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Stability Comparison of ZnO and TiO₂-based Perovskite Solar Cells on Polymer Substrates

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Abstract: Device up-scaling and long-term stability constitute two major hurdles that the emerging perovskite solar technology will have to overcome before commercialization. Here, a comparative study was carried out between ZnO and TiO₂ electron-selective layers, two materials that allow for low-temperature processing of perovskite solar cells on polymer substrates. While the use of TiO₂ is well established on glass substrates, ZnO was chosen because it can be readily printed at low-temperature, and offers the potential for large scale roll-to-roll manufacturing of flexible photovoltaics at a low cost. However, rapid degradation of CH₃NH₃PbI₃ was observed when deposited on ZnO, therefore the influence of the perovskite film preparation conditions on its morphology and degradation kinetics was investigated. This study showed that CH₃NH₃PbI₃ could withstand higher temperature on TiO₂ than ZnO, and that TiO₂-based perovskite devices were more stable than their ZnO analogues.

Introduction

The International Energy Agency predicts that solar photovoltaics (PV) will contribute to 16 % of the global electricity generation by 2050,^[1] thereby playing a key role in the efforts to reduce carbon dioxide emissions. With power conversion efficiencies (PCE) beyond 20 %^[2] only six years after their first report,^[3] perovskite solar cells are positioning themselves as a potential contributor to the future PV solution. But, rather than competing with the well-established silicon PV technology for residential rooftop application, this promising PV thin film technology could take advantage of the low-temperature processing of perovskite materials and be effective in a wide variety of consumer driven applications. Flexible and lightweight

devices could be provided by the use of polymers as substrates. However, these attractive polymer substrates come with a low-temperature processing restriction for the metal oxide electron selective layer, which few groups have addressed so far. Recent reports show that excellent PCEs of over 12 % could be attained with a thin TiO₂ layer by means of atomic layer deposition^[4] and spin coating of a suspension of crystalline TiO₂ nanoparticles.^[5] Very recently, flexible perovskite solar cells have reached new highs with reports of 14-15 % PCEs for devices employing Zn₂SO₄ particles,^[6] surface nanostructured NiO_x,^[7] and amorphous TiO₂.^[8]

Although TiO₂ is the most commonly used material for the electron selective layer in perovskite solar cells, ZnO nanorods have been investigated as alternatives.^[9-11] The good performance of these ZnO-based perovskite devices has been attributed to effective charge collection in the CH₃NH₃PbI₃/ZnO based system^[9] and to the enhanced light harvesting provided by the nanorod arrays.^[10] Before the emergence of perovskite solar devices, conventional metal oxides such as TiO₂ and ZnO had been extensively explored as the electron-selective layer in dye-sensitized solar cells (DSCs) and organic photovoltaic devices.^[12-17] One of the advantages of using ZnO over TiO₂ as an electron transport layer lies in its higher electron mobility. ZnO exhibits an electron mobility of 200-300 cm² V s⁻¹ for the bulk material and ≈1000 cm² V s⁻¹ for single-crystal nanowires.^[18-21] This is one order of magnitude higher than TiO₂, which makes it an ideal choice for an electron-selective contact. In addition, crystalline ZnO nanoparticles can be synthesized at low temperature and ZnO thin films can be prepared by means of solution processed deposition methods that broaden their application to thermally sensitive substrates.

The first report of a flexible perovskite solar cell used ZnO nanorods grown by chemical bath deposition and obtained a PCE below 3 % on polymer substrates.^[22] In 2013, Kelly and co-workers employed an electron-selective layer, spin coated from a suspension of ZnO nanoparticles and reported a PCE of 15.7 % for devices assembled on conductive indium doped tin oxide (ITO) glass and 10.2 % on ITO coated polyethylene terephthalate (ITO-PET) substrates. This demonstrated the ability to attain high efficiencies on flexible substrates.^[11]

Another attractive property of ZnO is its ability to be printed on a variety of substrates. This property has been widely exploited by the organic photovoltaics community.^[23-25] Since ZnO layers can be readily deposited by solution processing methods, the intention here was to print ZnO on polymer substrates and move towards larger scale devices. However, concerns arose about the stability of the perovskite film on ZnO; the characteristic dark CH₃NH₃PbI₃ film turned yellow after a few

