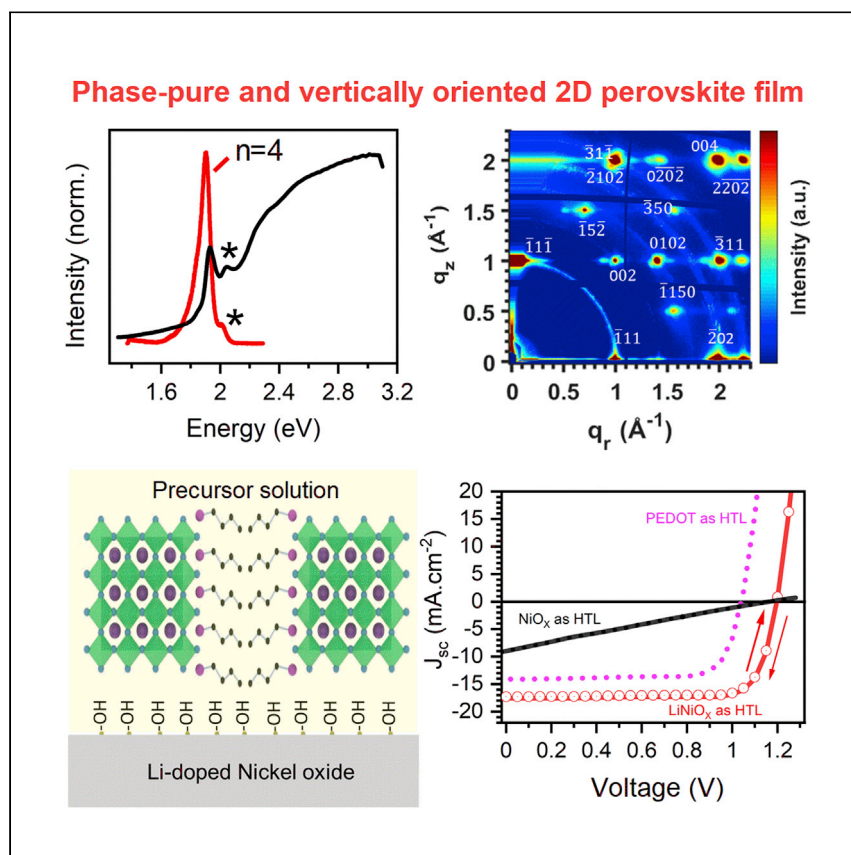


Article

High-phase purity two-dimensional perovskites with 17.3% efficiency enabled by interface engineering of hole transport layer



Sidhik et al. report a high-efficiency 2D hybrid perovskite solar cell with an open circuit voltage of 1.22 V by using Li-doped nickel oxide as the hole transport layer with a phase-pure vertically oriented thin film.

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Highlights

High-phase purity 2D perovskite films with near-perfect vertical orientation

Lithium doped nickel oxide as HTL improves the 2D perovskite film quality

High efficiency of 17.3% enabled by an open circuit voltage of 1.22 V

Enhanced stability with $T_{99} = 400$ h at 1 sun and T_{90} of 100 h at 5 suns



Article

High-phase purity two-dimensional perovskites with 17.3% efficiency enabled by interface engineering of hole transport layer

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SUMMARY

State-of-the-art p-i-n-based 3D perovskite solar cells (PSCs) use nickel oxide (NiO_x) as an efficient hole transport layer (HTL), achieving efficiencies >22%. However, translating this to phase-pure 2D perovskites has been unsuccessful. Here, we report 2D phase-pure Ruddlesden-Popper BA₂MA₃Pb₄I₁₃ perovskites with 17.3% efficiency enabled by doping the NiO_x with Li. Our results show that progressively increasing the doping concentration transforms the photoresistor behavior to a typical diode curve, with an increase in the average efficiency from 2.53% to 16.03% with a high open-circuit voltage of 1.22 V. Analysis reveals that Li doping of NiO_x significantly improves the morphology, crystallinity, and orientation of 2D perovskite films and also affords a superior band alignment, facilitating efficient charge extraction. Finally, we demonstrate that 2D PSCs with Li-doped NiO_x exhibit excellent photostability, with T₉₉ = 400 h at 1 sun and T₉₀ of 100 h at 5 suns measured at relative humidity of 60% ± 5% without the need for external thermal management.

INTRODUCTION

Organic-inorganic hybrid perovskites have gained a great deal of attention in the field of photovoltaics due to the rapid increase in efficiency from 3% to 25%.¹ The state-of-the-art p-i-n based three-dimensional (3D) perovskite solar cells (PSCs) achieve high efficiencies by using a nickel oxide (NiO_x) or lithium (Li)-doped NiO_x hole transport layer (HTL) with high-charge carrier mobility, desired wettability, and enhanced stability.^{2–5} However, the 3D perovskites lack long-term intrinsic stability. Several strategies have been implemented to improve stability, including replacing the methylammonium cation with multicomponent cation-based perovskites such as formamidinium, methylammonium, and cesium cation or adding interfacial barrier layers between the perovskite absorber and the transport layers.^{6–9} The introduction of 2D Ruddlesden-Popper perovskites with the general formula (RNH₃)₂A_{n–1}M_nX_{3n+1}, where RNH₃ represents the bulkier alkyl ammonium cation, A stands for smaller organic or alkyl metal cation, M and X represent the group IVA metal cation and the halogen, and n is an integer that represents the number of the perovskite slabs sandwiched between the bulky ammonium bilayers, indicating the purity of the 2D perovskites.^{10–12} Recent work on 2D PSCs has shown that they not only inherit the attractive physical properties of 3D but also possess a

