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# Coordinating light management and advance metal nitride interlayer enables MAPbI<sub>3</sub> solar cells with >21.8% efficiency

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## ABSTRACT

Due to the continuous increase in power conversion efficiencies (PCEs), perovskite solar cells (PSCs) are widely considered as the most promising technology for third generation photovoltaics. Improving optical absorption while reducing electrical losses is still a challenge towards attaining PCE values closer to the Shockley-Queisser limit. However, frequently used strategies to improve light absorption (e.g. via texturing the front surface) often cause electrical recombination losses. Here, we successfully relaxed the competing mechanisms between electrical and optical properties by integrating a modulated textured substrate and an amorphous metal nitride interface modification layer to combine enhanced light scattering and reducing interfacial recombination losses in PSCs. This comprehensive electro-optical management presents several advantages, including increased light absorption, promoting bandgap alignment and passivating the underlying perovskite defects. Consequently, the resulting MAPbI<sub>3</sub> solar cells exhibit a high open-circuit voltage of 1.17 V and the concomitant high PCE of 21.84%. In addition, we also use numerical simulations to propose approaches towards achieving high efficiency (PCE>30%) PSCs. Besides expanding the pool of available strategies for improving the efficiency of PSCs, from photon management to interface engineering, our work also offers a systematic guidance for the design and fabrication of high performance photovoltaic devices.

## 1. Introduction

Hybrid organic-inorganic halide perovskite materials have been studied extensively due to their excellent optoelectronic properties, such as long carrier lifetime and large absorption coefficient, making them excellent candidates as photoabsorbers for next generation photovoltaics. Recently, the power conversion efficiency (PCE) of perovskite solar cells (PSCs) has soared to a certified 25.5% [1–6], gradually approaching the theoretical limit (31%) without angular restriction [7]. Several challenges, such as exceeding the theoretical PCE limit, the long-term instability, and the toxicity of lead, still need to be addressed large-scale developments of perovskite photovoltaics [2–5]. Since PSCs are a sunlight-to-electricity converter, to overcome the above problems, effective light management and well-designed bulk/interface properties

are principally required.

Among various strategies that have been demonstrated to improve device performance, using materials and device architectures that increase light trapping has been proven to be particularly effective. Recent studies proposed that the combination of advanced materials synthesis with manipulation of the incident light path using nanostructures could increase the PCE beyond the Shockley-Queisser limit, due to the enhanced internal field intensity and photo-excited charge flux [1,8,9].

Incorporating a unique scattering media or texturing the photoabsorber layer was particularly effective among various methods used for light trapping. For example, random substrate texturing was shown to achieve a maximum optical enhancement in the photoabsorber of the solar cells [10]. Subsequently nanopatterned TiO<sub>2</sub> layers with conical shaped moth-eye structures were used to enhance light harvesting [11],

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yielding a *PCE* of 17.48%. Highly textured TiO<sub>2</sub> nanorods were also used as electron transport layer (ETL) for PSCs to improve light trapping and charge extraction [12].

Despite the above-mentioned advantages related to light-trapping, the afore-mentioned reports also remind us that enhanced light harvesting is accompanied by a degradation of crystallinity of the perovskite films, due to the imperfect interface contact, resulting in a performance-offset for PSCs. Previously, we observed that depositing a perovskite layer on a modulated textured surface (MST) results in an inhomogeneous film with some pinholes and cracks;<sup>1</sup> the perovskite absorber will directly connect with the electrode via these imperfect pinholes and cracks, causing recombination losses and instability at the perovskite/ETL interface. Therefore, although the textured substrates could boost light absorption in PSCs, this approach is not effective for improving PSCs performance, and reducing the charge recombination at the perovskite/ETL interface is still a crucial challenge.

Attempts have been made to insert an interface modification layer (IML) between the perovskite and ETL to eliminate the texture-induced recombination. For example, a compact TiO<sub>2</sub> film has been adopted as hole blocking layer for PSCs to suppress the shunt path and interface recombination. We deposited an ultrathin WO<sub>x</sub> layer on the ETL as buffer layer to enhance the interfacial charge transfer and reduce electron-hole recombination, yielding an efficiency of over 20% for MAPbI<sub>3</sub> solar cells [13]. Tan et al. used a SnO<sub>2</sub>-KCl composite as ETL in planar PSCs to passivate the trap states at the ETL/perovskite interface, and effectively reduce interfacial recombination [14]. All these successful cases are based on the fact that the interlayer must have suitable bandgap and sufficient charge transporting ability. Otherwise, the IML will even offset the merits of interface passivation and degrade device performance. [14,15] Thus, developing an appropriate IML to engineer the critical hetero-interface to reduce the electrical losses under the premise of improving light management is promising towards further improving the efficiency of PSCs.

To fulfill these requirements, the IML deposited on the textured substrates should present high conductivity, a favorable bandgap alignment between perovskite and ETL. Moreover, this IML should be better prepared by vacuum based processes to ensure it is uniformly coated on the textured substrates. In this framework, we proposed that titanium nitride (TiN<sub>x</sub>) may be a very promising alternative as IML due to its quasi-metallic conductivity and excellent optical and chemical stability [16]. Previously, TiN<sub>x</sub> has been implemented on metal diffusion barriers in microelectronics, and as anode for photoelectrochemical water splitting [16]. Recent findings also suggest that thin TiN<sub>x</sub> film with bandgap of ~3.2 eV could concurrently act as hole-blocking layer and an electron selective layer in n-Si solar cells, exploiting its superior conductivity and appropriate band alignment [16–18]. Nevertheless, for PSCs, few studies using TiN<sub>x</sub> as a functional material have been reported until now, regardless of the implementation technique, the ultimate PSCs performance, and the corresponding mechanisms.

Accordingly, to fully use the optical enhancement without sacrificing the electrical characteristics of the PSCs, an efficient “light management & interface engineering” strategy is proposed herein: an MST fluorine doped SnO<sub>2</sub> (MST-FTO) is used as light-scattering media to boost light absorption in the device, and an amorphous TiN<sub>x</sub> IML prepared by magnetron sputtering is integrated with the MST substrates to suppress the recombination losses. Compared with traditional PSCs, the MST-FTO improves the haze factor over three times in the 300–700 nm wavelength range; while the TiN<sub>x</sub> IML partitions the perovskite absorber and the rough MST-FTO. As an additional benefit, the appropriate energy level position and high electron mobility of TiN<sub>x</sub> films accelerate electron extraction and block holes, thereby inhibiting electron-hole recombination at the interface. Ultimately, the upgraded MST-MAPbI<sub>3</sub> solar cells exhibit the highest *Voc* of 1.17 V with *PCE* of 21.84%. Moreover, approaches to attain > 30% efficiency of PSCs has also been explored by numerical simulation. The concurrent improvement in optical and electrical properties brought by light management and

interface engineering is thus extremely promising for high performance PSCs in low-cost and large-area production.