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minutes of heating to 100 °C on ZnO indicating degradation of the perovskite film. Therefore, the influence of the processing conditions on the morphology and stability of the perovskite film was investigated. Kelly and co-workers reported that the decomposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ in air was exacerbated when deposited on ZnO, and showed that the devices stored under ambient conditions (relative humidity 30–40 %; temperature 21–23 °C) rapidly degraded.^[26] The same group examined the thermal instability of $\text{CH}_3\text{NH}_3\text{PbI}_3$ when deposited on ZnO and proposed that a two-step perovskite deposition process was necessary to avoid temperature induced film degradation.^[27] Here, state-of-the-art efficiencies exceeding 10 % were attained for ZnO-based perovskite solar cells on polymer substrates by means of a one-step gas-assisted perovskite deposition method.^[28] A comparison was made between the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$ systems, which demonstrated a higher stability for the TiO_2 -based devices, and the influence of the heat treatment on the morphology and decomposition of the perovskite film examined.

Results and Discussion

Device Fabrication and Photovoltaic Performance

Previously, we developed a method to reproducibly construct TiO_2 -based perovskite solar cells on polymer substrates with efficiencies up to 12.3 %.^[5] After optimization of the titania layer thickness (70–80 nm), a PCE of 13.4 % was attained when scanning from forward bias to short-circuit (FB-SC, Figure 1a). Figure 1b shows the steady state efficiency of 12.9 % at the point of maximum power, obtained when applying a bias of

0.84 V.

Figure 1. Current density-voltage curves and photovoltaic parameters obtained when scanning from forward bias to short-circuit (FB-SC) and from short-circuit to forward bias (SC-FB) for (a) an IZO/ TiO_2 / $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Spiro-MeOTAD/Au, and (c) an IZO/5L ZnO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Spiro-MeOTAD/Au flexible

devices. Steady-state measurement obtained when applying a bias of (b) 0.84 V on the TiO_2 -based device, and (d) of 0.79 V on the ZnO-based device.

On average, devices gave an open-circuit photovoltage, V_{oc} , of 1020 ± 30 mV, a short-circuit photocurrent density, J_{sc} , of 16.8 ± 0.8 mA cm^{-2} , a fill factor, FF, of 0.69 ± 0.09 , and a PCE, of 11.8 ± 1.8 %. With the exception of the evaporated metal contact, each layer in the device was deposited by means of spin coating.

In order to develop techniques more suitable for up-scaling, ZnO was considered for the dense blocking film as it is a good candidate for roll-to-roll printing.^[25] The feasibility of the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$ system was established on small devices. The thickness and coverage of the ZnO layer were optimized to produce efficient flexible perovskite solar cells on polymer substrates. A suspension of ZnO nanoparticles, synthesized according to a published procedure,^[11] was spin coated onto an indium doped zinc oxide (IZO) coated PET substrate. The photoactive perovskite layer was deposited by means of a gas-assisted fast crystallization method,^[28] 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (spiro-MeOTAD) was used as hole transport material, and Au as metal contact. Devices with an IZO/ZnO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Spiro-MeOTAD/Au architecture were fabricated with different ZnO film thicknesses by varying the number of ZnO layer (L) deposition cycles (Experimental Section). The current density-voltage ($J-V$) curves and parameters of devices fabricated with 3L, 4L, 5L and 6L of ZnO are provided in Figure S1 (Supporting Information). For devices constructed with 3 to 5 ZnO layers, V_{oc} , J_{sc} , FF, and PCE improved with the number of deposited ZnO layers, and started to decrease after the fifth layer. The best photovoltaic performances were obtained for a device constructed with a 5L ZnO blocking film, with a V_{oc} of 988 mV, a J_{sc} of 14.7 mA cm^{-2} , a FF of 0.71, and a PCE of 10.3 %, when scanning in the FB-SC direction at a rate of 100 mV s^{-1} (Figure 1c). A steady-state measurement with an applied bias of 0.79 V gave a more accurate PCE of 9.0 % (Figure 1d). Incident photon-to-electron conversion efficiency (IPCE) curves for TiO_2 and ZnO based devices are available in the Supporting Information (Figure S2). The 5L ZnO blocking film exhibited a relatively high roughness and a film thickness varying from 40 to 80 nm, as illustrated in the FIB-SEM cross-sectional image (Figure 2) and top surface SEM and AFM images (Figure S3, Supporting Information). The root mean roughness, determined by AFM, was 11 nm on a 1×1 μm^2 section. Combined with the $J-V$ results, this analysis indicated that good coverage of the IZO-PET substrate was obtained after spin coating 5 layers of ZnO suspension, therefore the rest of the study was carried out using this optimum 5L ZnO electron-selective film.

