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## PAPER



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# Efficient, flexible and mechanically robust perovskite solar cells on inverted nanocone plastic substrates<sup>†</sup>

Mohammad Mahdi Tavakoli,<sup>a</sup> Qingfeng Lin,<sup>a</sup> Siu-Fung Leung,<sup>a</sup> Ga Ching Lui,<sup>a</sup> Hao Lu,<sup>b</sup> Liang Li,<sup>b</sup> Bin Xiang<sup>c</sup> and Zhiyong Fan\*<sup>a</sup>

Utilization of nanostructures on photovoltaic devices can significantly improve the device energy conversion efficiency by enhancing the device light harvesting capability as well as carrier collection efficiency. However, improvements in device mechanical robustness and reliability, particularly for flexible devices, have rarely been reported with in-depth understanding. In this work, we fabricated efficient, flexible and mechanically robust organometallic perovskite solar cells on plastic substrates with inverted nanocone (i-cone) structures. Compared with the reference cell that was fabricated on a flat substrate, it was shown that the device power conversion efficiency could be improved by 37%, and reached up to 11.29% on i-cone substrates. More interestingly, it was discovered that the performance of an i-cone device remained more than 90% of the initial value even after 200 mechanical bending cycles, which is remarkably better than for the flat reference device, which degraded down to only 60% in the same test. Our experiments, coupled with mechanical simulation, demonstrated that a nanostructured template can greatly help in relaxing stress and strain upon device bending, which suppresses crack nucleation in different layers of a perovskite solar cell. This essentially leads to much improved device reliability and robustness and will have significant impact on practical applications.

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## Introduction

Organometallic perovskite materials have demonstrated intriguing physical properties, such as high optical absorption, a direct band gap, low defect density, and a long carrier diffusion length up to 175  $\mu$ m.<sup>1–4</sup> These characteristics make them promising candidates for high performance photovoltaic (PV) applications.<sup>5–7</sup> In fact, lead halide perovskite thin film solar cells have achieved a record high power conversion efficiency (PCE) of 20.1%, which is close to the record of single junction crystalline Si solar cells.<sup>8–13</sup> Besides high PCE, low material and device fabrication cost is also advantageous, especially when compared with inorganic material based solar cells.<sup>14,15</sup> There are a number of different processes reported

for the fabrication of perovskite films, including sequential deposition,<sup>16,17</sup> co-deposition,<sup>18,19</sup> a vapour-assisted solution process (VASP),<sup>20</sup> vacuum deposition,<sup>21-23</sup> spray coating,<sup>24</sup> and chemical vapor deposition.<sup>25</sup> In these processes, perovskite film preparation temperatures are all below 120 °C. This suggests the compatibility of the fabrication process with various types of low thermal budget substrates, including plastics, for potential flexible solar cell applications. In fact, even though flexible perovskite thin film solar cells have not been widely explored, there have been a few reports on planar perovskite film based flexible solar cells fabricated on polyethylene terephthalate (PET), polyacrylonitrile (PEN), titanium foil, etc.26-34 Although these devices have demonstrated a decent PCE in the range of 6 to 15%, repetitive bending of the planar devices may lead to the accumulation of stress and strain inside both the active layer, *i.e.* perovskite light absorber, and the passive layer, i.e. electron and hole transporters and electrodes. In addition, the higher thermal expansion coefficient of a plastic substrate over that of the solar cell device layers may also introduce stress and strain in the device during the fabrication process, as well as in the practical operation when the device is exposed to solar radiation. These stresses and strains can release and develop into crack lines on the device, consequently quickly degrading the device performance.



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<sup>&</sup>lt;sup>a</sup>Department of Electronic and Computer Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China. E-mail: eezfan@ust.hk

<sup>&</sup>lt;sup>b</sup>College of Physics, Optoelectronics and Energy, Jiangsu Key Laboratory of Thin Films, Soochow University, Suzhou, 215006, P. R. China

<sup>&</sup>lt;sup>c</sup>Department of Materials Science & Engineering, CAS Key Lab of Materials for Energy Conversion, University of Science and Technology of China, Hefei, Anhui 230026, China

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Recently, we reported the fabrication of efficient lead halide perovskite thin film solar cells on a flexible glass substrate.<sup>35</sup> Flexible glass substrates have an excellent thermal budget and low thermal expansion coefficient; however, the bendability of the resulting device could be further improved.

