

Electronic Supplementary Information

Tuning the Fermi-Level of TiO₂ Mesoporous Layer by Lanthanum Doping towards Efficient Perovskite Solar Cells

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This file includes Experimental section, Figure S1-S5, Table S1.

Experimental Section

Preparation of La/TiO₂ nanocomposite and paste: The La/TiO₂ nanocomposite was obtained from a wet approach, where the entire synthetic procedure was conducted in the ambient air. In the synthesis process, 1 g P25-TiO₂ was added into the amount of 0.1M nitrite acid solution with vigorous stirring. The solution was heated at 80 °C in a period of 2 h, forming a light blue translucent solution. After that, 0.05g La (NO₃)₃ was added to mixed solution and stirred for 2 h at least under vigorous stirring at 80 °C. The prepared samples were then transferred to a 100 mL Teflon autoclave and maintained for 12 h at 200 °C. After cooling down to ambient temperature, the white precipitates were centrifuged at 8000 rpm for 10 min, washed with ethanol, deionized water, ethanol respectively for three times, and dried at 60 °C for 6 h. After finishing all drying process, the power was calcined in air at 500 °C for 4 h (5 °C /min). TiO₂ (La/TiO₂) nanocomposite pastes were prepared as follows: 1 g TiO₂ (La/TiO₂) power and 0.52 g ethyl cellulose were added to the mixture of 10.68 g ethanol and 4.06 g terpineol. The solvents were removed by rotary evaporation at about 50 °C for 2 h. We obtained the white TiO₂ (La/TiO₂) pastes.

Synthesis of CH₃NH₃I: CH₃NH₃I (MAI) were firstly synthesized by the reaction of 24 mL CH₃NH₂ (40% in methanol, Sigma-Aldrich) and 10 mL HI (57 wt% in water, Sigma-Aldrich) in a 100 mL round-bottom. Keep in dark place at 0 °C for 2 h with stirring. The precipitate was collected using a rotary evaporator through carefully removing the solvents at 50 °C for 1 h. The white product was formed, which was recrystallized with ethanol. After filtration, the precipitate was washed with diethyl ether for three times at least and finally collected and dried at 60 °C in a vacuum oven for 24 h.

Fabrication of perovskite solar cell: The Fluorine-doped SnO₂ glass (FTO) substrate was washed with deionized water, ethanol, acetone and isopropanol by ultrasonication respectively. The FTO substrate was then treated with an UV/Ozone cleaner for 15 min. The TiO₂ blocking

layers (bl-TiO₂) were deposited onto the FTO by spray pyrolysis using a titanium diisopropoxide bis (acetylacetonate) solution (75 % in 2-propanol, Sigma-Aldrich) which was diluted in 1-butanol (99.8%, Sigma-Aldrich) at 1:39 volume ratio on 450 °C. The mesoporous TiO₂ layer was deposited onto the bl-TiO₂/FTO substrate by spin-coating the prepared TiO₂ and La/TiO₂ pastes. After annealing at 125 °C for 30 min, the as-deposited TiO₂ films were gradually heated to 525 °C in air, and then baked at this temperature for 30 min to remove organic components. The precursor solution of perovskite was prepared by mixing CH₃NH₃I with PbI₂ (99%, Sigma-Aldrich) at 1:1 mole ratio in anhydrous N,N-dimethylformamide (99.8%, Sigma-Aldrich) at room temperature for 60 min. Prior to using, the films were treated with UV/Ozone for 10 min. Then 55 μL CH₃NH₃PbI₃ precursor was coated onto the prepared mp-TiO₂ or mp-La/TiO₂ nanocomposite/bl-TiO₂/FTO substrate (around 1.9 cm × 1.9 cm) by spin-coating process at 5000 rpm in the glove box. After that, 180 μL anhydrous chlorobenzene (99.8%, Sigma-Aldrich) was dropped quickly onto the centre of the substrate after the spin-coating process. The obtained film was annealed at 100 °C for 10 min. After cooling to room temperature, 55 μL spiro-OMeTAD solution was deposited by spin-coating on the perovskite layer as the hole transport layer (HTL). The spiro-OMeTAD solution was prepared by mixing 72.3 mg spiro-OMeTAD (99.1%, Luminescence Technology Corp.) in 1 mL chlorobenzene. After 30 min stirring at room temperature, 28.8 μL 4-tert-butylpyridine (96%, Sigma-Aldrich), 17.5 μL of a stock solution of 520 mg mL⁻¹ lithium bis (trifluoromethylsulphonyl) imide (99.95%, Sigma-Aldrich) in acetonitrile (99.8%, Sigma-Aldrich) were added and stirred continuously for 3 h. Finally, 80 nm thick gold electrodes were deposited using thermal evaporation as a back contact.

