Supporting Information

Ultrathin atomic layer deposited TiO\(_2\) for surface passivation of hydrothermally grown 1D TiO\(_2\) nanorod arrays for efficient solid state perovskite solar cells

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S1 Methods:

S1.1 Synthesis of TiO\(_2\) nanorods:

Firstly, laser-patterned, FTO-coated glass substrates (TEC15, Pilkington) were cleaned by ultrasonication in an alkaline, aqueous washing solution, rinsed with deionized water, ethanol and acetone. A 20–40-nm-thick TiO\(_2\) compact layer was then deposited on the substrates by spin coating of (0.15M and 0.3M commercial titanium diisopropoxidebis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) diluted in ethanol (1:39, volume ratio) as precursor and subsequently annealed in air at 450\(^\circ\)C for 30min. The TiO\(_2\) nanorods were deposited directly onto patterned FTO substrate using our previous technique [1]. Briefly, titanium(IV) isopropoxide (TTIP) were hydrolyzed in equal volumes of HCl:H\(_2\)O at 180\(^\circ\)C for 3h. The films were washed several times with water/ethanol and used for further process.

S1.2 TiO\(_2\) by atomic layer deposition (ALD) passivation.

The few nanometer ultrathin TiO\(_2\) layers on TiO\(_2\) NR were deposited using a laminar-flow thermal atomic layer deposition (ALD) reactor (CN1, Atomic Classic, Korea).
The reactor chamber temperature was kept at 250°C. The Titanium isopropoxide (TTIP, Ti(OCH(CH\textsubscript{3})\textsubscript{2})\textsubscript{4}, UP Chemical, Korea) precursor (70°C) and deionized water (room temperature) were used as the Ti precursor and oxidant gas, respectively. One ALD TiO\textsubscript{2} growth cycle consists of the following steps: TTIP pulse (2 s), purge (10 s), H\textsubscript{2}O pulse (0.2 s), and purge (15 s). Nitrogen gas (200 sccm, 99.999%) was used for each purge step. The thickness of TiO\textsubscript{2} films was monitored using an ellipsometer (Gaetner, Stokes Ellipsometer LSE) on a witness Si wafer. Approximately, 12 cycles of ALD led to 1 nm growth of TiO\textsubscript{2}.

**S2. Preparation of Methylammonium lead iodide (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3})**

Methylammonium lead iodide (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}) was synthesized as per previous literature with few modifications [2, 3]. Briefly, drop-wise addition of hydroiodic acid to a solution of methylamine (aqueous, 40 wt %, TCI Chemicals) in an ice bath followed by stirred for 2 h, and the solvent was evaporated using a rotary evaporator. The resulting white solid CH\textsubscript{3}NH\textsubscript{3}I product was washed with diethyl ether. The perovskite solution was prepared by dissolving equimolar amounts of CH\textsubscript{3}NH\textsubscript{3}I and lead iodide (PbI\textsubscript{2}) in anhydrous γ-butyrolactone (GBL). The clear filtered yellow solution was spin coated on top of the 1D TiO\textsubscript{2} films followed by heat treatment on a hot plate for 10 min to form dark-brown colored crystalline CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}. The hole transport material (HTM) was prepared by standard procedure reported elsewhere with few modifications [3]. The 180 mg 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD, Merck) dissolved in 1mL chlorobenzene (99.8%, Aldrich) with addition of 37.5 µL bis(trifluoromethane)sulfonimide lithium salt (LiTFSI, 99.95%, Aldrich) (170 mg mL\textsuperscript{-1}) in acetonitrile and 17.5 µL 4-tert-butylpyridine (TBP, 96%, Aldrich). The CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}-deposited 1D TiO\textsubscript{2} films were coated with HTM solution using the spin-coating method at 3000 rpm for 30 s. Then the substrates were transferred to a vacuum chamber and evacuated to a pressure of 2×10\textsuperscript{-6} mbar. For the Au-counter electrode, a 80 nm thick Au was deposited on the top of the HTM over layer by thermalevaporation (growth rate ~0.5 Å/s) at pressure of 2×10\textsuperscript{-6} mbar. The active areas of all devices were 0.09 cm\textsuperscript{2}.

