Origin of the Thermal Instability in CH₃NH₃PbI₃ Thin Films Deposited on ZnO

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ABSTRACT: The rapid development of organometal halide perovskite solar cells has led to reports of power conversion efficiencies of over 20%. Despite this excellent performance, their instability remains the major challenge limiting their commercialization. In this report, we systematically investigate the origin of the thermal instability of perovskite solar cells fabricated using ZnO electron transport layers. Through in situ grazing incidence X-ray diffraction experiments and density functional theory calculations, we show that the basic nature of the ZnO surface leads to proton-transfer reactions at the ZnO/CH₃NH₃PbI₃ interface, which results in decomposition of the perovskite film. The decomposition process is accelerated by the presence of surface hydroxyl groups and/or residual acetate ligands; calcination of the ZnO layer results in a more thermally stable ZnO/CH₃NH₃PbI₃ interface, albeit at the cost of a small decrease in power conversion efficiency.

INTRODUCTION

Methylammonium lead iodide (CH₃NH₃PbI₃) and other closely related organolead halide perovskites have revolutionized the field of photovoltaics by combining high power conversion efficiencies (PCEs) with inexpensive starting materials and simple device fabrication procedures. Although initial examples of perovskite solar cells displayed relatively modest power conversion efficiencies, the development of this technology has progressed extremely rapidly. The introduction of solid-state hole conductors and optimization of the device configuration and cell components resulted in further improvements in PCE, from 15% in 2013 to over 20% today.3–11 This dramatic increase in device performance means that perovskite solar cells are rapidly becoming competitive with CdTe and multicrystalline Si technologies, suggesting their enormous commercial potential in the rapidly growing photovoltaic industry.

In these state-of-the-art perovskite solar cells, both hole- and electron-transport layers are required to selectively and efficiently extract charge carriers from the perovskite semiconductor.12,13 One of the most commonly used cell designs is produced by spin-coating a CH₃NH₃PbI₃ precursor solution onto a TiO₂ electron-transport layer, followed by thermal annealing at ca. 100 °C and subsequent deposition of a 2,2′,7,7′-tetakis(N,N-di-4-methoxyphenylamino)-9,9′-spirobi fluorene (Spiro-OMeTAD) hole-transport layer.9,14–17 In this one-step spin-coating procedure, thermal annealing is necessary in order to drive off both residual solvent and any chloride-containing precursors, and to crystallize the perovskite film. In order to reduce the processing temperature of these devices (temperatures of up to 550 °C are typically used to sinter the TiO₂ films),6,16 our group has previously employed compact films of ZnO nanoparticles as the electron-transport layer, and achieved PCEs of close to 16%.10 In the subsequent deposition of perovskite films onto these ZnO layers, a two-step deposition method was employed.8,18 PbI₃ thin films were immersed in a solution of CH₃NH₃I, converting them to the dark brown perovskite back into a bright yellow films (Figure 1). Similarly, any attempt to deposit perovskite films on the ZnO surface by a one-step spin-coating process (which necessitates thermal annealing), met with failure. This apparent thermal instability of the ZnO/CH₃NH₃PbI₃ bilayer will undoubtedly have a deleterious effect on the long-term stability of finished devices. Nominal operating cell temperatures of ca. 50 °C are common for commercially available photovoltaic modules, and in extreme environments (areas with high air temperatures and above average insolation), the temperature of an operating cell can easily exceed 85 °C. If perovskite solar cells containing ZnO electron-transport layers are to be developed for real world applications, it is imperative that the...
underlying decomposition mechanism be identified and addressed.

In this work, we use a combination of in situ absorbance spectroscopy, in situ grazing incidence X-ray diffraction (GIXRD), and Density Functional Theory calculations to elucidate the decomposition mechanism of thermally annealed ZnO/CH$_3$NH$_3$PbI$_3$ films. We show that the thermal decomposition of the perovskite film is driven by acid−base chemistry at the ZnO/CH$_3$NH$_3$PbI$_3$ interface; deprotonation of the methylammonium cation by the ZnO surface leads to the formation of methylamine and PbI$_2$. More acidic metal oxide surfaces (such as TiO$_2$ or ITO) therefore produce more thermally stable films. We demonstrate that thermally annealing the ZnO films prior to perovskite deposition eliminates basic hydroxyl groups and residual acetate ligands from the surface, ultimately leading to a substantial improvement in the thermal stability of the perovskite films.