In this work, we utilized a facile molding process to fabricate flexible plastic substrates with inverted nanocone (i-cone) structures on the surface. These nanostructured substrates were used as the templates to accommodate lead halide perovskite thin film solar cells. Compared with the reference cell fabricated on a flat substrate, it was shown that the device PCE could be improved by 37%, and reached up to 11.29% on i-cone plastic substrates due to the optical light trapping effect in the nanocone arrays. More interestingly, it was discovered that the PCE of an i-cone device remained more than 90% of the initial value even after 200 mechanical bending cycles, which is remarkably better than for the flat reference device, which degraded down to only 70% in the same test. Our experiments and mechanical simulation results show that the residual stresses and strains in a nanostructured device can be greatly relaxed upon device bending, which suppresses crack nucleation in different layers of a perovskite solar cell. This essentially improves the device reliability and robustness and is beneficial for practical applications.

## **Results and discussion**

Hexagonally ordered i-cone plastic substrates were fabricated by a scalable and low-cost process in three steps, as shown in Fig.  $1a_1-a_4$ . First, an alumina i-cone array was prepared by a multi-step anodization process in an acidic solution with a



**Fig. 1** Schematics of fabrication of the i-cone epoxy substrate.  $(a_1, a_2)$  Drop casting of PDMS solution on the AAO i-cone template and curing at 80 °C.  $(a_3)$  Drop casting of epoxy solution on nancone PDMS and curing under UV light.  $(a_4)$  Epoxy substrate after peeling off from the PDMS mold. (b) Angular view SEM image of nanocone arrays of PDMS with an aspect ratio of 0.5; the inset shows the top view SEM image of the same sample. (c) The angular view SEM image of i-cone arrays of epoxy with an aspect ratio of 0.5; the inset shows the top view SEM image of the same sample.

suitable direct-current (DC) voltage, followed by wet etching on the imprinted aluminum foil, as reported by us elsewhere.<sup>36,37</sup>

Fig. S1<sup>†</sup> shows SEM images of the i-cone AAO arrays with an aspect ratio (i-cone height/pitch) of 1.0. In the next step, the alumina i-cone array was employed as a template to mold a bifunctional poly-dimethylsiloxane (PDMS) nanocone array. Specifically, a 10 nm-thick gold layer was thermally evaporated on the alumina i-cone template as an anti-sticking layer. Thereafter, PDMS solution was drop cast on the gold-coated i-cone template, followed by a degassing and curing process at 80 °C for 2 h. The nanocone PDMS mold was obtained by peeling it off directly from the i-cone template. The top and angular view SEM images of the nanocone PDMS molds with different aspect ratios are shown in Fig. 1b and S2.† After obtaining the PDMS nanocone mold, epoxy solution was poured on the PDMS, followed by overnight UV curing, as shown in Fig. 1a<sub>3</sub>. Finally, the epoxy plastic film was peeled off from the PDMS molds, resulting in an i-cone array structure on the surface of the epoxy film. Fig. 1c and S3<sup>†</sup> illustrate the top and angular view SEM images of the epoxy plastic substrates with different i-cone aspect ratios.

In order to fabricate perovskite thin film solar cells on i-cone substrates, a two-step evaporation process was employed, as shown in Fig.  $2a_1-a_4$ . Here, a sub-100 °C process was used to fabricate a standard device architecture based on epoxy substrates. Specifically, an i-cone plastic substrate was firstly deposited with 300 nm-thick indium-doped tin oxide (ITO), followed by 40 nm-thick zinc oxide (ZnO) as an n-type compact layer using sputtering. Afterwards, the organohalide perovskite material (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) was deposited on the compact layer using sequential thermal evaporation of PbI<sub>2</sub> and MAI in a vacuum evaporator, followed by annealing at 100 °C for 1 h in an argon environment in order to promote crystallization and complete the reaction.

