

Supporting Information for

Enhancing photocurrent of perovskite solar cells via modification of $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ heterojunction interface with amino acid

1. Experimental section

1.1 Preparation of nanocrystalline TiO_2 paste

TiO_2 nanoparticle precursor was synthesized by sol-gel method. 72 mL titanium tetraisopropoxide (TTIP, 96%, Acros) was added to 430 mL of 0.1 M HNO_3 under vigorous stirring for 30 min. Then the solution was heated to 85–90 °C and kept constantly stirring for 8 h for peptization. After being filtered to remove the large particles, the solution was transferred to an autoclave for hydrothermal treatment at 240 °C for 12 h. While cooling to room temperature, the whitely colloidal suspension was collected and washed with water for several times. After drying, the TiO_2 particles with a size of ~20 nm were obtained and subsequently added with ethanol. Ethyl cellulose (Aldrich), acetic acid and terpeneol (Aldrich) were then added into the prepared ethanol solution. The ethanol was removed from the solution using a rotary evaporator to obtain a viscous paste. The composition of TiO_2 /terpeneol/ethylcellulose/acetic acid was 1/6/0.5/0.1. To fabricate the mesoporous TiO_2 layer, the paste was then diluted with ethanol for controlling the layer thickness.

1.2 Synthesis of methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$)

Hydroiodic acid (30 mL, 0.227 mol, 57 wt.% in water, Acros) and methylamine (27.8 mL, 0.273 mol, 40% in methanol, TCI) were stirred in the ice bath for 2 h. Then, the precipitates were recovered by evaporation at 50°C for 1 h. The products were dissolved in ethanol, recrystallized from diethyl ether and finally dried at 60°C in vacuum oven for 24 h.

1.3 Fabrication of perovskite solar cells

FTO glasses (~7 $\Omega \text{ sq}^{-1}$, Solaronix) were cleaned with acid solution (volume ratio of $\text{H}_2\text{O} : \text{H}_2\text{O}_2 : \text{HCl}_{(\text{aq})} = 6 : 1 : 1$), alkaline solution (volume ratio of $\text{H}_2\text{O} : \text{H}_2\text{O}_2 : \text{NH}_3_{(\text{aq})} = 5 : 1 : 1$) and isopropanol for 20 min respectively. A 60-80 nm thick compact TiO_2 as blocking layer was deposited by spin-coating the 0.15 M titanium(diisopropoxide)bis(2,4-pentanedionate) (75%, Alpha) in 1-butanol (Aldrich)

solution on cleaned FTO, which was then heated at 125°C for 5 min. After cooling to room temperature, the same process was repeated twice but with 0.3 M titanium(diisopropoxide)bis(2,4-pentanedionate) in 1-butanol solution. The sample was subsequently heated to 500°C for 15 min and then immersed in 0.02 M TiCl₄ (Aldrich) aqueous solution at 70°C for 30 min. After heating to 500°C for 15 min again, the obtained compact TiO₂ layer was deposited with mesoporous TiO₂ film by spin coating the as-prepared nanocrystalline TiO₂ paste at 5,000 rpm for 30 s and then sintering at 500°C for 30 min. For the glycine treatment, the sintered TiO₂ film was immersed into a 10⁻³ M glycine (99+%, Acros) aqueous solution overnight, washed with water and ethanol to remove the un-chelated residuals and dried under vacuum.

Under the controlled atmospheric conditions in a glove box, PbI₂ (Acros) was dissolved in N,N-dimethylformamide with stirring at 70°C for over 12 h. 1 M PbI₂ solution was then spin-coated onto the as-prepared TiO₂ film at 3,000 rpm for 20 s and dried at 70°C for 10 min. After cooling to room temperature, the film was rinsed with 2-propanol and subsequently dipped into a CH₃NH₃I solution in 2-propanol (10 mg mL⁻¹) for 20 s, rinsed with 2-propanol again and dried at 70°C for 30 min to form CH₃NH₃PbI₃.

The hole transporting material was deposited onto the CH₃NH₃PbI₃ film by spin coating (4,000 rpm for 30 s) the solution containing 72.3 mg 2,2',7,7'- tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD) in 1 mL chlorobenzene, 28.8 mL 4-tert-butylpyridine, and 17.5 mL of 520 mg mL⁻¹ lithium bis(trifluoromethylsulphonyl)imide in acetonitrile as additives. Finally, 50 nm thick Au as the counter electrode for perovskite solar cells was deposited on top of the hole transporting material by thermal evaporation.