■ EXPERIMENTAL SECTION

Film Formation. All films were deposited on glass substrates that had been cleaned by sequentially sonicating in dilute Extran 300 detergent, acetone, and isopropanol for 30 min, followed by drying in an oven at 120 °C for 2 h. ZnO/CH$_3$NH$_3$PbI$_3$ films were prepared according to the following procedures. The ZnO nanoparticle solution was spin-coated onto the glass substrate at 3000 r.p.m. for 30 s. The procedure was repeated three times to obtain a continuous smooth film. If the films were to be thermally treated, they were placed on a hot plate (with temperature ranging from 25 to 400 °C) for 30 min in a N$_2$-filled glovebox (<0.1 ppm of O$_2$ and H$_2$O). Thin film samples on glass substrates were placed directly on top of a 2.54 cm × 2.54 cm, 10 W polyimide film heater (Omega). The temperature was monitored by a K-type thermocouple (Omega) mounted directly to the sample surface with copper tape, and a proportional-integral-derivative (PID) controller used to provide temperature feedback control to the

Solar Cell Fabrication. Solar cells were fabricated on precleaned ITO-coated glass substrates with a sheet resistance of 20 Ω/□. The ZnO/perovskite film on ITO was prepared using the same procedure as listed above. The P3HT-based hole-transfer layer (20 mg of P3HT, 3.4 μL of 4-tert-butylpyridine, and 6.8 μL of a lithium-bis(trifluoromethanesulfonyl)imide (Li-TFSI) solution (28 mg Li-TFSI/1 mL acetonitrile) all dissolved in 1 mL chlorobenzene) was deposited by spin coating at 1000 r.p.m. for 30 s. Finally, a 150 nm thick silver layer was deposited by thermal evaporation at a base pressure of 2 × 10$^{-6}$ mbar. Completed devices were stored in a N$_2$-purged glovebox (<0.1 ppm of O$_2$ and H$_2$O). Prior to the evaporation of the Ag top contact, all device fabrication steps were carried out under ambient conditions.

GIXRD Measurements. GIXRD measurements were conducted at the Hard X-ray MicroAnalysis (HXMA) beamline of the Canadian Light Source (CLS). An energy of 17.998 keV (λ = 0.6888 Å) was selected using a Si (111) monochromator. GIXRD patterns were collected on a SX165 CCD camera (Rayonix) placed at a distance of 139 mm from the sample with a 30 s acquisition time. A lead beamstop was used to block the direct beam. Thin film samples on glass substrates were placed directly on top of a 2.54 cm × 2.54 cm, 10 W polyimide film heater (Omega). The temperature was monitored by a K-type thermocouple (Omega) mounted directly to the sample surface with copper tape, and a proportional-integral-derivative (PID) controller used to provide temperature feedback control to the