Figure 2. FIB-SEM cross-sectional image of an IZO/5L ZnO/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Spiro-MeOTAD/Au flexible device.

Figure 3. XRD patterns of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films on IZO-PET prepared under varied annealing conditions deposited on (a) ZnO, and (b) TiO_2 . Only low angles are represented here due to a broad peak at $2\theta \approx 26^\circ$ related to the IZO-PET substrate. Full XRD patterns are available in the Supporting Information, Figures S5 and S6.

Having demonstrated that state-of-the-art flexible perovskite solar cells could be fabricated employing a ZnO electron-selective film, the impact

t of the heat treatment on the morphology of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was investigated, as well as potential pathways for the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ deposited on ZnO. Interest in this aspect was raised when transferring the protocol conventionally applied for TiO_2 -based perovskite solar cells to ZnO-based solar cells. Prolonged heating time (for instance, 10 min at 100°C) resulted in the degradation of the dark perovskite film to a yellow color (Figure S4, Supporting Information). This phenomenon was not observed on TiO_2 , thus the effect of perovskite film preparation conditions on the photovoltaic performance of the resulting devices was explored.

Perovskite Layer Heat Treatment

The XRD patterns of ZnO and perovskite films deposited on a Si wafer (Figure S5, Supporting Information) showed that the tetragonal phase of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was formed after heating for 1 min to 100°C .^[29] The perovskite films deposited on ZnO coated IZO-PET were heated to 70°C , 90°C and 110°C for 1 min, 5 min and 10 min, and XRD patterns of the resulting films were obtained (Figure 3a and Figure S6). For ease of data analysis, only low angles are reported in Figure 3a, thus removing the large peak at $2\theta \approx 26^\circ$ related to the IZO coated polymer substrate. Full XRD patterns are available in Figure S6 (Supporting Information). XRD analyses of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films treated at 90°C for 10 min, and at 110°C for 5 min exhibited a peak at $2\theta \approx 12.8^\circ$ corresponding to PbI_2 (110) diffraction. It is known that $\text{CH}_3\text{NH}_3\text{PbI}_3$ can degrade to form PbI_2 in the presence of water according to Equation 1.^[30]

The formation of PbI_2 , therefore, indicated the degradation of the perovskite film on ZnO. The XRD study showed that while the $\text{CH}_3\text{NH}_3\text{PbI}_3$ film did not degrade at 70°C when kept at this temperature for up to 10 min, it started to decompose when heated to 90°C for 10 min, when deposited on ZnO. At 110°C , the degradation was more rapid and already visible after only 5 min. This suggested a strong temperature dependence of the

Figure 4. SEM images of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films deposited via the gas-assisted method and annealed on ZnO at (a) 70°C , (b) 90°C , and (c) 110°C for 10 min; and on TiO_2 at (d) 70°C , (e) 90°C , and (f) 110°C for 10 min.

Figure 5. Current density-voltage curves of the flexible devices constructed under various $\text{CH}_3\text{NH}_3\text{PbI}_3$ annealing conditions with (a) ZnO, and (b) TiO_2 as the electron selective layer.

stability of the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$ system. As a comparison, perovskite films were deposited on TiO_2 and heated to 110 °C, 130 °C and 150 °C for 10 min and 30 min. As illustrated in the low angle XRD patterns of the resulting films (Figure 3b and Figure S7), degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was not apparent for films prepared at 110 °C but became evident from the presence of lead iodide for films treated at 150 °C for 10 min, and at 130 °C for 30 min. Full XRD patterns are available in Figure S7 (Supporting Information). This study clearly demonstrated a strong correlation between the heating conditions and the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ on ZnO or TiO_2 . Moreover, it showed that degradation was much faster when $\text{CH}_3\text{NH}_3\text{PbI}_3$ was deposited on ZnO. Heating to 110 °C for 10 min completely degraded the perovskite film deposited on ZnO, whereas a temperature of 150 °C was necessary to initiate the degradation of the film on TiO_2 in the same time. In both cases, the degradation temperature was below that observed for pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ single crystals, which undergo decomposition at 240 °C.^[31] It is worth noting that the decomposition of a thin perovskite film, deposited on a metal oxide in a non-dry environment, will differ from that of a single crystal in dry conditions.