2. Supplementary figures

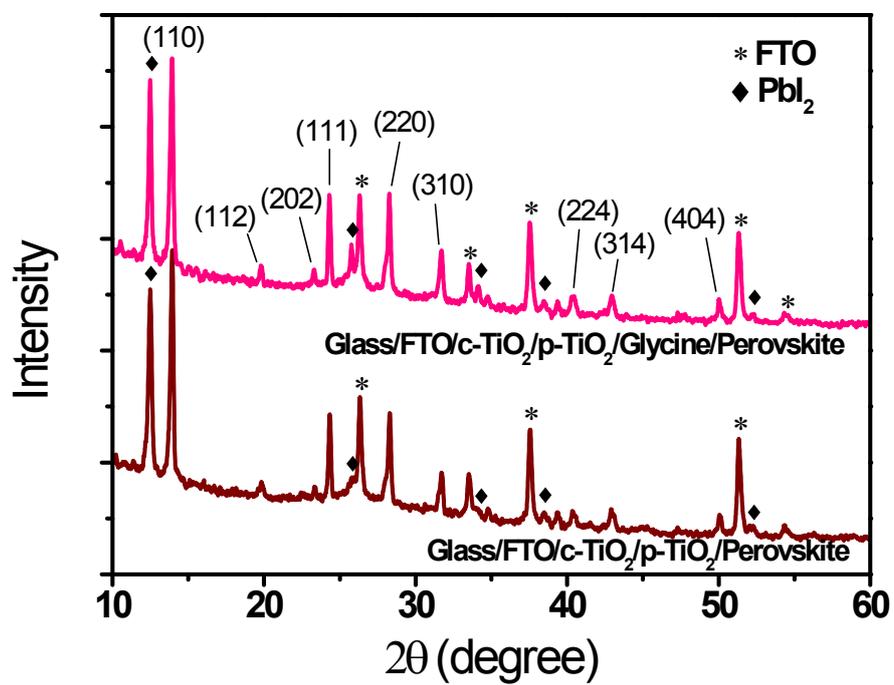


Figure S1. XRD patterns of CH₃NH₃PbI₃ formed on p-TiO₂ with and without glycine treatment.

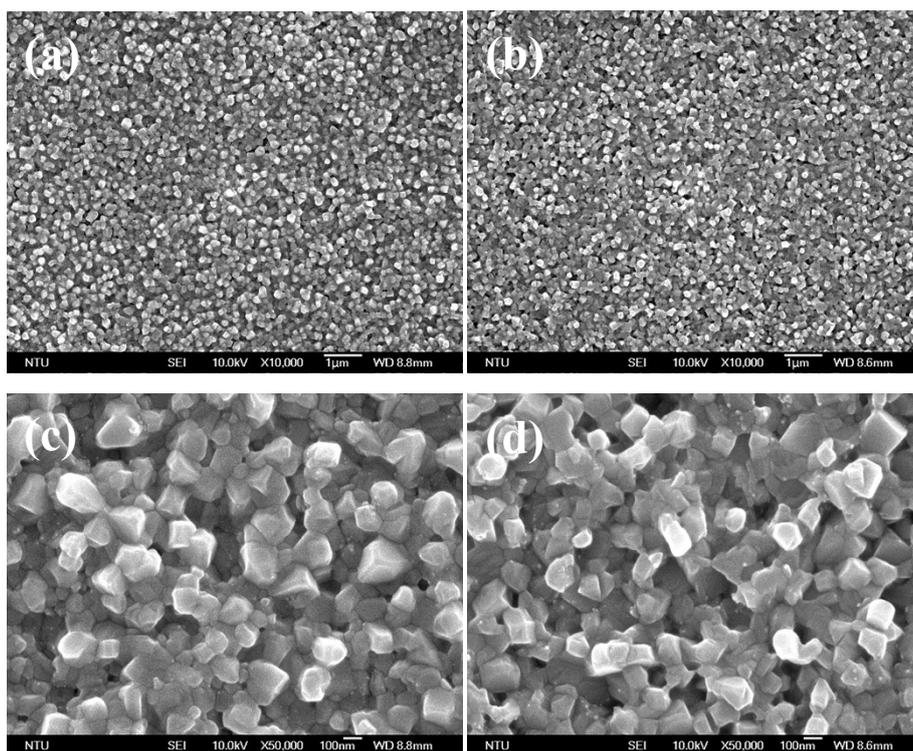


Figure S2. SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ formed on (a, c) p- TiO_2 and (b, d) glycine-treated p- TiO_2 .

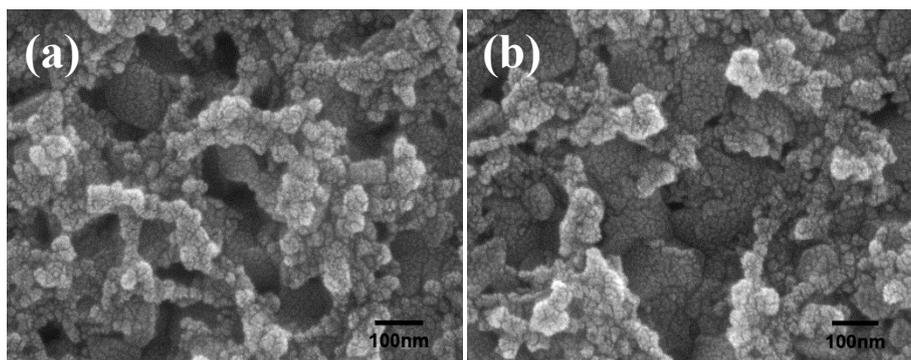


Figure S3. SEM images of PbI_2 deposited on (a) c-TiO_2 and (b) glycine-treated c-TiO_2 by spin-coating $\sim 0.1\text{M}$ PbI_2 in DMF solution.