

Centimetre-scale perovskite solar cells with fill factors of more than 86 per cent

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Owing to rapid development in their efficiency¹ and stability², perovskite solar cells are at the forefront of emerging photovoltaic technologies. State-of-the-art cells exhibit voltage losses^{3–8} approaching the theoretical minimum and near-unity internal quantum efficiency^{9–13}, but conversion efficiencies are limited by the fill factor (<83%, below the Shockley–Queisser limit of approximately 90%). This limitation results from non-ideal charge transport between the perovskite absorber and the cell's electrodes^{5,8,13–16}. Reducing the electrical series resistance of charge transport layers is therefore crucial for improving efficiency. Here we introduce a reverse-doping process to fabricate nitrogen-doped titanium oxide electron transport layers with outstanding charge transport performance. By incorporating this charge transport material into perovskite solar cells, we demonstrate 1-cm² cells with fill factors of >86%, and an average fill factor of 85.3%. We also report a certified steady-state efficiency of 22.6% for a 1-cm² cell ($23.33 \pm 0.58\%$ from a reverse current–voltage scan).

Nitrogen-doped titanium oxide (titanium oxynitride, TiO_xN_y) has been widely investigated for photocatalysis^{17,18}, but rarely in perovskite solar cells (PSCs). PSCs incorporating solution-processed TiO_xN_y have been reported, but device performances have not exceeded that of PSCs with standard TiO_x electron transport layers (ETLs)^{19,20}, because the stoichiometric control required to optimize metal oxide transport layer properties is challenging with solution processing. Instead, we report here a reverse-doping method to produce high-quality TiO_xN_y films by oxidizing sputtered titanium nitride thin films using a controlled annealing temperature in an oxygen atmosphere (details are provided in the Methods). In addition to producing high-quality TiO_xN_y films, sputtering is already widely used in the photovoltaic and electronics industries and is therefore a promising deposition method for commercial fabrication of PSCs.

TiO_xN_y film composition and morphology

To understand the effect of the annealing process on the physical and electronic properties of TiO_xN_y , we prepared films (thickness ~50 nm) with seven different annealing conditions: as deposited (room temperature), 300 °C, 350 °C, 400 °C, 450 °C, 500 °C and 550 °C. There is no significant difference in the morphology of the resulting TiO_xN_y films (Extended Data Fig. 1), and they are similar to the bare fluorine-doped tin oxide (FTO)-coated glass substrates.

We next investigate the elemental composition of TiO_xN_y using X-ray photoelectron spectroscopy (XPS). As shown in Fig. 1a, the Ti^{2+} oxidation state²¹ is present in the as-deposited TiN film as evidenced by the

presence of O 1s (refs. ^{15,22}; Fig. 1b) and O–Ti–N (refs. ^{18,23,24}) XPS peaks (Fig. 1c). The appearance of Ti^{3+} and Ti^{4+} states after annealing at 300 °C indicates partial oxidation of the TiN, and oxidation increases at higher temperatures. For samples annealed at 450 °C and above, only the highest Ti^{4+} oxidation state is present^{15,21}. Meanwhile, the TiN (refs. ^{18,23}) peak weakens and eventually disappears at higher annealing temperatures, and two new N 1s core-level peaks (NO_x (refs. ^{18,23,25}) and $\gamma\text{-N}_2$ (refs. ^{23,26}) (chemisorbed N_2)) are observed (Fig. 1c). This further demonstrates that the chemical states of Ti and N within TiO_xN_y lattices continuously change as the oxidation temperature increases. More details of the XPS analysis can be found in the Methods.

By combining the elements' relative peak areas and sensitivity factors (Extended Data Fig. 2), we calculate that the atomic ratio of O/Ti (N/Ti) is 0.58 (0.62) for the as-deposited film. The O/Ti atomic ratio increases with annealing temperature, reaching a peak of 2.24 at 500 °C before decreasing. In contrast, the N/Ti ratio decreases monotonically with annealing temperature. However, N atoms remain in the TiO_xN_y film at higher temperatures, with N/Ti ratios of 0.08 and 0.07 for samples annealed at 500 °C and 550 °C, respectively.

High-resolution transmission electron microscopy (TEM) imaging (Extended Data Fig. 3a) shows that the as-deposited film is not completely crystalline and features an amorphous contrast along with a distribution of crystalline particles with characteristic sizes ranging from 10 nm to 20 nm. A survey of the first two diffraction rings from the polycrystalline pattern in Fig. 2a reveals diffracting planes corresponding to distances of $d_1 = 2.45 \pm 0.07 \text{ \AA}$ and $d_2 = 2.12 \pm 0.06 \text{ \AA}$, which can be respectively assigned to the cubic phases of TiO (ref. ²⁷) and TiN (ref. ²⁷).

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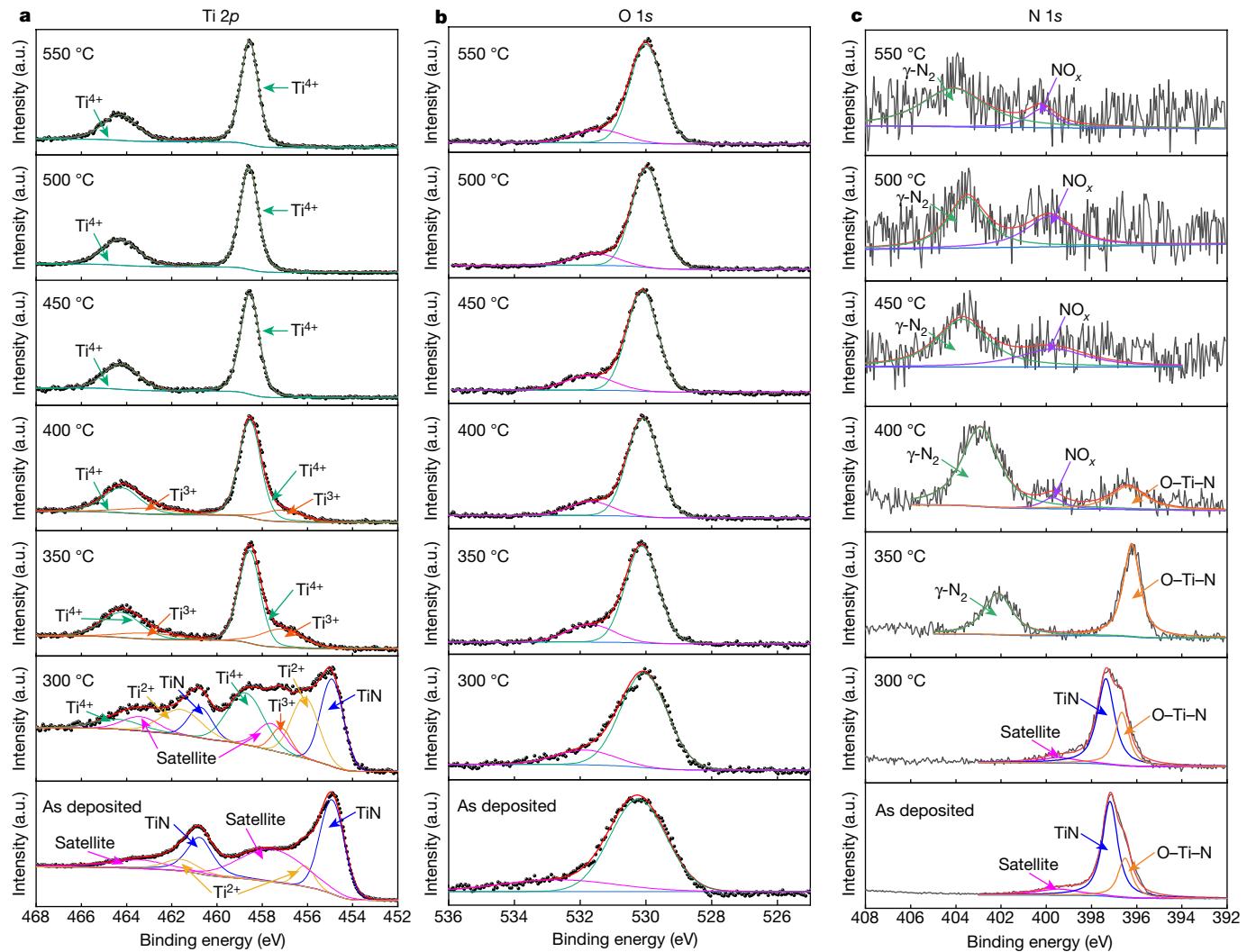


Fig. 1 | XPS characterization of TiO_xN_y films annealed at different temperatures. **a–c,** Evolution of the chemical state of Ti (**a**), O (**b**) and N (**c**) in TiO_xN_y films under different oxidation conditions. Note that the Ti 2p peaks centred at binding energies of ~ 457.5 eV and ~ 463.4 eV and the N 1s peak centred

at ~ 399.5 -eV binding energy can be ascribed to the satellite features of TiN. The black data points in **a**, **b** and the black line in **c** are raw data; the red lines in **a** to **c** are envelope curves.

($d_{(111),\text{TiO}} = 2.411 \text{ \AA}$, $d_{(200),\text{TiO}} = 2.088 \text{ \AA}$; $d_{(111),\text{TiN}} = 2.445 \text{ \AA}$, $d_{(200),\text{TiN}} = 2.117 \text{ \AA}$). Detailed parameters for simulation are summarized in Supplementary Table 1. Given the XPS result, which shows a large concentration of N relative to O, and the difficulty of differentiating the cubic TiO from the cubic TiN (Extended Data Fig. 2), we conclude that the observed crystalline phase has a composition of the type TiO_xN_y . Similar analysis of the films annealed at 300 °C, 350 °C and 400 °C indicates that these are also largely composed of the cubic TiO_xN_y phase (Fig. 2 and Extended Data Fig. 4). Note that there are two rings in the diffraction patterns of the sample annealed at 400 °C (Fig. 2c), which can be allocated to the tetragonal anatase crystal phases of TiO_xN_y (ref. ²⁸).

The combined evidence of the XPS and TEM analysis shows that oxidation at low temperatures (<400 °C) starts a restructuring process in which TiN and TiO crystals transform into amorphous TiO_xN_y , which then continues to form TiO_xN_y crystals under oxidation at high temperatures (>450 °C). Compared with the as-deposited sample and those annealed at 300 °C, 350 °C and 400 °C, an increased crystalline fraction is observed for the TiO_xN_y film annealed at 450 °C and above (Extended Data Figs. 3 and 4). The diffraction patterns of the sample annealed at 450 °C are dominated by a combination of tetragonal anatase and rutile phases of TiO_xN_y (ref. ²⁸), accompanied by the complete disappearance of the cubic TiO_xN_y phase (Extended Data Fig. 4d).