- DOI: 10.1021/acs.chemmater.5b01598
- Chem. Mater. 2015, 27, 4229−4236
Initially, both annealing for 5 min at successively higher temperatures. A ZnO layer. Spectra were reacquired immediately after glass substrates, both with (Figure 1a) and without (Figure 1b) experiments were replicated in the bulk, where CH₃NH₃PbI₃ of the perovskite thermal stability (Figure 1c). These and PEDOT:PSS substrates were very similar to ITO in terms degraded faster than those prepared without the ZnO layer, perovskite solar cells containing a ZnO electron-transport layer that yellow spots began to appear in ITO/ZnO/CH₃NH₃PbI₃ spectra for CH₃NH₃PbI₃ thin further probe this thermal instability, we measured absorbance after heating to temperatures as high as 200 °C with that of PbI₂ (Figure S1 in the Supporting Information). In contrast, perovskite CH₃NH₃PbI₃ appeared to be thermally stable when deposited CH₃NH₃PbI₃ and SiO₂/CH₃NH₃PbI₃ films using in situ absorption spectroscopy and an environmental chamber²⁴ with carefully controlled relative humidity (RH). The in situ absorbance data obtained at 98 ± 2% RH are shown in Figure S3 in the Supporting Information. Upon exposure to moisture, the absorption onset at 760 nm gradually disappears, along with a rapid decrease in the intensity of the high energy absorption band. The decomposition rate can be quantified by plotting the absorbance at 410 nm (where the change in absorbance is greatest) as a function of time. The normalized data (Figure 1d) indicate that rather than accelerating the decomposition of the CH₃NH₃PbI₃ film, the ZnO layer actually appears to protect the perovskite from the effect of moisture. Previous studies have shown that the CH₃NH₃PbI₃ perovskite can reversibly absorb moisture to form CH₃NH₃PbI₁·H₂O; further hydration of the film yields (CH₃NH₃)₄PbI₆·2H₂O and Pbl₂.²⁴⁻²⁶ Because the underlying ZnO film is hydrophilic, it may act to trap H₂O at the ZnO surface, dehydrating the CH₃NH₃PbI₁·H₂O that is produced on the initial absorption of water, and regenerating the dark brown CH₃NH₃PbI₃. Once the ZnO surface becomes saturated with moisture, the perovskite would be expected to rapidly decompose; however, initially this competitive dehydration process results in an attenuation of the decomposition rate, which is consistent with the data in Figure 1d. Comparing the time needed for the normalized absorbance to drop to halfway between its initial and final values (τ₁/₂), τ₁/₂ = 14.3 and 3.5 h for the SiO₂/ZnO/CH₃NH₃PbI₃ and SiO₂/CH₃NH₃PbI₁ samples, respectively.
Clearly, water vapor cannot be responsible for the reduced stability of the perovskite films deposited on ZnO. This is confirmed by thermally annealing both samples inside a nitrogen-filled glovebox; the sample deposited on ZnO again decomposes into yellow byproducts (Figure S4 in the Supporting Information).

To further elucidate the decomposition mechanism, we carried out in situ GIXRD measurements on a SiO$_2$/ZnO/CH$_3$NH$_3$PbI$_3$ thin film that was heated to 100 °C in air. The combination of a fast area detector with the high brightness of a synchrotron X-ray source allows the rapid decomposition process to be followed in real time. Snapshots of the in situ GIXRD patterns at various time points are shown in Figure 2, with the first 24 min of collected data combined into Movie S1 (shown at 85× normal speed). The amorphous glass substrate contributed to a relatively strong scattering background signal in the range of $q = 12-23$ nm$^{-1}$, where the scattering vector ($q = 4\pi\sin(\theta)/\lambda$); however, ring patterns are also observed at $q \approx 10$, 20, and 23 nm$^{-1}$, and are in good agreement with reflections from the (110), (220), and (310) lattice places of CH$_3$NH$_3$PbI$_3$. When the film was heated to 100 °C for 13 min (Figure 2b), a new feature at $q \approx 9$ nm$^{-1}$ appeared, which is consistent with reflection from the (001) planes of PbI$_2$ and in good agreement with the benchtop pXRD data (Figure S2 in the Supporting Information). After ca. 20 min, the perovskite (110) feature has completely disappeared (Figure 2d). The azimuthally integrated intensity of the in situ GIXRD data is plotted as a function of both scattering vector and time (Figure 2e). These data show that after ca. 13 min of heating at 100 °C, the features due to the perovskite disappear and are immediately replaced by those of PbI$_2$. This suggests that the perovskite decomposes into PbI$_2$ in a single step, without the formation of any intermediate phases.

