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Supporting Information

Water-Repellent Perovskite Solar Cell

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Experimental section

Fabrication of Pyramid-shaped PDMS films:

The pyramid-shaped master used in this work was produced by mechanical cutting method. The procedure is described in detail elsewhere.¹ After the preparation of the pyramid-shaped masters, the UV-curable polyurethane-acrylate (PUA) prepolymer solution was drop-dispensed on the master and covered by a flexible polyethylene-terephthalate (PET) film (~50 µm thickness). Subsequently, the PUA was cured by UV exposure ($\lambda = 250$ to ~400 nm, intensity of ~100 W/cm², Fusion Cure System, Minuta Tech, Korea) for a few tens of seconds and the inverse pyramid PUA replica on the PET film was de-mold from the master. After overnight curing (>12 h) of PET film mold, to ensure a rigidity of PUA structures, polydimethylsiloxane (PDMS) precursor (Sylgard 184 Silicon elastomer, Dow Corning) and curing agent with a 10:1 ratio by weight was poured on the negative pyramid PET film mold and was placed at 70 °C for 1 h. Then, the fully cured pyramid-shaped PDMS film was gently peeled off from the PET film mold.

Preparation of the Anti-reflection and Self-cleaning Surfaces :

The Ar ion treatment with fluorocarbon source of octafluorocyclobutane, C_4F_8 was performed on the fabricated surface of pyramid-shaped PDMS by chemical plasma deposition for a few tens of seconds (2000 W ICP power, 10 V bias voltage, 25 mTorr pressure, Ar ion 30 sccm / C_4F_8 150 sccm gas flow rate) in an inductively coupled plasma (ICP) etching system. (Versaline ICP, Plansma-Therm inc.).

Fabrication of Perovskite Solar Cells:

The fluorine-doped tin oxide-coated (FTO) glass substrate was purchased from Pilkington (TEC-8, $8\Omega/sq$) and cleaned sequentially using UVO treatment for 15 min and sonication process with detergent liquid, acetone, ethanol and DI water. A compact blocking layer TiO₂ was deposited by spin-coating titanium diisopropoxide dis(acetylacetonate) (Sigma-Aldrich, 75 wt% in isopropanol) 0.15 M in 1-butanol (Sigma-Aldrich, 99.8%) solution at 2000 rpm for 40 sec and sintered at 125 °C for 5 min. Mesoporous 50-nm sized TiO₂ nanoparticles layer was formed on the TiO₂ blocking layer using TiO₂ paste, which consist of TiO₂ precursor, terpineol, ethylcellulose and lauric acid with a nominal ratio of 1.25: 6: 0.9: 0.3 wt%. To deposite on the substrate in liquid phase, 1.4 g of synthesized TiO₂ paste was diluted in 10 mL ethanol. The diluted TiO₂ paste solution was spin coated on the TiO₂ blocking layer at 2000 rpm for 20 s and annealed at 550 for 1h. After UVO treatment for 30 min, the substrate was immersed in titanium chloride solution (TiCl₄, Sigma-Aldrich, > 98 %) 20 mM in DI water at 90 °C for 10 min in water bath, followed by washing with DI water and sintered at 500 °C for 30 min. The CH₃NH₃PbI₃ perovskite active layer was deposited on the mesoporous TiO₂ layer by using two-step process. First, 1 M (1.844 g) of PbI₂ (Sigma-Aldrich, 99 %) in 4 mL of N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%) was spin-coated on the substrate at 6000 rpm for 20 s and dried sequentially at 40 °C for 3 min and 100 °C for 10 min. Second, 0.3 g of the home-made methylammonium iodide² in 30 mLof 2-propanol (Sigma-Aldrich, 99.5%) was spun on the substrate at 3000 rpm for 20 sec and the same drying process with previous step was carried out. After washing with pure 2-propanol to remove unreacted perovkite residue, the hole transport material (HTM) was deposited on the substrate by spin coating a 72.3 mg of spiro-MeOTAD solution in 1 ml Chlorobenzen with 28.8 µL of 4-tertbutyl pyridine and 17.5 µL of lithium bis(trifl uoromethanesulfonyl) imide solution of 520 mg Li-TSFI in 1 ml acetonitrile (Sigma-Aldrich,

99.8 %) at 4000 rpm for 20 s. For the counter electrode, gold (Au) was thermally deposited on the top of the HTM by evaporation under $\sim 10^{-6}$ Torr vacuum condition through a shadow mask.