## 2. Results and discussion

Generally, the morphological characteristics of interfaces will directly affect light scattering, thereby influence the light incoming into the cell [8,19]. To visually illustrate this light trapping effect, the schematics of the light paths are depicted in Fig. 1a. When the incident light encounters an MST medium, the optical path of scattered light becomes much longer than the practical thickness of the photoabsorber. This is equivalent to increasing the optical thickness ( $L_o$ ) of the film with the identical electrical thickness ( $L_E$ ), which is an effective way to fully harness the potential of the optical absorption and achieve high efficiency devices. Fig. 1b exhibits the photographic images of the regular FTO and MST-FTO substrates. The surface of MST-FTO substrate is “whiter” than that of the FTO substrate. This occurs because the incident light was scattered in different directions by the undulating particles of the MST-FTO. This interface scattering is helpful to increase the optical path of neighboring perovskite layers, thus improving photon utilization [1,9]. We examined surface morphology by scanning electron microscopy (SEM) for different substrates (Fig. 1c–d). The MST-FTO presents much larger grains and rougher morphologies than the regular FTO substrates, conferring a better light scattering ability to the MST-FTO. The grain size distribution of the polycrystalline FTO is 30–100 nm, which is smaller than that of the MST-FTO (50–310 nm) (Fig. S1). Atomic force microscopy (AFM) was used to further evaluate the surface morphology and roughness of the FTO and MST-FTO substrates (Fig. 1e). The root mean square (RMS) of MST-FTO (21.0 nm) is almost three times larger than that of FTO (7.5 nm). Then, we evaluated the light-scattering ability of the substrates via the haze factor, which is also determined by the geometry of the nanostructured substrate. The haze factor gained from the variation between vertical transmittance (VT) and total transmittance (TT) (Fig. S2) is given by [8,20]:

$$\text{Haze} = \frac{TT - VT}{VT} \times 100\% \quad (1)$$

The haze factor of MST-FTO is higher than that of FTO in the 300–700 nm spectral region of (Fig. 1f) and the average values are 17.7 and 4.9, respectively (Inset. 1 f). The larger haze factor also indicates that the MST-FTO can more effectively scatter the incident light. In addition, we carried out optical simulations based on FTO and MST-FTO substrates to theoretically ascertain their light harvesting capability. Fig. 1g shows the two-dimensional optical absorption distribution in the perovskite layer, and the corresponding optical simulation parameters have been illustrated in Supplementary Note 3 and Fig. S3. Compared with the electrical field distribution in the FTO-based sample, a strong light scattering, due to the higher surface roughness of the MST-FTO substrate, is found in perovskite films based on MST-FTO, resulting in more intense absorption. This can also be experimental verified by comparing the optical absorbance of the perovskite films deposited on different substrates. As shown in Fig. 1h, the absorbance of the MAPbI<sub>3</sub>/MST-FTO is much higher than that of the MAPbI<sub>3</sub>/FTO, which indicates that more photons can be converted into electrons in the MST-based photoabsorber and it is feasible to increase the light absorption of the perovskite layer by modulating the surface roughness.

We then fabricated PSCs on FTO and MST-FTO substrates to confirm the effect of enhanced light harvesting on device performance. We expect that the MST devices should have better performance than the regular ones due to the increased light absorption in the perovskite layer. The statistical photovoltaic parameters of 20 devices with FTO and MST-FTO substrates were collected in Fig. 2a–d. The current density-voltage (*J-V*) curves and parameters of the best-performance PSCs with different substrates (FTO and MST-FTO) are shown in Fig. S6 and Table S1. Surprisingly, the *PCE* of the MST-FTO-based devices are even lower than that of the FTO devices, although MST-FTO based devices

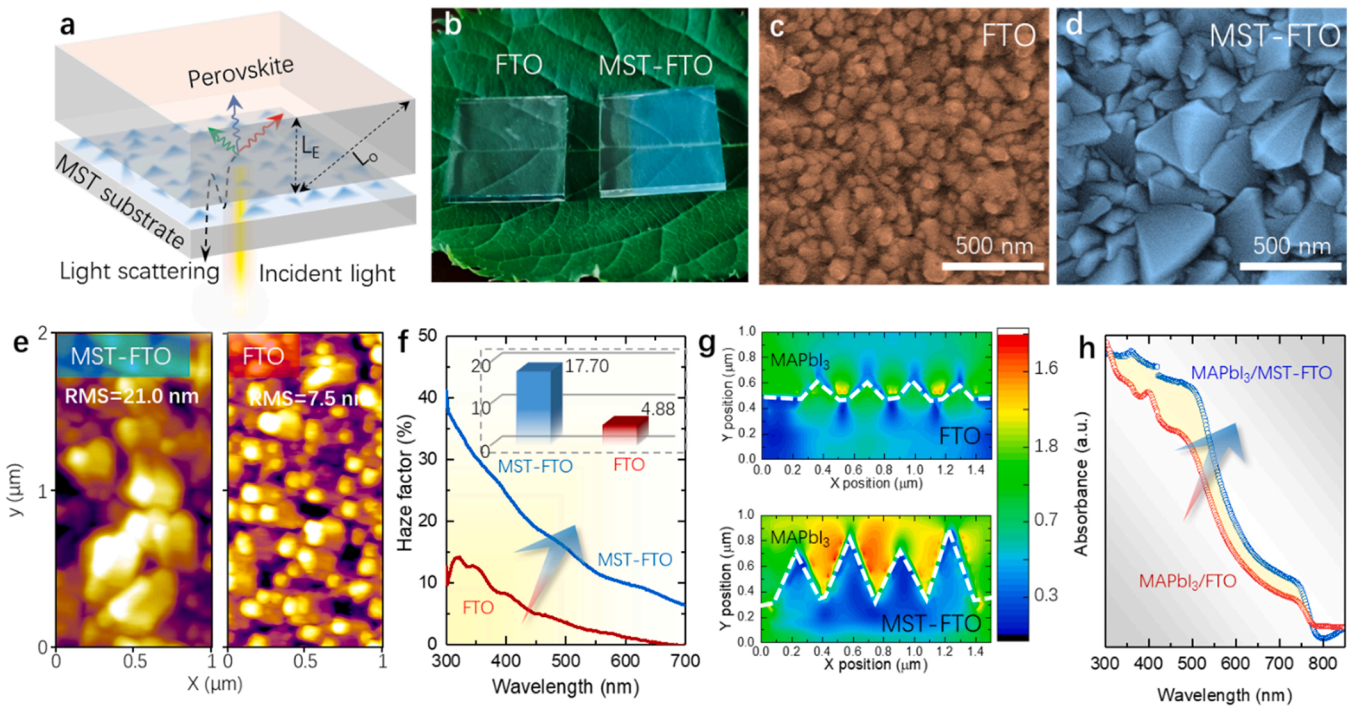


**Fig. 1.** Characterization of MST substrate. (a) Schematic of the light path within the perovskite films grown on a MST substrate. (b) Images of FTO and MST-FTO substrates. (c-d) SEM and (e-f) AFM images of FTO and MST-FTO substrates, respectively. (f) Haze factor of the FTO and MST-FTO substrates. Inset f: the average value of the haze factor from 300 to 700 nm. (g) The simulated absorption distribution of 600 nm wavelength incident light within the films based on FTO and MST-FTO substrates, respectively. (h) The absorbance of the MAPbI<sub>3</sub>/MST-FTO and MAPbI<sub>3</sub>/FTO.