The XRD pattern and photoluminescence (PL) of the assynthesized perovskite on the plastic i-cone are shown in Fig. S4.<sup>†</sup> The XRD pattern of the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film indexed in Fig. S4a<sup>†</sup> indicates that the perovskite layer has a cubic crystal structure.<sup>38</sup> In addition, the PL spectrum of the perovskite film



**Fig. 2** (a) Schematic fabrication process of a perovskite solar cell based on the i-cone-epoxy substrate. (b) Cross sectional SEM images of the perovskite solar cell based on the i-cone-epoxy substrate with 0.5 aspect ratio. (c) Top view SEM image of the perovskite film on the i-cone-epoxy substrate with 0.5 aspect ratio.

demonstrates a strong and narrow peak at 780 nm (under laser excitation at 405 nm) due to the radiative recombination of electron and hole pairs.  $^{22,30,39}$ 

Fig. S5<sup>†</sup> shows the SEM images of the perovskite layer deposited on i-cone epoxy substrates with different aspect ratios. As can be seen, the i-cone substrates were covered by a uniform layer of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and, according to the SEM images and XRD patterns, the perovskite films have a high crystallinity with perfect surface coverage. To complete the structure, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyldevice amine)-9,9'-spirobifluorene (Spiro-OMeTAD) as a hole transfer layer was spin coated on the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> layer (3500 rpm for 45 s) with a thickness of ~200 nm, and finally, 100 nm-thick gold was deposited on the Spiro-OMeTAD layer by thermal evaporation as a carrier collector. Fig. 2b, c and S6<sup>†</sup> show the top view and cross section of the planar and i-cone-based devices with different aspect ratios, from which it can be easily observed that each layer has been uniformly coated on the substrates.

Fig. 3 shows the optical measurement and device characterization of the perovskite solar cells with a pitch size of 1.2  $\mu$ m and different aspect ratios of i-cones. The reflectance spectra of the devices were recorded with an integrating sphere quantitatively. As shown in Fig. S7,† a perovskite film has an absorption edge at 780 nm with an optical band gap of ~1.59 eV. As is clearly observable in Fig. 3a, when the i-cone perovskite devices are illuminated with light from the epoxy side, they have much lower reflectance than the planar control device on a flat epoxy substrate. This is simply due to the light trapping effect in the nanocone arrays. Among the devices with different aspect ratios, the 1.0-aspect-ratio device shows the lowest broadband reflection due to the better light trapping effect. Furthermore, the 0.5-aspect ratio device.



Fig. 3 (a) Measured reflectance spectra, (b) simulated reflectance spectra using FDTD software, (c) J-V characteristics, and (d) EQE measurements of perovskite solar cell devices based on flat and i-cone-epoxy substrates with different aspect ratios.

In order to utilize the best pitch size of i-cone nanostructures, we fabricated perovskite films on the i-cone substrates with different pitch sizes of 0.5, 1.0, 1.2, and 1.5  $\mu$ m. The results of the optical absorption measurement indicate that the 1.2  $\mu$ m pitch is the best structure, as shown in Fig. S8.<sup>†</sup>

To verify the optical measurement results, finite-difference time domain (FDTD) simulations were carried out for the devices, resulting in simulated reflection spectra. As can be seen in Fig. 3b, the simulation results are consistent with the experimental results especially for the wavelength range above the band-gap. In addition, to investigate how light is absorbed in each layer in the device structure, the generation rate profiles of i-cone based perovskite solar cells and the planar device were plotted, as shown in Fig. S9.† In the simulation, the electromagnetic plane waves propagated upward to simulate the real situation. The reddish colored region, *i.e.* hot zone, in Fig. S9<sup>†</sup> represents the region with a high generation rate of electron-holes inside the perovskite active layer. It is particularly obvious that the planar device has a very small hot zone area compared with the i-cone device and the aspect ratio 1.0 device has the largest hot zone area, across almost the entire perovskite layer. This reveals the effectiveness of the i-cone structures for improving light absorption, and it is in good agreement with the results in Fig. 3a and b.

The optical study showed that the i-cone structures have the potential for efficient light absorption. Meanwhile, the performances of i-cone epoxy based devices were measured together with the flat reference device. The current density–voltage (J–V) characteristics of the devices under 1 sun illumination are shown in Fig. 3c. The short current density ( $J_{sc}$ ) and open circuit voltage ( $V_{oc}$ ) extracted from the J–V curves are summarized in Table 1. The results indicate that the  $J_{sc}$  increases significantly, from 13.9 to 19.2 mA cm<sup>-2</sup>, as the aspect ratio increases from 0 (the flat device) to 0.5 due to the enhancement of the light absorption capability, as shown in Fig. 3a. However it reduces to 15.6 mA cm<sup>-2</sup> by further increasing the aspect ratio to 1.0.

