

Electronic Supplementary Information (ESI)

CH₃NH₃PbI₃ planar perovskite solar cells with anti-reflection and self-cleaning function layer

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Experimental

Materials

Acetone (Aldrich), methanol (Aldrich), ethanol (Aldrich), isopropyl alcohol (IPA: Aldrich), n-hexane (Aldrich), methylamine (40 % in methanol, Junsei), diethyl ether (Aldrich), toluene (Aldrich), acetonitrile (Aldrich), N, N-dimethylformamide (DMF, Aldrich), tert-butyl pyridine (t-BP: Aldrich), Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI: Aldrich), titanium diisopropoxide bis(acetylacetonate) (Aldrich), buffer oxide etchant (BOE: CHEMI TOP Co., LTD.), 5% hydrofluoric (HF) acid (Aldrich), potassium hydroxide (KOH: Aldrich), hydrochloric acid (HCl: Aldrich), hydrogen peroxide (H₂O₂: Aldrich), trichloro (1H, 1H, 2H, 2H-perfluorooctyl) silane (FOTS: Aldrich), hydriodic acid (HI: 57% in water, Aldrich), PbI₂ (Aldrich), poly-triarylamine (PTAA: EM index), Sylgard 184 (Dow Corning Co.), Si □100□ wafers (p-type, boron-doped; iTASCO), and F-doped tin oxide (FTO, Pilkington, TEC8) were used.

Synthesis of CH₃NH₃I (MAI) powder

MAI was prepared by reacting 50 mL HI and 50 mL methylamine in a 250-mL round-bottom flask at 0 °C for 2 h under magnetic stirring. The precipitate product was recovered by evaporating the solvents through rotary evaporator at 50 °C for 1 h. The product was then dissolved in ethanol, recrystallized from diethyl ether, and finally dried at room temperature in a vacuum oven for 24 h. The white MAI powder was then poured in a vial and was stored in a desiccator.

Fabrication of micro-pyramidal structured Si (MPS-Si) molds

Si substrates with a size of 2×2 cm² were ultrasonically cleaned with acetone, methanol, and deionized (DI) water, and subsequently dried with nitrogen (N₂) gas flow. Prior to the wet etching, the Si substrates were subsequently dipped into to BOE, 5wt% HF acid solutions, and DI water for 1 min, followed by the N₂ gas blow. And then, in order to form the MPS-Si molds, the Si samples were dipped into etchant solution mixed with KOH:IPA:DI water (1:0.5:8.5 vol%) at a temperature of 75 °C for 40 min. Finally, the MPS-Si molds were dipped into HCl:H₂O₂:H₂O (1:1:5) mixture solution at 80 °C for 10 min, to remove the remaining potassium impurities on their surface.

Preparation of inverted micro-pyramidal structured polydimethylsiloxane (IMPS-PDMS) and flat-PDMS layers

A PDMS solution, prepared by the mixture of base resin and curing agent (Sylgard 184, Dow Corning Co.) with a 10:1 weight ratio, was poured on the MPS-Si molds, and subsequently cured at 75 °C for 2 h in an oven. By peeling off the PDMS film from the MPS-Si mold, the IMPS-PDMS layers were finally prepared. For comparison, the flat-PDMS layers were also fabricated using the Si substrate with a planar surface via the same pattern transfer patterning process.

Characterization instruments for the IMPS-PDMS layer

The surface morphologies of the fabricated samples were observed by using a field-emission scanning electron microscopy system (LEO SUPRA 55, Carl Zeiss). The optical properties were characterized by using a UV-vis-NIR spectrophotometer (Cary 5000, Varian) with an integrating sphere. The water contact angles were measured and averaged at three different positions on the surface of the samples by using a contact angle measurement system (Phoenix-300, SEO Co., Ltd.) with 5 □L droplets of DI water.

