Supporting Information

Thiourea Interfacial Modification for High Efficient Planar Perovskite Solar Cells

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Experimental Section

Materials and synthesis

Thiourea, $TiCl_4$, CH_4N_2(FA)I, CH_3NH_3(MA)Br, absolute ethanol, and benzyl alcohol were bought, from Shaanxi Xi'an Polymer Light Tech. Corp. China. $PbBr_2$, PbI_2, CsI, anhydrous dimethyl sulfoxide (DMSO) and anhydrous dimethylformamide (DMF) were bought, from Sigma-Aldrich. These reagents and solvents were used directly (without further purification) unless otherwise mentioned.

The low-temperature TiO_2 was synthesized by solvothermal reaction of $TiCl_4$ (1 mL), absolute ethanol (4 mL) and benzyl alcohol (20 mL) at 85 ºC for 12 h referred to the literature reported by Tan et al.[1] Thiourea solutions with concentration of 0.05, 0.1 and 0.2 $mol \cdot L^{-1}$ (M) were made by mixing predetermined quantities of thiourea into ethanol, respectively. Perovskite precursor solution was made by dissolving $PbBr_2$ (0.2 M), PbI_2 (1.15 M), MABr (0.14 M), FAI (1.10 M), and CsI (0.07 M) in anhydrous DMSO/DMF (volume ratio: 1:4) mixed solvent according to Saliba et al. reported previously,[2] which formed a precursor solution with compositions of $Cs_{0.07}FA_{1.1}MA_{0.14}Pb_{1.35}I_{3.47}Br_{0.414}$. The solution was heated at 80 ºC for 10 min under stirring and nitrogen atmosphere and filtrated with 0.45 μm PTFE filters before using it.

Device fabrication

Figure S1 displays the diagram of the fabrication process of perovskite films. F-doped SnO_2 conducting glass (FTO, 1.5 × 1.5 cm^2) was washed with detergent solution, distilled water and alcohol for 20 min, successively. A TiO_2 electron transport layer was solidified onto the FTO substrate by spin-spraying the synthesized TiO_2 solution at a spin speed of 2000 rpm for 20 s and then was sintered at 120 ºC for 2 min. The spin-spraying was repeated for three times to reach the thickness requirement of the devices. The TiO_2 electron transport layer was modified with thiourea by spin-spraying the synthesized thiourea solution on the

FTO/TiO_2 at a spin speed of 2000 rpm for 20 s, and then heating at 120 ºC for 15 min to evaporated ethanol completely. The resultant film was surface treated with ultraviolet-ozone for 20 min.

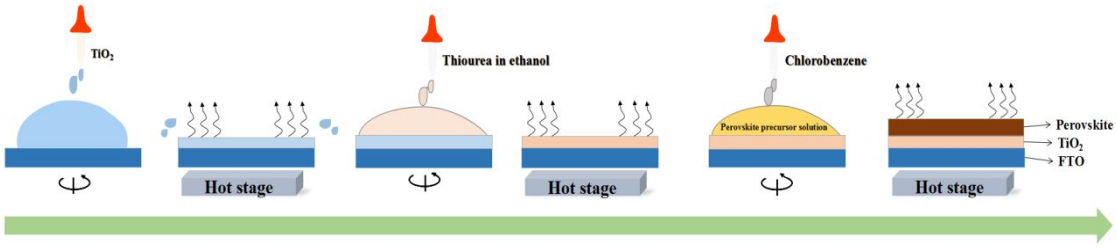

Figure S1. Diagram of the fabrication of FTO/thiourea-modified TiO_2/perovskite films.

Perovskite layer was fixed on the thiourea-modified TiO_2/FTO by spin-spraying the synthesized perovskite precursor solution (20 mL) at a spin speed of 6500 rpm for 20 s and then sintered at 100 ºC for about 40 min. The hole transport layer (HTL) of spiro-MeOTAD was spin-sprayed on the perovskite/TiO_2/FTO at a spin speed of 4000 rpm for 20 s. Finally, ~80 nm thickness of Au counter electrode was evaporation-coated on the HTL, thus a planar perovskite solar cell with architecture of Au/spiro-MeOTAD/perovskite/thiourea-modified TiO_2/FTO was fabricated.