At the highest temperature investigated, the film annealed at 550 °C features large tetragonal crystals with sizes of greater than 20 nm with similar crystal phases to those of the film annealed at 500 °C (Fig. 2d and Extended Data Fig. 4e, f).

Optoelectronic properties of TiO_xN_y film

The as-deposited TiN film has a workfunction (WF) of ~ 4.32 eV (Fig. 3a) and an optical bandgap (E_g) of ~ 3.25 eV (Extended Data Fig. 5), similar to literature values²⁹. The WF values of the samples annealed at 300 °C, 350 °C, 400 °C, 450 °C, 500 °C and 550 °C are 4.32 eV, 4.29 eV, 4.14 eV, 4.08 eV, 4.16 eV, 4.14 eV and 4.28 eV, respectively, which are associated with the free-carrier density (or doping density) change and/or surface dipoles within the TiO_xN_y films. Figure 3b shows the energy level distribution of TiO_xN_y films for different annealing temperatures, extracted by combining data from ultraviolet photoelectron spectroscopy (UPS) spectra (Fig. 3a) and E_g measurements (Extended Data Fig. 5).

In addition to the WF change, the energy difference (ΔE) between the Fermi level (E_F) and the conduction band minimum of TiO_xN_y increases with higher annealing temperatures. This indicates a reduction in free-carrier density (or doping density) of the n-type TiO_xN_y , which we quantify using Hall effect measurements (Fig. 3c). The charge carrier

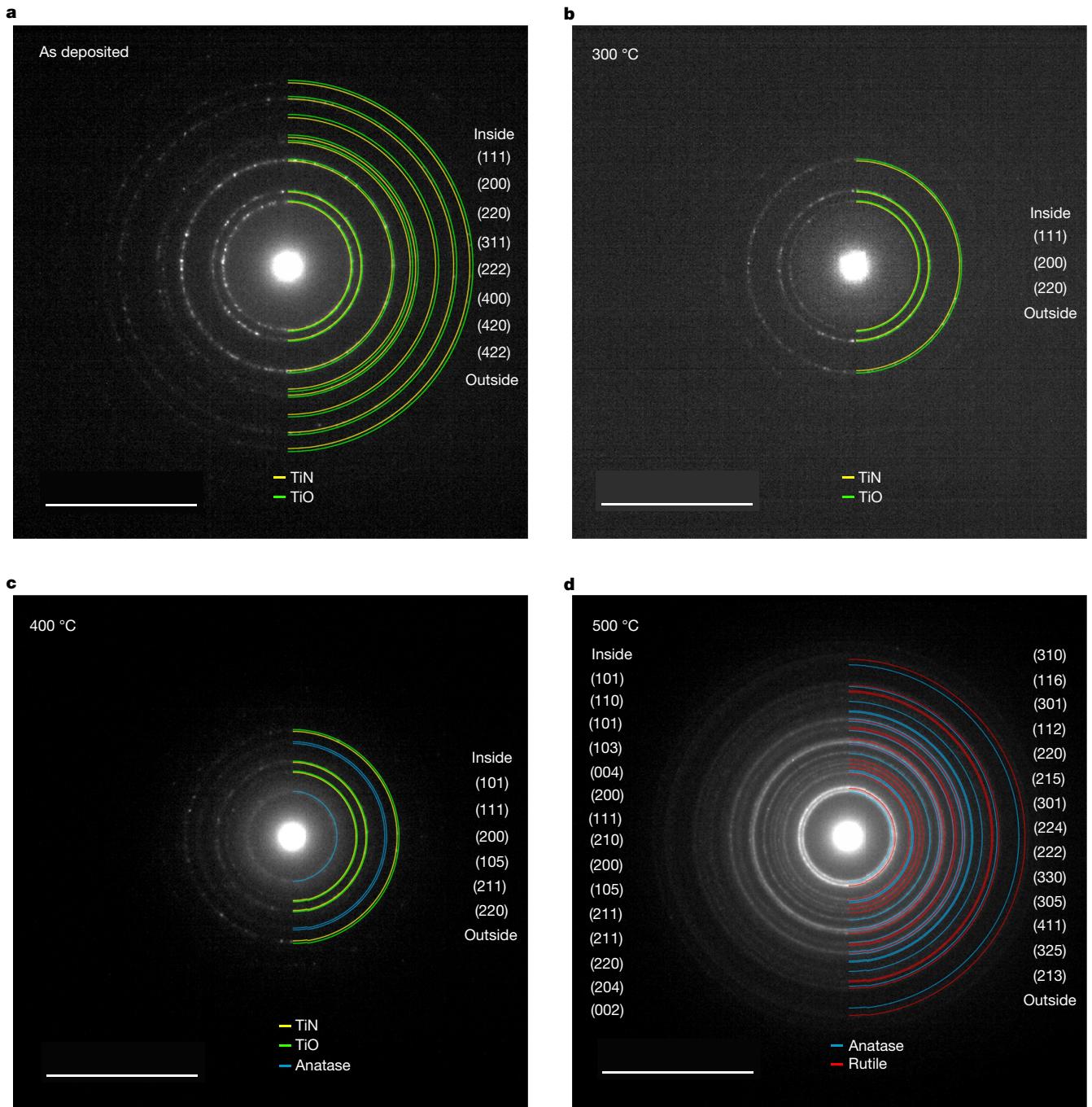


Fig. 2 | TEM characterization and simulation of the diffraction pattern.

a, TiO_{xN_y} without annealing (as deposited). **b–d**, TiO_{xN_y} annealed at 300 °C (**b**), 400 °C (**c**) and 500 °C (**d**). Scale bars, 10 nm⁻¹. The crystal phases of the TiO_{xN_y} annealed at 300 °C and 400 °C are cubic TiO_{xN_y} mixtures. Note that it is unusual for the rutile phase of TiO_{xN_y} to form at the relatively low annealing temperature of 450 °C. In contrast, solution-processed TiO_x forms an anatase phase when annealed at 500 °C and 550 °C (Supplementary Fig. 1). Anatase is

often the first TiO_x crystal phase to form in many fabrication processes, owing to its low surface energy³³, even though it is not an equilibrium phase for TiO_x in terms of the lattice stability. It typically converts to rutile, a more thermally stable phase, at temperatures above 550 °C (ref. ³³). However, studies suggest that the phase transition temperature strongly depends on impurities (or dopants) as well as on the morphology of the sample^{33–35}. This may explain the formation of rutile TiO_{xN_y} phase in the sample annealed at 450 °C.

density decreases steadily with increasing annealing temperatures up to 400 °C, followed by a drop of approximately three orders of magnitude between the samples annealed at 400 °C ($5.1 \times 10^{20} \text{ cm}^{-3}$) and 450 °C ($5.0 \times 10^{17} \text{ cm}^{-3}$). This coincides with the formation of the higher oxidation state of Ti, and loss of N from the TiO_{xN_y} lattice, as discussed previously. The carrier density decreases to $3.4 \times 10^{16} \text{ cm}^{-3}$ for an annealing temperature of 550 °C. Consequently, the conductivity of the films exhibits a similar trend to the free-carrier density; the

Hall mobility has an opposite trend (Fig. 3c). For comparison, we note that a control film made from solution-processed pure TiO_x (ref. ¹⁵) annealed at 500 °C has a much lower carrier density ($4.5 \times 10^{14} \text{ cm}^{-3}$) and conductivity ($9.8 \times 10^{-5} \text{ S cm}^{-1}$) than both the TiO_{xN_y} samples annealed at 500 °C and 550 °C. The detailed Hall effect results are summarized in Extended Data Table 1.

Despite the bandgap of the TiO_{xN_y} undergoing no significant change with annealing temperature (Extended Data Fig. 5), samples annealed

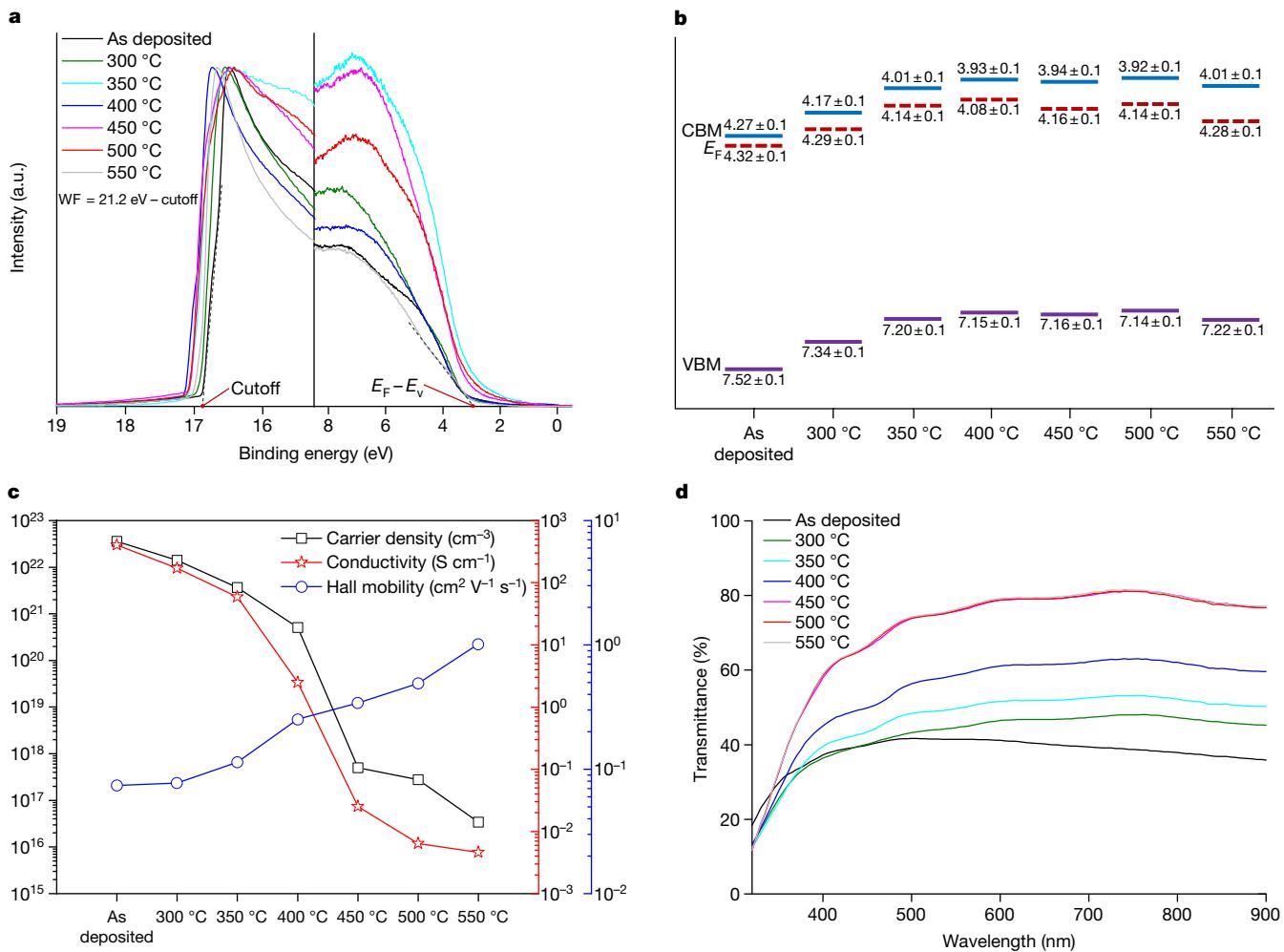


Fig. 3 | Optoelectronic properties of TiO_{xN_y} films annealed at different temperatures. **a**, WF and valence band maximum (VBM) of TiO_{xN_y} films determined by UPS spectra. **b**, Energy level distribution of TiO_{xN_y} films. CBM, conduction band minimum. **c**, Carrier density, conductivity and Hall mobility of TiO_{xN_y} films. **d**, Optical transmittance of TiO_{xN_y} films (deposited on FTO

substrates). Note that the VBM is determined by the sum of WF and $(E_F - E_v)$, where E_v represents VBM; the CBM is determined by $\text{VBM} - E_g$. The detailed data of the UPS and Hall effect measurements are also provided in Supplementary Tables 2 and 3, respectively.