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superior intrinsic stability.^{10,13–15} However, the 2D perovskites still lag in efficiency as compared to their 3D counterpart due to two key limitations. First, despite the near-perfect vertical orientation of the 2D layers, the charge transport is limited by the recombination of carriers at the organic-inorganic interfaces due to the imperfect crystal packing in thin films resulting in field-dependent transport.¹³ This places an upper limit on the thickness of the 2D film (~220 nm) resulting in inefficient light absorption in comparison with a 3D perovskite film with >500 nm thickness.^{16–18} Second, thin films exhibit heterogeneity in the layer thickness (also known as phase purity or *n*-value), which has been shown to result in losses in the overall open circuit voltage because the photogenerated charge carrier funnels to the lowest energy level. As a result, the majority of p-i-n-based 2D perovskite photovoltaic devices have been fabricated on PEDOT: PSS (poly 3,4-ethylene dioxythiophene: poly 4-styrene sulfonate), which typically yields an open circuit voltage of 1 V due to the lower ionization energy (IE) of the 2D perovskites and significant interfacial recombinations due to ionic interaction and inferior crystallinity of perovskites on PEDOT.^{11,13,19,20} There have also been reports on using alternative organic HTLs, such as poly (triarylamine) (PTAA); however, its hydrophobicity makes wetting of the perovskite solution difficult.²¹ Beyond the organic HTLs, there have been very few reports on using inorganic HTLs such as NiO to produce stable 2D PSCs. These devices also show relatively low efficiencies, which were attributed to the increased resistance of 2D perovskites with the NiO_x HTL.^{22,23} In addition, these devices used a 2D perovskite thin film with a mixture of 2D and 3D phases, making it challenging to understand the interfacial characteristics between the 2D perovskite and the inorganic HTL.^{22,23}

In this work, we show that by using Li-doped NiO_x as an HTL in combination with high-phase purity (~97%) BA₂MA₃Pb₄I₁₃ 2D perovskites, we can tailor the film crystallinity, orientation, and energy level alignment to achieve a solar cell with a champion efficiency of 17.3%. The higher efficiency was enabled by a high V_{OC} of 1.22 V resulting from the high-purity 2D perovskite, which lends a homogeneous energy landscape (~97%) with a negligible contribution from impurities (higher *n* values). External quantum efficiency (EQE) measurements show that the contribution of impure phases is 0.6 mA/cm², which is <5% of the total J_{SC}, also consistent with the phase purity obtained from absorbance and X-ray diffraction (XRD) measurements.^{12,23} Analysis of the photovoltaic devices revealed that with increasing Li doping concentration in the NiO_x, the behavior transformed from a linear photoresistor (average PCE = 2.53%) to a diode curve (average PCE = 16.03%). Comparison of grazing incidence wide-angle X-ray scattering (GIWAXS) measurements performed on PEDOT: PSS and Li-doped NiO_x revealed a drastic improvement in the morphology and crystallinity, along with a near-perfect vertical orientation of the 2D perovskite thin films grown on Li-doped NiO_x, thereby enabling efficient charge transport and extraction. Photoemission spectroscopy indicated that the Li doping in NiO_x results in a shallower VBM, resulting in a better energy alignment between the VBM of the 2D perovskite and that of the Li-doped NiO_x, which was further validated by observing a 2-fold quenching of the PL signal compared to bare NiO_x substrate. Finally, the use of a stable Li-doped NiO_x HTL further accentuates the stability of 2D perovskites and results in excellent stability with almost no degradation (T₉₉ = 400 h) at 1 sun and a T₉₀ of 100 h at 5 suns measured at 60% ± 5% relative humidity at maximum power point (MPP) tracking without any external thermal management. These results demonstrate that by combining an appropriate HTL with high-phase purity 2D perovskites, one can realize high-efficiency solar cells without compromising operational stability. We anticipate that this work will lay the foundation for a 2D perovskite photovoltaic technology, with efficiencies that are on par with 3D perovskites but much superior stability.

RESULTS AND DISCUSSION

Fabrication and characterization

The NiO_x films were fabricated following a previous report with small modifications,²⁴ in which the precursors are dissolved in anhydrous ethanol for 3 h for pristine NiO_x and 12 h for Li-doped NiO_x, followed by spin coating on the substrate and sintering at 450°C for 30 min. The 2D perovskite solution of BA₂MA₃Pb₄I₁₃ was prepared by dissolving the synthesized high-purity crystals in dimethylformamide (DMF) with 5 wt% methylammonium chloride (MACl) for 6 h at 70°C (Figure S1). Following this, the 2D perovskite films were fabricated by a single-step process detailed in the Method details.

Figure 1 describes the surface chemistry, thin-film morphology, and spectroscopic characteristics of the fabricated NiO_x HTLs and the 2D perovskite, BA₂MA₃Pb₄I₁₃. The surface energy of the underlying NiO_x HTL plays a major role in controlling the morphology of 2D perovskite film. Contact angle measurements were performed by drop casting the 2D perovskite solution onto the Li-doped and pristine NiO_x surfaces. The Li-doped NiO_x showed enhanced wettability compared to the pristine NiO_x film (Figures 1A and 1B). This indicates that the introduction of Li in the NiO_x HTL increases the surface energy of the NiO_x substrate and leads to improved interfacial properties of the 2D perovskite film, which is studied in detail using the X-ray photoelectron spectroscopy (XPS) measurements. The Ni 2p_{3/2} spectra of the NiO_x and Li-doped NiO_x are presented in Figures 1C and 1D. The deconvolution of the Ni 2p_{3/2} binding energies in the NiO_x can be fitted to NiO (Ni²⁺, 853.4 eV), Ni₂O₃ (Ni³⁺, 855.7 eV), and a shake-up satellite peak (861.02 eV). The Li-doped NiO_x shows an additional peak of Ni(OH)₂ (856.8 eV) attributed to the adsorption of H₂O due to the presence of Li in the film.²⁵ The ratio of the integrated area of the Ni²⁺/Ni³⁺ bonding states was observed to increase from 0.6 to 1.05 with the introduction of Li in the NiO_x, resulting in an improved conductivity.^{26–29} The O 1s XPS spectra are depicted in Figure S2. The deconvolution of the O 1s peaks can be fitted to the lattice oxygen (529.38 eV) and oxygen vacancies (531.38 eV).³⁰ With the introduction of Li in the NiO_x, we observed an additional peak at 530.3 eV, which can be assigned to the interaction of Li with the oxygen (Li-O).^{26,28} In addition, the Li-doped NiO_x consists of adsorbed O or H₂O (533.0 eV) on the surface. The presence of these –OH groups on the surface of Li-doped NiO_x makes it superhydrophilic, which is also verified by the contact angle measurements (see Figure 1B). In addition, we observed a slight increase in the O vacancies, which may be due to the intercalation of Li in the NiO_x lattice.^{25,27} Furthermore, to visualize the morphological characteristics of the fabricated films, we performed atomic force microscopy (AFM) and scanning electron microscopy (SEM) measurements. The root-mean-square (RMS) roughness of the NiO_x surface increased from 5.3 to 6.3 nm, with a slight increment in the grain size, following the introduction of Li (Figure S3). After depositing the 2D perovskite film on top of both the NiO_x surfaces, we measured the cross-sectional SEM image, which indicates similar thicknesses of the 2D perovskite film (~200–250 nm) (Figures 1E and 1F). The 2D perovskite films grown on top of the Li-doped NiO_x surfaces appear to be bulk-like, with few grain boundaries. In contrast, films on the pristine NiO_x surface nucleate with several significantly large densities of grain boundaries and non-uniform cross-sections, which were also confirmed by the surface SEM and AFM measurements (Figures 1G, 1H, and S4). We obtained an ultra-smooth film on top of Li-doped NiO_x (RMS roughness = 3.9 nm) as compared to the one grown on pristine NiO_x (RMS roughness = 8.3 nm), enabled by the superhydrophilic nature of the Li-doped NiO_x substrate increasing the adhesion with the perovskite solution.^{31–34} The optical