Device fabrication

A blocking TiO₂ layer (bl-TiO₂) with ~ 50 nm of thickness was deposited on a cleaned FTO glass substrate (2.5 cm×2.5 cm) by a spray pyrolysis deposition method with 20 mM of titanium diisopropoxide bis(acetylacetonate) solution at 450 °C. We repeated the spraying process about 40 times to spray 40 mL solution manually by using a glass type atomizer. A 0.1 mL of 40 wt% MAPbI₃/DMF solution with a HI solution (40 wt% MAPbI₃ solution in DMF/hydriodic acid = 1 mL/0.1 mL) was then spin-coated on the bl-TiO₂/FTO substrate at 3000 rpm for 200 s and the resulting film was fully dried on a hot plate at 100 °C for 2 min in air under 25 % relative humidity. PTAA/toluene (15 mg/1 mL) with 7.5 μL Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (170 mg/1 mL) and 7.5 μL tert-butyl pyridine (t-BP)/acetonitrile (1 mL/1 mL) additives was spin-coated on the MAPbI₃/bl-TiO₂/FTO substrate at 3000 rpm for 30 s. Finally, Au counter electrode with ~60 nm of thickness was deposited by thermal evaporation. Whole experiments were conducted at ambient atmosphere under controlled relative humidity (~25 %). The active area was fixed to 0.16 cm². For IMPS-PDMS AR layer and flat-PDMS AR layer equipped MAPbI₃ perovskite solar cells, we just covered the IMPS-PDMS AR layer and flat-PDMS AR layer on the FTO glass/bl-TiO₂/MAPbI₃/PTAA with additives/Au substrates.

Device characterization

The external quantum efficiency (EQE) was measured by a power source (ABET 150W Xenon lamp, 13014) with a monochromator (DONGWOO OPTORN Co., Ltd., MonoRa-500i) and a potentiostat (IVIUM, IviumStat). The current density-voltage (J-V) curves were measured by a solar simulator (Peccell, PEC-L01) with a potentiostat (IVIUM, IviumStat) under illumination of 1 sun (100 mW·cm⁻² AM 1.5G) and a calibrated Si-reference cell certificated by JIS (Japanese Industrial Standards). The J-V curves of all devices were measured by masking the active area with a metal mask of 0.096 cm² aperture.

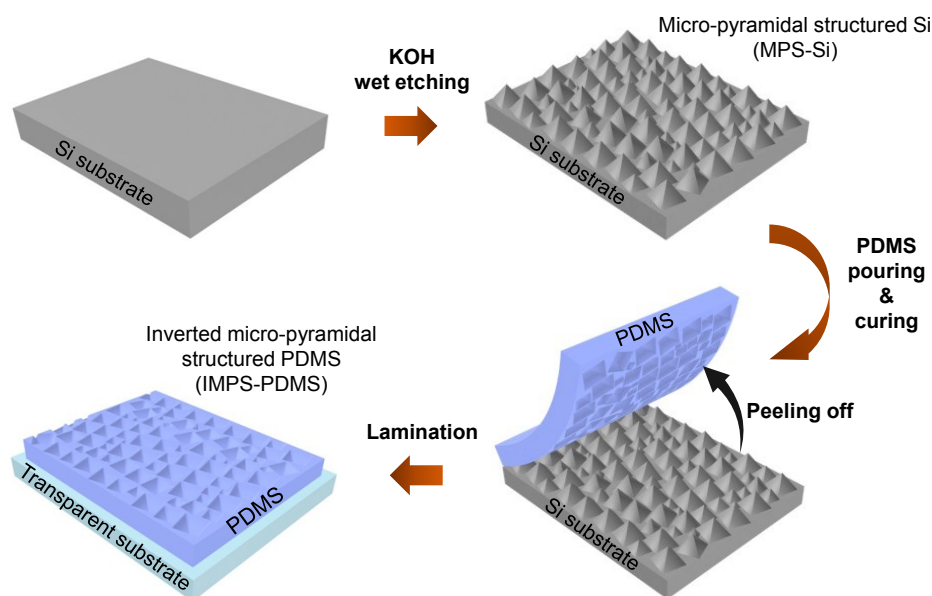


Fig. S1. Schematic diagram of fabrication steps for the inverted micro-pyramidal structured PDMS (IMPS-PDMS) via the soft lithography using a micro-pyramidal structured silicon substrate (MPS-Si) as a mold and its lamination on transparent substrates.