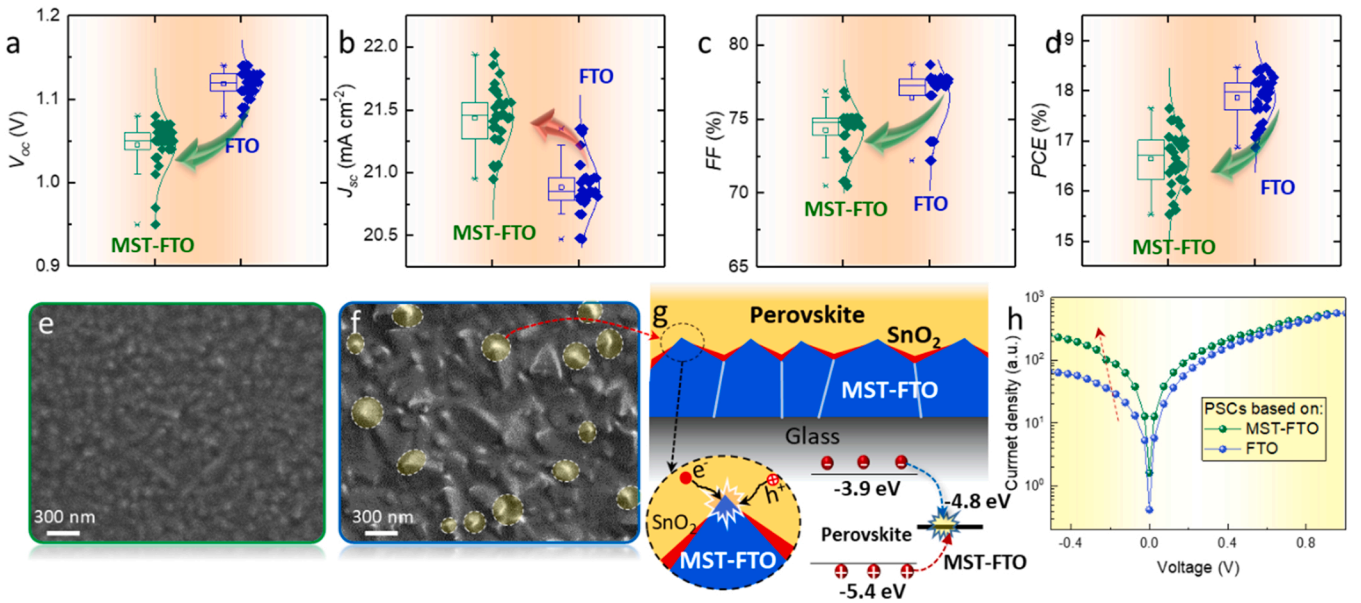


**Fig. 2.** Influence of the MST substrates on the PSCs. (a-d) Device performance obtained with FTO and MST-FTO substrates. Top-view SEM images of the SnO<sub>2</sub> layer spin-coated on (e) FTO and (f) MST-FTO substrates, respectively. (g) Schematic diagram of the heterointerface and the charge recombination behavior. (h) The  $J-V$  characteristics of devices measured in the dark.

enable a higher short-circuit current density ( $J_{sc}$ ) than the FTO based devices (MST-FTO cell ~22.08 mA cm<sup>-2</sup>; FTO cell ~20.92 mA cm<sup>-2</sup>). We measured the integrated reflectance spectra of MST-FTO and FTO substrates, as well as the internal quantum efficiency (IQE) and EQE of FTO- and MST-FTO devices (Fig. S4). The difference between the IQE and EQE of the FTO device and MST-FTO device are almost the same, indicating that almost all incident light is absorbed by the perovskite. The degradation is mainly caused by the decline of the open-circuit

voltage ( $V_{oc}$ ) and fill factor (FF). The champion device with MST-FTO only exhibits a PCE of 17.21%, lower than the one based on the FTO substrate (18.33%). We further evaluated the perovskites quality on bare FTO and bare MST-FTO substrates (without ETLs) by SEM and XRD measurements, respectively. The crystallinity and the grain size of FTO- and MST-FTO perovskite are almost the same (Fig. S7-8), indicating that the large roughness of MST-FTO is not the main reason for the performance degradation. Considering that all the device preparation

processes are identical, we thereby attribute the performance degradation to the interface properties of the ETL/perovskite. The SEM (Fig. 2e-f) and AFM (Fig. S9) show that the ETLs (SnO<sub>2</sub>) were fully covered on the FTO substrate while some bare tips can be found on the MST-FTO substrate, which implies that the highly textured MST-FTO pierces the ETL and comes directly into contact with the perovskite layer. Cross-sectional SEM images also confirm the above observations (Fig. S10).

On this basis, we illustrate the reason for  $V_{oc}$  and  $FF$  degradation in Fig. 2g. The rough MST-FTO pierces the ETL and directly connects with the perovskite layer, so that the photogenerated holes cannot be effectively blocked at the interface, thereby causing significant electron-hole recombination. The relationship between  $V_{oc}$  and interface recombination can be expressed as follows [21]:

$$V_{oc} = \frac{\phi_B}{q} - \frac{nkT}{q} \ln \left( \frac{qN_V S_{it}}{J_{sc}} \right) \quad (2)$$

where  $S_{it}$ ,  $\phi_B$ ,  $q$ ,  $kT$ , and  $N_V$  are the interface recombination velocity, effective barrier, elementary charge, thermal energy, and effective density of states in the valence band, respectively.

Therefore, an increase in  $S_{it}$  will degrade the  $V_{oc}$  of the device. Fig. 2h shows an obvious increase in the dark current density for the MST-FTO based device compared with that of the planar FTO-based device. The corresponding plots of  $dV/dJ$  versus  $(J_{sc}-J)^{-1}$  and linear fitting curves of the devices under illumination is shown in Fig. S11 and Table S2. The MST-FTO based PSCs have higher  $A$  and lower  $R_{sh}$ , demonstrating substantial electron-hole recombination within the cells. Therefore, to improve the PSCs performance, it is urgent to develop an appropriate strategy that can maintain the optical enhancement without sacrificing the electrical properties.