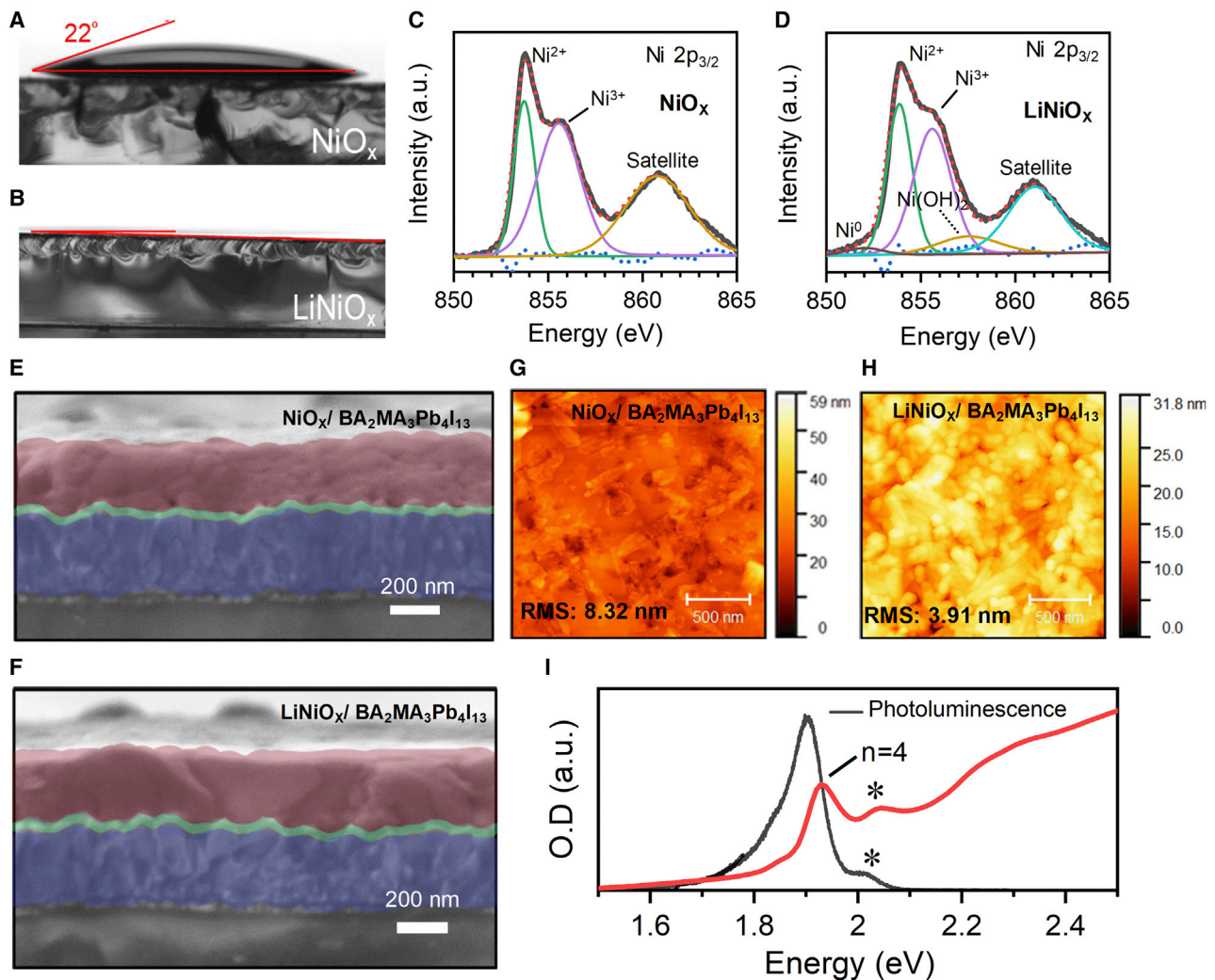


Figure 1. Morphological and spectroscopic characteristics of the 2D perovskite film on NiO_x

(A and B) Contact angle measurement showing wettability of (A) pristine NiO_x surface and (B) Li-doped NiO_x surface.

(C and D) Deconvolution of the $\text{Ni } 2p_{3/2}$ spectra of the NiO_x and Li-doped NiO_x films indicating the Gaussian fitted peaks of different oxidation states of Ni. The dotted red line indicates the fitted $\text{Ni } 2p_{3/2}$ spectra, and the dotted blue line denotes the residual spectra.

(E and F) Cross-sectional scanning electron microscopy image of the 2D perovskite films grown on top of the NiO_x (E) and (F) the LiNiO_x surface, indicating the variation in morphology.

(G and H) Atomic force microscopy image of the fabricated $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D perovskite film on the NiO_x - and Li-doped NiO_x surface for evaluating the root-mean-square roughness.