at 400 °C and below exhibit low optical transmittance across the visible spectrum (Fig. 3d), which we attribute to strong free-carrier absorption³⁰. A substantial increase in transmittance for films annealed at temperatures of 450 °C and above coincides with the compositional, structural and electronic transition identified above. Thus, the combination of high conductivity and high optical transmittance for films annealed above 450 °C indicates that TiO_{xN_y} films produced in this way have potential as high-performance ETLs for PSCs.

Solar cell characterization

Having investigated the physical, electronic and optical properties of the TiO_{xN_y} films, we next investigate their use as ETLs in n-i-p PSCs. The devices studied here feature a structure of glass/FTO/ TiO_{xN_y} (~40 nm)/meso- TiO_2 (~50 nm)/PMMA:PCBM/Cs_{0.05}FA_{0.9}MA_{0.05}PbI_{2.74}Br_{0.26} (~500 nm)/PMMA/P3HT:CuPc (~65 nm)/Au (Fig. 4a and Extended Data Fig. 6). Here meso- TiO_2 represents mesoporous TiO_2 , PMMA (ref.⁵) and PMMA:PCBM (ref.⁵) are ultrathin interface passivation layers consisting of poly(methyl-methacrylate) and PMMA:[6,6]-phenyl-C61-butyril-acid-methyl-ester), respectively, and P3HT:CuPc (ref.⁸) is a blended hole transport layer (HTL) consisting of poly(3-hexylthiophene) and copper phthalocyanine. Solution-processed compact TiO_x (ref.¹⁵) substitutes TiO_{xN_y} as the ETL in the control cells.

As shown in Fig. 4a, our champion TiO_{xN_y} -based cell with an active area of 1-cm² yielded a PCE of 23.36% (23.38%) with V_{OC} ~ 1.193 V (1.200 V), J_{SC} ~ 22.80 mA cm⁻² (22.89 mA cm⁻²) and fill factor (FF) ~ 0.859 (0.851) from reverse (forward) scan in-house measurements. The TiO_x -based control cell exhibited a maximum PCE of 21.65% (V_{OC} ~ 1.172 V, J_{SC} ~ 22.75 mA cm⁻² and FF ~ 0.812) and 21.22% (V_{OC} ~ 1.171 V, J_{SC} ~ 22.70 mA cm⁻² and FF ~ 0.798) from reverse and forward scans, respectively. External quantum efficiency (EQE) spectra and perovskite optical bandgap (E_g ~ 1.57 eV) plots confirm the accuracy of the measured photocurrent as demonstrated by a discrepancy <2% between the integrated J_{SC} from the EQE spectra and the J_{SC} measured from the $J-V$ curve (Fig. 4b). Another cell was submitted to an independent testing centre and achieved a certified efficiency of $-23.33\% \pm 0.58\%$ with a FF of $86.68\% \pm 0.01\%$ from a reverse $J-V$ scan, and a steady-state efficiency of -22.6% (Supplementary Fig. 2). This is, to our knowledge, the highest certified efficiency for 1-cm² PSCs¹ and the highest FF reported for a PSC of any size (Supplementary Tables 4 and 5).

The $J-V$ parameter distribution plots in Fig. 4c and Extended Data Fig. 7a illustrate the reproducibility of our 1-cm² PSCs. The average PCE of the TiO_{xN_y} -based cells is $23.09\% \pm 0.11\%$ with an average FF ~ 0.853 ± 0.005 , while that of the TiO_x -based cells is $21.26\% \pm 0.33\%$ (average FF ~ 0.793 ± 0.014). There is little difference in both V_{OC} and J_{SC} between the TiO_{xN_y} - and TiO_x -based cells (Extended Data Fig. 7a), so

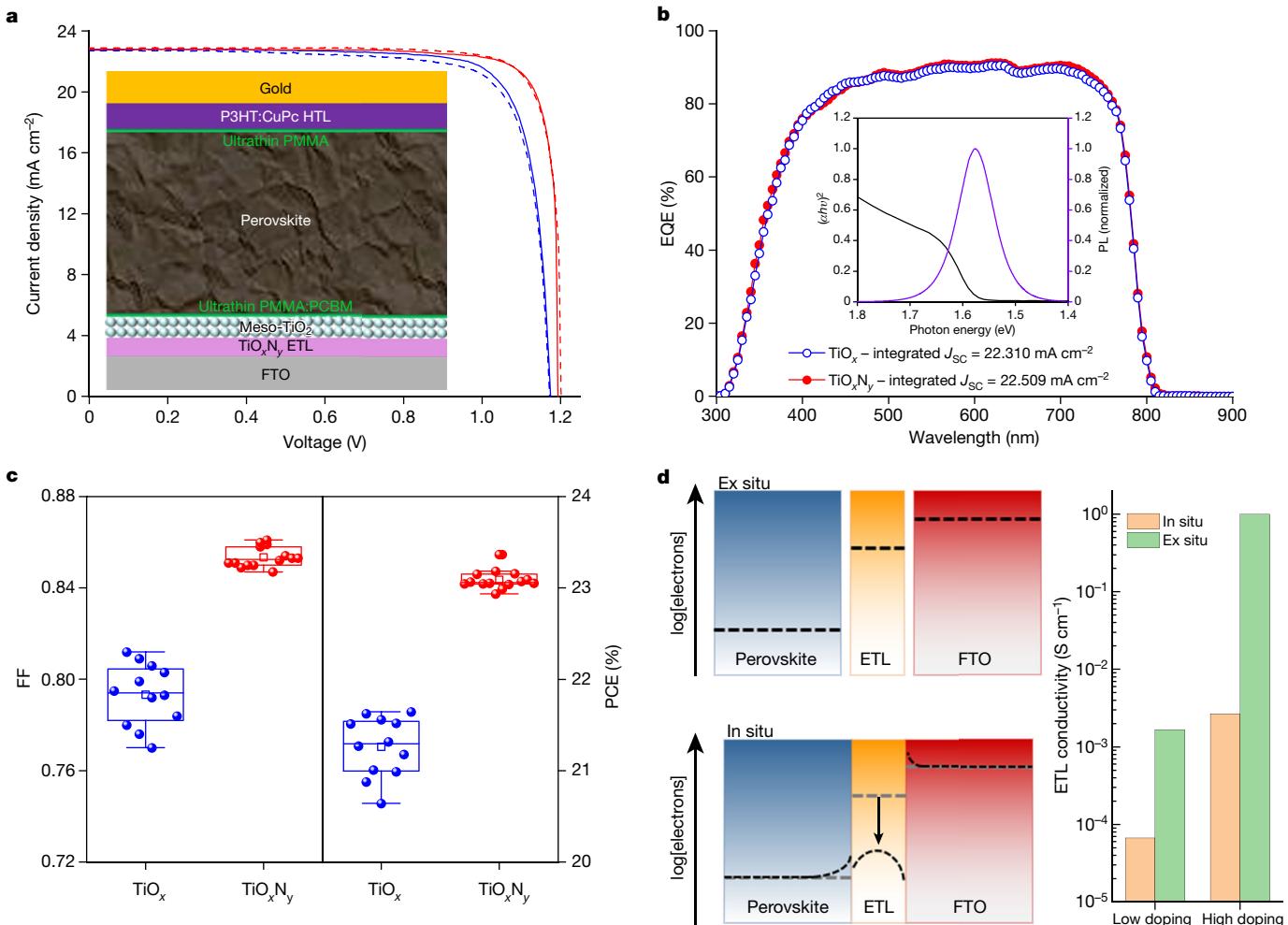


Fig. 4 | Device characterization and simulation. **a**, J - V curves of the champion 1- cm^2 TiO_x -based cell (control, in blue) and the 1- cm^2 TiO_xN_y -based cell (in red). The solid and dashed lines represent reverse and forward J - V scans, respectively; the TiO_xN_y -based cell device structure is shown in the inset. Note that the TiO_xN_y ETLs were fabricated at 500 °C and all J - V curves of the cells (effective area, 1.2 cm^2) were measured using an aperture mask (certified area, 1.0189 cm^2). Given that the meso- TiO_2 must be annealed at 500 °C to completely remove the organic compounds from the TiO_2 paste, the TiO_xN_y ETLs processed at low temperature (<500 °C) are not selected for our PSCs in this work. **b**, EQE spectra of the TiO_x -based cell and the TiO_xN_y -based cell.

UV-Vis absorption and steady-state photoluminescence (PL) spectra of the $\text{Cs}_{0.05}\text{FA}_{0.9}\text{MA}_{0.05}\text{PbI}_{2.74}\text{Br}_{0.26}$ film are plotted in the inset. **c**, FF and PCE distribution for the TiO_x -based cells (12 cells) and the TiO_xN_y -based cells (14 cells). **d**, Left:, schematic representation of the intrinsic (ex situ) free electrons of the perovskite, ETL and FTO materials themselves (top) and the in situ free electrons of these different layers within the perovskite/ETL/FTO layer stack (bottom); the ETL layer can become fully depleted, and the equilibrium free-carrier density falls by orders of magnitude below the ex situ dopant concentration. Right, diagram of the ex situ and in situ conductivity of two doping levels of the ETL (right).

the efficiency gains for TiO_xN_y -based cells are dominated by the higher FF that results from improved electron transport. A similar trend was also found between the TiO_xN_y - and TiO_x -based PSCs fabricated with indium tin oxide (ITO)-coated glass substrates (see Supplementary Fig. 3 and discussion in the Methods).