As mentioned, engineering the hetero-interface by incorporating an IML to reduce the interfacial recombination has proven to be effective for improving device performance [10,19,20]. For practical applications, IML materials should exhibit several properties, including excellent electron selectivity, hole blocking properties, low resistivity, etc. Moreover, the IML should be deposited through a non-solution route to enable the IML homogenously covering the rough surface. Herein, a transition metal nitride-TiN<sub>x</sub> was firstly used as IML to improve the interface properties. The stable composition range of TiN<sub>x</sub> is TiN<sub>0.37</sub>~TiN<sub>1</sub> [16,17,24,25], and the nitrogen content can be varied within a certain range without changing the TiN<sub>x</sub> structure. The crystal structure of the standard TiN nanoparticles (NPs) and our sputtered TiN<sub>x</sub> films was investigated, respectively. Grazing-incidence XRD (GIXRD) measurements confirm that standard TiN<sub>x</sub> NPs exhibit several peaks at 36.8°, 42.7°, and 62.1°, which are assigned to the (111), (200), and (220) planes (Fig. 3a) [25,26]. In contrast, no well-defined peaks can be found for the sputtered TiN<sub>x</sub> film, which is therefore considered to be amorphous. Since the films were deposited without heating, the precursor has less kinetic energy to find the optimal binding sites, causing the microstructure of the TiN<sub>x</sub> film to be disordered [24]. This amorphous phase is usually accompanied by a nonstoichiometric configuration, as also confirmed by X-ray photoelectron spectroscopy (XPS) (Fig. S12). The XPS spectra of Ti 2p and N 1s acquired from the TiN<sub>x</sub> film and the corresponding fits are shown after the binding energy axis correction. The peaks appeared at 455 eV, 456.8 eV and 458.6 eV, referring to Ti-N, Ti-O and Ti-N-O bonding respectively, which are characteristic peaks of high resolution Ti 2p of TiN<sub>x</sub> according to previous studies. [28,29] The coexistence of Ti-O, Ti-N-O bonding is due to the inevitable partial oxidation of TiN<sub>x</sub> during handling. The N 1s core-level spectra with at

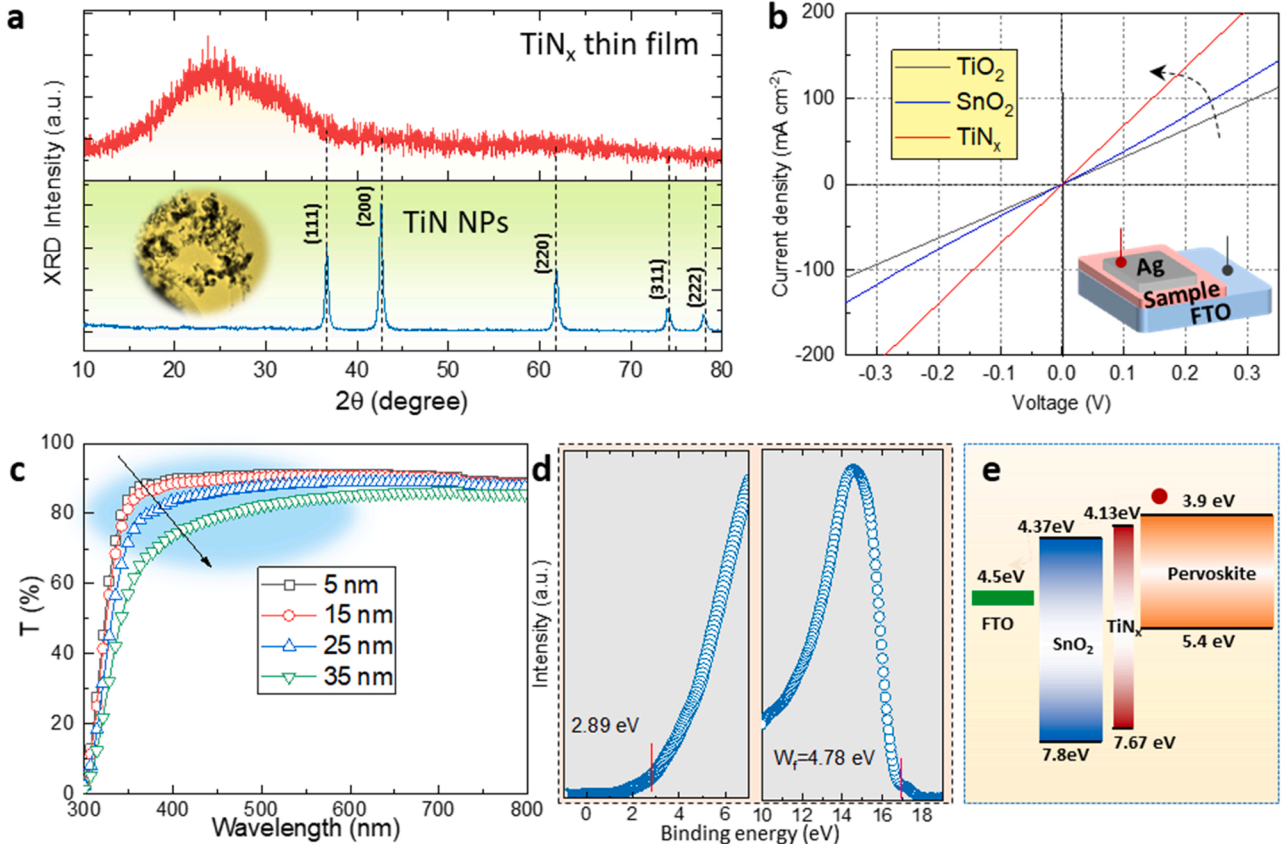


**Fig. 3.** Characteristics of the TiN<sub>x</sub> IML. (a) XRD patterns for the TiN<sub>x</sub> NPs and the amorphous phase of TiN<sub>x</sub> film deposited by magnetron sputtering. The inset in the below figure shows the TEM image of the TiN<sub>x</sub> NPs. (b) J-V curves of devices with the structure of FTO/sample/Ag for evaluating the conductivity of samples. All the samples have similar thicknesses (~15 nm). (c) The optical transmission of the TiN<sub>x</sub> films with different thicknesses. (d) The valence band, and secondary-electron cut-off region of UPS spectra of the TiN<sub>x</sub> film. (e) Schematic diagram of the energy levels.