(I) Absorption characteristics of the $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D perovskite film. The star symbol represents the $n = 3$ impurity peak in the film. No notable variation in the absorption was observed in the 2 samples under study.

absorbance characteristics of $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D perovskite thin-film fabricated on both the NiO_x substrate showed no clear distinction and are depicted in Figure 2I. We directly compared the absorption spectra of 2D perovskite thin films with the 2D perovskite crystals of $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ (see Figure S5), which shows a dominant $n = 4$ phase with a small $n = 3$ impurity and negligible higher-order impurities. The percentage of phase purity was evaluated by normalizing the thin film absorption with its absorption coefficient reported by Song et al.,³⁵ and was found to be $\sim 97\%$ (Figure S6). The photoluminescence (PL) spectra indicate a strong peak at 1.92 eV (644 nm) corresponding to the excitonic absorption of $n = 4$ phase, with a small shoulder (~ 2.02 eV) indicating $n = 3$ phase impurity. The degree of phase

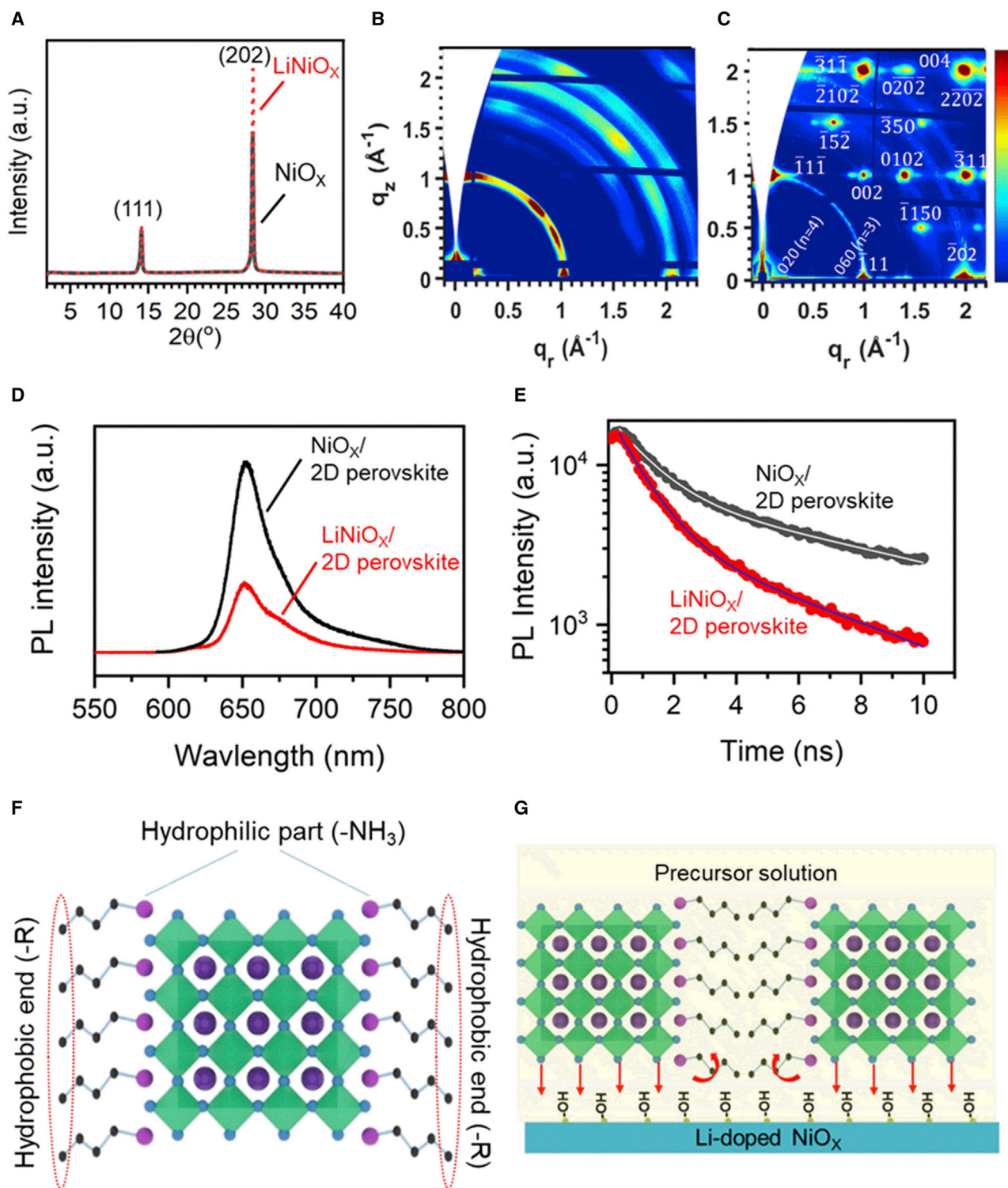


Figure 2. Orientation and interfacial characteristics of 2D perovskite on NiO_x surfaces

(A) Grazing incidence X-ray diffraction measurement of the $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ perovskite film grown on the 2 surfaces under investigation showing the variation in orientation.

(B and C) GIWAXS 2D diffraction pattern of the $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D perovskite film fabricated on the pristine NiO_x -doped (B) and (C) the Li-doped NiO_x .

purity was further confirmed by abrading the thin films and measuring the XRD pattern of the powder (see Figure S7). To understand the mechanism that leads to high-phase purity 2D perovskite, we performed *in situ* XRD measurement on the thin films during their growth, as illustrated in Figure S8.

This was performed by spin coating the 2D perovskite $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ precursor solution on a glass slide, which was kept at room temperature without annealing to slow down the kinetics of nucleation and film formation. The evolution of the XRD pattern was monitored for 80 min immediately after spin coating. The diffraction peaks corresponding to different phases of 2D perovskite were identified and monitored as a function of time. We observed a peak at $q = 1 \text{ \AA}^{-1}$ after 1 min, indicating the formation of a perovskite phase, after which the 2D perovskite peaks start evolving. After a few minutes, the $n = 3$ phase forms rapidly and over time transforms into the thermodynamically stable $n = 4$ phase (ΔG transformation of $n = 3$ to $n = 4$ is negative) by using the existing or unused precursor solution,³⁶ which can be verified by the increase in peak intensity of the $n = 4$ phase, following a decrease in the $n = 3$ phase. This method bypasses the intermediate gel stage, which is usually observed in all of the perovskite film formation techniques, hence avoiding broad phase distribution.^{16,17,37}