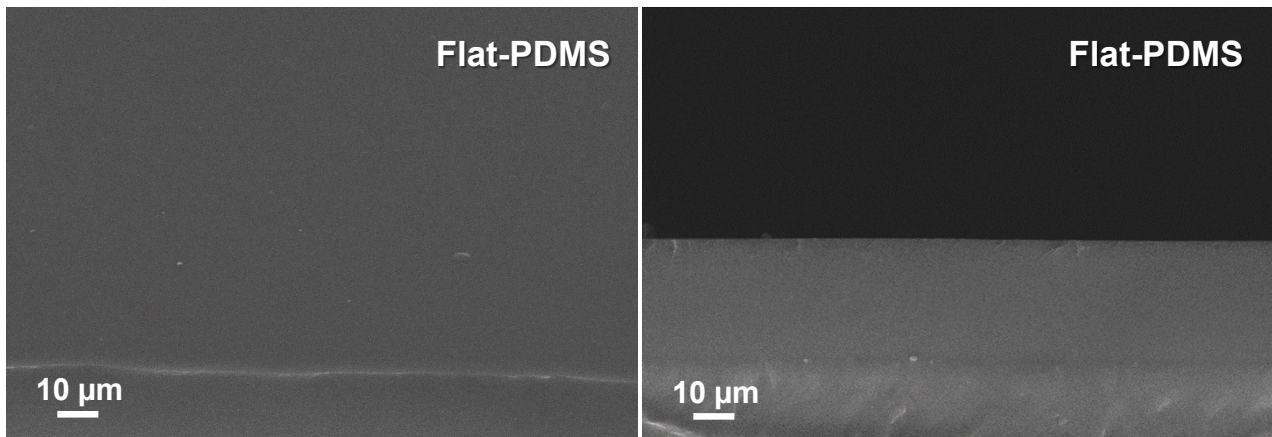


Fig. S2. 30°-tilted and cross-sectional SEM images of the flat-PDMS layer without any patterns.

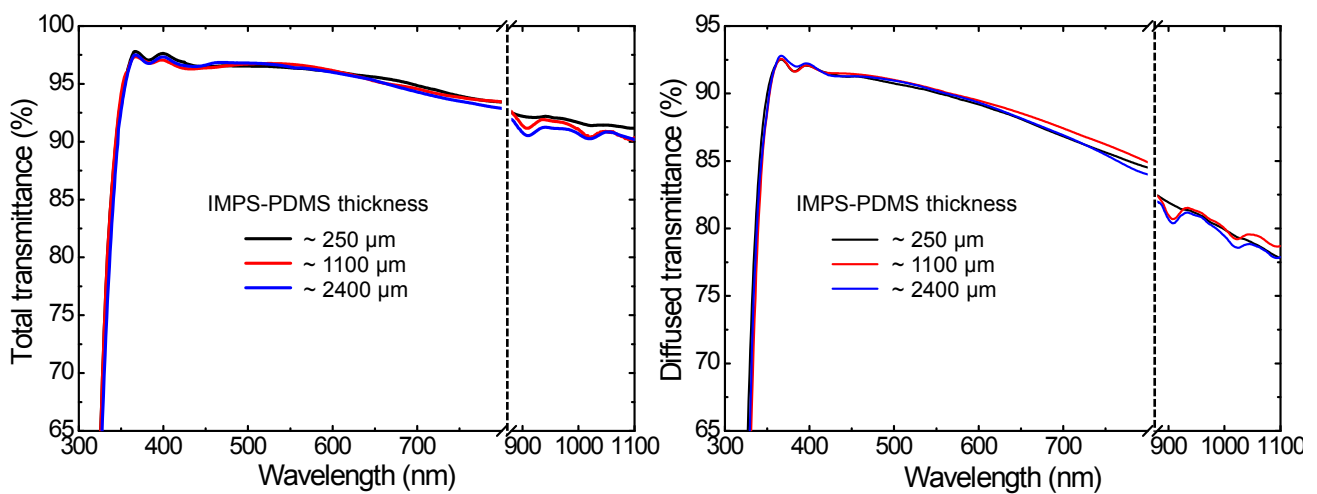


Fig. S3. Measured total and diffuse transmittance spectra of IMPS-PDMS layer with different thickness.

