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Supporting information for:

# Modifying Perovskite Solar Cells with L(+)-cysteine at the Interfaces between Mesoporous $TiO_2$ and Perovskite

Pengfei Wu, Baohua Zhao, Xiaotong Ma, Chengben Liu, Yanli Chen, Guangwu Yang*, Xiyou Li*

School of Materials Science and Engineering, Institute of New Energy, College of Science, China University of Petroleum (East China), Qingdao, 266580, China

# Experimental section

## Materials

All chemicals and reagents were used as received without any further purification. Substrates are fluorine-doped tin oxide (FTO) conducting glass, which were washed sequentially in an ultrasonic bath with KOH/isopropyl alcohol-saturated solution, distilled water, acetone, and ethanol alcohol.

## Measurements

Absorption spectra were recorded on a U-3900 UV-vis spectrophotometer (Japan Hitachi). Steady-state and time-resolved photoluminescence (PL) spectra were taken using a fluorescence spectrometer (FLS980, Edinburgh, England). IR spectra were recorded by using a Spectrum One instrument (German Perkinelmer). Laboratory powder X-ray diffraction patterns were collected on a Rigaku Ultima IV X-ray diffractometer with a Cu Ka source (40 kV, 40 mA). The morphology of the samples were observed on a field-emission scanning electron microscope (SEM, Quant 250FEG) equipped with an energy-dispersive X-ray (EDX) detector. The contact angle was measured on an OCA20 contact angle measuring instrument (Dataphysics, Germany). Current-voltage (I-V) data of PSCs and electrochemical impedance spectroscopy (EIS) were collected on an electrochemical workstation (CHI-760) in solar plot mode under xenon lamp irradiation. The xenon lamp used in the measurement was calibrated by a commercial standard Si cell (Newport). The external quantum efficiencies (EQEs) were detected by the dual phase lock-in amplifier (SR830) and the grating spectrometer (Omni-λ300).

## Solar cell fabrication

Fluorine-doped tin oxide (FTO) glass substrates with dimension of 1.75 cm × 1.2 cm were patterned by etching with zinc powder and 2M hydrochloric acid. The precursor solution of the block $TiO_2$ layer (bl-$TiO_2$) composed of 1-butanol and titanium diisopropoxide bis(acetylacetonate). The bl-$TiO_2$ was applied to FTO by spincoating at 3000 rpm for 20 s and sintered at 500 °C for 30 min. The mp-$TiO_2$ (18NR-T TiO2 paste, purity >99%) was then coated at 4000 rpm for 30 s and annealed at 500 °C for 30 min. For the perovskite layer, a precursor solution composed of $CH_3NH_3I$, $PbI_2$ and $PbCl_2$ in a molar ratio of 4:1:1 with N,N-dimethylformamide as solvent was spin-coated at 4000 rpm for 30 s and then annealed at 100 °C for 60 min. Spiro-OMeTAD as hole transport layer, was subsequently deposited following the literature method.[37] Finally, 80 nm thick Au as a counter electrode was deposited. The active area of fabricated PSCs is 0.06 $cm^2$

### L-cy modification onto mp-$TiO_2$ surface

The as-obtained FTO/bl-$TiO_2$/ mp-$TiO_2$ substrate was dipped into different L-cy solutions (solvent: methyl alcohol, ethyl alcohol, isopropanol and water) with a series L-cy concentration (0.5 mM, 1 mM and 1.5 mM) at room temperature for a certain time (0.5h, 1h, 1.5h, 2h), and then the substrates were washed thoroughly by absolute ethanol three times to remove physically absorbed L-cy molecules. Finally they were dried at 353 K in a vacuum oven for 90 min.

## The Young's equation

When dropping liquid on a solid substrate, there will be a certain angel at the line of three-phase contact described by one of the mostly used physical equations, namely Young's equation(1)

$$cos\theta\gamma_{\iota v} = \gamma_{sv} - \gamma_{s\iota} \qquad (1)$$

where $\gamma_{\iota v}$ is liquid surface energy, $\gamma_{sv}$ is solid surface energy and $\gamma_{s\iota}$ is solid-liquid surface energy. According to the equation, it is clear understood that when $\gamma_{\iota v}$ is the same as $\gamma_{s\iota}$, the solid energy will go up with the contact angels decreasing. The contact angels between different thiadiazole derivatives containing perovskite films and DMF were investigated.