The crystallinity of the 2D perovskite films was analyzed using grazing incidence X-ray diffraction (GIXRD) (Figure 2A). We observed two dominant diffraction peaks at 14.16° and 28.38° corresponding to the (111) and (202) planes. The full width at half-maximum (FWHM) of the (202) plane reduced from 0.26 for the pristine NiO_x to 0.22 for Li-doped NiO_x , indicating an increase in the correlation length and thus an enhancement in crystallinity of the perovskite film grown on top of the Li-doped NiO_x HTL. We also observed a preferential orientation in the (101) plane confirmed by the increased intensity of the (202) diffraction peak with respect to the (111) peak. The considerable variation observed in the orientation of the 2D perovskite film between the pristine and Li-doped NiO_x HTLs motivated an in-depth 2D crystallographic measurement using GIWAXS presented in Figures 2B and 2C. The GIWAXS pattern was analyzed and indexed depicting the presence of $n = 3$ and $n = 4$ phases with a negligible amount of higher-order n -values in the film, matching well with the absorption spectra. However, the two scattering patterns showed a striking difference in orientation. The 2D perovskite film fabricated on the pristine NiO_x exhibited halo rings, which depict the random orientation of the 2D perovskite slabs within the grains of the polycrystalline film (Figure 2B). In contrast, the films grown on top of Li-doped NiO_x showed near-circular discrete Bragg spots along the same ring, indicating preferential orientation (Figure 2C). Moreover, the presence of prominent (111) and (202) reflections in the q_r direction indicate a strongly preferred vertical orientation.¹³ An azimuthal angle-dependent intensity integration of the GIWAXS for the (111) diffraction peak ($q = 1.0 \text{ \AA}^{-1}$) corroborates the strong preferred orientation of the 2D film on the Li-doped NiO_x HTL compared to the pristine HTL (Figure S9). The reduction in the FWHM and mosaicity evaluated from the angular profile of the (111) diffraction peak (in the Li-doped NiO_x 2D film) is associated with an increase in correlation lengths as shown by the GIXRD measurements (Figures S9 and S10). To further verify the quality of the 2D perovskite

(D) Photoluminescence measurement to probe the bulk of the 2D perovskite film grown on the 2 NiO_x surfaces to evaluate the charge transfer phenomenon.

(E) The time-resolved photoluminescence spectra of the 2D perovskite film grown on top of the 2 NiO_x surfaces to extract the charge carrier lifetime to elucidate the charge transfer to the HTL.

(F) Schematic representation of $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ molecular seed with PbI_2 octahedra and the butylammonium molecule.

(G) Schematic showing the orientation of the $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ film on the Li-doped NiO_x substrate.

film and elucidate the charge transfer mechanism in both films, we performed a series of PL and time-resolved PL measurements. The PL intensity measured for both the 2D perovskite films (without the electron transport layer and the metal contact) is presented in Figure S11A. The PL peak observed at 750 nm corresponds to the edge states or lower energy states, which were probed at a lower fluence of 1 sun ($100 \text{ mW} \cdot \text{cm}^{-2}$).^{14,38} At lower fluences, all of the excitons primarily decay by populating the lower energy states. It has been reported that the lower energy states are surface localized in vertically oriented films, while they are distributed in the bulk of the film in a randomly oriented film.³⁸ The $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D perovskite film fabricated on top of Li-doped NiO_x yields much stronger PL intensity as the excitons can diffuse to the surface and efficiently transfer their energy in a near-single crystalline out-of-plane oriented film. Our recent result shows the exciton diffusion length of 100 nm in a near-single crystalline vertically oriented film.³⁹ In contrast, the film on top of bare NiO_x , shows a more random orientation giving lower PL emission intensity, presumably due to non-radiative recombination resulting from exciton dissociation at the organic-inorganic interfaces distributed in the film. Hence, this PL measurement probes the quality of the 2D perovskite surface that is used for charge dissociation in optoelectronic devices. Also, the redshift in the PL can be caused by the larger grain size verified by the morphological characterization.^{39–41} Furthermore, we performed time-resolved PL (TRPL) measurements to quantify the carrier lifetime of these edge states in both films (Figure S11B). The obtained TRPL curves are fitted with a tri-exponential decay model to extract the carrier lifetime. Table S1 presents the fitted parameters of the tri-exponential fit of the TRPL decay, in which τ_1 , and τ_2 correspond to two types of trap-assisted recombination, and τ_3 is ascribed to the radiative recombination process in the perovskite grains. We observed a significant increase in the average carrier lifetime from 2.72 to 19.72 ns for the 2D perovskite films grown on top of Li-doped NiO_x HTL, indicating a reduction in non-radiative recombination on the 2D perovskite surface.

We further increased the fluence to probe the dominant $n = 4$ phase in the $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D perovskite film. The PL consists of a dominant $n = 4$ phase ($\sim 653 \text{ nm}$), small $n = 3$ impurity ($\sim 620 \text{ nm}$), and a decaying tail in the near-infrared region (NIR), which can be assigned to edge states or higher-order states (see Figure 4D). We observed a significant quenching in the PL intensity of the $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D perovskite fabricated on Li-doped NiO_x when compared to the bare NiO_x as HTL. This phenomenon indicates an efficient charge transfer from the bulk of the 2D perovskite to the Li-doped NiO_x caused due to the reduced surface charge trapping. The time-resolved PL measurements were conducted with an excitation wavelength of 500 nm. Table S2 summarizes the fitting parameters of the TRPL decay for both samples. The Li-doped $\text{NiO}_x/\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ sample shows a decay time of 6.97 ns, whereas the $\text{NiO}_x/\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ sample showed a longer decay time of 16.29 ns, indicating that the Li-doped NiO_x has faster and more efficient hole extraction capabilities than the bare NiO_x , which significantly increases the current density and fill factor (FF) of the solar cells^{42–44} (see Figure 4E).

The remarkable change in the morphology, crystallinity, and orientation of the 2D perovskite film can be attributed to the strongly hydrophilic nature of the Li-doped NiO_x caused by the hydroxyl ($-\text{OH}$) groups present on the surface. Similar results were reported by Kim et al.⁴⁵ for the MAPbI_3 film, in which they intentionally introduce the $-\text{OH}$ groups on the NiO_x substrates to make the film hydrophilic. The reduced Gibbs free energy for hydrophilic surface results in several nucleation centers, owing to accelerated nucleation kinetics and grain boundary formations.^{46–48} At this point in our single-step deposition (immediately after spin coating), the

perovskite grains will be small but densely packed. As we are not using an antisolvent method or a hot casting approach, the light-brown 2D perovskite film contains residual DMF. As a result, upon thermal annealing, the perovskite grains further redissolve and coalesce together to form large grains with enhanced crystallinity, similar to the Ostwald ripening process observed in the post-annealing treatment by isopropyl alcohol.^{27,49} However, a relatively less hydrophilic surface leads to few nucleation centers,⁴⁵ and the perovskite grains are not packed enough to grow into a larger grain during the annealing process as verified by the AFM and SEM images (see Figures 1G, 1H, and S4).