PSCs fabricated with TiO_xN_y ETLs annealed at 550 °C exhibited a lower average PCE of $21.42\% \pm 0.32\%$ with substantial FF losses (Extended Data Fig. 7b, c) compared to cells processed at 500 °C. This is due to the order-of-magnitude reduction in carrier density in the sample annealed at 550 °C compared to that annealed at 500 °C.

We performed scanning electron microscopy (SEM), X-ray diffraction and time-resolved photoluminescence measurements to investigate the effect of ETL composition on subsequently deposited perovskite films. As seen in Supplementary Fig. 4, we found no evidence of changes in the surface morphology (from SEM images), or in crystal structure, orientation or crystallinity (from X-ray diffraction measurements) of perovskite films deposited on the different substrates. There was also little difference in the time-resolved photoluminescence decay

measurements, consistent with the experimental cell V_{OC} values. This suggests that the very high FFs of the TiO_xN_y -based perovskite cells are derived from the improved electronic property of the TiO_xN_y film itself.

To explain how TiO_xN_y can significantly increase FF, we employed numerical one-dimensional, multilayer ionic-electronic numerical device simulations. Our focus is on the electrostatics of the perovskite/ETL/FTO layer structure. The empirical data suggest that increased dopant density is the only electronic factor that conclusively distinguishes TiO_xN_y from TiO_x . Yet a simple analytical treatment based on ex situ conductivity of the ETL layers cannot explain the difference in FF. For 50-nm ETL layers, the optimum TiO_xN_y ($N_D = 3 \times 10^{17} \text{ cm}^{-3}$) reduces the voltage losses relative to TiO_x ($N_D = 5 \times 10^{14} \text{ cm}^{-3}$) by only ~3 mV at the maximum power point (MPP) current of 22 mA cm^{-2} (where the electron mobility $\mu_e = 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). This is a small fraction of the experimental mean MPP voltage loss of approximately 80 mV. Instead, our model explains the resistance-related FF loss by showing that heavy doping of the ETL layer protects against electron depletion that can occur in

regions of positive space charge at the perovskite/ETL and FTO/ETL heterojunctions. Equilibrium conditions in the perovskite/ETL/FTO structure deplete the ETL of electrons to concentrations that can be orders of magnitude below the fixed dopant density (Fig. 4d). At the TiO_x dopant density of $5 \times 10^{14} \text{ cm}^{-3}$, the equilibrium free-electron concentration can be closer to 10^{13} cm^{-3} , introducing many tens of millivolts of voltage loss in the ETL at MPP currents (see Extended Data Fig. 8 for details). Our simulations suggest that although modifications of the WF alignment between these materials, and in particular the ETL and FTO layer, can mitigate the effect to some extent, high doping ($\gtrsim 10^{17} \text{ cm}^{-3}$) in the ETL layer will, in general, be necessary (although not sufficient) to achieve PSC FFs above approximately 85%.

We conclude this work by investigating the cell stability³¹. As seen in Extended Data Fig. 9a, the unencapsulated TiO_xN_y -based cell exhibited a steady-state PCE of -22.82% after 250 h of MPP voltage (V_{MPP}) tracking under continuous 1 sun illumination in nitrogen, retaining -98.7% of its initial efficiency (-23.12%). Similarly, the TiO_x -based cell (-20.24%) retained -96.5% of its initial efficiency (-20.97%), demonstrating no significant difference in light-soaking stability between the unencapsulated cells with different ETLs (Extended Data Fig. 9b). Two cells of each type were also subjected to damp-heat exposure in the dark. For these tests, an additional MoO_x (-10 nm)/indium zinc oxide (-40 nm) barrier layer was deposited between the HTL and the gold electrode resulting in a reduced FF relative to the unencapsulated cells reported above. All four individual cells retained >90% of their initial efficiencies after 1,000 h. Time-dependent power output and $J-V$ curves are presented in Supplementary Figs. 5 and 6 showing the cell performance evolution during the degradation tests. Although both the light-soaking and damp-heat stability tests show promising results, these are not sufficient to guarantee the stability of perovskite cells under real operating conditions where thermal, light and humidity stressors act simultaneously³¹. According to the literature^{2,32}, the combination of these conditions can accelerate degradation of the perovskite active layer, even in the presence of stable charge transport layers and encapsulation. As the perovskite used in this work was not optimized to withstand such conditions, a more stable composition such as those reported in refs.^{2,32} would be necessary to realize the full benefits of the TiO_xN_y ETL.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41586-021-04216-5>.

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Methods

Materials

Lead iodide (99%), lead bromide (99.999%), lead chloride (99.999%), caesium iodide (99.999%), dimethylformamide (DMF, 99.99%), dimethyl sulfoxide (DMSO, 99.99%), poly(methyl methacrylate) (PMMA, MW - 120,000), [6,6]-phenyl-C61-butyric-acid-methyl-ester (PCBM, 99.5%), copper phthalocyanine (CuPc, 99%), chlorobenzene (CB, 99.8%), titanium (IV) isopropoxide (TTIP, 99.999%), isopropyl alcohol (IPA, 99.5%), ethyl alcohol (99.5%), hydrochloric acid (HCl, 37%) and ITO-coated glass substrates (ITO, $8\text{--}12\ \Omega\text{ sq}^{-1}$) were purchased from Sigma Aldrich. FTO-coated glass substrates (FTO, $7\ \Omega\text{ sq}^{-1}$), formamidinium iodide (FAI), formamidinium bromide (FABr), methylammonium bromide (MABr) and TiO₂ paste (30 NR-D) were purchased from Greatcell Solar. Methylammonium chloride (MACl) was purchased from Xi'an Polymer Light Technology Corp. Poly(3-hexylthiophene) (P3HT) was purchased from 1-Materials. The titanium nitride sputtering target was purchased from AJA International. All chemicals were used as received without further purification.

Preparation of FTO and ITO substrates

The FTO and ITO substrates were sequentially cleaned in detergent, distilled water, acetone, isopropyl alcohol and ethyl alcohol for 20 min in an ultrasonic bath, and then dried with nitrogen. Cleaned FTO and ITO substrates were exposed to approximately 30 min of UV-O₃ treatment before the subsequent deposition step. Note that Sigma Aldrich's ITO product information (<https://www.sigmaaldrich.com/AU/en/product/aldrich/578274?context=product>) says that "ITO coated float glass is only offered with a SiO₂ passivation layer applied directly on the glass prior to ITO coating. The passivation layer is intended to minimize the leaching of alkali oxides into liquid crystals, which can have a detrimental effect on the volume resistivity of the liquid crystal."

Preparation of nitrogen-doped titanium ETLs

First, titanium nitride thin films were deposited on the pre-cleaned FTO (ITO) substrates by radiofrequency magnetron sputtering at 300 W and 20 sccm Ar gas using a titanium nitride target under a pressure of 1.5 mtorr. Second, the pre-fabricated titanium nitride thin films were then transferred to a furnace, and annealed at different temperatures ranging from 300 °C to 550 °C for 45 min under a controlled oxygen atmosphere, where the time of oxygen flow (gas flow $\sim 5\text{ l min}^{-1}$) was fixed at 5 min (note that the timing was calculated at the beginning of the annealing period). Samples were then cooled to 200 °C in the furnace before being removed.

Preparation of solution-processed titanium oxide ETLs

Compact TiO_x thin films of ~50 nm were deposited on the pre-cleaned FTO (ITO) substrates according to our previous work¹⁵, where the compact TiO_x precursor solution contained 369 µl TTIP and 35 µl 2 M HCl in 5 ml anhydrous IPA.

Preparation of mesoporous titanium oxide scaffold layers

Mesoporous TiO₂ scaffold layers of ~40 nm were deposited on the FTO/TiO_xN_y or FTO/TiO_x substrates according to our previous work⁵, where the mesoporous TiO₂ precursor solution was prepared from 30 nm TiO₂ paste diluted in ethyl alcohol (1:9, w/w). All samples were annealed at 500 °C for 30 min under dry air.

Preparation of precursor solution

The Cs_{0.05}FA_{0.9}MA_{0.05}PbI_{2.74}Br_{0.26} perovskite precursor solution contains 0.065 M CsI, 1.15 M PbI₂, 0.11 M PbBr₂, 1.1 M FAI, 0.045 M FABr, 0.065 M MABr, 0.01 M PbCl₂, 0.01 M MACl in 1 ml anhydrous DMF/DMSO (4:1, v/v). PMMA:PCBM (ref.⁵) passivation precursor solution was prepared by dissolving 0.5 mg PMMA and 1.5 mg PCBM into 1 ml CB. PMMA (ref.⁵) passivation precursor solution was prepared by

dissolving 0.25 mg ml⁻¹ PMMA in CB. P3HT:CuPc (ref.⁸) HTL precursor solution was prepared with a 10:1 (v/v) ratio blend of P3HT (12 mg ml⁻¹ in CB)/CuPc (5 mg ml⁻¹ in CB).

Device fabrication

For the ultrathin passivation layer deposition, ~100 µl PMMA:PCBM precursor solution was dropped onto the FTO/TiO_xN_y (or TiO_x)/meso-TiO₂ substrates and deposited by spin-coating at 5,000 r.p.m. with a ramp of 5,000 r.p.m. s⁻¹ for 30 s, then annealed at 100 °C for 10 min. Cs_{0.05}FA_{0.88}MA_{0.07}PbI_{2.56}Br_{0.44} thin films were then deposited on the passivated substrates by a two-step spin-coating programme: first at 2,000 r.p.m. with a ramp of 200 r.p.m. s⁻¹ for 10 s, and then at 4,000 r.p.m. with a ramp of 1,000 r.p.m. s⁻¹ for 20 s. The perovskite precursor film was immediately transferred into a custom-built vacuum flash³⁶ system where a two-step vacuum procedure was applied: first, the system was immediately pumped down to a low pressure of ~100 mtorr and held for 20 s; the pressure was then increased to ~1.2 torr and held for another 10 s. The pump valve was then turned off and left to return to atmospheric pressure. After the vacuum flash treatment, the perovskite sample was immediately annealed on a hotplate at 100 °C for 120 s. The sample was then returned to the spin-coater and cooled down by fast rotation at 5,000 r.p.m. with a ramp of 5,000 r.p.m. s⁻¹ for 60 s. Next, the PMMA passivation treatment was applied: first, ~100 µl PMMA solution (0.25 mg ml⁻¹ in chlorobenzene) was dropped onto the perovskite sample and left for 2 s; second, the sample was spin-coated for 15 s at 5,000 r.p.m. with a ramp of 5,000 r.p.m. s⁻¹; finally, the sample was annealed on a hotplate at 100 °C for 60 min. The P3HT:CuPc HTL was deposited via spin-coating at 2,000 r.p.m. with a ramp of 500 r.p.m. s⁻¹ for 30 s. Finally, ~100 nm gold was deposited through a shadow mask (cell area 1.2 cm²). All depositions were conducted in a nitrogen-filled glovebox.