Clearly, a reaction takes place between the ZnO nanoparticles and the CH$_3$NH$_3$PbI$_3$ thin film. Additionally, based on both literature reports and our own observations (Figure 1c), the same reaction does not take place on either TiO$_2$ or ITO. The contrast between ZnO and TiO$_2$ is striking; both are n-type semiconductors with very similar band structures and energies, and therefore have very similar electronic behavior. Chemically, however, the two materials are quite different; TiO$_2$ surfaces are typically slightly acidic (with isoelectric points in the range of 4–8), whereas ZnO surfaces tend to be more basic (with isoelectric points >8.7).29 This suggests that deprotonation of the methylammonium cation (which has a $pK_a$ of ~10.6)50 by the ZnO surface may be the root cause of the thermal decomposition. To validate this hypothesis, we carried out theoretical calculations on the ZnO/CH$_3$NH$_3$PbI$_3$ interface and compared them to previously reported data for the TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface.3,32

Our model ZnO/perovskite interface is based on a clean 6 × 6 × 3 wurtzite ZnO slab exposing the apolar (1010) surfaces, on which a 3 × 5 × 3 tetragonal CH$_3$NH$_3$PbI$_3$ perovskite slab exposing the (110) surface was “depotted” (Figure 3). Because of the expected flexibility of the perovskite lattice, the ZnO experimental lattice parameters were used. The two slabs are ideal in terms of lattice matching, showing a maximum lattice mismatch of only 1.7 and 2.3% on the $a$ and $b$ cell dimensions, respectively. The perovskite slab shows CH$_3$NH$_3$I terminations on both sides, which implies an interaction with the semiconductor surface mainly occurring through formation of I–M (M = Zn or Ti) chemical bonds to undercoordinated surface metal atoms and hydrogen bonds between methylammonium cations and surface oxygen atoms. Geometry optimizations performed for the ZnO/perovskite interface by scalar relativistic PBE calculations yielded an interaction energy of 19.5 eV (calculated with respect to the optimized ZnO and CH$_3$NH$_3$PbI$_3$ perovskite slabs), compared with 24.2 eV for the TiO$_2$/perovskite interface (i.e., 1.3 vs 1.6 eV under perovskite-interface bond formation). Our data therefore suggest a less effective adhesion of CH$_3$NH$_3$PbI$_3$ on ZnO compared to TiO$_2$. Most notably, inspection of the optimized ZnO/perovskite structure shows deprotonation of two surface methylammonium molecules (out of a total of 15 CH$_3$NH$_3^+$ cations located in proximity of the ZnO surface) to produce methylamine, with the released protons being adsorbed on vicinal surface oxygen atoms. An even higher number of deprotonated methylammonium molecules (4 out of 15 total) is found upon optimization of the CH$_3$NH$_3$PbI$_3$ (001) surface on ZnO. This behavior is not exhibited in the TiO$_2$/perovskite interface, for which all the methylammonium molecules retained their protons and clearly reflects the different acid–base properties of the ZnO and TiO$_2$ semiconductors.

These results support the idea that ZnO is basic enough to deprotonate the methylammonium cation; however, in order to determine whether surface hydroxyl groups or residual organic ligands influence the decomposition process, we carried out...
FT-IR spectroscopy on drop-cast ZnO films that were thermally annealed at increasingly elevated temperatures (Figure 4a). The as-prepared ZnO film exhibits bands at 3410, 1580, and 1420 cm⁻¹, which are assigned to the stretching modes of surface hydroxyl groups (3410 cm⁻¹) and residual acetate ligands (1580 and 1420 cm⁻¹) left over from the nanoparticle synthesis. When the films are annealed at successively higher temperatures, the hydroxyl stretch gradually disappears, as do the acetate stretching bands. By 400 °C, there are essentially no hydroxyl groups left on the surface, with only a small amount of the acetate ligand remaining.