The preferential out-of-plane orientation observed on the Li-doped NiO_x substrate was attributed to the presence of –OH groups on the surface. In a 2D perovskite, the polar (–NH₃) group is attached to the lead iodide slabs and the hydrophobic alkyl groups protrude out (see Figure 2F). As a result, when a solution containing the 2D perovskite slabs is introduced on a superhydrophilic Li-doped NiO_x, the PbI₂ octahedra have more affinity to bind on the surface, while the hydrophobic long alkyl chain tries to stay well inside the solution, inducing an out-of-plane orientation⁵⁰ (see Figure 2G). This mechanism was also verified for lower *n* values (*n* < 4), which have a natural tendency to orient horizontally (along the stacking axis).¹⁶ We could achieve a preferential vertical orientation depicted by strong (111), (202) peaks and the missing low-angle peaks (see Figure S12). Hence, in a single-step deposition technique, a hydrophilic surface leads to the formation of dense, compact, crystalline, and oriented 2D perovskite films.

Device evaluation

Considering the drastic change in morphological, orientation, and interfacial characteristics of the 2D perovskite film fabricated on Li-doped NiO_x, we fabricated a p-i-n junction photovoltaic device, FTO/NiO_x/BA₂MA₃Pb₄I₁₃/PCBM/Ag with varying doping levels of Li. The fabricated devices with pristine NiO_x as the HTL exhibited a highly resistive behavior under light, having an average efficiency of 2.5% ± 0.5% corresponding to a FF of 27.32% ± 1.0% (Figures 3A, 3B, and S13). We also tested the hot casting approach for growing 2D perovskite film on the pristine NiO_x, which also resulted in a resistive J-V characteristic (Figure S14). Furthermore, we fabricated a series of 2D PSCs with Li-doped NiO_x as the HTL. Figure 3A depicts the variation in the power conversion efficiency (PCE) of the 2D PSCs with varying doping levels of Li salt from 0 mol% to 10 mol%. A large improvement in the average device performance from ~2.53% to ~16.03% was observed with an increase in the doping concentration (0 to 10 mol%), with the greatest improvements observed in the FF and the current density (*J*_{SC}) (Figure S13). The corresponding J-V characteristics are depicted in Figure 3B. The champion device with Li-doped NiO_x (10 mol% Li doping) as the HTL exhibited a PCE of ~17.3% (*J*_{SC} = 17.04 mA · cm⁻², *V*_{OC} = 1.22 V, and FF = 83%) corresponding to a major increase in the FF and the *J*_{SC} (Figures 3C and S9C). These devices showed negligible hysteresis verified by the J-V characteristics measured under different scan directions and scan speeds (Figures 3C and S15). The champion PEDOT: PSS device gave an efficiency of 13.2% corresponding to a *V*_{OC} of 1.05 V and FF of 77.0%. The considerable increase in *V*_{OC} observed for the NiO_x-based 2D PSCs can be attributed to improved band-level alignments. The EQE of the best device is presented in Figure 3D. The average EQE is in good agreement with the *J*_{SC} extracted from the J-V characteristics, with a <5% difference arising from a slight spectral mismatch between the two sources. In addition, the EQE shows a small photogeneration in the NIR below the band gap of *n* = 4 2D perovskite of 1.85 eV. This corresponded to a current density of 1 mA · cm⁻² arising from the impurities within the film, which is merely 5.6% of the total *J*_{SC} of 17.04 mA/cm².

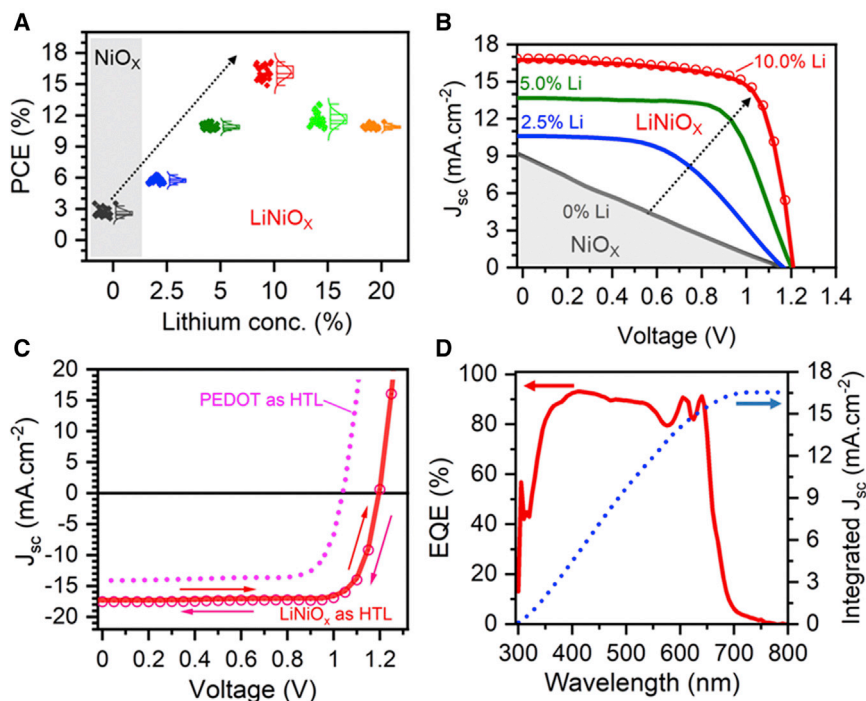


Figure 3. Photovoltaic characteristics of the 2D perovskite solar cell with the NiO_x HTL

(A) The statistics showing the change in the power conversion efficiency of the 2D perovskite solar cell fabricated on NiO_x with varying levels of Li doping.

(B) J-V characteristics of the fabricated 2D perovskite device with varying levels of Li doping.

(C) J-V characteristics of the champion device fabricated on Li-doped NiO_x and PEDOT:PSS as an organic HTL. The arrows indicate the scanning direction, and the characteristics exhibit negligible hysteresis behavior.

(D) The external quantum efficiency (EQE) of the champion 2D perovskite device fabricated on top of Li-doped NiO_x.