Solar cell characterization

All devices were tested under 1 sun conditions (100 mW cm⁻², AM 1.5G) in a solar simulator system (Wavelab Inc.). The light intensity was calibrated using a certified Fraunhofer CalLab reference cell. All J-V curves were measured at a 20 mV s⁻¹ scan rate with an aperture mask (certified area is $\sim 1.0189\text{ cm}^2$) in a custom-built measurement jig under nitrogen flow. Note that the reverse scan is from V_{oc} to J_{sc} (forward bias \rightarrow short circuit, 1.2 V \rightarrow -0.1 V), and the forward scan is from J_{sc} to V_{oc} (short circuit \rightarrow forward bias, -0.1 V \rightarrow 1.2 V). EQE was measured using the d.c. measurement module on a commercial EQE system (CEP-25ML, Bunkoukeiki). For the TiO_xN_y perovskite cell, the estimated spectrum mismatch correction is 98.36% based on the comparison between the integrated current density calculated from the EQE response and the current density measured under the solar simulator. No preconditioning protocol was applied before the characterization.

The performance distribution of TiO_xN_y-based PSCs fabricated with ITO substrates is shown in Supplementary Fig. 3. The average PCE of TiO_xN_y cells is $22.78\% \pm 0.17\%$ (champion PCE ~ 23.09%) with FF $\sim 0.842 \pm 0.006$ (champion FF ~ 0.849), while that of TiO_x ('Control') cells is $21.03\% \pm 0.27\%$ (champion PCE ~ 21.47%) with FF $\sim 0.785 \pm 0.012$ (champion FF ~ 0.802). Note that the performance of ITO-based TiO_xN_y or TiO_x cells is lower than that of the corresponding FTO-based TiO_xN_y or TiO_x cells. This is because the sheet resistance of ITO substrates (initially $8\text{--}10\ \Omega\text{ sq}^{-1}$) increases to $\sim 26\text{--}30\ \Omega\text{ sq}^{-1}$ when annealed at 500 °C for 30 min, while that of FTO substrates (~7 Ω sq⁻¹) does not change. For this reason, the slightly decreased performance of ITO-based cells originates from the increased sheet resistance of the ITO substrates.

Damp-heat test

The damp-heat (85 °C, 85% relative humidity) tests under dark conditions were performed using a climate test chamber (Weiss Technik). When measuring the cells during the aging, samples were removed from the chamber and allowed to cool down to room temperature. Note that

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the perovskite cells used for the damp-heat tests included an additional barrier layer deposited on the HTL before the gold electrode. The barrier layer consisted of -10 nm MoO_x deposited by thermal evaporation followed by -40 nm of indium zinc oxide deposited by sputtering. The function of the MoO_x was to prevent sputtering damage to the underlying HTL. The rest of the cell fabrication was identical to the process described above. Cells were then encapsulated between two pieces of glass and the edges were sealed with polyisobutylene³⁷.

Film characterization

The top morphology of bare FTO and FTO/ TiO_xN_y samples was imaged with a non-contact tapping-mode atomic force microscope (Asylum Research). XPS and UPS measurements were carried out on an XPS machine (Escalab 250 Xi, Thermo Fisher), with a monochromatic Al K α (1486.7 eV) X-ray source for XPS and a He I (21.2 eV) gas discharge lamp for UPS. The detailed XPS peak analysis is presented below.

As shown in Fig. 1a, the Ti^{2+} oxidation state is present in the as-deposited TiN film, with the $\text{Ti}2p$ peaks centred at binding energies of -456.1 eV and -461.6 eV (ref. ²¹). In addition, the O1s XPS peak indicates the presence of a significant amount of O even in the as-deposited sample (Fig. 1b). This might be caused by the natural oxidation of the TiN sputtering target during storage or by oxidation from residual oxygen in the chamber during the sputtering process. For the sample annealed at 300 °C, the $\text{Ti}2p$ core-level peaks are at binding energies of -457.1 eV and -458.6 eV/-464.4 eV, which can be respectively ascribed to Ti^{3+} and Ti^{4+} oxidation states^{15,21}, indicating that the TiN starts oxidizing at 300 °C under oxygen atmosphere. Both the TiN and Ti^{2+} peaks vanish when annealed at 350 °C, while the Ti^{3+} peaks reduce when the annealing temperature is increased from 350 °C to 400 °C. There is no evidence of Ti^{3+} peaks in films annealed at 450 °C and above.

For the O1s XPS spectra (Fig. 1b), the dominant peaks at all temperatures are centred at binding energies of -530.1 eV to -530.5 eV, which we attribute to titanium oxides^{15,22} (TiO_x), while the smaller peaks at higher binding energies of -532.0 eV can be assigned to hydroxyl groups or O_2 (refs. ^{15,22}).

As shown in Fig. 1c, the N1s core-level peak of the as-deposited sample could be deconvoluted into three different N species. The peak centred at -397.2-eV binding energy and its satellite are indicative of TiN (refs. ^{18,23}); while the smaller peak centred at a lower binding energy of -396.5 eV can be allocated to O-Ti-N (refs. ^{18,23,24}), suggesting that the oxidation state of Ti is present in the as-deposited TiN film. This oxidized TiN (that is, O-doped TiN) is the early stage of TiO_xN_y .

The relative height of the O-Ti-N peak increases when oxidized at 300 °C and becomes the dominant N1s peak at 350 °C. A new peak centred at a higher binding energy of -402 eV is observed for the sample annealed at 350 °C, which we attribute to chemisorbed nitrogen, also denoted as $\gamma\text{-N}_2$ (refs. ^{23,26}). In addition, the TiN peak vanishes when annealed at 350 °C, consistent with the $\text{Ti}2p$ core-level peak analysis (Fig. 1a). Therefore, the 350 °C oxidized film is dominated by N-doped TiO_x (Extended Data Fig. 2). Note that the slight shift of the O-Ti-N peak to a lower binding energy of -396.2 eV might be caused by the transition of the dominant chemical state of TiO_xN_y from O-doped TiN_y to N-doped TiO_x.

For the sample annealed at 400 °C, a new peak is observed at a binding energy of -400 eV, which can be ascribed to the NO_x functional group^{18,23,25}. For this sample, the peak intensity of O-Ti-N decreases and the $\gamma\text{-N}_2$ peak shifts to a slightly higher binding energy of -403 eV. This is because the oxidation states of Ti within the sample annealed 400 °C are dominated by Ti^{4+} (Fig. 1a), and O-rich N-doped TiO_x lattices are formed after annealing at 400 °C (see Extended Data Fig. 2). Note that the O-Ti-N peak cannot be detected for TiO_xN_y films annealed at 450 °C and above.

In general, for non-metal-doped TiO_x , substitutional doping of the O lattice site is preferred in O-deficient conditions, while interstitial doping is favoured in O-rich conditions¹⁸. Here the O-Ti-N species in N1s core-level peaks is associated with both O substitutional doping in TiN_y or N substitutional doping in TiO_x lattices, while the NO_x peaks can be attributed to N interstitial doping in O-rich TiO_x lattices^{18,23,25}.

The TiO_xN_y lattices will be eventually oxidized into pure TiO_x lattices with further increasing the annealing temperature (>550 °C) as the reaction of oxidation of TiN to TiO_2 is thermodynamically favourable^{18,34}, where the relevant chemical reaction equation is $\text{TiN} + \text{O}_2 \rightarrow \text{TiO}_2 + 1/2 \text{N}_2$.

UV-Vis transmittance and absorption spectra

UV-Vis transmittance and absorption spectra were measured using a PerkinElmer Lambda 1050 UV/Vis/NIR spectrophotometer. An FEI Verios scanning electron microscope and a Helios Nanolab 600 FIB system were used to investigate the surface morphology and cross-sectional SEM images of the perovskite samples, respectively. The TEM measurements were performed in a JEOL 2100F operating at 200 keV. The simulation of the polycrystalline TEM diffraction patterns was performed using the JEMS³⁸ code as implemented on version 4.6131U2018.

Data availability

The data that support the findings of this study are available from the corresponding authors on reasonable request.

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Author contributions J.P. conceived the idea, designed the overall experiments and led the project. J.P. optimized the sputtered TiO_xN_y thin films. J.P. and Y.W. prepared and characterized the perovskite cell devices. F.K. and F.B. performed the TEM measurements and analysis. D.W., T.P.W. and K.J.W. conducted the device numerical simulation. Y.J. and J.X. performed the XPS/UPS measurements and analysis. D.Z. supervised the XPS/UPS measurements and analysis. Y.W. performed the Hall effect measurements and analysis. W.L. performed the EQE measurements. T.L. and Y.L. performed the atomic force microscopy measurements. T.D. and H.S. performed the steady-state and time-resolved photoluminescence, UV-Vis transmittance and absorption measurements. L.L. and O.L.C.L. conducted the SEM measurements. K.R.C. and T.P.W. supervised the project. J.P. wrote the manuscript. All authors contributed to the discussion of the results and revision of the manuscript.

Competing interests The Australian National University has filed a PCT patent (PCT/AU2021/051266) related to the subject matter of this manuscript.

