In-situ Formation of Inorganic Healing Overlayer for Interface-Stabilized All-Inorganic CsPbIBr₂ Perovskite Solar Cells

Junshuai Zhang,^a Qiyao Guo,^a Yuanyuan Zhao,^b Jialong Duan,^{a,*} and Qunwei Tang^a

^a Institute of Carbon Neutrality, College of Chemical and Biological Engineering, Shandong

University of Science and Technology, Qingdao 266590, PR China

^b College of Mechanical and Electronic Engineering, Shandong University of Science and

Technology, Qingdao 266590, PR China

Email address: duanjialong@sdust.edu.cn

Experimental Details

Materials

Cesium iodide (CsI, 99.9%), dimethylsulfoxide (DMSO, 99.7%) were purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Lead iodide (PbI₂, > 99.99%) was purchased from Xi'an Polymer Light Technology Corp. (Xi'an, China). Lead bromide (PbBr₂, 99.0%) was obtained from Macklin reagent Co. Ltd. (Shanghai, China). The low-temperature carbon paste (99.0%) was purchased from Shanghai MaterWin New Materials Co., Ltd. All materials and reagents were acquired from commercial sources and used without further purification.

Assembly of all-inorganic perovskite solar cells

FTO glasses were firstly etched with HCl and Zn powder, and then completely washed with deionized water, isopropanol and ethanol. Next, the cleaned FTO substrates were treated with plasma for 180 s before use. The compact TiO_2 (*c*-TiO₂) layer was fabricated by spin-coating an

ethanol mixture of titanium isopropoxide (0.5 M) and diethanolamine (0.5 M) on FTO substrate at 7000 rpm for 30 s, followed by annealing at 500 °C for 2 h. The perovskite precursor solution was firstly constructed by fully dissolving CsI (260 mg, 1.0 mmol), PbBr₂ (367 mg, 1.0 mmol), PbI₂ (4.6 mg, 0.01 mmol) in 1.0 mL DMSO. Then 90 μ L precursor solution was spin-coated onto plasma-treated FTO/*c*-TiO₂ surface at 1000 rpm for 10 s and 3000 rpm for 50 s. Next, the wet film was heated at 30 °C for 1 min and then 260 °C for 5 min, respectively. After naturally cooling down, Zirconium *n*-propoxide solution with various concentrations dissolved in isopropanol was spin-coated onto the perovskite surface at 4000 rpm for 30 s and then the film was annealed at 200 °C for 5 min. Finally, the carbon electrode was deposited with an active area of 0.09 cm² by a doctor-blade coating method and heated at 70 °C for 10 min.

Measurements and characterizations

The morphologies of the prepared perovskite films were observed by scanning electron microscope (SEM, Hitachi S-4800). The detailed chemical states of perovskite films were estimated by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, USA). The crystal phase was determined utilizing X-ray diffraction (XRD) in a Bruker D8 Advanced diffractometer with a Cu K α radiation source. Ultraviolet-visible (UV-vis) absorption spectra were evaluated by means of Meipuda UV-3200 spectrophotometer in the range of 400-700 nm under continuous illumination. Photoluminescence (PL) spectra were detected by Hitachi F-4500 fluorescence spectrophotometer with an excitation wavelength of 410 nm. Time-resolved PL (TRPL) spectra were evaluated by the Delta Flex Fluorescence Lifetime System (Horiba Scientific Com., Japan) excited by a 500 nm laser. Photocurrent density-voltage (*J-V*) curves of devices were measured on an electrochemical workstation (CHI660E) under irradiation of simulated solar light (Newport, Oriel Class 3A, 91195A, AM 1.5G, 100 mW cm⁻², calibrated by a standard silicon solar cell). External quantum efficiency

(EQE) spectra were obtained using an IPCE kit from Enli Technology Co., Ltd. The light stability was performed under constant irradiation by a xenon lamp at temperature (T = 25 °C) and relative humidity (RH = 50%), and the error bar in corresponding figure is originated from the unstable light intensity. To evaluate the operational stability of PSCs during 60 days, the obtained PSCs were stored in AKL drybox with automatic adjustment function at constant temperature and humidity (T = 25 °C, RH = 10%). Capacitance-voltage (C-V) curves were recorded at a frequency of 5 kHz with an amplitude of 5 mV under dark at bias voltages from 0 to 1.80 V. The contact angles of water on the freshly-prepared CsPbIBr₂ perovskite films were measured by a drop shape analyzer (KRüSS, DSA25, Germany) at temperature (T) of 25 °C and relative humidity (RH) of 50%.



Fig. S1 (a) The XRD patterns and (b) absorption spectra of perovskite films with and without ZrO₂ capping layer.

Fig. S2 Cross-sectional SEM images of (left) control and (right) ZrO₂ layer capped PSCs.



Fig. S3 Characteristic *J-V* curves of PSCs treated by Zirconium *n*-proposide precursor solution with various concentrations.



Fig. S4 Cs 3d, I 3d and Br 3d XPS spectra of perovskite films with and without ZrO_2 layer.



Fig. S5 The dependence of J_{sc} on light intensity of PSCs with and without ZrO_2 layer.



Fig. S6 (a) V_{oc} decay curves of PSCs and (b) the corresponding calculated carrier lifetime.



Fig. S7 Normalized parameters of PSCs under dry air condition.

Sample A_1 A_2 τ_1 (ns) τ_2 (ns) τ_{Ave} (ns) Control 0.850 0.150 0.195 3.07 0.626 0.214 0.286 0.945 $w ZrO_2$ 0.786 3.37

Table S1. The specific carrier lifetime parameters of $FTO/CsPbIBr_2$ films with and without ZrO_2 layer obtained from Fig. 2f.