Device characterization: The morphology and particle size of obtained samples were examined by scanning electron microscopy (SEM, JEOL 6701F) operated at 10 kV. The TEM image and EDS maps were characterized by TEM (JEM 2100F) with an accelerating voltage of 200 kV. The structure of materials has been evaluated with an X-ray diffractometer (Rigaku D/max-2500, Rigaku Corporation, Tokyo, Japan) using filtered Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) by measuring the diffraction angle (2θ) between 15° and 80° with a scanning rate of 2° min⁻¹ and

a step size of 0.02° . Raman spectra were recorded on a DXR Raman Microscope (Thermo Scientific) with a laser wavelength of 532 nm and a spot size of 1.1 μm . AFM experiments were carried out in a glovebox under an argon atmosphere at room temperature and pressure (Multimode 8, Bruker). The UV–Vis spectra were measured on a Shimadzu UV/Vis 2600 spectrophotometer with an integrating sphere. Samples were analyzed on Thermo Scientific ESCALab 250Xi using UPS. The gas discharge lamp was used for UPS, with helium gas admitted and the He I (21.22eV) emission line employed. The helium pressure in the analysis chamber during analysis was about 2E^{-8} mbar. The data were acquired with -10V bias. Current-voltage characteristics were measured with a solar simulator (Newport, USA) equipped with 450 W Xenon lamp (OSRAM) and a Keithley 2420 source meter. Light intensity was adjusted using a NREL-certified Si solar cell with a KG⁻² filter for approximating AM 1.5G light (100 mW cm^{-2}). The active area of solar cells were defined by a 0.16 cm^2 non-reflective metal mask. The mask was measured using a microscope (ECLIPSE LV150N, Nikon).

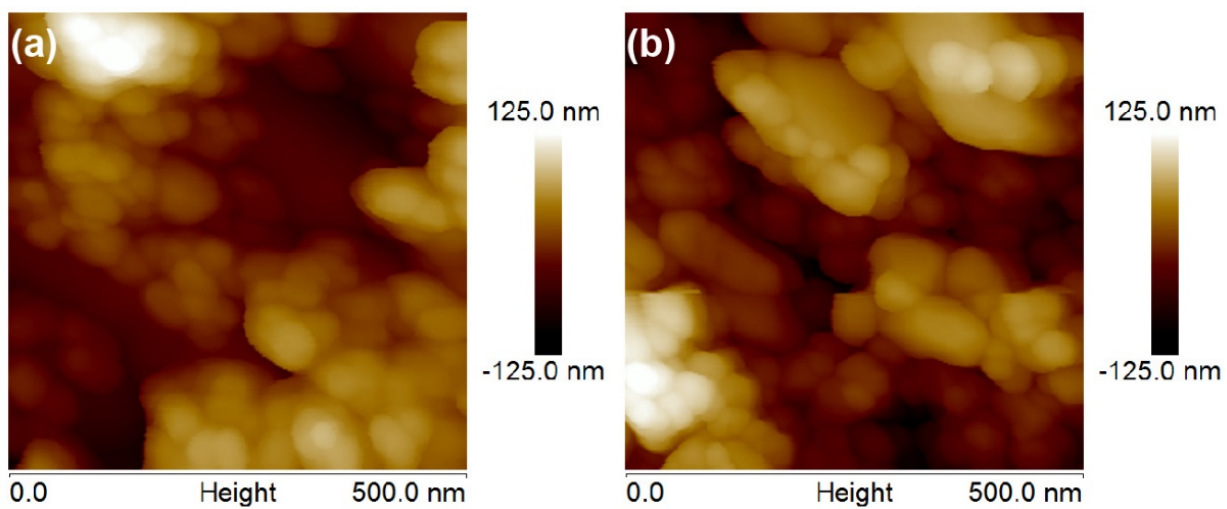


Fig. S1. AFM topographic images of TiO₂ (a) and La/TiO₂ (b) nanocomposite.

