



# Cesium Iodide Interface Modification for High Efficiency, High Stability and Low Hysteresis Perovskite Solar Cells



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## ABSTRACT

Each interface is crucial to perovskite solar cells (PSCs), so the interface modification is often used to improve the PV performances. In this manuscript, an environment-friendly cesium iodide (CsI) interface layer between the mesoporous TiO<sub>2</sub> (mp-TiO<sub>2</sub>) and the MAPbI<sub>3</sub> perovskite active layer was introduced to improve the PV performances and stabilities of PSCs and significantly reduce hysteresis of the device. After optimizing, the PSC employing a CsI-modified mp-TiO<sub>2</sub> as electron transporting layer (ETL) could obtain a high fill factor (FF) of 0.79 with an increased power conversion efficiency (PCE) of 17.10% and a low hysteresis index (HI) of 0.10 under illumination of AM 1.5G, while FF of 0.75 and PCE of 14.38% for PSC without CsI interface modification. The enhanced PV performances can be attributed to the improved surface morphology of mp-TiO<sub>2</sub>, the lower work function (WF) of TiO<sub>2</sub>, the passivation of surface trap states, the improved perovskite crystallization and reduced grain boundaries. Besides, the reduced WF of TiO<sub>2</sub> results in the enhanced built-in potential, which promotes the charge separation, transport and collection.

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## 1. Introduction

Perovskite solar cells (PSCs) have opened up a new horizon for the development of a series of inorganic-organic metal halide perovskite materials in PV applications [1–5]. Methylammonium lead halide perovskites (MAPbX<sub>3</sub>) are known as particularly promising light absorbers for the advantages of optimal band gaps, long-range exciton diffusion lengths, high absorption coefficients and simple solution approaches [6–12]. The champion power conversion efficiency (PCE) of PSC has jumped to 22.1% [13], which indicates that they have great potential to compete with traditional silicon solar cells and other thin-film solar cells in the next few years.

Interface modification is identified as an efficient approach for improving the device performance by significantly promoting electron injection, enhancing electron transfer and reducing the charge recombination [14–17]. To obtain high-quality perovskite films, it is critical to control the surface properties of the electron transporting layer (ETL). To date, some groups have found that introducing interlayers on top of the ETL was an effective method

to enhance the PV performances and stabilities of PSCs [18–26]. For example, Wang et al. reported a multifunctional polyethyleneimine interlayer between the ETL and the perovskite active layer to achieve uniform perovskite thin films with low defect densities [21]. In addition, Li et al. reported a new method for improving the interfacial compatibility by introducing a self-assembled monolayer of 4-aminobenzoic acid between the TiO<sub>2</sub> layer and the perovskite active layer, obtained high-quality perovskite films with fewer traps, better carrier transport and energy level matching [22]. Ito et al. introduced a blocking layer of Sb<sub>2</sub>S<sub>3</sub> between mesoporous TiO<sub>2</sub> (mp-TiO<sub>2</sub>) and perovskite active layer, which could improve light stability of device by passivating the interface between mp-TiO<sub>2</sub> and MAPbI<sub>3</sub> and reducing surface oxygen vacancies of mp-TiO<sub>2</sub> [23]. However, Sb<sub>2</sub>S<sub>3</sub> is relatively toxic and formed at 300 °C. Therefore, exploring an eco-friendly and low-temperature interlayer for improving their stabilities by passivating the interface between mp-TiO<sub>2</sub> and MAPbI<sub>3</sub> and reducing surface oxygen vacancies of mp-TiO<sub>2</sub> is imperative for long-term operation of PSCs.

In this manuscript, a promising CsI interlayer between the mp-TiO<sub>2</sub> and the MAPbI<sub>3</sub> perovskite active layer is reported. Notably, Xiao et al. reported a solution-processed CsI interlayer in inverted polymer solar cells to improve device efficiency and stability [27]. We expect that deep trap states present at the mp-TiO<sub>2</sub>/MAPbI<sub>3</sub>

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interface could potentially be addressed by passivating the interface between mp-TiO<sub>2</sub> and MAPbI<sub>3</sub> via CsI interface modification. Simultaneously, the CsI interlayer maybe helpful to improve the PV performances and stabilities of PSCs and significantly reduce hysteresis of the device.