Subsequently, the impact of the perovskite layer preparation conditions on the morphology of the films deposited on ZnO and TiO_2 was investigated. Figure 4 shows SEM images of the perovskite films, prepared by a gas-assisted method and heated to 70 °C, 90 °C, and 110 °C for 10 min on ZnO (Figure 4a-c), and on TiO_2 (Figure 4d-f). A strong correlation exists between the heat treatment and film morphology when $\text{CH}_3\text{NH}_3\text{PbI}_3$ was deposited on ZnO. At 70 °C, although there was a reasonable coverage of the blocking layer, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films were comprised of small crystals, a few tens

of nanometers in size, leaving quite a few holes in the perovskite matrix (Figure 4a). A similarly rough morphology was observed for a film prepared at 90 °C for 1 min (Figure S8d, Supporting Information). Interestingly, the morphology changed dramatically upon prolonged heating at 90 °C, leading to large crystals of a few hundreds of nanometers (Figure 4b). After 10 min of heating, the perovskite film resembled that of a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film deposited on TiO_2 (Figure 4e). In addition, small elongated crystals were also visible, which was in agreement with the presence of PbI_2 , as apparent from the XRD analysis. At 110 °C, the crystals grew more rapidly and the formation of PbI_2 was significant after 10 min (Figure 4c). However, when the perovskite films were treated on TiO_2 under the same conditions, the morphology of the films was not greatly impacted (Figure 4d-f). Further to this, the perovskite films on TiO_2 were kept at 110 °C, 130 °C, and 150 °C for 10 min and analyzed by SEM (Figure S9c-e, Supporting Information). At high temperature, particularly at 150 °C (Figure S9e), the size of the perovskite crystals increased. This revealed that contrary to the films prepared on ZnO, the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films prepared on TiO_2 could withstand higher temperatures without significant degradation. $\text{CH}_3\text{NH}_3\text{PbI}_3$ films on TiO_2 were also kept for 30 min at 110, 130 and 150 °C, and SEM images show the progressive change in morphology after 30 min heat treatment (Figure S10a-c, Supporting Information). Flakes of lead iodide became apparent in the low magnification image of the sample treated at 130 °C for 30 min (Figure S10b). At 150 °C, the edge of the perovskite film turned yellow (a visual indication of PbI_2) after prolonged heating time (Figure S10c).

The performance of the resulting photovoltaic devices constructed on ZnO and TiO_2 with a range of perovskite processing conditions was investigated. Figure 5a shows that the best-performing ZnO-based device in this study was obtained when heating the perovskite film to 90 °C for 10 min. This was related to the perovskite film morphology and good coverage of the ZnO layer, illustrated in Figure 4b. Conversely, the device constructed with a decomposed perovskite film (110 °C/10 min) showed very poor photovoltaic performance. Details of the $J-V$ characteristics when scanning the devices in both FB-SC and SC-FB directions are listed in Tables S1 and S2 (Supporting Information). A range of photovoltaic performances was observed depending on the perovskite formation conditions, demonstrating again the strong impact of the latter in the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$ system. Figure 5b shows the photovoltaic performances of the TiO_2 -based flexible devices constructed with the perovskite films prepared under various conditions. No significant difference was observed for the films heated to 110 and 130 °C for up to 30 min. However, the photovoltaic performance of devices made with films prepared at 150 °C was poorer, in keeping with observed degradation of the $\text{CH}_3\text{NH}_3\text{PbI}_3$ films at this temperature. Details of the $J-V$ parameters of these devices can be found in Tables S3 and S4 (Supporting Information).