The trend of the  $J_{sc}$  for different aspect ratio devices was verified with external quantum efficiency (EQE) measurements, as presented in Fig. 3d. The increase of the  $J_{sc}$  initially can be attributed to the improved light-trapping with a higher aspect ratio.<sup>40</sup> However, the reduction of the  $J_{sc}$  for the highest aspect ratio 1.0 i-cone device is contradictory to the optical study results. This can be explained by the excessive thickness

 
 Table 1
 Figures of merit for perovskite solar cell devices based on flat and i-cone epoxy substrates

		_	Fill	Highest	Average
Device	$V_{\rm oc}$ (V)	$\int_{\rm sc}$ (mA cm <sup>-2</sup> )	factor (%)	efficiency (%)	efficiency (%)
Flat	0.94	13.9	63.2	8.25	$6.3 \pm 1.5$
0.25 aspect ratio	0.87	15.9	69.9	9.66	$7.4 \pm 1.2$
0.5 aspect ratio	0.87	19.2	67.6	11.29	$10.2\pm0.8$
1.0 aspect ratio	0.86	15.6	62.3	8.36	$7.1\pm0.9$

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un-uniformity for a high aspect ratio i-cone device. As can be seen from Fig. S5 and S6,† for low aspect ratio structures, the perovskite film can rather conformally cover the nanostructure with uniform thickness. However, the perovskite film thickness is not uniform on aspect ratio 1.0 i-cones, mainly due to the directionality of thermal evaporation. Particularly, the film is thicker at the tip of the i-cones than at the valley. The consequence is that the carrier collection distance, especially for holes, is much longer at the tip of the perovskite nanocones. From the FDTD simulations, shown in Fig. S9,† it is apparent that high generation occurs in the proximity of the nanocone tip, where the carrier collection distance is long. Thus the overall carrier collection efficiency is compromised. Note that this issue is caused by the directionality of thin film deposition with thermal evaporation. If a more conformal coating method, e.g. vapor deposition, is applied, the non-uniformity issue can be alleviated and the device performance can be much improved.

Meanwhile, it can be seen from Fig. 3c that the  $V_{\rm oc}$  of the devices decreases monotonically by increasing the aspect ratio from 0 to 1.0. This is also an indication of increased carrier recombination. Consequently, the perovskite solar cell based on the 0.5-aspect-ratio i-cone epoxy demonstrates the highest performance, with a PCE of 11.29%, which represents a 37% improvement compared with the flat reference device, as shown in Table 1. Notably, the device on 1.0-aspect-ratio i-cone epoxy shows the highest optical absorption as shown in ESI Fig. S7.† In this kind of device, high concentrations of photocarriers are generated at the tip of the perovskite i-cones, as shown in ESI Fig. S9.† However it has the lowest PCE in all nanostructured devices. In fact, it can be seen from the crosssectional SEM image of the aspect ratio 1.0 device in Fig. 2a, the perovskite material fills in the nanocone very well and a flat layer of the spiro film is deposited on top. Thus, the generated holes at the nanocone tips have a long transport distance to reach the spiro-OMeTAD HTL layer. This increases carrier recombination and degrades the device performance. As a result, we employed the 0.5-aspect-ratio i-cone epoxy-based perovskite solar cell to further study the device performance and mechanical properties. In order to study the effect of the scan direction on PCE, the perovskite solar cell was measured in both the forward and reverse scan directions. As shown in Fig. S10,<sup>†</sup> the result confirmed that there is only a marginal difference in the J-V curves.

It is worth pointing out that the angle of solar irradiation varies over time during a day and thus, angular light absorption should be measured for a practical case. In our study, the angular absorption of the i-cone based and flat perovskite solar cells was investigated for different angles of light, varying from 0° (normal incidence) to 60° in 10° intervals, using a halogen light source and an integrating sphere, as shown in Fig. 4a. Interestingly, the absorption of the i-cone based device remains almost unchanged from 0° to 60°; however, for the flat reference device, the absorption monotonically decreases by as much as 11% with the highest incident angle of 60°. Furthermore, the  $J_{\rm sc}$  and PCE of the i-cone and flat devices



Fig. 4 (a) Angular absorption, (b) angular PV measurements of perovskite solar cells based on flat and 0.5-aspect ratio-i-cone-epoxy substrates, (c) photograph of the bending setup and, (d) efficiency stability depending on bending cycles in perovskite solar cells based on flat and 0.5-aspect ratio i-cone substrates.