**Table 1S** The contact angle and solid interface energy for droplets of DMF on bare and L-cy modified mp-$TiO_2$ substrate

| | bare mp-$TiO_2$ | L-cy modified mp-$TiO_2$ |
|---|---|---|
| The contact angel | 17° | 7.9° |
| The solid interface energy | 35.73 mN/m | 37.04 mN/m |

**Table 2S** Fitting parameters used in the equivalent circuit modeling of impedance spectra of the devices based on bare mp-$TiO_2$ and L-cy modified mp-$TiO_2$

| | Device based on bare mp-$TiO_2$ | Device based on L-cy modified mp-$TiO_2$ |
|---|---|---|
| $R_s$ （Ω） | 19.68 | 19.44 |
| $R_{ct}$ （Ω） | 129.8 | 116.0 |

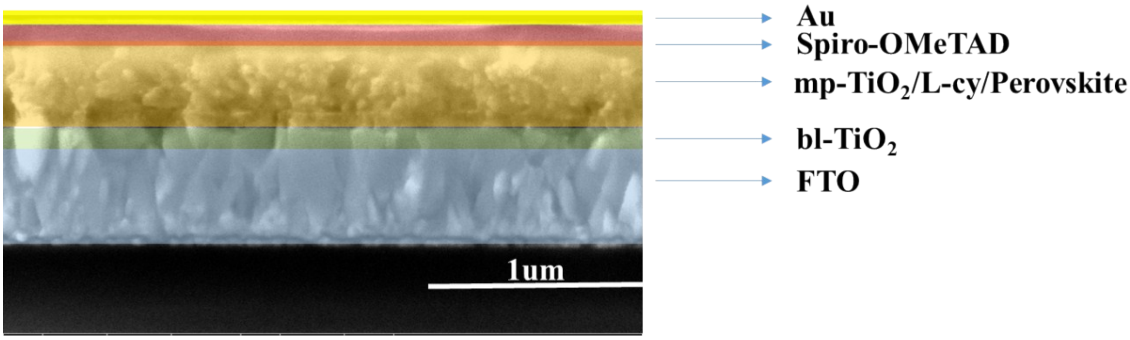

**Fig. 1S** The cross-section SEM image of the device with L-cy modified mp-$TiO_2$ containing the FTO cathode and Au anode.