Characterization

Current density-voltage (J-V) curves of perovskite solar cells were recorded under the white light illumination with a light intensity of 100 $mW \cdot cm^{-2}$ (AM 1.5G). The incident light intensity was calibrated by using a NREL-calibrated Si cell equipped with a filter of KG-2. With the same instruments, Tafel curves of TiO_2 ETL were recorded by measuring FTO/TiO_2/Au multilayer films in dark, and the trap state densities of perovskite layers were investigated by measuring FTO/TiO_2/perovskite/Au multilayer films in dark. The time resolved photoluminescence (TRPL) spectra and the steady state photoluminescence (PL) spectra were obtained by using the time-correlated single photon counting system (TCSPC, model: Omni-l Monochromator). The surface morphology and roughness of the TiO_2 films

were observed by using a conductive atomic force microscope (AFM, model: Mutimode-8J). The contact potential difference (CPD) was recorded with a Kelvin probe force microscopy (KPFM, model: SPA-400). The ultraviolet-visible (UV-Vis) transmittance and absorption spectra were recorded with an UV/Vis-NIR spectrometer (model: Lambda 950). Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS) were measured on a multifunctional photoelectron spectroscopy (model: Kratos Axis Ultra DLD) in an ultra-high vacuum seal chamber with a vacuum degree < 10^{-10} Torr, HeI radiation line (21.22 eV) from a discharge lamp. Impedance spectra (IS) for PSCs were measured on an electrochemical workstation (model: ZAHNER IM6e) in dark. During the impedance measurement, a 20 mV alternating current (AC) was provided to ensure a liner response of the impedance analyzer. The sweeping frequency ranged from 100 mHz to 1 MHz.[3,4]

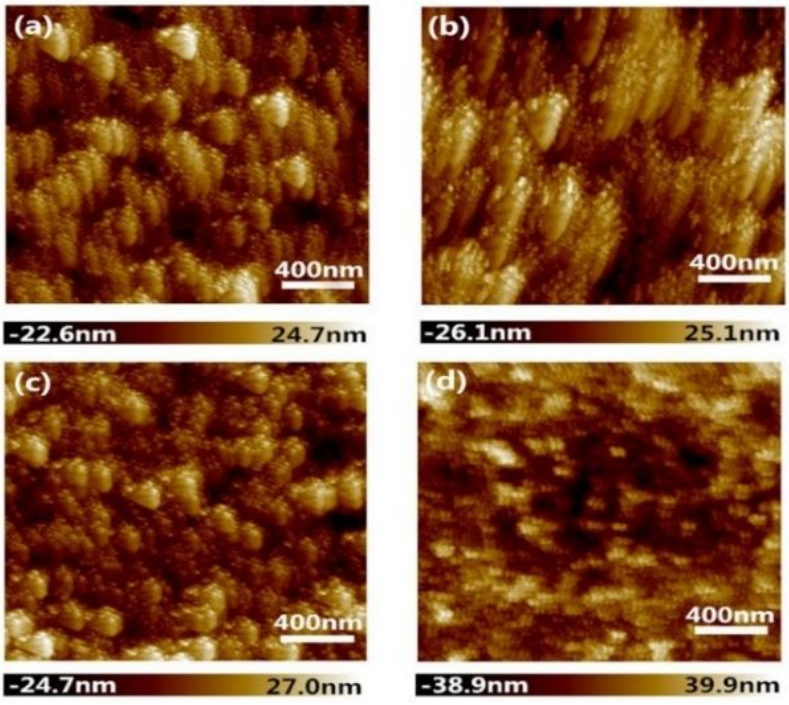

Figure S2. AFM images of TiO_2 films modified with different thiourea concentrations of (a) 0 M, (b) 0.05 M, (c) 0.1 M, and (d) 0.2 M.

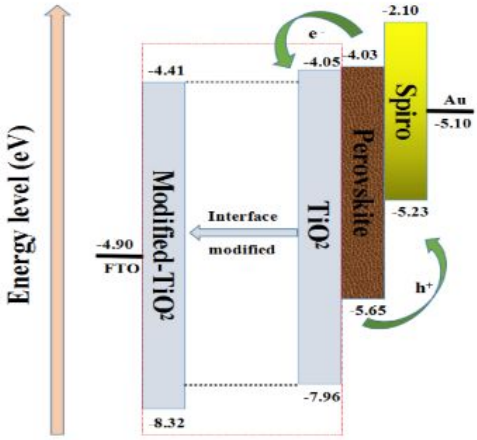

Figure S3. Schematic energy level diagram of FTO/TiO_2/perovskite/spiro-OMETAD/Au devices with and without thiourea modification (the energy level position of TiO_2 calculated from UPS analysis).

References

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(4) Tu, Y.; Wu, J.; Zheng, M.; Huo, J.; Zhou, P.; Lan, Z.; Lin, J.; Huang, M., TiO_2 quantum dots as superb compact block layers for high-performance $CH_3NH_3PbI_3$ perovskite solar cells with an efficiency of 16.97%. *Nanoscale* **2015**, *7*, 20539-20546.