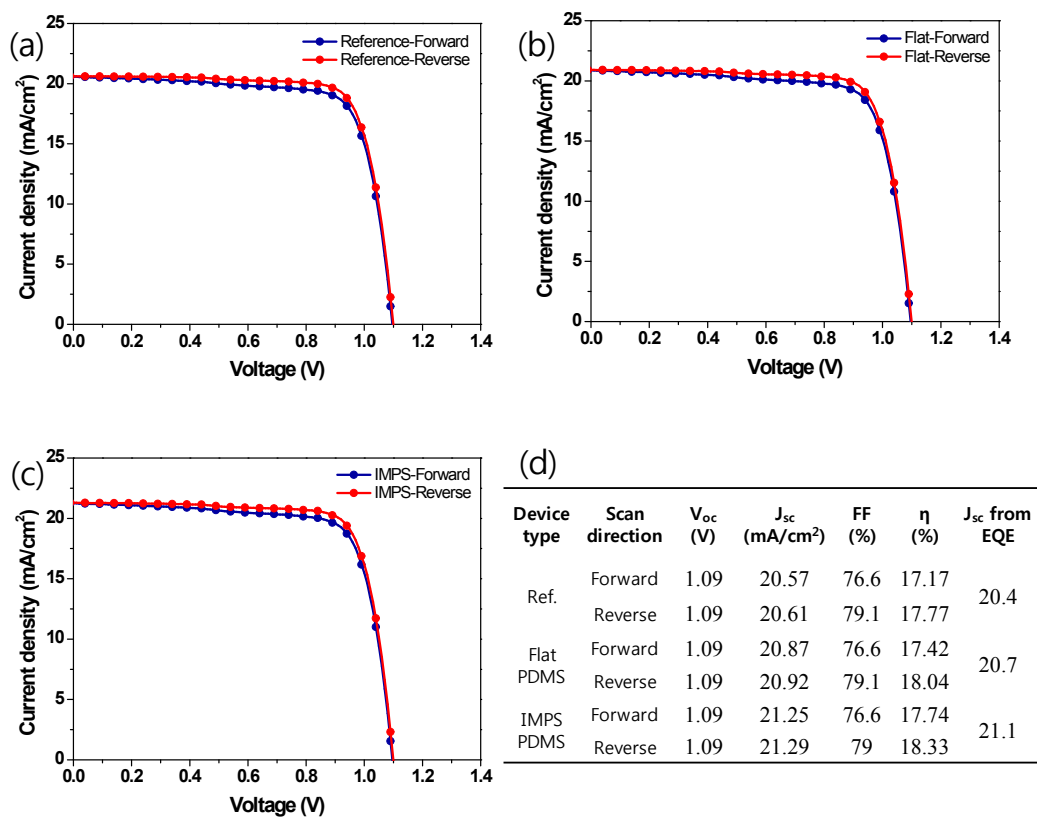


Fig. S4. (a-c) The J-V hysteresis for forward and reverse scan condition and (d) summary of photovoltaic properties and J_{sc} values calculated from EQE spectra of reference (a), flat-PDMS (b), and IMPS-PDMS (c) device.