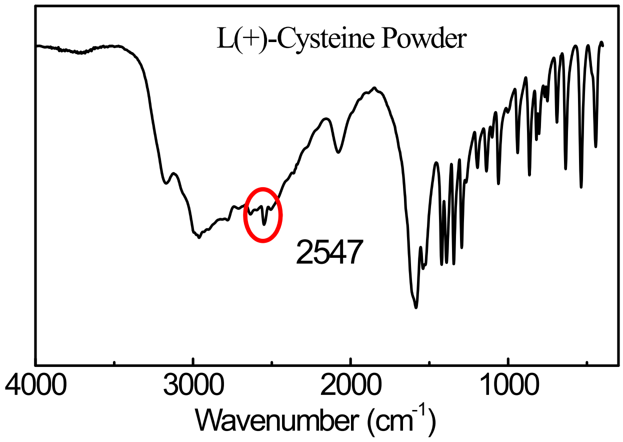

**Fig. 2S** The FTIR spectra of the L-cy powder.

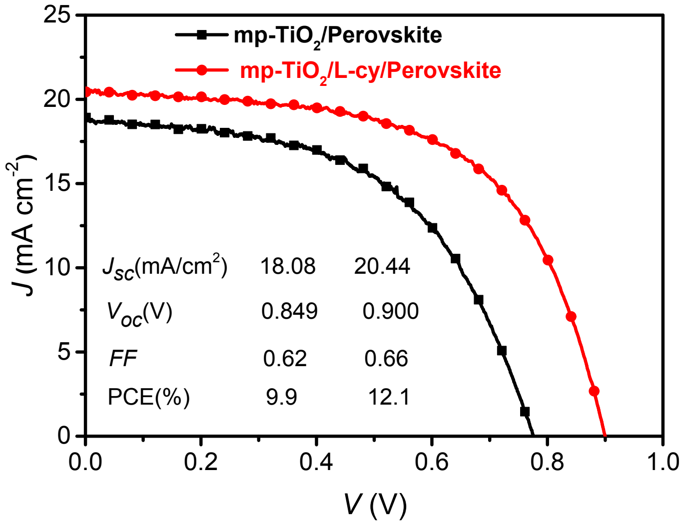

**Fig. 3S** *J-V* curves for the champion devices (1 $cm^2$) based on bare mp-$TiO_2$ and on modified mp-$TiO_2$.

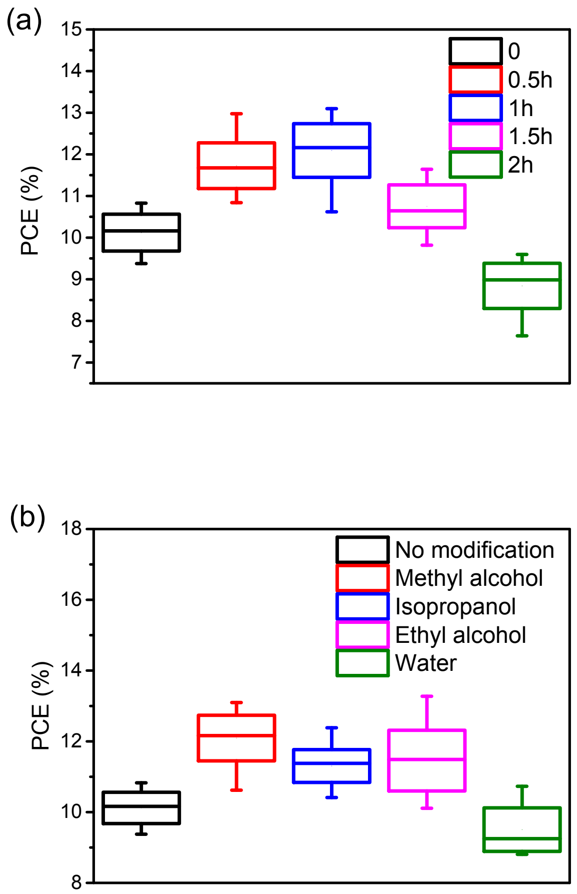

**Fig. 4S** Histograms of PCE for the devices based on L-cy modified mp-$TiO_2$: (a) with different dipping time; (b) in different solvents.

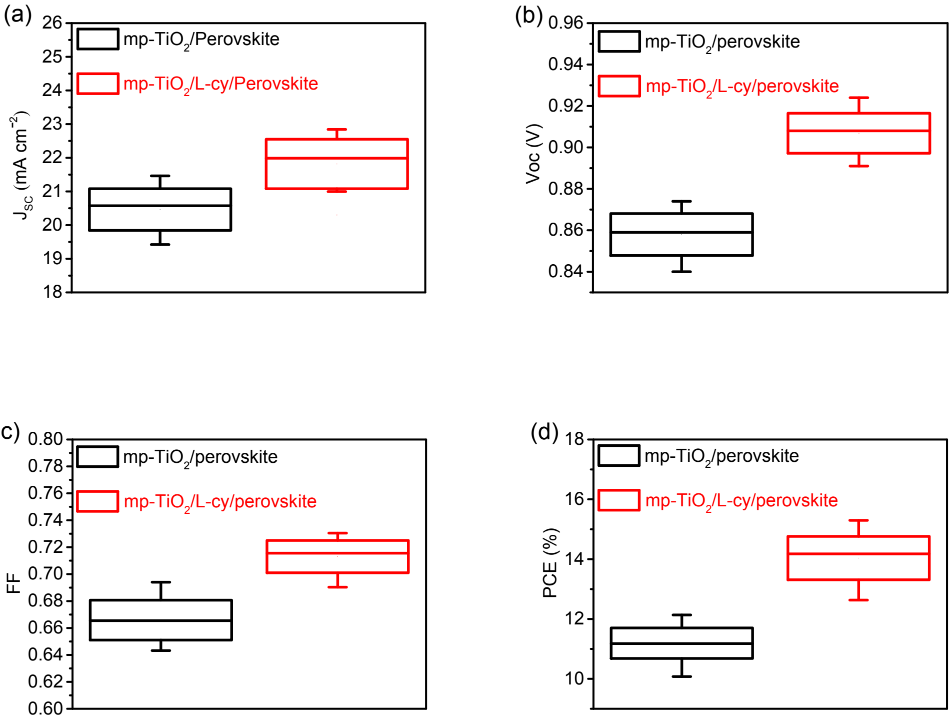

**Fig. 5S** Histograms of (a) $J_{SC}$; (b) $V_{OC}$; (c) $FF$; (d) PCE for the devices based on bare mp-TiO$_2$ and on L-cy modified mp-TiO$_2$.

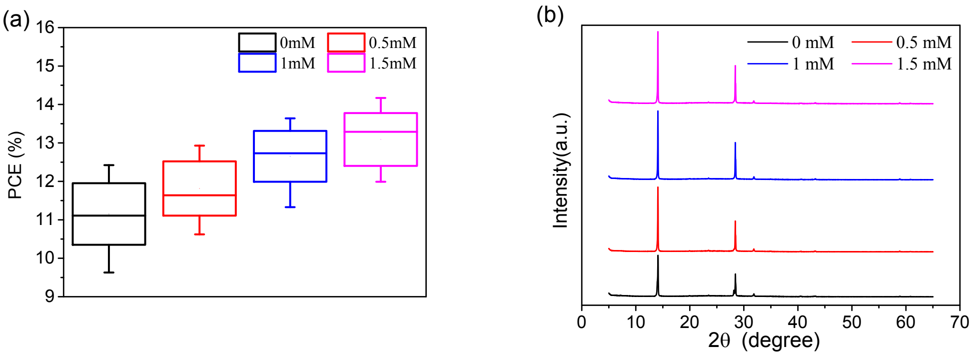

**Fig. 6S** (a) Histograms of PCE for the devices and; (b) XRD patterns of perovskite film based on bare mp-TiO$_2$ and on TiO$_2$ modified with different concentration methanol solutions.