Device Stability

In addition to the clear correlation between the perovskite processing temperature and film degradation in the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$ system, an interesting phenomenon was detected during $J-V$ characterization of the flexible devices fabricated on ZnO. This was not observed for TiO_2 -based devices. Figure 6a shows the change in photovoltaic performance upon multiple scans of the same device from forward bias to short-circuit at a scan rate of 100 mV s^{-1} . Under illumination, the cell performance initially rapidly plummeted by 50 % in PCE and gradually stabilized after about 25 min of

testing. This drop in performance originated from a 17 % loss in V_{oc} , and 42 % loss in J_{sc} . Conversely, a slight performance increase (13 % in PCE) was detected upon repeated scanning of a TiO_2 -based device (Figure 6b). As the devices heated under AM 1.5G, the effect of temperature on the perovskite film degradation was suspected to be responsible for the decrease in device performance in the $CH_3NH_3PbI_3/ZnO$ system. This observation and the instability of the perovskite film even at moderate temperatures, raised concerns about the general stability of ZnO-based devices.

The stability of ZnO-based devices, without encapsulation, has been investigated by several groups. Bi et al. reported that the efficiency of devices stored in air at room temperature decreased from 5.0 % to 4.3 % over a period of 500 h.^[10] Liu et al. showed rapid degradation of a ZnO-based device, resulting in a 50 % PCE loss over a period of 10 h, under ambient conditions.^[26] In this study, the stability of encapsulated, flexible perovskite devices with IZO/ZnO/ $CH_3NH_3PbI_3$ /Spiro-MeOTAD/Au and IZO/ TiO_2 / $CH_3NH_3PbI_3$ /Spiro-MeOTAD/Au

Figure 6. Development of the current density-voltage curve over a number of scans of (a) an IZO/ZnO/ $CH_3NH_3PbI_3$ /Spiro-MeOTAD/Au device and (b) an IZO/ TiO_2 / $CH_3NH_3PbI_3$ /Spiro-MeOTAD/Au device on PET substrate, tested under AM 1.5G from forward bias to short-circuit, at a scan rate of 100 mV s^{-1} . Insets give normalized $J-V$ parameters as a function of scan number for each device.

Figure 7. Stability of the ZnO and TiO_2 -based perovskite flexible devices stored under ambient conditions (average ambient temperature of $22.5 \pm 0.2 \text{ }^\circ\text{C}$, relative humidity ranging from 40 to 80 %, and constant ambient illumination of 400 lux). Normalized PCE are calculated as the ratio of the measured PCE at a given time t , to the initial PCE at $t = 0$.

architectures was assessed under ambient conditions (average temperature of $22.5 \pm 0.2 \text{ }^\circ\text{C}$, relative humidity ranging from 40 % to 80 %, and constant ambient illumination of 400 lux). These devices were encapsulated according to a published procedure^[32] to limit the impact of external factors, such as ambient moisture and oxygen, on the cell degradation. Figure 7 shows that the ZnO-based device rapidly dropped in efficiency after a few hours of storage under ambient conditions, whereas the TiO_2 -based devices remained more stable.

The PCE of the ZnO-based device gradually declined over a period of 900 h to zero. The TiO_2 -based devices maintained a stable PCE for 500 h, then progressively degraded and failed after 1500 h of storage, possibly due to the moisture ingress through the edges of the encapsulation material. This decline could also correspond to the high relative humidity of over 70 % measured in the laboratory for consecutive days, which could have accelerated the moisture ingress through the edges and led to the device failure. This comparative stability study confirmed that a device constructed with a ZnO blocking layer was less stable than one fabricated with TiO_2 .

Studies on the Degradation Mechanism

In order to understand the origins of the exacerbated degradation of $CH_3NH_3PbI_3$ on ZnO, further experiments were undertaken. First, thermogravimetric analyses were carried out on ZnO and TiO_2 powders to determine whether the device degradation was correlated to a greater amount of water adsorbed on the oxide surface. Metal oxides, such as ZnO and TiO_2 , chemically adsorb water molecules to form surface hydroxyl groups or coordinate to free sites on metal centers. These groups can physisorb additional water molecules via hydrogen bonding. The temperature at which the chemisorbed water can be removed depends on the nature of the oxide and it has been suggested to be higher for ZnO than for TiO_2 due to the stronger bonding force of hydroxyl groups to surface metal atoms in ZnO.^[33] In this work, the temperature sensitivity of the polymer substrates restricted the cell fabrication process to $150 \text{ }^\circ\text{C}$. For this reason, we focused on the impact of the desorption of weakly physisorbed water from the hydroxylated surface. The mass losses measured at $120 \text{ }^\circ\text{C}$, which were associated to the removal of physically adsorbed water, were 1.5 % for titania (Figure 8a), and 2.2 % for zinc oxide (Figure 8b).