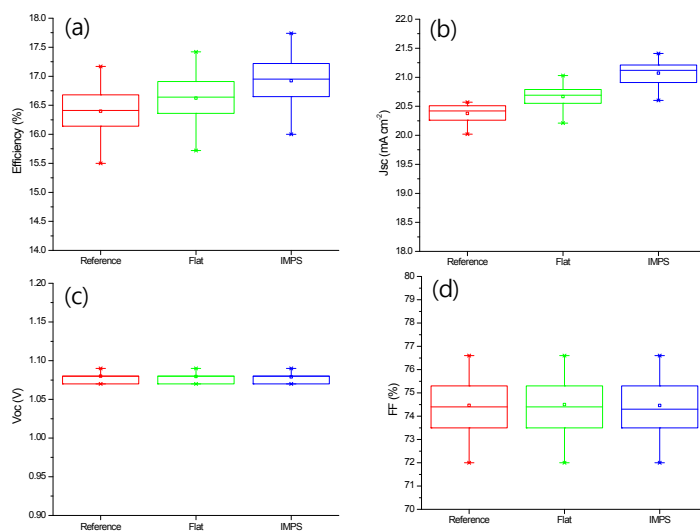


Fig. S5. Statistical photovoltaic data of each 20 sample of reference, flat-PDMS, and IMPS-PDMS device. (a) Efficiency, (b) J_{sc} , (c) V_{oc} , and (d) FF.

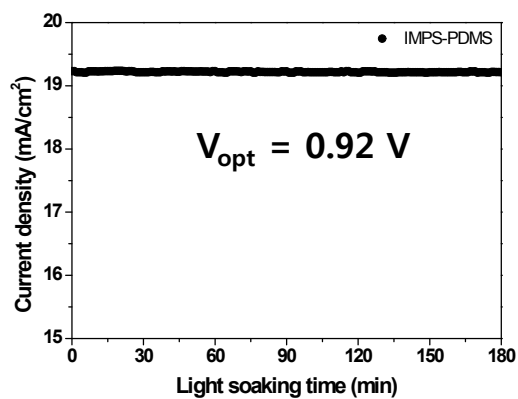


Fig. S6. Stabilized efficiency of IMPS-PDMS device. The J_{sc} variation with continuous light soaking of 1 Sun by applying optimal bias voltage ($V_{opt} = 0.92$ V) at maximum power point.

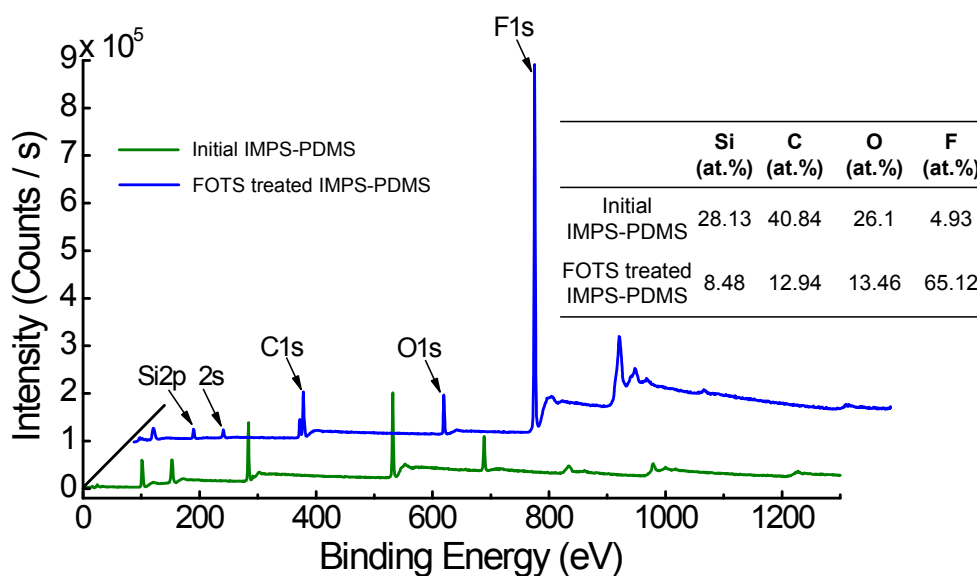


Fig. S7. XPS spectra and atomic composition of IMPS-PDMS layer before and after the FOTS surface modification treatment.