To further understand the substantial increase in PCE, we studied the electronic characteristics of the NiO_x and Li-doped NiO_x HTLs using correlated optical and electronic measurements. This enables the evaluation of the relative change in conductance and measurement of the variation in band levels in the device architecture. We measured the *I*-*V* characteristics of the NiO_x films (with varying concentrations of Li-doping) spin coated on top of the fluorine-doped tin oxide (FTO) and sintered, with a top metal contact (Ag). Compared to the pristine NiO_x, we observed an increase in conductance (more than a factor of 2) with the introduction of 10% Li (Figure 4A). Upon further increase in the doping (15, 20 mol%), the conductance is substantially reduced, indicating that the excess Li⁺ may act as scattering centers for charges. Figure S16 shows the *T*_{auc} plot calculated from the absorbance of the corresponding films, where we observed a reduction in band gap from 3.7 to 3.6 eV with the introduction of 10% Li in the NiO_x film. The Li-induced change in energy of the NiO_x VBM with respect to the vacuum level (i.e., the IE) was measured using ambient photoemission yield spectroscopy (PYS; see Method details). Ultra-high vacuum measurements using ultraviolet (UV) photoemission spectroscopy (UPS) were also performed. The NiO_x IE was observed to decrease from 5.22 to 5.10 eV with ambient photoemission and from 5.0 to 4.8 eV with UPS upon Li doping (Figure 4B). This result is consistent with our previous theoretical prediction indicating that Li doping pushes NiO_x states to a better band-level alignment with the perovskite states at the VBM.⁵¹ Most important, we observed a shift of the NiO_x Fermi level toward the VBM by ~0.18

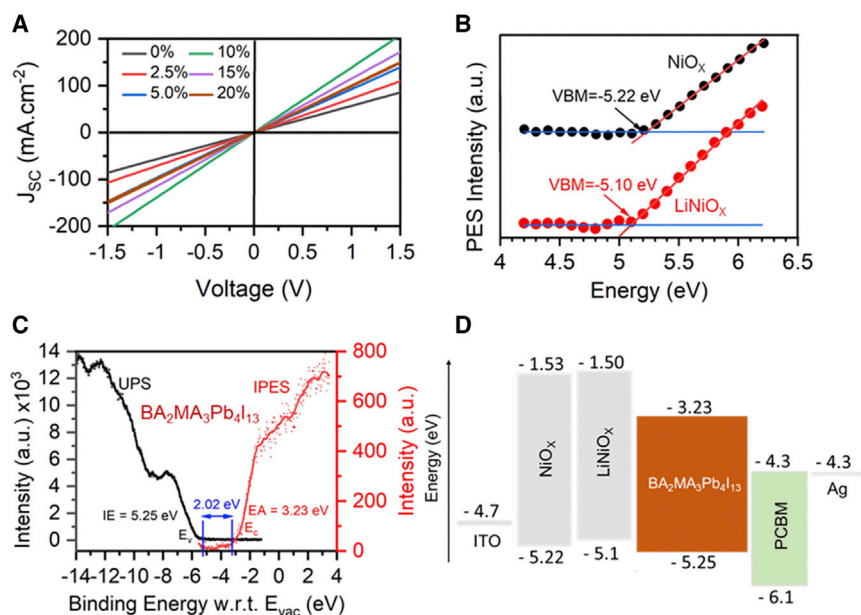


Figure 4. Electronic characteristics of 2D perovskite solar cell with pristine and Li-doped NiO_x

(A) Current-voltage characteristics of the NiO_x film, with varying doped Li levels indicating an increase in conductance verified by the change in the slope of the curve.
 (B) Plot showing the variation in the position of the valence band maximum (VBM) with respect to the vacuum level (i.e., ionization energy [IE]) of the 2 NiO_x surfaces obtained by photoemission yield spectroscopy (PYS).
 (C) Plots showing the determinations of the electron affinity (EA) by inverse photoemission spectroscopy (IPES) and the extracted VBM w.r.t. the vacuum level (i.e., IE) by ultraviolet photoemission spectroscopy (UPS) of the high purity BA₂MA₃Pb₄I₁₃ 2D perovskite film. The Fermi level reference for both UPS and IPES was determined on a clean Au surface.
 (D) Band diagram of the solar cell assumed from measured energy levels and work functions of various constituents, showing probable charge extraction paths.

eV, from 0.78 eV in the pristine NiO_x film to ~0.6 eV in the Li-doped NiO_x film, consistent with the rise in NiO_x conductance (Figure 4A) due to increased p-type doping achieved by Li incorporation (see Figure S17). Furthermore, we extracted the VBM with respect to the vacuum level (i.e., IE of the high-purity BA₂MA₃Pb₄I₁₃ 2D perovskite film using the UPS), and the electron affinity (EA) using the inverse photoemission spectroscopy (IPES) (Figures 4C and S18). The Fermi level reference for these combined UPS and IPES experiments was determined on a clean Au surface. Using these results, an energy diagram representing the solar cell architecture with the band energies evaluated is presented in Figure 4D. As one cannot measure energy-level alignment at buried interfaces, the diagram provides a view of the device's electronic structure assuming vacuum-level alignment at each interface. Nevertheless, we observe an appropriate step-like VBM alignment for the Li-doped NiO_x to the BA₂MA₃Pb₄I₁₃ 2D perovskite for efficient hole extraction through the doped, more conductive HTL, which helps in fabricating highly efficient photovoltaic devices.⁵¹

Finally, to evaluate the photostability of the device, we performed measurements under continuous light soaking with the air mass 1.5 global (AM 1.5G) filter for the 2D PSCs with Li-doped NiO_x. We recorded the variation in PCE at the MPP as a function of illumination time and light power, as illustrated in Figure 5. The devices were encapsulated using UV-curable epoxy and measured under 60% ± 5%

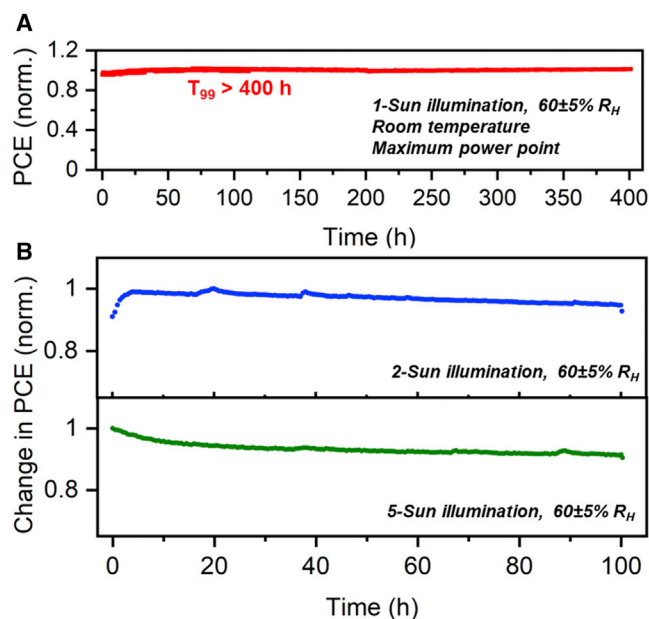


Figure 5. Photostability of 2D perovskite photovoltaic devices

(A) Photostability of 2D perovskite photovoltaic devices under continuous 1 sun ($100 \text{ mW} \cdot \text{cm}^{-2}$) illumination measured on an encapsulated device at a relative humidity of $60\% \pm 5\%$.