The difference observed between ZnO and TiO₂ was not significant enough to explain the dramatically faster degradation of CH₃NH₃PbI₃ when deposited on ZnO. Furthermore, a significant mass loss of 9.7 % was observed in the second heating step from 120 to 500 °C for the zinc oxide sample, versus 2.8 % for TiO₂, which could relate to the release of surface hydroxyls or organic molecules from the synthesis (mainly acetate ligands, see Experimental Section and published procedure^[11]) bound to the surface of ZnO. IR spectroscopy was carried out in conjunction with TGA/STDA analyses to clarify the weight losses observed at high temperature. The ZnO samples were heated to 120, 150, 250 and 400 °C and their respective spectra are shown in Figure S11. With this low temperature process, a considerable number of ligands could remain adsorbed on the surface due to the ZnO small particle size (5 nm). For the ZnO films heated to 120 and 150 °C, the presence of acetate ligands was confirmed by IR spectroscopy which shows absorption bands of the characteristic stretch vibrations of alkyl C–H at 2963 cm⁻¹, C=O at 1563 cm⁻¹ and C–O at 1409 cm⁻¹ (Figure S11). Surface hydroxyl groups were also detected on these samples (3364 cm⁻¹). This implied that under the cell fabrication conditions, both hydroxyl and acetate ligands were present on the surface of ZnO. In addition, IR spectra of ZnO films heated to 250 and 400 °C showed that the band intensity of the acetate ligand significantly decreased at 250 and 400 °C (Figure S11). To mimic the cell fabrication conditions, ZnO was heated to 150 °C and the powder was collected to run additional TGA/SDTA analyses with plateaus at 120, 250 and 400 °C (Figure S12). The weight loss measured between 120 and 250 °C (0.7 wt %) was interpreted as the loss of both hydroxyl groups strongly bound to the surface of ZnO and some

acetate ligands, presumably as acetic acid (Figure S12a). Between 250 and 400 °C, the weight loss (2.6 wt %, Figure S12a) and exothermic peak (Figure S12b) were attributed to the combustion of acetate ligands. Furthermore, any remaining hydroxyl groups would be converted into oxo groups with the release of water for the most part in the 200–400 °C range^[34]. This study showed that perovskite decomposition already occurred at 100 °C on ZnO. Thus, film degradation was more likely to result from reaction with the surface hydroxyl groups or acetate ligands than desorption of these groups that are strongly bound to the surface of ZnO. Cheng et al. also observed exacerbated degradation of CH₃NH₃PbI₃ on ZnO, which they attributed to the high number of hydroxyl groups on the surface of solution processed ZnO nanoparticles.^[35] They found that intercalating an organic layer between the ZnO and perovskite layers, or vacuum sputtering ZnO, significantly delayed the perovskite decomposition.^[35] Yang et al. used Density Functional Theory (DFT) calculations to show that the basicity of ZnO^[36] could lead to the deprotonation of the methylammonium cation and degradation of the perovskite film.^[27] In comparison, TiO₂ has a lower basicity (isoelectric points in the range of 4–8)^[36] than ZnO (isoelectric point > 8.7),^[36] which is in favor of a higher stability of the perovskite material at the CH₃NH₃PbI₃/TiO₂ interface. Nevertheless, it is important to note that acetate ligands present on the ZnO surface could affect the surface chemistry. Alternatively, the formation of zinc iodide could be responsible for the degradation of ZnO-based devices. Further to the degradation of CH₃NH₃PbI₃ in the presence of water, leading to the formation of CH₃NH₃I and PbI₂ (Equation 1), CH₃NH₃I can decompose into CH₃NH₂ and HI (Equation 2).^[37]

Water, whether present on the surface of the metal oxides or in trace amounts in the N₂ filled glovebox will play a role in the perovskite degradation. This decomposition pathway is common to CH₃NH₃PbI₃/TiO₂ and CH₃NH₃PbI₃/ZnO systems, and therefore does not explain the accentuated degradation visible on ZnO. However, the reaction of HI with ZnO in the CH₃NH₃PbI₃/ZnO system could result in the formation of ZnI₂ (Equation 3) or related zinc iodide species^[38] and H₂O, while TiO₂ is inert to HI.