The influence of this thermal pretreatment on the stability of the perovskite film was then evaluated. CH₃NH₃PbI₃ films were deposited on heat-treated ZnO films, and the ZnO/CH₃NH₃PbI₃ films were then heated to 100 °C (Figure 4b). Absorbance spectra were then acquired as a function of time (Figure S5 in the Supporting Information). For those films deposited on untreated ZnO, the first signs of degradation occur after ca. 7 min; after 15 min, a substantial amount of decomposition has occurred, in good agreement with the kinetic data acquired by GIXRD (Figure 2e). In contrast, the perovskite films deposited on preannealed ZnO retain most of their dark brown color. After 25 min of heating, the films pretreated at <200 °C are predominantly yellow, while those pretreated at 200 and 300 °C are beginning to show signs of decomposition. By 40 min of heating, only the sample pretreated at 400 °C (which contains the lowest concentration of surface hydroxyl groups and acetate ligands) has not decomposed, and its absorbance spectrum (Figure S5 in the Supporting Information) still resembles that of CH₃NH₃PbI₃ deposited directly onto glass. However, after 80 min of heating, even the sample pretreated at 400 °C begins to decompose. Increasing the temperature further (to 500 °C) results in only a modest increase in stability (Figure S6 in the Supporting Information). The rate of decomposition appears to be strongly correlated to the number of surface hydroxyl groups and residual acetate ligands that are present on the ZnO nanoparticle layer. However, as predicted by the theoretical calculations (Figure 3), even in the absence of these groups, the perovskite still appears to undergo thermal decomposition due to proton-transfer reactions taking place at the ZnO/CH₃NH₃PbI₃ interface.

Other methods of surface treatment, such as UV/ozone cleaning and soaking in dilute HCl, were explored to see whether they could also stabilize the ZnO/CH₃NH₃PbI₃ interface. Although the ZnO layer was stable to dilute HCl (Figure S7 in the Supporting Information), neither treatment was as effective as thermal annealing in stabilizing the perovskite film (Figure S8 in the Supporting Information). After 15 min of heating to 100 °C, perovskite films deposited on either the ozone or HCl-treated ZnO films had decomposed. The stability of the perovskite deposited on ozone-treated ZnO was slightly higher than that deposited on untreated ZnO (likely as a result of the removal of residual acetate ligands); however, it was still inferior to films deposited on thermally annealed ZnO. To determine whether the method of ZnO deposition has a significant effect on the stability of the ZnO/CH₃NH₃PbI₃ interface, we explored alternate methods of preparing ZnO films. A Zn film was first prepared on glass by thermal evaporation, and was then oxidized in air at 400 °C for 1 h. It was observed that CH₃NH₃PbI₃ films deposited on this substrate start to decompose after 70 min when annealed at 100 °C (Figure S9 in the Supporting Information). Given the similarity of this data to that obtained from ZnO nanoparticle films annealed at 400 °C (Figure 4), we conclude that although residual acetate ligands or surface hydroxyl groups accelerate the decomposition process, it is the basic ZnO surface that is the fundamental driver of the perovskite thermal decomposition.

Although thermal annealing of the ZnO films results in a substantial improvement in the thermal stability of the perovskite film, it is unclear what impact this annealing process has on device performance. To determine the effect of the thermal pretreatment on cell performance, we tested ITO/ZnO/CH₃NH₃PbI₃/P3HT/Ag devices with ZnO layers either deposited at room temperature or after annealing at 400 °C. Sixty devices of each type were prepared and measured. To estimate the steady-state power conversion efficiency (PCE), we obtained current–voltage curves at a relatively slow sweep rate of 0.1 V/s, and the devices were measured from forward bias (FB) to short-circuit (SC) and also from SC to FB (Figure 5a). Devices fabricated using unannealed ZnO electron-transport layers displayed noticeably higher PCEs and less hysteresis than those prepared from the annealed ZnO films.
The average PCE of the devices with unannealed ZnO layers was 10.3 ± 0.5%, with the champion device reaching a PCE of 11.4%, while the devices with thermally annealed ZnO layers displayed average PCEs of 6 ± 1% with the champion device having a PCE of 7.9% (Figure 5a and Table S1 in the Supporting Information). The IPCE spectra indicated similar current densities for the two device types (Figure 5b). Integrating the product of the IPCE spectra and the AM1.5G photon flux yields calculated short-circuit current densities of 16.6 mA cm$^{-2}$ for both devices, in reasonable agreement with the $J_{sc}$ values obtained from the $J$−$V$ curves. Because the average $J_{sc}$ and $V_{oc}$ are essentially unchanged between the two sets of devices (Table S1 in the Supporting Information), the difference in PCE is explained almost entirely by the reduction in fill factor. The fill factors of the devices with annealed ZnO layers are only two-thirds those of the analogous devices without annealing. This is at least in part due to changes in the morphology of the ZnO electron-transport layer. The ZnO nanoparticles agglomerated after annealing at 400 °C, with the particle size increasing substantially (Figure 5c, d). The minimum crystallite size (as determined from a Scherrer analysis of the pXRD data) increases from 8 to 13 nm after annealing (Figure S2 in the Supporting Information). These morphological changes result in a discontinuous ZnO film with large gaps, providing pathways to the ITO substrate beneath (Figure 5d). This in turn creates pathways for hole recombination at the ITO electrode, leading to a decrease in the shunt resistance and a drop in the power conversion efficiency. At the same time, the thermal instability of ITO also makes a substantial contribution to the overall decline in device performance; analogous experiments carried out on FTO show a less severe drop in device performance after thermal annealing of the ZnO electron transport layer (Table S1 in the Supporting Information).