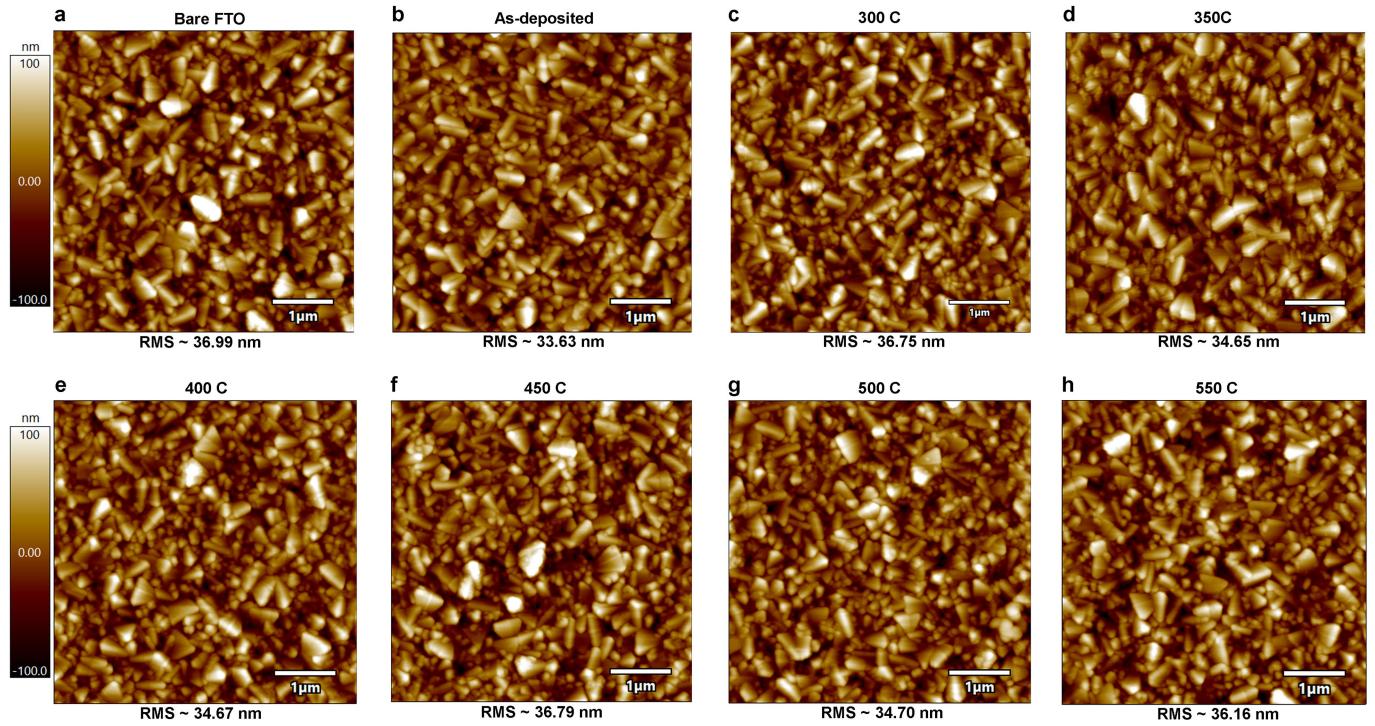
Additional information

Supplementary information The online version contains supplementary material available at <https://doi.org/10.1038/s41586-021-04216-5>.

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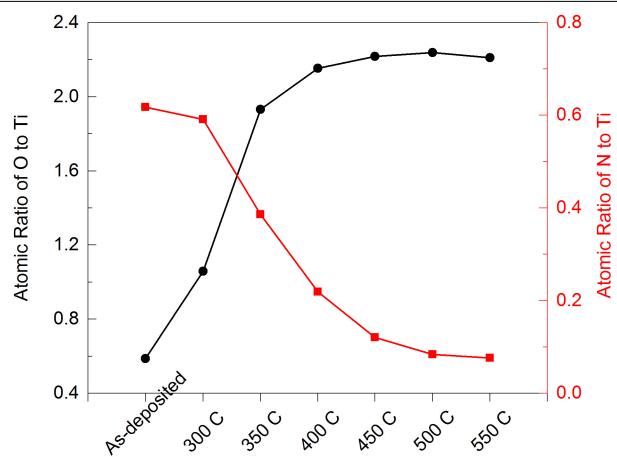
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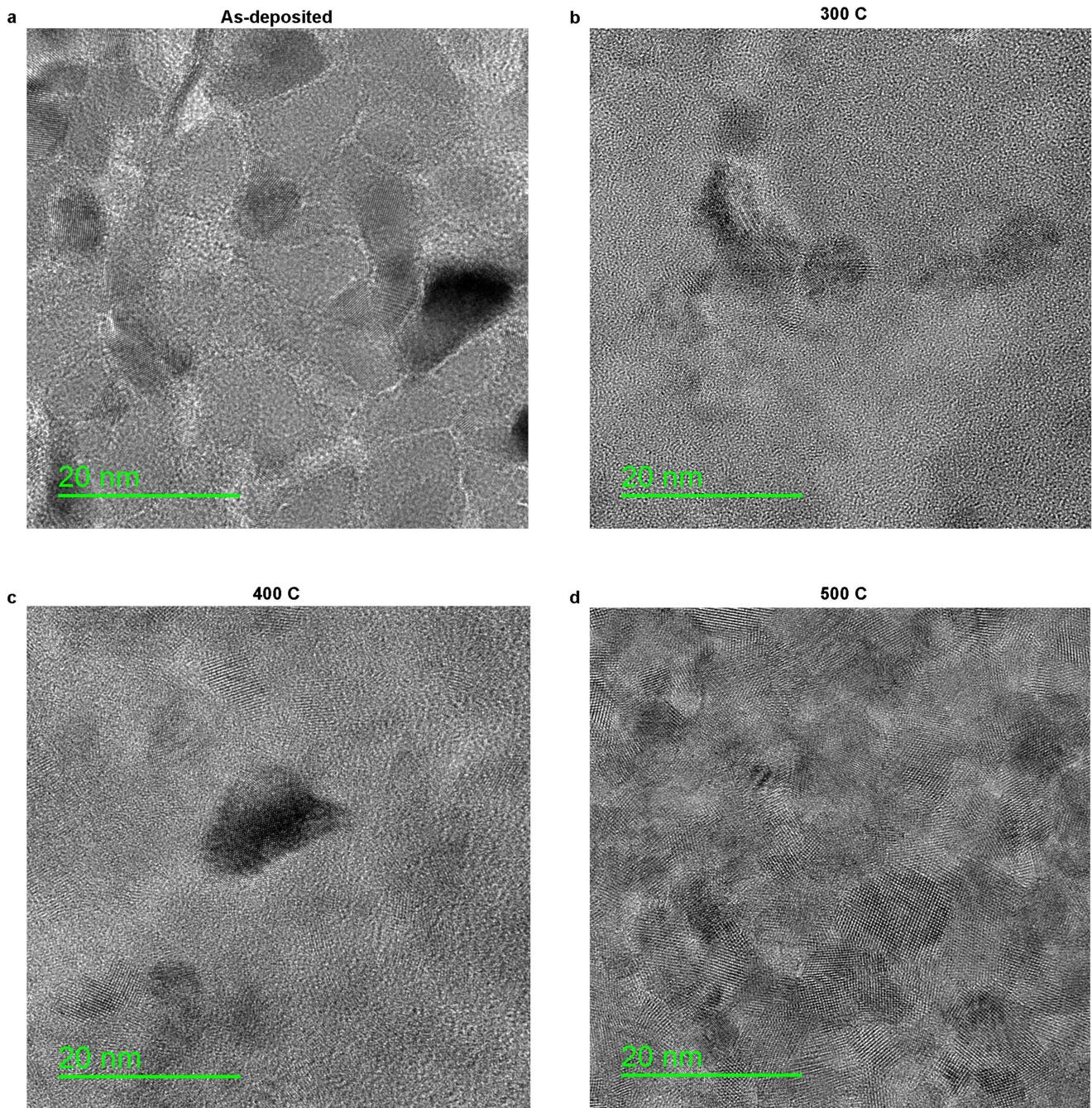
Extended Data Fig. 1 | Surface morphology characterisation by AFM. **a**, Bare FTO substrate. **b**, FTO/TiN substrate without post-annealing treatment (labeled as ‘As-deposited’). **c**, FTO/TiO_xN_y substrate annealed at 300°C (labeled as ‘300 C’). **d**, FTO/TiO_xN_y substrate annealed at 350°C (labeled as ‘350 C’). **e**, FTO/TiO_xN_y substrate annealed at 400°C (labeled as ‘400 C’). **f**, FTO/TiO_xN_y substrate

annealed at 450°C (labeled as ‘450 C’). **g**, FTO/TiO_xN_y substrate annealed at 500°C (labeled as ‘500 C’). **h**, FTO/TiO_xN_y substrate annealed at 550°C (labeled as ‘550 C’). Note that the legend of ‘RMS’ represents root mean square of the surface roughness.

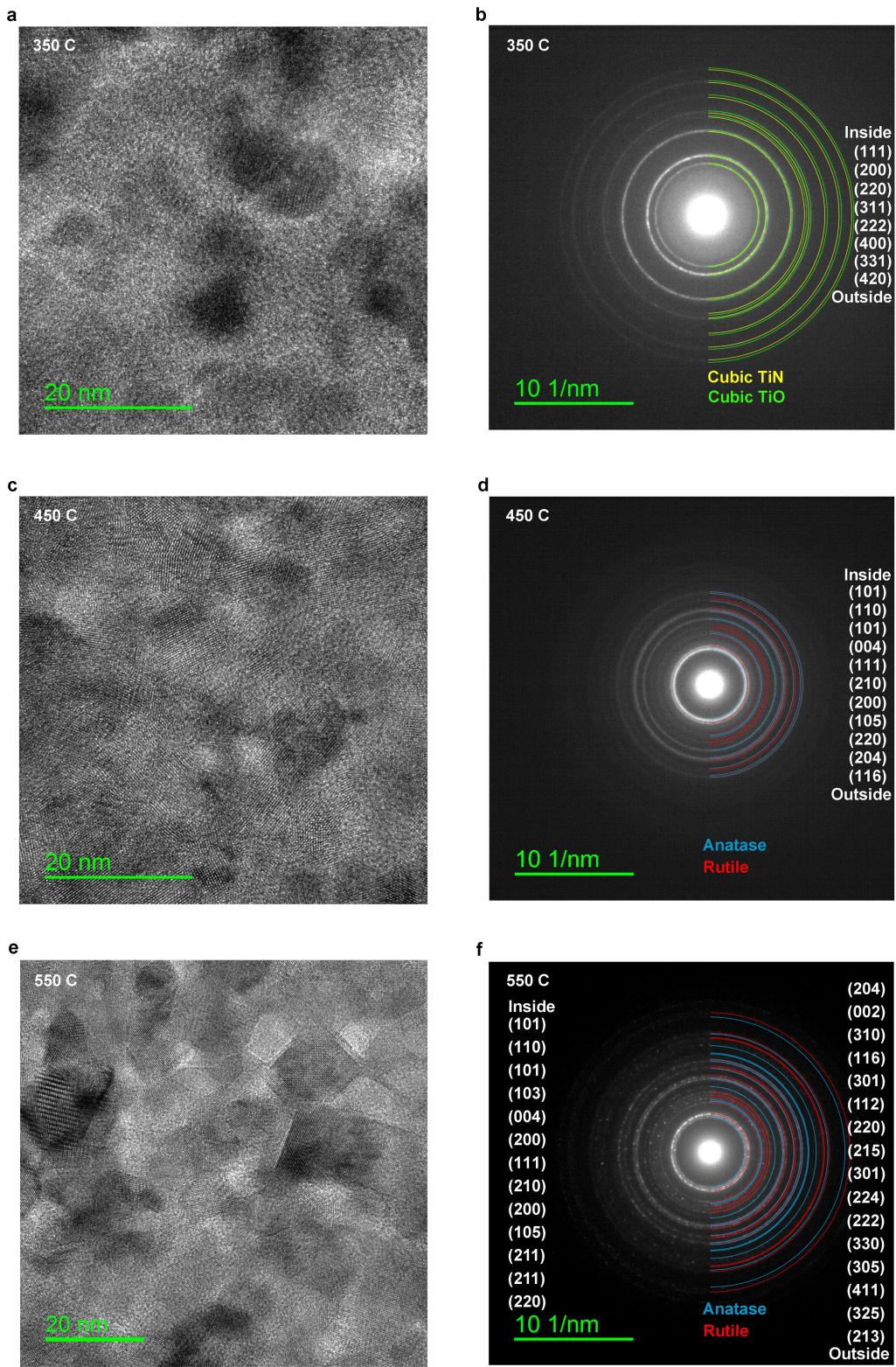
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Extended Data Fig. 2 | XPS element analysis. The atomic ratio of O to Ti and N to Ti for TiO_xN_y thin films annealed at different temperatures.