This reaction cascade could then trigger a new decomposition cycle, and could therefore explain the rapid perovskite film degradation. Moreover, it leads to the formation of more water, which has itself been identified as a degradation catalyst (see Equation 1).^[30] Raman spectroscopy was conducted on the perovskite films deposited on TiO₂ and ZnO (Figure S13 and Figure S14, Supporting Information) but was unable to unambiguously demonstrate the presence of zinc iodide species in the degraded CH₃NH₃PbI₃/ZnO system. Several reasons may have hindered the observation of ZnI_x features: (a) only trace amounts of zinc iodide species were formed which fell under the Raman detection threshold, (b) hygroscopic ZnI₂ could have decomposed prior to film encapsulation, and (c) the perovskite film degradation did not emanate from the reaction between ZnO and HI. Therefore, the formation of zinc iodide species and their contribution to the observed accelerated CH₃NH₃PbI₃ degradation cannot be excluded, but this process is unlikely to be the main source of degradation. Furthermore, from IR spectroscopy and thermogravimetric analyses, the main source of degradation originated from the reaction between CH₃NH₃PbI₃ and hydroxyl groups or acetate ligands on the surface of ZnO.

Figure 8. Thermogravimetric analysis curves of the titania and zinc oxide powders used as electron-selective layers in this study. The temperature profile is plotted in the orange dashed line.

Conclusions

Perovskite solar cells were successfully constructed on polymer substrates giving state-of-the-art PCEs of 13.4 % with TiO_2 as the electron-selective layer, and 10.3 % with ZnO , after film thickness optimization. Concerns about the thermal stability of ZnO -based devices arose during their fabrication. An assessment of device stability under ambient conditions revealed that the TiO_2 -based devices were more stable than the ZnO -based devices. The influence of the preparation conditions of the perovskite film on its morphology was investigated. There was a clear correlation between the perovskite morphology and the temperature treatment for the films deposited on ZnO . XRD analyses revealed that lead iodide formed after heating a perovskite film to 110 °C for only 5 min, indicative of a very rapid degradation. Conversely, $\text{CH}_3\text{NH}_3\text{PbI}_3$ films deposited on TiO_2 did not degrade when treated under the same conditions. A more severe treatment was necessary to affect the perovskite film deposited on TiO_2 (i.e., 150 °C for 10 min or 130 °C for 30 min). The photovoltaic performance of the resulting devices was significantly impacted by the perovskite film morphology as a result of the heating conditions, particularly in the case of ZnO . In both systems, the formation of lead iodide led to poor device performance. However, a strong relationship between the underlying metal oxide and the degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ was identified, and exacerbated degradation in the presence of ZnO was monitored. Given the instability of the perovskite layer in the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$ system, the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ system is concluded to be more suitable for low-temperature solution processing applications. If acetate ligands constitute the main degradation source, low-temperature vacuum sputtering or atomic layer deposition of ZnO remain viable alternatives, at the expense however of the device manufacturing cost.

Experimental Section

Materials: All chemicals and substrates were purchased and utilized as described previously.^[5]

Blocking layer: ZnO nanoparticles were synthesized according to a published procedure.^[11] Before use, the 6 mg mL^{-1} ZnO nanoparticle solution was filtered through a 0.45 mm PVDF syringe filter. To deposit one layer of ZnO nanoparticles (1L), 20 μL of the ZnO suspension was spin coated onto the IZO-PET substrate at 3000 rpm for 30 s. This procedure was repeated until the required number of ZnO layers was obtained, i.e., for devices constructed with 3L, 4L, 5L and 6L, 20 μL of ZnO suspension was spin coated 3, 4, 5 and 6 times, respectively. After the final layer deposition, the ZnO films were heated to 150 °C for 1 h. For the comparative study, TiO_2 based devices were fabricated using a suspension of crystalline anatase nanoparticles synthesized according to a hydrothermal method published elsewhere.^[5, 39] 20 μL of a 16 mg L^{-1} TiO_2 suspension in ethanol was spin coated onto IZO-PET at 2000 rpm for 60 s. The films were then heated to 150 °C for 1 h.