## 2. Experimental section

### 2.1. Materials

2,2',7,7'-tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) and TiO<sub>2</sub> paste (Dyesol, 18NR-T) were purchased from Xi'an Polymer Light Technology Corp. Tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine) cobalt (III) bis(trifluoromethylsulphonyl)imide (FK209-Co(III)-TFSI, 99%) was purchased from Shanghai Materwin New Materials Technology Co., Ltd. Cesium iodide (CsI, 99.999%) was purchased from Aladdin. Lead iodide (PbI<sub>2</sub>, 99%), lithium bis(trifluoromethylsulphonyl)imide (LiTFSI, 95%), 1-butanol (99.8%), titanium diisopropoxidebis (acetylacetonate) (75 wt% in isopropanol), anhydrous N,N-dimethylformamide (DMF, 99.8%), 4-tert-butylpyridine (TBP, 96%), acetonitrile (99.8%) and chlorobenzene (CB, 99.8%) were purchased from Sigma Aldrich. Titanium tetrachloride (TiCl<sub>4</sub>, 99.0%) was purchased from Tianjin Fu Chen Chemical Reagents Factory. Methylammonium iodide (MAI) was synthesized according to the reported procedure [4]. All materials were used without further purification.

Fluorine-doped tin oxide (FTO) coated glasses (Tec 7, Pilkington) were patterned by etching with Zn powder and 2 M HCl. To prepare 1.2 mM MAPbI<sub>3</sub> precursor solution, 553.2 mg PbI<sub>2</sub> and 190.8 mg MAI were dissolved in 1.0 mL DMF with stirring. A Spiro-OMeTAD solution was prepared by dissolving 72.3 mg Spiro-OMeTAD, 28.8 μL TBP, 29.0 μL of a stock solution of 300.0 mg mL<sup>-1</sup> FK209-Co(III)-TFSI in acetonitrile and 17.5 μL of a stock solution of 520.0 mg mL<sup>-1</sup> LiTFSI in acetonitrile in 1.0 mL CB.

### 2.2. Device fabrication

#### 2.2.1. Substrate preparation

The etched FTO substrates were cleaned with alkaline aqueous washing solution, deionized water, isopropanol, ethanol and finally treated under O<sub>3</sub>/ultraviolet for 15 min. The blocking layer TiO<sub>2</sub> (bl-TiO<sub>2</sub>, ~50 nm) was deposited on FTO glass by spin-coating 0.30 M solution of titanium diisopropoxidebis (acetylacetonate) in 1-butanol at 2000 r.p.m. for 50 s, which was further dried at 125 °C for 10 min. The bl-TiO<sub>2</sub> substrates were treated by 40 mM TiCl<sub>4</sub> aqueous solution at 70 °C for 30 min, rinsed by deionized water and ethanol and then annealed at 500 °C for 30 min. After cooling to room temperature, the mesoporous layer was formed by spin-coating TiO<sub>2</sub> paste diluted in anhydrous ethanol (1:4, weight ratio) at 3000 r.p.m. for 30 s, then annealed at 500 °C for 30 min. Prior to their use, the films were stored in a drying oven with 50 °C and humidity less than 20%.

#### 2.2.2. CsI interface layer preparation

The CsI-modified mp-TiO<sub>2</sub> films were prepared by spin-coating a solution of 10 mg mL<sup>-1</sup> CsI dissolved in isopropanol directly on the mp-TiO<sub>2</sub> at 1500 r.p.m. for 30 s and then annealed at 60 °C for 5 min in the glovebox. The same operation was repeated 3 times.

#### 2.2.3. Perovskite solar cell fabrication

The synthesis of MAPbI<sub>3</sub> was carried out by a one-step deposition technique, which was deposited onto mp-TiO<sub>2</sub> by spin-coating with 3000 r.p.m. for 55 s. At the remaining spin time of 49 s [28], 100.0 μL CB was quickly added onto the MAPbI<sub>3</sub> film. After spin-coating, the substrate was annealed at 100 °C for 10 min. The Spiro-OMeTAD solution was further deposited on the surface

of MAPbI<sub>3</sub> film by spin-coating at 4000 r.p.m. for 30 s. The obtained devices were then left overnight in a dry box full of oxygen. Finally, 80 nm of gold was thermally evaporated under vacuum of about 10<sup>-6</sup> Torr, at a rate of about 0.5 nm s<sup>-1</sup>, to complete the devices. The active area is 0.09 cm<sup>2</sup>. Apart from the preparing gold electrodes, the high-temperature sintering process, the overnight oxidation process [29] of Spiro-OMeTAD and other procedures were performed in a glove box filled with argon.