■ CONCLUSION

Although the high efficiencies of perovskite solar cells give them tremendous market potential, their instability remains the single greatest barrier to their commercialization. Here, we have clearly identified the origin of the thermal instability observed in perovskite solar cells fabricated using ZnO electron-transport layers. The basic nature of the ZnO surface leads to deprotonation of the methylammonium cation, leading to loss of methylamine and the formation of PbI$_2$. The process is accelerated by the presence of surface hydroxyl groups and/or residual acetate ligands, and removal of these groups by calcination results in a more thermally robust perovskite film (albeit at the cost of a small decrease in device PCE, and a substantial increase in the required processing temperature). These results are expected to help guide the development of perovskite solar cells that are capable of withstanding even the harsh conditions and high temperatures often encountered in areas with high photovoltaic potential.

■ ASSOCIATED CONTENT

* Supporting Information

Additional experimental details, absorption spectra, pXRD data, photographs of annealed films, tabulated device performance parameters. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.Sb01598.
ACKNOWLEDGMENTS

Research described in this paper was performed at the Canadian Light Source, which is supported by the Canada Foundation for Innovation, the Natural Sciences and Engineering Research Council of Canada (NSERC), the University of Saskatchewan, the Government of Saskatchewan, Western Economic Diversification Canada, the National Research Council Canada, and the Canadian Institutes of Health Research. Technical support from HXMA beamline scientist Dr. Chang-Yong Kim is gratefully acknowledged. NSERC and the University of Saskatchewan are acknowledged for financial support. T.L.K. is a Canada Research Chair in Photovoltaics.

REFERENCES


Supplementary Information

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METHODS

Synthesis of ZnO Nanoparticles: ZnO nanoparticles were prepared by previously reported procedures.1, 2 Concisely, zinc acetate dihydrate (2.95 g, 13.4 mmol) was first dissolved in methanol (125 mL) with stirring at 65 °C. A 23 mg·mL\(^{-1}\) solution of KOH in methanol (65 mL) was then added dropwise at 60–65 °C over a period of 15 min. The solution was stirred for another 2.5 h at 65 °C. After cooling to room temperature, the supernatant was decanted and the precipitate was washed twice with methanol (2 × 20 mL). A ZnO nanoparticle solution with a concentration of 6 mg·mL\(^{-1}\) was obtained by dispersing the precipitate in n-butanol (170 mL). The solution was filtered through a 0.45 μm PVDF syringe filter.

Synthesis of CH\(_3\)NH\(_3\)PbI\(_3\) Powder: Perovskite powder was synthesized from an equimolar mixture of PbI\(_2\) and CH\(_3\)NH\(_3\)I in N,N-dimethylformamide. In a typical process, 460 mg (1 mmol) PbI\(_2\) and 159 mg (1 mmol) CH\(_3\)NH\(_3\)I were added to 2 mL N,N-dimethylformamide with constant stirring. The perovskite powder was obtained by evaporation to dryness and drying the resulting solid at 120 °C overnight.