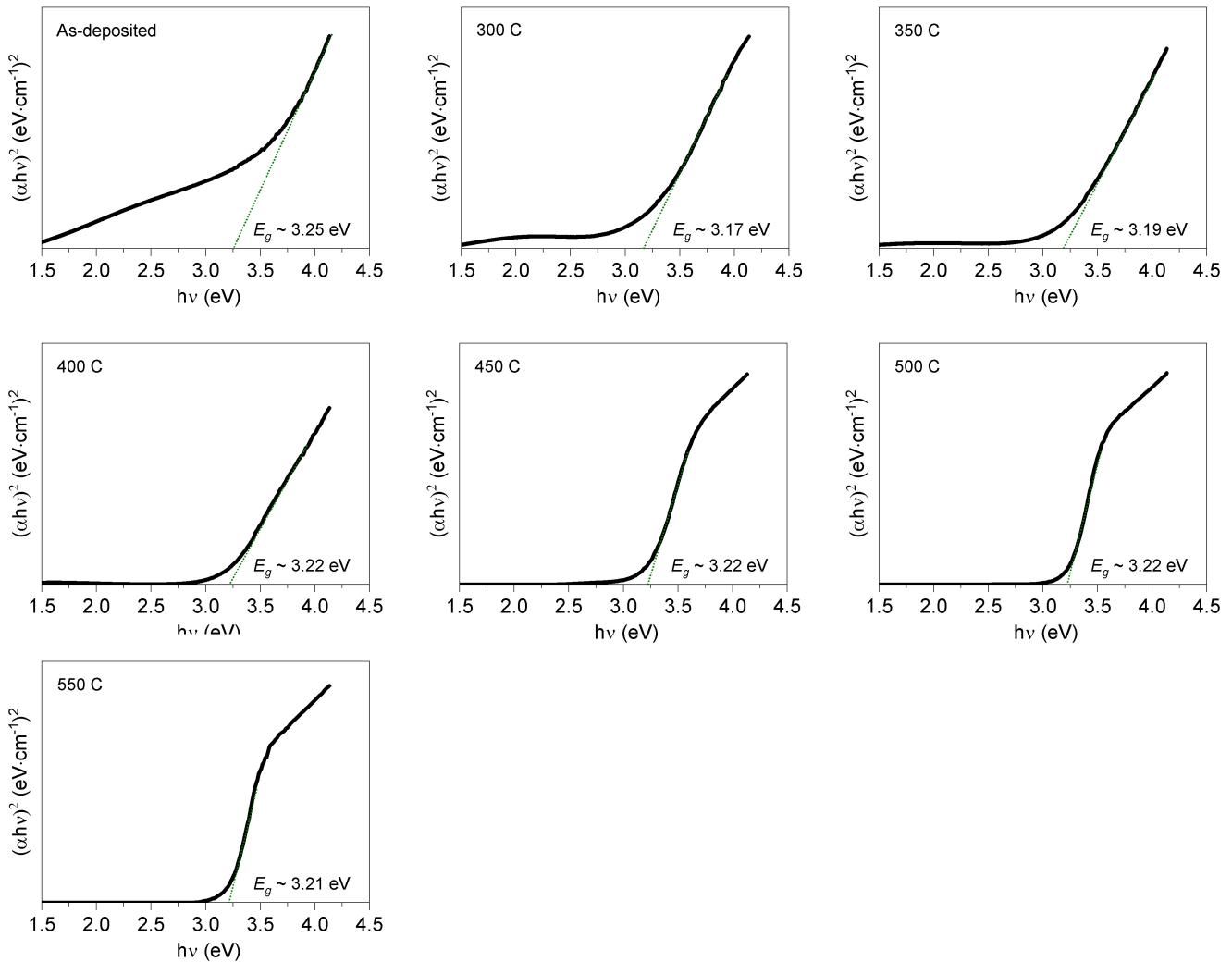


Extended Data Fig. 3 | TEM characterisation. **a**, TiO_xN_y without annealing ('As-deposited'). **b**, TiO_xN_y annealed at 300°C. **c**, TiO_xN_y annealed at 400°C. **d**, TiO_xN_y annealed at 500°C.



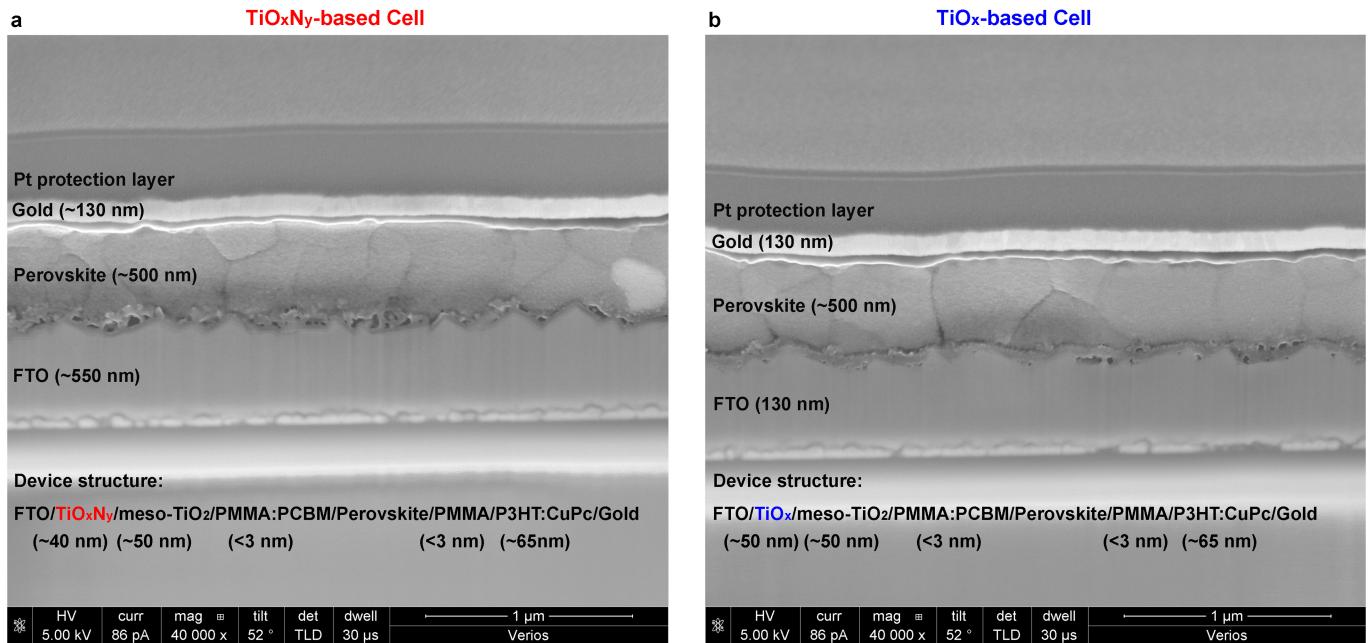
Extended Data Fig. 4 | TEM characterisation and simulation of the diffraction pattern. **a** and **b**, TiO_xN_y annealed at 350°C. **c** and **d**, TiO_xN_y annealed at 450°C. **e** and **f**, TiO_xN_y annealed at 550°C. Note that the

non-continuous diffraction ring visible in Fig. 4f diffraction pattern is caused by the low crystal density within the specimen.



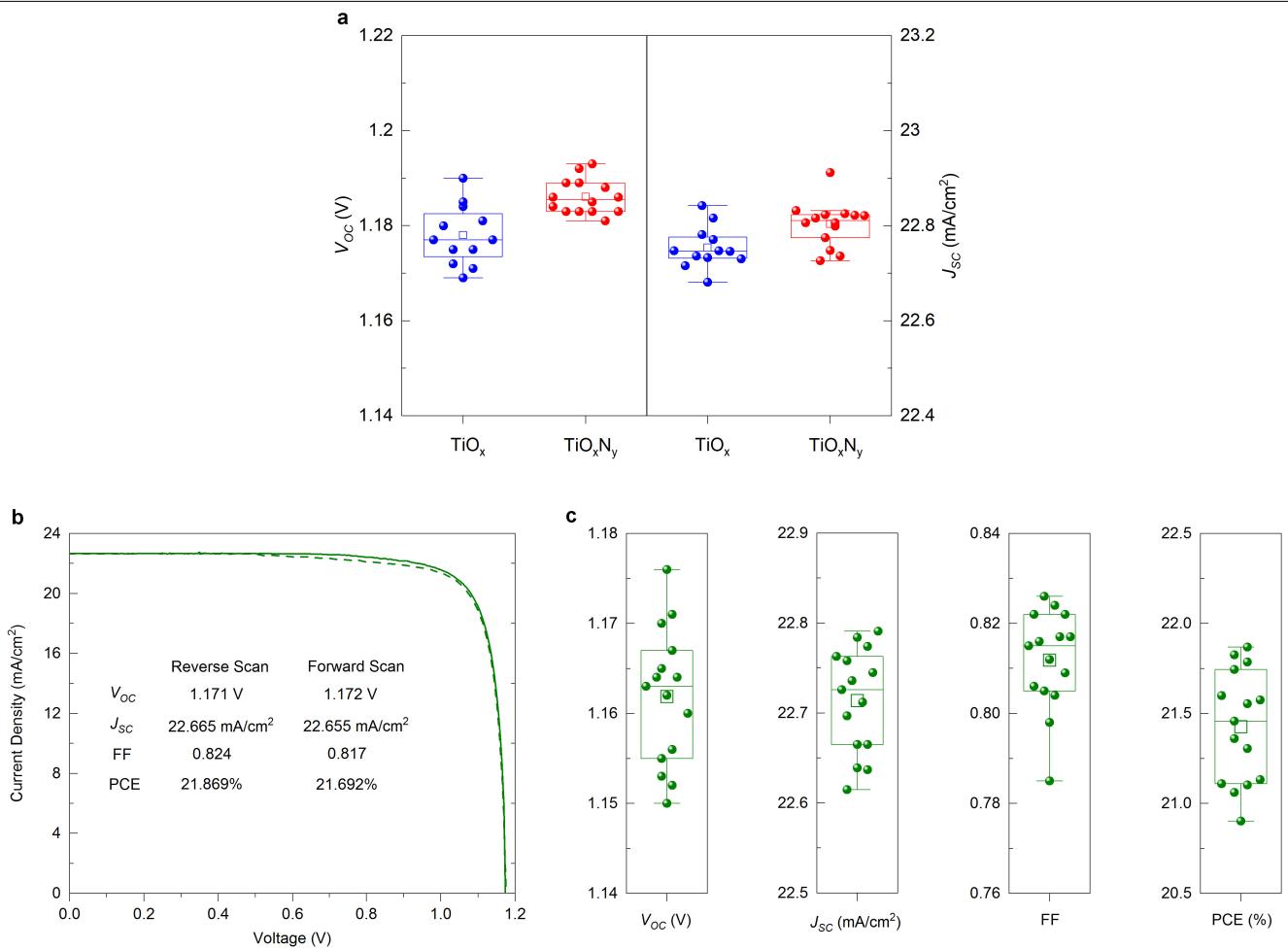
Extended Data Fig. 5 | Optical bandgap characterisation. Tauc plots for the as-deposited TiN film and TiO_xN_y films annealed at different temperatures. Note that all films (~50 nm) were deposited on quartz substrates.