### 2.2.4. Device measurement and characterization

Scanning electron microscopy (SEM) was performed using a JEOL JSM-7600F device. Atomic force microscopy (AFM) measurements were obtained using a SPA-300 AFM (Seiko, Japan) and the scanning range of the AFM images is 2 μm × 2 μm. The contact angle tests for films of mp-TiO<sub>2</sub> substrates without and with CsI interface modification were performed with a standard DSA25 (KRUSS, Germany) Contact Angle Measurement Instrument. The X-ray diffraction (XRD) analysis of the perovskite films was characterized by a D1 Evolution (JORDAN VALLEY, USA) using Cu-Kα radiation at a coincident scan rate of 6° min<sup>-1</sup>. The ultraviolet photoelectron spectroscopy (UPS) spectra were performed with EscaLab 250Xi. The light source of UPS is a HeI discharge lamp (*hν* = 21.22 eV). Absorption spectra of the MAPbI<sub>3</sub> perovskite films on FTO/bl-TiO<sub>2</sub>/mp-TiO<sub>2</sub> substrates were determined with SHIMADZU (model UV1700) ultraviolet to visible (UV-vis) spectrophotometer. The μ-PL spectra were measured using an integrated Raman system (Horiba JY HR800) with an Olympus 15X NUV lens (NA=0.32). A 325 nm helium-cadmium (He-Cd) laser was used as the excitation source. The laser power density on the film surface was about 2 W cm<sup>-2</sup> and the wavelength scale was from 500 to 900 nm. PL lifetime measurement was performed on a lifetime spectrometer (FLS 920, Edinburgh Instrument). The excitation source is a 405 nm pulsed laser diode and the monitored wavelength is 534 nm. The photocurrent-voltage (*J-V*) characteristics of the PSCs were measured with a fixed active area of 0.09 cm<sup>2</sup> using a CH Instruments 660C electrochemical workstation (Shanghai CH Instruments Co., China) under illumination of a simulated sunlight (AM 1.5G, 100 mW cm<sup>-2</sup>) provided by a short-arc xenon lamp (CHF-XW-500W, Trusttech Co. Ltd., Beijing, China). The scan rate is 0.1 V/s, which is a frequently-used parameter. The measurement of the incident photo-to-current conversion efficiency (IPCE) was obtained by a commercial setup (Qtest Station 2000 IPCE Measurement System, CROWNTECH, USA). Electrochemical impedance spectroscopy (EIS) were tested using a CH Instruments 660C electrochemical workstation (Shanghai CH Instruments Co., China) with a 20 mV amplitude over a frequency range of 10<sup>-1</sup> Hz to 10<sup>5</sup> Hz under illumination of AM 1.5G. The Init E (mV) was 800 mV. The impedance parameters were simulated by fitting of impedance spectrum through Z-view software.

## 3. Results and discussion

### 3.1. Morphological characterization

SEM and AFM (Fig. 1) measurements were used to study the surface morphologies of the films. CsI interface modification could improve the mp-TiO<sub>2</sub> film smoothness, and at the same time partially block the pinholes in the mp-TiO<sub>2</sub> film. After CsI interface modification, the quality of MAPbI<sub>3</sub> film on FTO/bl-TiO<sub>2</sub>/mp-TiO<sub>2</sub> substrate was improved from the results of SEM (Fig. 1d) and AFM (Fig. 1h), which was also verified by contact angle tests for the films (Fig. 2). The root-mean-square (rms) roughness values given by AFM were 15.37, 15.06, 10.93, and 13.26 nm for the mp-TiO<sub>2</sub>, mp-TiO<sub>2</sub>/CsI, mp-TiO<sub>2</sub>/MAPbI<sub>3</sub>, and mp-TiO<sub>2</sub>/CsI/MAPbI<sub>3</sub> films, respectively. It could be found that the large grain size of perovskite film is corresponding to large surface roughness. All the rms values were

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