Sn dopant). This work presents a new method to develop industry-scale metal-doped TiO_2-based ETLs for low-temperature-processed PSCs to reduce the cost of manufacture. Potentially, this metal-doped TiO_2 nanomaterials can be used in several other technological areas, including catalysis [34,35], gas sensors [36,37], lithium-ion batteries [38], waste remediation [39] and biocompatible materials [40].

2. Experimental section

2.1. Materials

A majority of materials were acquired from Alfa-Aesar. The CH_3NH_3I (MAI) was first synthesized by the reaction of 24 mL CH_3NH_2 (33 wt% in absolute ethanol, Alfa) and 30 mL of HI (57 wt% in water, Alfa) in a 300 mL flask at 0 °C for 2 h. The precipitate was then evaporated at 55 °C for 1 h. MAI was dissolved in ethanol, then recrystallized from diethyl ether, and finally dried at 60 °C in oven for 24 h.

2.2. Fabrication of perovskite solar cells

F-doped SnO_2 (FTO) substrates with a sheet resistance of 8 Ω^{-2} and an optical transmission of greater than 82% in the visible range were used. After thoroughly washing with acetone, isopropanol and de-ionized water, the clean FTO glasses were treated under UV-ozone for 15 min. An aqueous solution of $TiCl_4$ was diluted to 200 mM at 0 °C. The $NbCl_5$ of different molar ratio (0.5%, 1%, 3%, 5%) was dissolved in concentrated hydrochloric acid. ($TaCl_5$, WCl_6 or $SnCl_4$ of different molar ratio were dissolved in ethyl alcohol.) Then, the $NbCl_5$ ($TaCl_5$, WCl_6, or $SnCl_4$) solution was dropped into the $TiCl_4$ solution. The FTO were then put into this solution and retained in an oven at 70 °C for 1 h in a closed beaker. After 1 h, the FTO were washed with de-ionized water and dried at 100 °C for 1 h.

The CH_3NH_3I and PbI_2 were stirred in a mixture of dimethyl sulfoxide (DMSO):γ-butyrolactone (GBL) (3:7, v/v) at 65 °C overnight under inert gas environment. The resulting solution was coated onto FTO/TiO_2 substrate by a two-step spin-coating procedure at 1000 rpm and at 4000 rpm for 15 and 25 s, respectively, and the toluene in final spin-stage was dropped onto the substrate during spin coating. The perovskite-precursor was dried on a hot plate at 100 °C for 10min. The HTM was then spin-coated at 3000 rpm for 30 s. The spin-coating formulation was prepared by dissolving 72.3 mg (2,2,7,7-tetrakis (N,N-di-pmethoxyphenylamine)-9,9-spirobifluorene) (Sprio-OMeTAD), 28.8 μl 4-*tert*-butylpyridine, and 17.5 μl of a stock solution of 520 mg/mL lithium bis(trifluoromethylsulphonyl)imide(LiTFSI) in acetonitrile in 1 mL chlorobenzene. Finally, Au was evaporated by Trovato thermal evaporation via a shadow mask at 3×10^{-8} Torr. The device area was fixed at 0.09 cm^2. Except for the preparation of titanium oxide in atmosphere, other layers of the device were fabricated in inert glovebox.

2.3. Instruments

The phase structure was characterized on a Rigaku(RINT-2500) X-ray diffractometer (Cu Ka radiation, $\lambda = 1.5418$ Å). SEM images was obtained via a field emission scanning electron microscope (JEM-7500 F). Ultraviolet–visible absorption spectra were recorded on a Shimadzu UV 3600 spectrophotometer at room temperature. XPS were detected on Multilab 2000 XPS system, using a monochromatic Mg Kα source and a charge neutralizer. All the binding energies were referenced to the C 1s peak of the surface adventitious carbon at 284.6 eV. The excitation wavelength, scanning speed, PMT voltage and slit width were set to be 320 nm, 1200 nm/min, 400 V and 10.0 nm, respectively. The UPS measurements were performed on a PHI5000 Versa Probe instrument. The UPS radiation was generated by a He-gas discharge lamp (He I α at 21.2 eV). The electron binding energy scale was calibrated using the Fermi edge of clean silver. The current density-voltage (J-V) characteristics were recorded with a Keithley 2400 source meter and 300 W collimated Xenon lamp (Newport) calibrated with the light intensity to 100 mW cm^{-2} under AM 1.5 G solar light condition by the certified silicon solar cell. The J-V curves were measured by reverse (forward bias (1.2 V)→short circuit (0 V)) or forward (short circuit (0 V)→forward bias (1.2 V)) scan. IPCE was achieved on a computer-controlled IPCE system (Newport). PL (excitation at 425 nm) was measured with Edinburgh Instruments (FLSP920). Impedance spectroscopy was measured by an ZAHENR Electrochemical Workstation, in the dark and at 0.8 V, with the frequency from 100 KHz to 0.1 Hz.

3. Results and discussion

A planar heterojunction structure was used to prepare the PSCs. Fig. 1 shows the scanning electron microscopy (SEM) image of an as-fabricated PSC and energy level diagram, as well as schematic diagram of the deposition of metal-doped TiO_2 thin films by a general LSDM. The cross-sectional SEM image (Fig. 1a) reveals a planar structure, consisting of FTO/metal-doped TiO_2 (60 nm)/$CH_3NH_3PbI_3$ (400 nm)/spiro-OMeTAD (250 nm)/Au (60 nm). For this device structure, the formation of a high-quality metal-doped TiO_2 layer under sub-100 °C is extremely important, directly determining the band alignment and charge transport. The doping method involves six procedures, as