Device Characterization: Current-voltage curves were measured inside a N\(_2\)-filled glovebox using a Keithley 2400 source-measure unit. The cells were illuminated by a 450 W Class AAA solar simulator equipped with an AM1.5G filter (Sol3A, Oriel Instruments) at a calibrated intensity of 100 mW/cm\(^2\), as determined by a standard silicon reference cell (91150V Oriel Instruments). The effective area of the cell was defined to be 0.0708 cm\(^2\) using a non-reflective metal mask. IPCE spectra were measured in air using a commercial IPCE setup (QE-PV-Si, Oriel Instruments).

Characterization: Powder X-ray diffraction was performed on a PANalytical Empyrean diffractometer configured with a copper X-ray source (\(\lambda = 1.54 \text{ Å}\)). UV-Vis absorbance spectra
were acquired on a Cary 6000i spectrophotometer. *In situ* UV-Vis measurements were made using a custom designed sample holder; the relative humidity was controlled by adjusting the relative flow rates of saturated water vapor and diluent carrier gas. FT-IR spectra were recorded in attenuated total reflectance mode using a Bruker Alpha FT-IR spectrometer. Scanning electron microscopy was carried out on a Hitachi SU8010 instrument operating at a 0.1 – 5.0 kV landing voltage.

**Figure S1.** Absorption spectra of pristine CH$_3$NH$_3$PbI$_3$ (black line) and PbI$_2$ (red line) thin films on glass.
Figure S2. Powder X-ray diffraction data. Bottom to top: Calculated patterns for tetragonal CH$_3$NH$_3$PbI$_3$ (dark red line), PbI$_2$ (dark yellow line), and ZnO (wurtzite, dark gray line). Experimental data for as-prepared ZnO nanoparticles (dark blue line), ZnO after annealing at 400 °C (purple line), perovskite powder (red line), 20:1 CH$_3$NH$_3$PbI$_3$:ZnO mixture (orange line), annealed perovskite powder (green line), and annealed mixture (blue line).
Figure S3. Absorbance spectra of (a) SiO$_2$/ZnO/CH$_3$NH$_3$PbI$_3$ and (b) SiO$_2$/CH$_3$NH$_3$PbI$_3$ films exposed to flowing N$_2$ gas at 98 ± 2% RH, with data collected at 15 min intervals.

Figure S4. Photograph of CH$_3$NH$_3$PbI$_3$ films after heating to 100 °C for 20 min inside a N$_2$-filled glovebox (< 0.1 ppm O$_2$ and H$_2$O): CH$_3$NH$_3$PbI$_3$ deposited on SiO$_2$ (left) and on SiO$_2$/ZnO (right).
Figure S5. Absorbance spectra of CH$_3$NH$_3$PbI$_3$ films deposited on thermally pre-treated ZnO layers and heated to 100 °C for (top to bottom): 0, 7, 15, 25, 40, and 80 min.
Figure S6. Photographs of CH$_3$NH$_3$PbI$_3$ films deposited on thermally pre-treated ZnO layers and heated to 100 °C for the indicated time: from left to right: pre-treated at 400, 500 °C and SiO$_2$/CH$_3$NH$_3$PbI$_3$.

Figure S7. Absorbance spectra of an as-prepared ZnO film (black line) and the same film after treatment with 1M HCl (red line).
Figure S8. Photographs of CH$_3$NH$_3$PbI$_3$ films deposited on pre-treated ZnO layers and heated to 100 °C for the indicated time (clockwise from top left): as-prepared ZnO, HCl treated ZnO, ozone treated ZnO, and SiO$_2$/CH$_3$NH$_3$PbI$_3$. 
Figure S9. Photographs of CH$_3$NH$_3$PbI$_3$ films deposited on different ZnO layers and heated to 100 °C for the indicated time (from left to right): SiO$_2$/CH$_3$NH$_3$PbI$_3$, ZnO nanoparticles (pre-treated at 400 °C) and ZnO prepared by thermal oxidation of evaporated Zn.
Table S1. Average device performance parameters. The associated uncertainties represent plus
or minus one standard deviation from the mean.

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<th>Device Structure</th>
<th># Cells</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
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<td>ITO/ZnO(25 °C)/CH$_3$NH$_3$PbI$_3$/P3HT/Ag</td>
<td>60</td>
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References