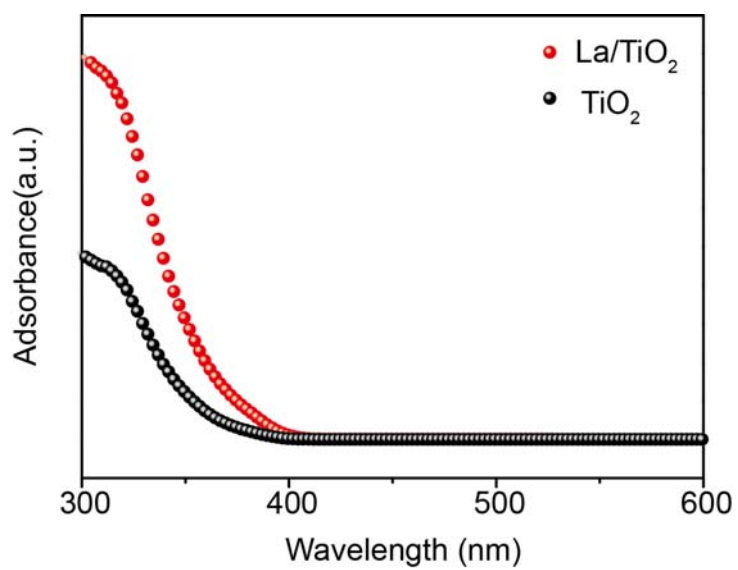


Fig. S2. UV-Vis absorption spectra of TiO₂ and La/TiO₂ nanocomposite

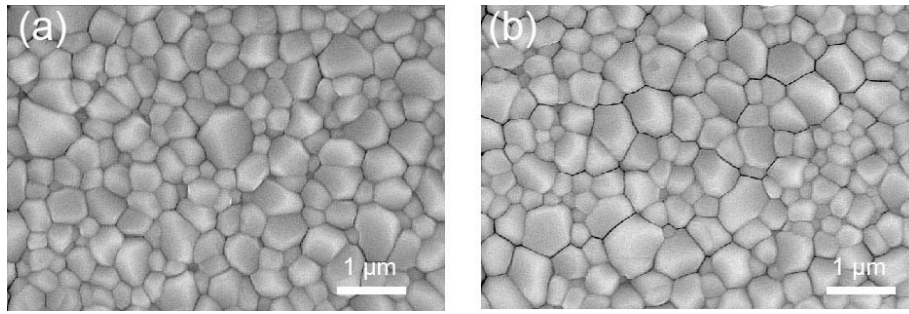


Fig. S3. SEM images of perovskite films on mesoporous TiO₂ (a) and La/TiO₂ (b) layers.

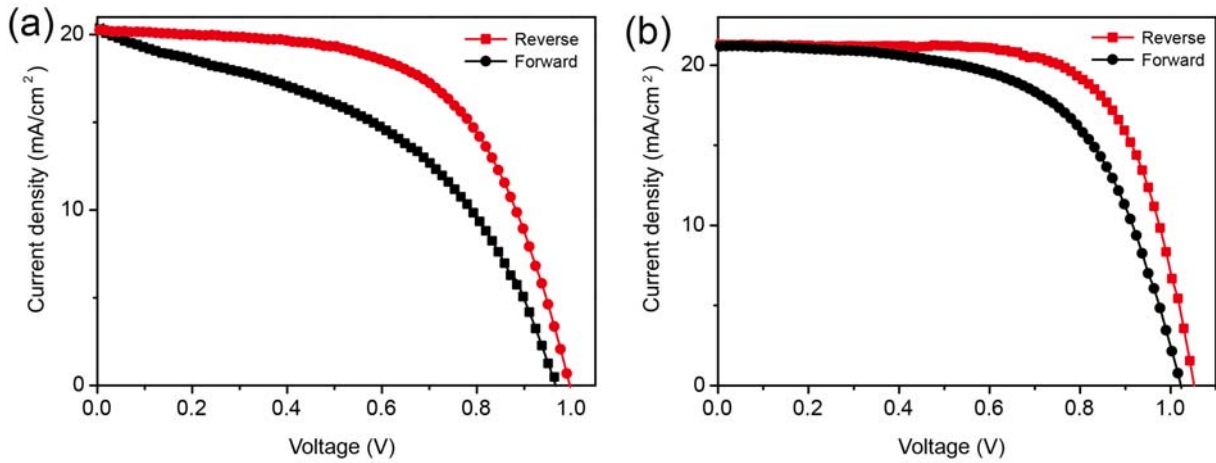


Fig. S4. J-V curves of PSCs with undoped (a) and La-doped (b) mp-TiO₂ layers, measured in both forward and reverse scan at 0.1 V/s scan rate.

Table S1. Photovoltaic parameters of PSCs with TiO₂ and La/TiO₂ mesoporous layer measured under reverse and forward scan.

	Scan direction	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	PCE (%)
TiO₂	Forward	0.97	20.53	45.06	8.98
	Reverse	1.00	20.28	60.01	12.11
La/TiO₂	Forward	1.02	21.20	60.34	13.06
	Reverse	1.05	21.30	68.92	15.42

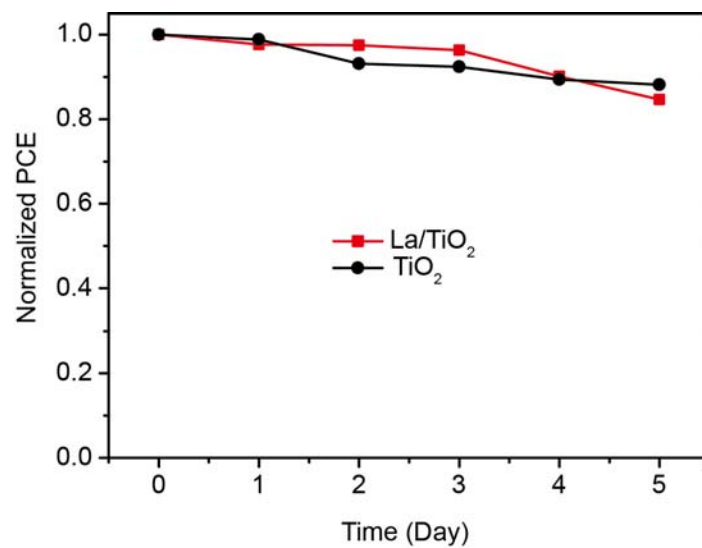


Fig. S5. Stability test on PSCs with undoped and La-doped mp-TiO₂, measured in ambient condition (40-50% RH) at room temperature (20-25 °C). The results are based on over 10 devices without encapsulation.