Device fabrication: The preparation of perovskite and spiro-MeOTAD solutions and film deposition were performed according to a published method.^[28] The perovskite films were heated to 100 °C for 1 min unless specified otherwise in a N_2 filled glovebox. Variations in perovskite preparation conditions are given in the main text. Hole conductor

deposition was conducted in a N_2 filled glovebox with the films only taken out of their environment to evaporate an 80 nm gold counter electrode.

Device encapsulation: The encapsulation process was carried out in a N_2 filled glovebox with H_2O and O_2 levels below 1 ppm. Viewbarrier® (Mitsubishi Plastic, Inc) was used as the plastic barrier film for the encapsulation of the flexible device. An adhesive layer (467MP, 3M) was laminated onto the barrier film and used as bonding material between device and barrier film. The adhesive coated barrier film was laminated at 100 °C onto the devices using an office-type laminator (Peach 3500) to seal the flexible solar device.

Characterization: Current density-voltage (J - V) curves of the solar cells were obtained by using a Keithley 2400 source meter under illumination of simulated sunlight, provided by an Oriel solar simulator equipped with an AM 1.5 filter. The devices were shielded by a black metal mask with an aperture area of 0.16 cm^2 . A Keithley 2400 source meter under the irradiation of a 300 W Xenon lamp equipped with an Oriel Cornerstone 260 monochromator was used to obtain the IPCE plots as a function of excitation wavelength ($\lambda = 300$ -900 nm). SEM images were obtained on a Quanta-ESEM microscope and cross-sectional images with a Nova Dual Beam FIB SEM. Crystallography data was obtained with a Philips vertical diffractometer with Cu K α radiation. The topography of the ZnO layer was determined using an Asylum Cypher High Resolution Atomic Force Microscope with a TapAI300-G probe in tapping mode (tip radius < 10 nm). Thermogravimetric measurements were made on a Mettler Toledo TGA/SDTA851[®] module. The titania and zinc oxide samples were first dried under vacuum overnight and subsequently exposed to air moisture for 24 h. The powders were heated from 25 °C to 120 °C at 10 °C min^{-1} , held at this temperature for 30 min, then heated at 10 °C min^{-1} to 500 °C in nitrogen. Isothermal heating was used for a better distinction between the heating steps, and related to the removal of physically adsorbed water.^[40, 41] For the supplementary TGA/STDA data (Figure S12), a ZnO film was initially heated at 150 °C for 1 h. The powder was collected and ran with a heating profile as follows: from 25 °C to 120 °C at 10 °C min^{-1} , held at 120 °C for 20 min, heated at 10 °C min^{-1} to 250 °C, held at 250 °C for 20 min, heated at 10 °C min^{-1} to 400 °C, held at 400 °C for 20 min, then heated at 10 °C min^{-1} to 500 °C, in nitrogen. For IR samples, ZnO films were heated at 120, 150, 250 and 400 °C for 1 h. IR spectroscopy was conducted on ZnO powder using a Thermo FTIR with ATR crystal. Raman spectroscopy was performed using an InVia Visible Renishaw microscope with a 514 nm excitation laser, 50x objective, and a 5 % laser intensity to avoid sample degradation.

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Entry for the Table of Contents

FULL PAPER

A comparison between $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{ZnO}$ and $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{TiO}_2$ -based perovskite solar cells on polymer substrates demonstrates higher thermal device stability when constructed on TiO_2 . Exacerbated degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ questions the viability of ZnO as an effective electron selective layer in low-temperature processed perovskite solar cells.

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Dehong Chen, Hasitha Weerasinghe,
Leone Spiccia, Yi-Bing Cheng,* and
Rachel A. Caruso*

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**Stability Comparison of ZnO and
 TiO_2 -based Perovskite Solar Cells
on Polymer Substrates**

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