least two different binding energies indicates the non-stoichiometric nature of the  $\text{TiN}_x$  film [29,30]. We subsequently evaluated the electrical and optical properties of the  $\text{TiN}_x$  film for PSCs applications. Fig. 3b shows J-V characteristics of the Ag/sample/FTO device (the sample is  $\text{TiN}_x$ ,  $\text{SnO}_2$ , and  $\text{TiO}_2$ ). With similar thickness (~15 nm), the  $\text{TiN}_x$  film possesses higher conductivity compared to standard  $\text{SnO}_2$  and  $\text{TiO}_2$ , which is conducive to transporting carriers (Fig. S13). As reported by Solovan et al., the high conductivity of  $\text{TiN}_x$  films can be attributed to the presence of metallic bonding with the d electrons of titanium, greatly improving the electron concentration (more than  $10^{23} \text{ cm}^{-3}$ ) [31]. Fig. 3c shows the optical transmittance of  $\text{TiN}_x$  films with different thickness. The 15 nm  $\text{TiN}_x$  film exhibits similar optical transmission compared to the 5 nm film. However, as the thickness is further increased to 35 nm, the transmission is observed to decline. This indicates that the  $\text{TiN}_x$  thickness should be thinner than 15 nm for PSCs applications in case of the extra parasitic absorption. Meanwhile, the haze factor of MST substrates with- and without- $\text{TiN}_x$  (Fig. S14) and the optical absorption of the perovskite layer (Fig. S15) are at similar levels, demonstrating that the ultrathin  $\text{TiN}_x$  IML does not deteriorate the light-scattering ability of the textured substrates.

In addition, to evaluate the feasibility of the  $\text{TiN}_x$  IML for PSCs applications, the energy level alignment at the  $\text{TiN}_x$ /perovskite interface was also studied. As shown in Fig. S16, the  $\text{TiN}_x$  IML has a gap of 3.2 eV, which is close to the value (3.4 eV) reported by Solovan et al. [31]. The work function (WF) of  $\text{TiN}_x$  is determined to be 4.78 eV, calculated by using the onset position in the UV photoelectron spectroscopy (UPS) spectrum of  $\text{TiN}_x$  after surface etching with  $\text{Ar}^+$  (Fig. 3d). The  $E_f-E_v$  value (2.89 eV) is obtained from the cutoff in the UPS spectrum. The parameters of the  $\text{SnO}_2$  ETL used in this study were also calculated, as shown in Fig. S17. The energy level structure of the hetero-interface is depicted in Fig. 3e based on these data. The large valence band offset of  $\text{TiN}_x$  can effectively block holes, thus avoiding electron-hole recombination at the interface [13,16]. Meanwhile, the conduction band offset at the  $\text{TiN}_x$ /perovskite interface is also conducive to the extraction of photo-generated electrons. Therefore, the cascade energy levels can improve device performance by eliminating the probability of carrier recombination, reducing the leakage current, and further enhancing the

interfacial charge transfer (Fig. S18).

Another factor that needs to be confirmed before the  $\text{TiN}_x$  IML is implemented in MST-PSCs is its influence on the growth of perovskite films, including the morphology, structure and interface defect density. The XRD patterns in Fig. 4a show that the reflection peaks of the perovskite film grown on the  $\text{TiN}_x$  surface has stronger intensity than that grown on the bare  $\text{SnO}_2$  substrate. Also, the SEM images show that the grain size of the perovskite grown on  $\text{TiN}_x$  surface is much larger than that on the bare  $\text{SnO}_2$  surface (Fig. 4b-c). We speculate that the difference of perovskite crystallization arises from the different surface conditions of the substrates. We collected liquid-state  $^1\text{H}$  NMR spectra of the perovskite precursor in the absence and presence of  $\text{TiN}_x$  in deuterated dimethyl sulfoxide- $d_6$  ( $\text{DMSO-}d_6$ ) to gain insights into the mechanism of the increasing grain size of the perovskite in the presence of  $\text{TiN}_x$  IML (Fig. 4d). The broad peak at 7.52 ppm originating from the four hydrogen atoms attached to nitrogen atoms of the  $\text{MA}^+$  shows a down shift by adding  $\text{TiN}_x$  to the perovskite precursor. Similar to previous work [32], the downshift can be attributed to the interaction between the hydrogen atoms of the  $\text{MA}^+$  and basic sites on  $\text{TiN}_x$ , which can delay the crystallization process of perovskite film. Moreover, since the amorphous  $\text{TiN}_x$  surface is rich in N, which has lone-pair electrons to terminate the uncoordinated  $\text{Pb}^{2+}$  dangling bonds of the perovskite layer, we anticipate that  $\text{TiN}_x$  can also interact with Pb to regulate the nucleation and act as an interfacial passivation layer to strengthen the interface contact (Fig. 4e). XPS measurements were conducted to confirm the interaction between  $\text{TiN}_x$  and the perovskite. The decreased binding energy of Pb 4  $f_{7/2}$  and Pb 4  $d_{5/2}$  peaks confirmed the interaction between Pb and N atoms (Fig. 4f). This assumption was further verified by comparing FTIR spectra of perovskite films grown on glass (control) and glass/ $\text{TiN}_x$  layer, respectively. The shift of the characteristic peak of N-H in FTIR spectra from  $1438 \text{ cm}^{-1}$  (control) to  $1426 \text{ cm}^{-1}$  ( $\text{TiN}_x$  sample) indicated a chemical interaction between Pb and N (Fig. 4g). These results imply that a suitable incorporation of  $\text{TiN}_x$  IML could delay the crystallization and effectively terminate the perovskite's sub-surface defects, thereby forming high quality perovskite films [32,33].

To further assess the effect of inserting the  $\text{TiN}_x$  IML, we acquired electrochemical impedance spectroscopy (EIS) data from the MST-PSCs