(B) Photocurrent stability as a function of illumination time and incident power (2- and 5-sun) measured on an encapsulated device at a humidity of $60\% \pm 5\%$.

relative humidity in the air. The device exhibits excellent stability under constant 1 sun illumination without additional UV filters showing $<99\%$ degradation for 400 h (Figure 5A). We further performed an accelerated test by monitoring the change in PCE under higher light intensities (2 and 5 suns illumination), as shown in Figure 5B. The devices exhibit a stable output for up to 5 suns illumination during the testing period. The degradation starts after several hours of light soaking for the higher intensities, most likely due to the increase in temperature of the device, which could be avoided by convective cooling of the devices. The enhanced photostability shown by the device is an indication of high-quality 2D perovskite film and its interface.

In summary, we showed a state-of-the-art Li-doped NiO_x -based $\text{BA}_2\text{MA}_3\text{Pb}_4\text{I}_{13}$ 2D PSC with a champion efficiency of 17.3%. The photovoltaic device with the pristine NiO_x showed a highly resistive behavior under light (average PCE = 2.53%), which was significantly improved with the introduction of Li (average PCE = 16.03%). The presence of Li in the NiO_x films not only improved the morphology and crystallinity of the 2D perovskite films but also altered the orientation of the 2D perovskite crystallite domains drastically. The preferred orientation has a beneficial effect on the reduction of non-radiative recombinations, leading to efficient charge carrier separation and transport. The electronic studies predicted the presence of a hole-extraction barrier between the 2D perovskite and pristine NiO_x , which was significantly reduced with the introduction of Li. In addition, we observed enhanced p-type doping in the Li-doped NiO_x , which increased the conductance of the layer significantly. The devices also showed enhanced photostability under rigorous testing conditions. This work could open up the field of 2D perovskites by providing an efficient HTL with low photovoltage losses and enhanced charge transfer characteristics. In addition, this could also provide a deeper understanding of the interface

between a pure 2D perovskite film and metal-oxide-based transport layers, which have never been studied.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Aditya D. Mohite (adm4@rice.edu).

Materials availability

This study did not generate new unique reagents.

Data and code availability

All data related to this study included in the article and [Supplemental information](#) will be provided by the lead contact upon reasonable request.

NiO_x solution preparation

The NiO_x solution was prepared by dissolving 0.1 M nickel acetate tetrahydrate and monoethanolamine (1:1) in anhydrous ethanol. The solution was left on the hot plate stirring at 70°C for 3 h. For preparing the Li-doped NiO_x solution, lithium nitrate at different mol% (2.5, 5, 10, 15, and 20) was added to the solution and left stirring at 70°C for >12 h.

2D BA₂MA₃Pb₄I₁₃ perovskite solution preparation

The perovskite solution was prepared by dissolving the synthesized 2D perovskite crystal powders of BA₂MA₃Pb₄I₁₃ in *N,N*-DMF with an additive of 5.0 wt% of MACl. The solution was aged on a hot plate at 70°C without stirring for 6 h.

Solar cell fabrication

The patterned FTO substrates were cleaned by sonicating in soap water, water, acetone, ethanol, and acetone (1:1) for 15 min each. The substrates were further dried under flowing N₂ and left under UV for 30 min. The NiO_x and Li-doped NiO_x solutions were immediately spin coated on the FTO at 5,000 rpm for 30 s, followed by 3-step annealing, 150°C for 10 min, 300°C for 15 min, and finally 450°C for 30 min. The entire fabrication process was carried out in ambient air. The sintering process at 450°C is critical for producing a highly reproducible Li-doped NiO_x film. The substrates were transferred to the Ar-filled glove box for the rest of the device fabrication process. The 2D perovskite solution was spin coated at 4,000 rpm for 30 s, followed by annealing at 100°C for 10 min. Furthermore, the PCBM solution (25 mg/mL) in chlorobenzene was spin coated at 1,000 rpm for 45 s, followed by thermal evaporation of 1 nm bathocuproine and then 100 nm Ag as the metal contact.

Ambient photoemission measurement

The VBM energy of NiO_x and Li-doped NiO_x films was measured by PES in the air (PYSAs, AC-2, Riken-Keiki). Briefly, the sample is scanned by tunable monochromatic UV light (4.2–6.2 eV), under ambient conditions, and the number of generated photoelectrons is measured at each excitation energy. Photoelectrons are only generated when the photon energy is higher than the ionization energy. The VBM is determined by finding the onset of the PYSAs spectra.

UV photoemission spectroscopy measurements

The UPS measurements were performed in ultrahigh vacuum (10⁻¹⁰ torr) at room temperature. HeI (21.22 eV) photons generated by a discharged lamp were used

to probe the work function (WF) and valence band edges. Valence band spectra were recorded and plotted on a logarithmic intensity scale due to the low density of states near the band edge. The ionization energy of the material is determined by combining the WF and valence band edge with respect to the Fermi level.

Solar cell characterization

The solar cells were characterized by taking current-voltage curves under a solar simulator with a light intensity equivalent to 1 sun ($100 \text{ mW} \cdot \text{cm}^{-2}$) with the air mass 1.5 G filter. The devices were covered with appropriate masks to reduce the error due to the edges. The EQE was measured by illuminating the active area of the device using the monochromatic light using a tungsten source (chopped at 150 Hz) while collecting the photocurrent by a lock-in amplifier in AC mode. The light source spectrum response was corrected by calibrated silicon diode (FDS1010, Thorlabs).

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2021.100601>.

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AUTHOR CONTRIBUTIONS

Conceptualization, S.S., Y.W., and A.D.M.; methodology, S.S., W.L., H.Z., X.Z., I.H., and I.S.; investigation, S.S. and Y.W.; formal analysis, S.S. and W.L.; writing – original draft, S.S. and A.D.M.; writing – review & editing, C.K., J.E., J.-C.B., A.B.M., A.K., M.G.K., A.A., B.T., M.H.K.S., and A.D.M.; supervision, J.E., M.G.K., and A.D.M.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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