**S3 Characterizations:**
The cross-sectional images were recorded by a field emission scanning electron microscope (FESEM; S-4700, Hitachi). Transmission electron microscopy (TEM) micrographs, selected area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) images were obtained by TECNAI F20 Philips operated at 200 KV. X-ray diffraction (XRD) measurements were carried out using a D/MAX Ultima III XRD spectrometer (Rigaku, Japan) with Cu K line of 1.5410 Å. The cells were illuminated using a solar simulator at AM 1.5 G for 10 s, where the light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter to 1 sun intensity (100 mW cm\(^{-2}\)). All devices were measured without any mask. However the device area was calculated as per active cross area of the FTO and Gold contact. For more details, please check Figure S2. The IPCE spectra were measured as a function of wavelength from 300 to 900 nm on the basis of a Spectral Products DK240 monochromator. All IPCE spectra were normalized to the measured J–V current for accurate comparison. The IPCE data was collected under the constant energy DC mode with delay time 10 ms under 50 \(\mu\)Wcm\(^{-2}\) light intensity. Impedance spectroscopy (IS) was conducted using Iviumstat (Ivium Technologies B.V., Eindhoven, the Netherlands) at an open-circuit potential at frequencies ranging from \(10^{-1}\) to \(10^5\) Hz with an AC amplitude of 10 mV. Z-view2.8d (Scribner Associates) was used to fit the IS spectra to the equivalent circuit based on the transmission line model. The DC bias potential was applied in 0.05 V step intervals.

**S4 Deposition of mesoporous TiO\(_2\) (mp-TiO\(_2\)) layer:**

For a comparison of our perovskite devices, we have also prepared perovskite devices based on mp-TiO\(_2\). The mp-TiO\(_2\) layer composed of 20-nm-sized particles was deposited by spin coating at 4,000 r.p.m. for 15s using a commercial TiO\(_2\) paste (Dyesol18NRT, Dyesol) diluted in ethanol (2:7, weight ratio). After drying at 125 °C, the TiO\(_2\) films were gradually heated to 500 °C, baked at this temperature for 15 min and cooled to room temperature. After cooling to room temperature, the substrates were treated in an 0.04M aqueous solution of TiCl\(_4\) for 30 min at 70 °C, rinsed with deionized water and again annealed at 500 °C for 20 min.

**References:**


Figure S1(a) XRD patterns of bare TiO$_2$ nanorods (black solid line) and ~4.8nm ALD TiO$_2$@1D TiO$_2$ nanorods (red solid line).
Figure S1 (b) XRD patterns of CH$_3$NH$_3$PbI$_3$ deposited onto bare TiO$_2$ nanorods and ~4.8nm ALD TiO$_2$@1D TiO$_2$ nanorods.
Figure S2 Perovskite device configuration (a) TiO$_2$ nanorods deposited on pattern FTO substrate (b) perovskite solution spin coated on FTO/TiO$_2$ (c) after annealing on a hot plate (d) complete fabricated device with gold contact (e) schematic representation of fabricated perovskite solar cell device configuration (contact area–0.09 cm$^2$) (Note: We have measured all devices without any masking, however the device area has been calculated as per laser pattern FTO and Gold cross contact area.)
Figure S3  Photovoltaic performance of perovskite solar cells based on TiCl$_4$ treated TiO$_2$ nanorods measured under AM 1.5 G illumination.
**Figure S4** Average photovoltaic performance of ten devices with their efficiency.
Figure S5 Forward and reverse scan characteristics of mp-TiO₂ based perovskite solar cell. (a) Typical Cross Section micrograph of perovskite solar cell based on mp-TiO₂. (b) Photovoltaic performance of perovskite solar cells based on mp-TiO₂ measured by forward and reverse scans with 10mV voltage steps and 50ms delay times under AM 1.5 G illumination.
Figure S6: Forward and reverse scan characteristics of champion cell. Photovoltaic performance of perovskite solar cells based on 4.8nm passivated TiO$_2$ nanorods measured by forward and reverse scans with 10mV voltage steps and 50ms delay times under AM 1.5 G illumination.
**Figure S7.** Hysteresis studies of perovskite solar cells based on various samples. The solar cell efficiencies were obtained from $J-V$ curves measured by forward and reverse scans with 10 mV voltage steps and 50ms delay under AM 1.5G illumination conditions.