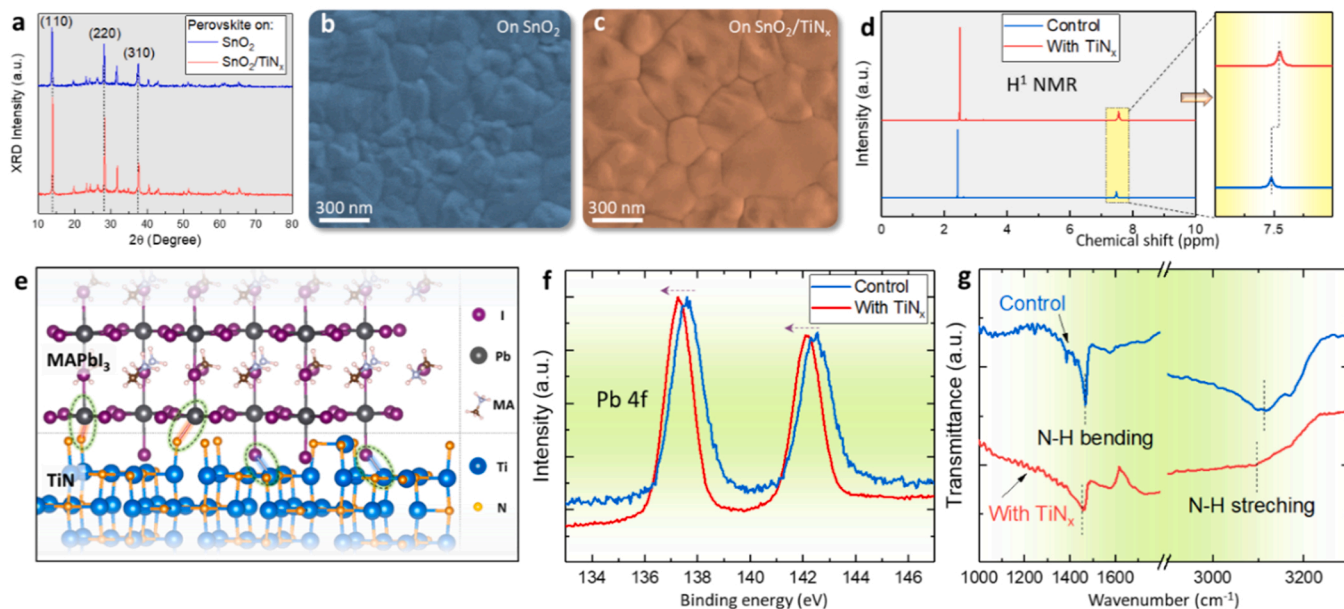


**Fig. 4.** Effect of  $\text{TiN}_x$  IML on the perovskite layer. (a) The XRD patterns of perovskite deposited on  $\text{SnO}_2$  and  $\text{SnO}_2/\text{TiN}_x$  substrates. (b-c) The SEM images of perovskite spin-on the  $\text{SnO}_2$  and  $\text{SnO}_2/\text{TiN}_x$  substrates (d)  $^1\text{H}$  NMR of perovskite solution, and perovskite +  $\text{TiN}_x$  collected in  $\text{DMSO-}d_6$ . The right figure is the scale magnification between 7 and 8 ppm. (e) The schematic diagram of interaction principle by perovskite and  $\text{TiN}_x$ . (f) The amplified spectra of Pb 4f signals of XPS results of the control and with  $\text{TiN}_x$ . (g) The FTIR spectra of perovskite films based on the control and with  $\text{TiN}_x$  substrates, for which the signals attributing to N-H are compared.

(Fig. S19). The arc found in the high frequency region is related to the impedance of the carrier transport ( $R_{tr}$ ) process, while the arc in the low frequency region is related to the impedance of the carrier recombination ( $R_{rec}$ ) process [3,15,19]. The MST-PSCs with  $TiN_x$  IML exhibits smaller  $R_{tr}$  and larger  $R_{rec}$  compared to the control device, indicating a better charge transfer efficiency and a lower interfacial charge recombination. This originates from the cascade energy levels and the suppressed interface recombination that occur after incorporating the  $TiN_x$  IML.

The semi-logarithmic plot of  $V_{oc}$  as function of light intensity for the devices and the slopes derived from the lines fitted linearly to the data are shown in Fig. S20. The control device exhibits a strong dependence of  $V_{oc}$  on the light intensity, with a slope of  $1.86 kT/q$ , where  $k$  is Boltzmann's constant,  $q$  is the elementary charge, and  $T$  is the absolute temperature. The device with  $TiN_x$  IML exhibits a lower slope of  $1.55 kT/q$ , indicating a lower trap-assisted Shockley-Read-Hall recombination in the device, which can be attributed to the enhanced perovskite crystallinity and the interface passivation [34]. In addition, Fig. S21 shows the open-circuit photovoltage decay (OCVD) curves of the PSCs. The cell with  $TiN_x$  IML shows slower  $V_{oc}$  decline and larger  $V_{oc}$  value than the control device, also demonstrating that the MST-PSCs with  $TiN_x$  IML have much longer carrier lifetime and slower charge recombination [3,9,22].

The above results indicate that the MST substrates can effectively improve the light harvesting of the device yet exhibit interface recombination losses; incorporating the  $TiN_x$  IML is a significant recipe to

improve the interface contact properties and construct a cascade of interface energy levels, thereby suppressing the recombination losses. Based on these findings, we upgraded the PSCs by integrating the MST substrates and the  $TiN_x$  IML and studied its influence on photovoltaic performance. Fig. 5a presents the schematic diagram and the cross-sectional SEM images of the upgraded MST-PSCs (dual-modulated by MST and  $TiN_x$  IML). Fig. 5b exhibits the  $J$ - $V$  characteristics of control PSCs and the upgraded MST-PSCs under AM 1.5 G irradiation ( $100 \text{ mW cm}^{-2}$ ). The detailed photovoltaic parameters of the PSCs are listed in Table 1. The control device exhibits a  $PCE$  of 19.55% with a  $V_{oc}$  of 1.15 V, a  $J_{sc}$  of  $21.73 \text{ mA cm}^{-2}$ , and a  $FF$  of 78.25%. In contrast, a significantly improved performance was obtained for the upgraded MST-PSCs, achieving a larger  $V_{oc}$  of 1.17 V, a  $J_{sc}$  of  $23.52 \text{ mA cm}^{-2}$ , a  $FF$  of 79.37%, yielding an impressive  $PCE$  of 21.84%. The improvement ratio of  $V_{oc}$ ,  $J_{sc}$ , and  $FF$  is 1.7%, 8.2%, and 1.4%, respectively. The increment in  $J_{sc}$  is attributed to enhanced light harvesting by the MST substrate, and we propose that the slight enhancement in  $V_{oc}$  and  $FF$  is likely related to the improved charge extraction due to the enlarged

**Table 1**

Comparison of the device performance of control and upgraded MST-PSCs.

| Sample            | $V_{oc}$ (V) | $J_{sc}$ ( $\text{mA cm}^{-2}$ ) | $FF$ (%) | $PCE$ (%) |
|-------------------|--------------|----------------------------------|----------|-----------|
| control           | 1.15         | 21.73                            | 78.25    | 19.55     |
| Upgraded MST-PSCs | 1.17         | 23.52                            | 79.37    | 21.84     |