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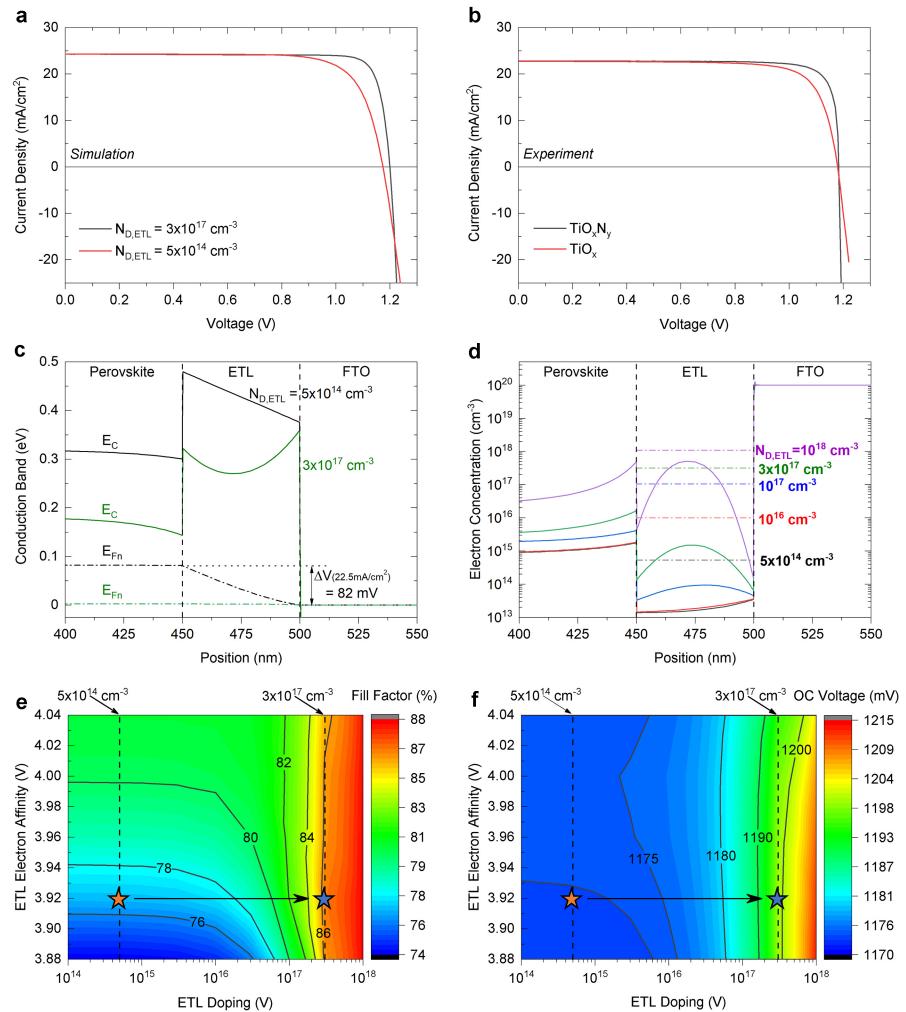
Extended Data Fig. 6 | Device structure. **a**, The cross-sectional SEM image of the TiO_xN_y-based cell with a structure of glass/FTO/TiO_xN_y (~40 nm)/meso-TiO₂ (~50 nm)/ultrathin PMMA:PCBM (<3 nm)/Perovskite (~500 nm)/ultrathin PMMA (<3 nm)/P3HT:CuPc (~65 nm)/Gold. **b**, The cross-sectional SEM image of the

TiO_x-based cell with a structure of glass/FTO/TiO_x (~50 nm)/meso-TiO₂ (~50 nm)/ultrathin PMMA:PCBM (<3 nm)/Perovskite (~500 nm)/ultrathin PMMA (<3 nm)/P3HT:CuPc (~65 nm)/Gold. Note that the meso-TiO₂ and perovskite represent mesoporous TiO₂ and Cs_{0.05}FA_{0.9}MA_{0.05}PbI_{2.74}Br_{0.26}, respectively.



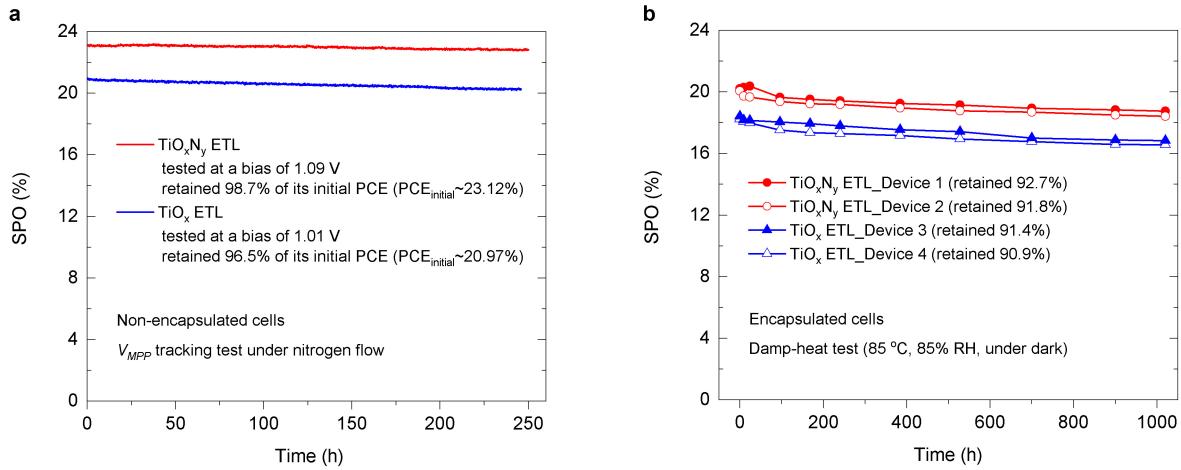
Extended Data Fig. 7 | Device characterisation. **a**, V_{oc} and J_{sc} distribution for the TiO_x-based cells (12 cells) and the TiO_xN_y-based cells (14 cells). **b**, The J - V curve of the perovskite cells based on the TiO_xN_y ETLs, which were annealed at

550°C. **c**, The J - V parameters distribution of the TiO_xN_y (annealed at 550°C) based cells (15 cells).



Extended Data Fig. 8 | Effects of electron transport layers with different carrier densities on the performance of perovskite solar cells. **a**, Simulated J - V curves where only ETL doping is varied using dopant densities taken from Hall effect measurements. **b**, Experimental J - V curves for the reference TiO_x and TiO_xN_y PSCs. Reduction in FF and increase in Ohmic series resistance is predominantly due to electron depletion in the ETL layer. **c**, Energy level diagram of electron quasi-Fermi levels and conduction band, illustrating the resistive voltage loss in the ETL for the lowly-doped cases. Note that Energy levels and electron concentrations are calculated at 22.5 mA/cm^2 for ETLs with doping densities equivalent to TiO_x ($5 \times 10^{14} \text{ cm}^{-3}$) and TiO_xN_y ($3 \times 10^{17} \text{ cm}^{-3}$). **d**, Electron concentration in the ETL for doping levels from $5 \times 10^{14} - 10^{18} \text{ cm}^{-3}$.

Note that the dash-dot horizontal lines mark the dopant defect concentration, indicating the magnitude of electron depletion. With the exception of extremely high doping at 10^{18} cm^{-3} , in no case does the free electron concentration reach even the same order of magnitude as the fixed dopant concentration. **e-f**, Contour plots of perovskite solar cell fill factor (**e**) and open-circuit voltage (**f**) across a range of ETL doping levels and electron affinity. Note that the stars mark the conditions simulated in Fig. 9a. The vertical dashed lines mark the doping levels of the TiO_x and optimized TiO_xN_y films fabricated in this work. Electron depletion from the ETL suggests that high doping is in general necessary to achieve fill factors on the order of 85% or above.



Extended Data Fig. 9 | Device stability characterisation. **a**, Light-soaking stability tests. **b**, Damp-heat stability tests. Note that SPO represents steady-state power output measured by maximum power point voltage (V_{MPP}) tracking under continuous 1 sun illumination intensity. The device structure of

the encapsulated cells is glass/FTO/TiO_xN_y (or TiO_x)/m-TiO_x/PMMA:PCBM/Perovskite/PMMA/P3HT:CuPc/MoO_x (~10 nm)/IZO (~40 nm)/Au, where the perovskite is Cs_{0.05}FA_{0.9}MA_{0.05}PbI_{2.74}Br_{0.26}. Details of encapsulation are provided in the experimental section.

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Extended Data Table 1 | Summarised parameters for the Hall-effect measurements

Sample	Type	Carrier Density (cm ⁻³)	Resistivity (ohm*cm)	Conductivity (S cm ⁻¹)	Hall Mobility (cm V ⁻¹ s ⁻¹)
As-deposited	n	3.6E+22	2.47E-3	4.05E+2	7.41E-2
300 C	n	1.4E+22	5.85E-3	1.71E+2	7.74E-2
350 C	n	3.7E+21	1.68E-2	5.94 E+1	1.14E-1
400 C	n	5.1E+20	4.01E-1	2.49E0	2.53E-1
450 C	n	5.0E+17	3.99E+1	2.50E-2	3.42E-1
500 C	n	2.8E+17	1.55E+2	6.43E-3	4.91E-1
550 C	n	3.4E+16	2.17E+2	4.60E-3	1.01E0
Solution-TiO _x	n	4.5E+14	1.02E+4	9.80E-5	5.26E-1