Characterization:

The morphologies of the fabricated hierarchical pyramid PDMS surfaces were examined by using high-resolution scanning electron microscope (SEM, HITACHI S-48000, Japan) at 5 kV. A 20 nm-thick Pt layer was deposited on the surfaces to avoid charging effect. The chemical components of the PDMS surfaces were detected by energy dispersive spectroscopy (EDS, JSM-7600F, JEOL KOREA). The transmittance and reflectance were measured by using UV/Vis spectrometer (PerkinElmer Lambda 45, USA) in the range from 300 to 800 nm. Current-voltage characteristics of perovskite solar cells were measured under AM 1.5G one sun illumination (100 mW/cm²) using a solar simulator (Oriel Sol 3A class AAA) equipped with a Keithley 2400 source meter and a 450 W Xenon lamp (Newport 6279NS). External quantum efficiency (EQE) was collected using IPCE system (PV measurement Inc.) equipped with a 75 W Xenon lamp (USHIO, Japan). The static contact angles (CAs) and rolloff angles (ROAs) of DI water on the fabricated PDMS films were measured by a contact angle analyzer (Drop Shape Analysis System DSA100, Kruss, Germany). To capture the optical images of CAs, a droplet of DI water (~5 µL) was gently placed onto the surfaces. The ROAs were measured by tiling the substrate until the droplet start to rolling-off on the surfaces.



Figure S1. (a-c) SEM images of micro pyramidal arrays before Ar ion treatment. There are no significant structural different between micro pyramidal arrays and H.P. structures (Figure 1b-d in the manuscript), but roughness of pyramid surface as shown in inset image of (c).



Figure S2. The photograph and schematics of fabricated perovskite solar cells device with multi-functional H.P. PDMS film.



Figure S3. (a,b) Refractive index profiles of the bare FTO glass and the FTO glass with a flat PDMS layer.



Figure S4. The path of the incident light (green) with reflection (red) and transmission (blue) between air and pyramid PDMS surfaces. The length and width of arrows roughly indicate the direction and intensity of each path way. Parentheses represent refractive indices.

The Snell's law is given as follows,

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

where n_1 and n_2 are the refractive indices of transmitting medium (air) and incident substrate (PDMS), θ_1 and θ_2 are the incidence and refraction angle of light, respectively. As illustrated in **Figure S4**, θ_3 and θ_4 occur at second reflection surface by double reflection effect. According to the above equation, the value of θ_2 is defined as 30° with assumption that the direction of incident light is perpendicular to the PDMS surface of substrate, $n_1 \sim 1$, $n_2 \sim 1.43$ and $\theta_1 \sim 45^\circ$. Sequentially, at second reflection surface the equation is summarized as,

$$\frac{\sqrt{6}}{2} = \sin\theta_4$$

so, $\theta_4 > 1$, which means that the second transmitting light into PDMS is totally reflected in the interface between air and pyramidal PDMS. In this case, the second reflective light is the only reflection light of the incident light at the interface between air and PDMS (see also **Figure 2d** in the manuscript). Also, the Fresnel's reflectance coefficient *R* is described as, in detail,

$$R(reflectance \ coefficient) = \frac{|r_s|^2 + |r_p|^2}{2}$$

$$r_{s} = \frac{n_{1}cos\theta_{1} - n_{2}cos\theta_{2}}{n_{1}cos\theta_{1} + n_{2}cos\theta_{2}}$$
$$r_{p} = \frac{n_{2}cos\theta_{1} - n_{1}cos\theta_{2}}{n_{1}cos\theta_{2} + n_{2}cos\theta_{1}}$$

where, *r* is the ratio of the reflective light amplitude to that of the incident light. The subscript *s* and *p* mean s-polarized and p-polarized light, respectively. It is noted that the calculated reflection coefficient of first reflection, *R* is ~3.94% based on the value of $r_s \sim 0.27$ and $r_p \sim 0.077$. Finally, the value *R* of total reflected light is estimated to be about 0.16% by the double reflection effect on the substrate.

Notes and references

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