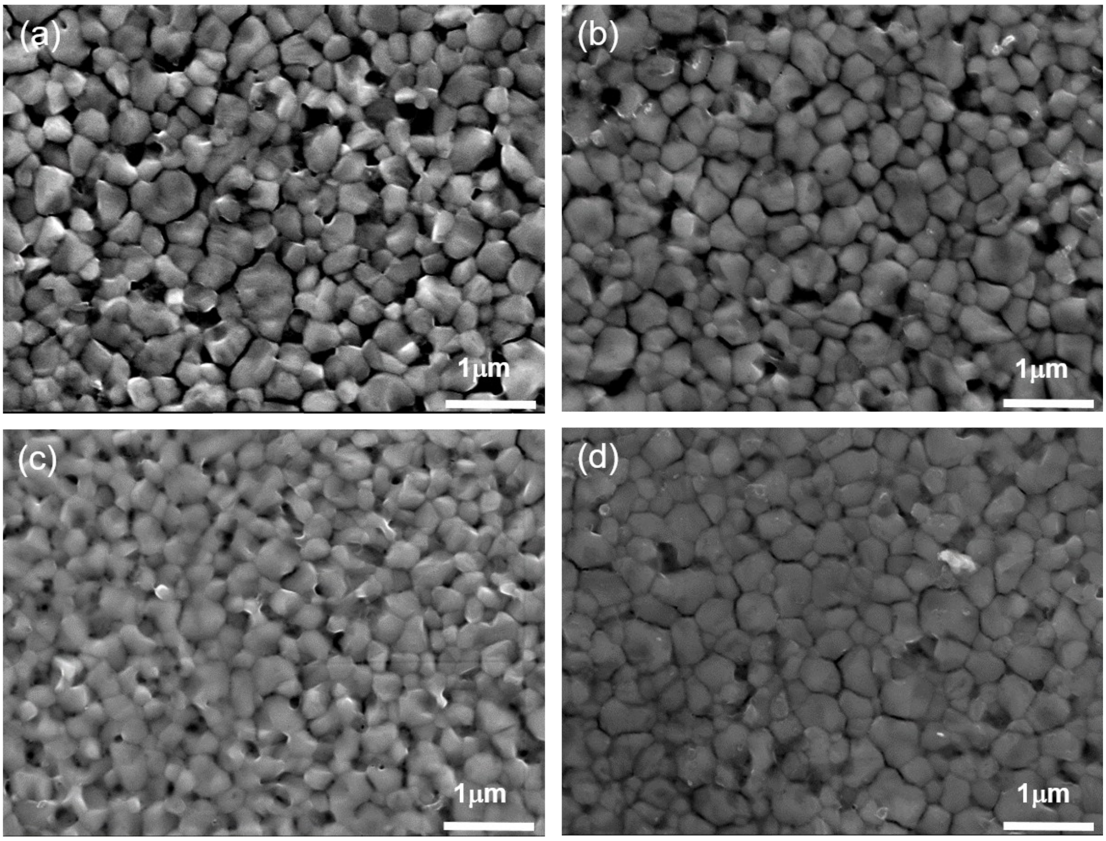

**Fig. 7S** Perovskite films on $TiO_2$ modified with different concentration methanol solution: (a) 0 mM; (b) 0.5 mM; (c) 1 mM; (d) 1.5 mM.

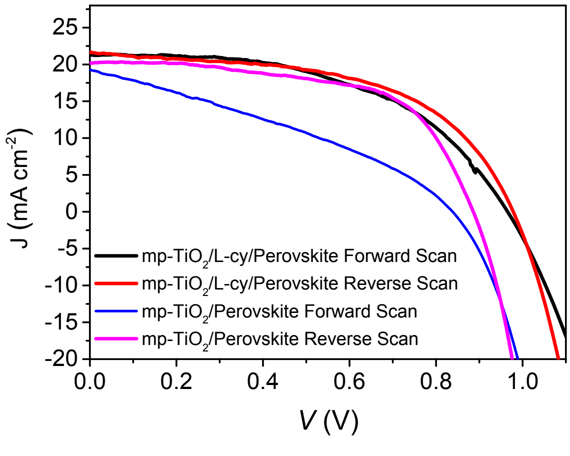

**Fig. 8S** Forward and reverse *J*-*V* curves for the champion devices based on bare mp-$TiO_2$ and on L-cy modified mp-$TiO_2$.