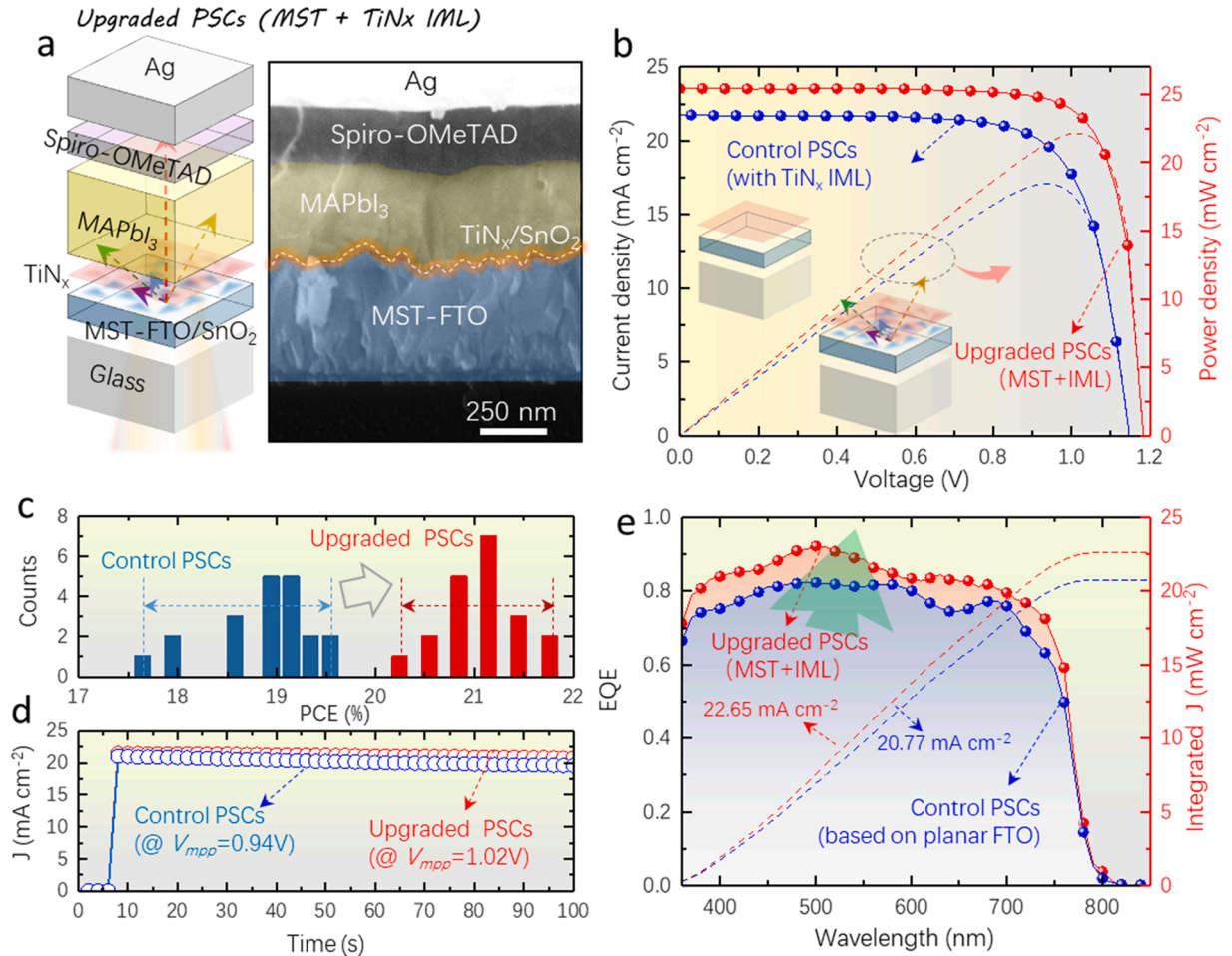


**Fig. 5.** Device performance. (a) Structure illustration and the cross-sectional SEM image of the upgraded MST-PSCs. (b)  $J$ - $V$  curves of control and upgraded MST-PSCs. (c) The  $PCE$  distribution of the control and upgraded MST-PSCs. 40 samples were fabricated, including 20 control cells and 20 upgraded MST-PSCs, respectively. (d) Photocurrent density taken from the  $V_{mpp}$  of the control and upgraded MST-PSCs. (e) EQE spectrum of the control and upgraded MST-PSCs.

interface area by the textured substrate. In addition, to verify the reproducibility of the upgraded MST-PSCs, we fabricated 40 devices in one batch (20 control PSCs, 20 upgraded MST-PSCs) to compare the *PCE* distribution (Fig. 5c). Compared with the control PSCs (*PCE* distribution from 17.57% to over 19.55%), higher *PCE*s were obtained from the upgraded cells mainly distributed in the 20.32–21.84% range. Fig. 5d shows the output stability of the devices by observing the change in current density of the PSCs at maximum power point voltage ( $V_{mpp}$ ) under continuous illumination. The  $V_{mpp}$  of the control- and upgraded MST-PSCs is 0.94 and 1.02 V, respectively. We found that both control- and upgraded MST-PSCs have highly stabilized current density outputs under continuous irradiation. In addition, the operational stability of the devices under maximum power point tracking with continuous light irradiation were evaluated by recording the *PCE* variation (Fig. S22). We found that the control cell and upgraded MST-PSCs show similar *PCE* decay tendency, maintaining more than 91.7% of initial *PCE* after 100 h continuous irradiation. These results imply that the control and upgraded PSCs have similar long-term stability and integrating the  $\text{TiN}_x$  and MST can improve device performance without sacrificing stability. External quantum efficiency (EQE) measurements were performed to examine the photoelectric response of the devices at different wavelength (Fig. 5e). The upgraded MST-PSCs exhibits a higher spectral response than that of the control PSCs over the 360–750 nm range, which is attributed to the MST-induced light harvesting effect. The  $J_{sc}$  values obtained by integrating EQE spectra are 22.65 and 20.77  $\text{mA cm}^{-2}$  for the upgraded- and control-devices, respectively, in good agreement with the values obtained by extrapolating from *J-V* measurements.

Based on these results, we further extend the horizons for conceptual

design high performance PSCs. As a polycrystalline thin film solar cell, the main limitations in *PCE* originates from defect-induced recombination losses and light absorpton losses [35]. The mainstream strategy to address this challenge is to passivate defects by using various chemical agents [36–38]. In addition, we propose that strengthening the built-in field is another promising way to overcome this problem because a stronger built-in field can more efficiently separate photo-excited charges before recombination, thereby reducing the recombination losses. For a given device, when the materials of each layer are determined (the potential difference within the device is constant), thinning the photoactive layer can improve the strength of the electric field ( $E = U/d$ , where  $U$  is the potential difference,  $d$  is the thickness of the photoactive layer). This has been verified by our numerical simulation presented in Fig. 6a (detailed simulation parameters are summarized in Table S4). However, a thin photoactive layer also limits optical absorption for the incident light, resulting in current losses [39]. As shown in Fig. 6b, the electron/hole current density ( $J_n/J_p$ ) depends directly on the optical thickness. The current density decreases as the optical thickness is increased from 100 to 600 nm and this attenuation becomes more significant when the perovskite layer is thinner than 400 nm. This indicates that a sufficient optical thickness is a necessary factor and the threshold thickness of the photoactive layer should be higher than 400 nm for designing and realizing high performance PSCs. Therefore, reducing the physical thickness (improve built-in field) and increasing the optical thickness simultaneously by regulating the MST architecture and interface engineering is a guideline for next generation PSCs (Fig. 6c). Correspondingly, Fig. 6d exhibits the numerically modeled  $\text{MAPbI}_3$ -based solar cells with different defect density and thickness of

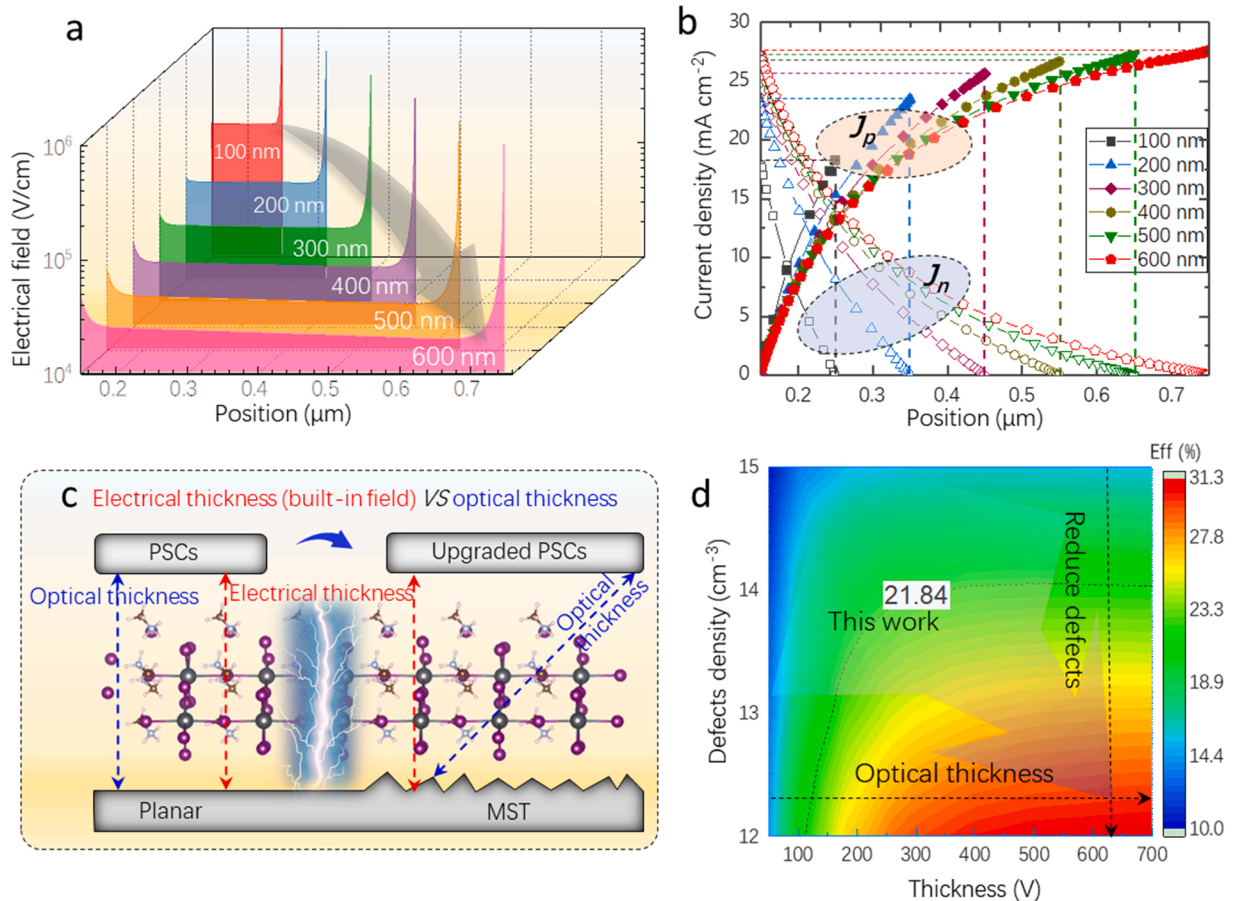


**Fig. 6.** Numerical understanding and designing for high performance PSCs. (a) Electrical field and (b) the current density within the perovskite photoabsorber. The thickness of the perovskite layer varies from 100 to 600 nm. (c) Schematic illustration for the optimization of the optical and electrical thickness in the PSCs. (d) *PCE* mapping as a function of defect density and optical thickness.

perovskite photoactive layer (Fig. 6d). This result shows that, as expected, the defects are the key factor that determines the *PCE*; while fine-tuning the thickness without sacrificing the optical absorption is also an effective way to improve device performance. The *PCE* can approach 30% when the defect density is lower than  $10^{13} \text{ cm}^{-3}$  and the optical thickness is higher than 400 nm, which indicates that reducing defects and managing light absorption are promising optimization strategies.

### 3. Conclusions and perspectives

Developing photo-electrical synergetic enhancement is one of the main challenges for next generation high performance PSCs. Herein we explored an upgraded MST-PSCs by integrating the MST light-harvesting substrates and multifunctional  $\text{TiN}_x$  IML to achieve this goal. Both experimental and theoretical simulation results show that the MST-substrate has a large haze factor that scatters the incident light and increases photon absorption in PSCs. Moreover, we addressed one of the most significant issues for obtaining commercial grade high performance MST-PSCs: achieving cascade energy levels and defect- and shunt-path free hetero-interfaces by the  $\text{TiN}_x$  IML to minimize interface recombination. The concurrent enhancement in optical and electrical properties yields an excellent *PCE* of 21.84% for  $\text{MAPbI}_3$  solar cells, which is 11.7% higher compared to standard  $\text{MAPbI}_3$  cells. In addition, by using numerical simulations we also propose approaches for further enhancing the efficiency (*PCE* > 30%) of PSCs.

As an extra perspective, we have shown that combining “*light management + interface engineering*” is a very promising approach for fabricating PSCs towards achieving >30% efficiency by relaxing the trade-off between optical enhancement and interface recombination losses. Next, the metal nitrides as interface modification layer (or even charge transport layer) of the PSCs, may have greater application potential than currently used metal oxide layers because of the inherent high-conductivity and the passivation capability for perovskites, which are provided by the lone pair electron of the N atoms. Finally, we hope our exploration on the light management and interface engineering of PSCs can be a reference toward developing high efficiency devices and trigger more effective approaches to realize versatile high performance photovoltaic devices.

### CRedit authorship contribution statement

**Fengyou Wang:** Conceptualization, Methodology, Writing. **Xin Li:** Data curation, Writing – original draft. **Jinyue Du:** Data curation, Writing – original draft. **Hui Duan:** Data curation. **Haoyan Wang:** Data curation. **Yue Gou:** Data curation. **Lili Yang:** Writing – review & editing. **Lin Fan:** Investigation. **Jinghai Yang:** Supervision, Validation. **Federico Rosei:** Writing – review & editing, Supervision.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2021.106765.

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