were also measured at different incident angles and are plotted in Fig. 4b. Interestingly, the absolute enhancement of the  $J_{\rm sc}$  and PCE for the i-cone device was nearly 5 to 7.5 mA cm<sup>-2</sup> and 2.2 to 4% for the flat device, respectively. As such, the improvement of PCE is more pronounced at higher incident angles. Particularly, the efficiency of the i-cone device for 60° incident angle was improved by 80% compared with the flat device. Note that by tilting the angle of the solar cell device away from the normal incidence of the sun light, the projection area of the device is reduced, and as a result, the actual PCE of the device needs to be calibrated according to the area reduction. These results confirm that the i-cone nanostructured substrates have an omnidirectional light absorption enhancement function, which is consistent with our previous observations on various other nanostructures.<sup>37,41–44</sup>

One of the most attractive features of a thin film solar cell is its flexibility, but this is only possible when the device is fabricated on a flexible substrate, such as metal foils or plastics. As the highest process temperature for perovskite solar cell fabrication in this work is only 90 °C, it enables a broad choice of plastic substrates. In this work, NOA 81 epoxy was cast onto nanostructured plastic films serving as substrates. This type of substrate has excellent flexibility. Fig. 4c shows a photograph of the bending setup to study the flexibility of the i-cone perovskite solar cells. The dependence of the device PCE on the bending angle is shown in Fig. S11a.† It is clear that the i-cone devices show only a marginal PCE change, but the planar device shows pronounced performance reduction upon bending.

Besides photovoltaic performance, device durability in repetitive bending tests was also measured, as it is one of the key characteristics to define the robustness of flexible devices. Specifically, we examined a device with a size of  $3 \times 1.5$  cm<sup>2</sup>

and bent it repetitively for up to 200 cycles, with a bending radius of 6 mm (120° angle) in each cycle. The  $V_{oc}$ ,  $J_{sc}$ , fill factor (FF) and PCE were measured and recorded after each bending cycle, as shown in Fig. 4d and S11b.† It is worth noting that the PCE of the i-cone device exhibits no significant decrease after 200 cycles, retaining 95% of the initial PCE value, while the PCE of the flat device drops to ~70% of its initial value. Changes in  $J_{sc}$ ,  $V_{oc}$  and FF are shown in Fig. 4d and S11b,† which show that all these parameters degrade after repetitive bending. These results clearly show that the flexible i-cone perovskite solar cell possesses excellent bending durability compared with the flat device.

During bending cycles, stresses and strains built into the thin films lead to the development of micro cracks and delamination, consequently deteriorating the device performance. In order to achieve further understanding of bending related device performance degradation, finite element modeling was carried out using a COMSOL Multiphysics 4.2a finite element code. A device with dimensions of  $10 \times 3 \ \mu m^2$  was modeled (Fig. S12<sup>†</sup>) by using Autodesk AutoCAD 2014 according to the FESEM images. As shown in Fig. 5a and b, the right end of the device is anchored and the left end of the device is pushed down by a 10 N force. Note that the thickness of the plastic substrate is reduced to 1.5 µm to reduce the simulation time. The simulation settings can be found in the Experimental section. The cross-sectional stress distribution is plotted in Fig. 5a and b for the flat and i-cone devices, respectively. As can be obviously observed from the planar device (Fig. 5a), concentrated stresses are built between the layers of the perovskite solar cell. Near to the fixed edge, the gold layer has the highest tensile stress since it is the top structure, which has the most tensile strain. And it also has a much higher Young's modulus (see the Experimental section) than the Spiro-OMeTAD underneath. The perovskite layer also has high tensile stress since it also has a higher Young's modulus than



Fig. 5 The results of finite element mechanical modeling for perovskite solar cells based on (a) flat and (b) 0.5-aspect ratio-i-cone-epoxy substrates. (c) and (d) are top view SEM images of devices based on flat and 0.5-aspect ratio-i-cone substrates after 200 bending cycles. The size of the model is  $10 \times 3 \mu m^2$ .

the Spiro-OMeTAD above. However, even though the ITO layer also has a high Young's modulus, since it is close to the mechanical neutral plane inside the simulation structure, the tensile stress is low. It is worth pointing out that in reality, the stress in the ITO layer is expected to be much higher, since the actual thickness of the plastic substrate is 200  $\mu$ m, instead of ~1.5  $\mu$ m as shown in Fig. 5. Intriguingly, when compared with the flat device, the i-cone device demonstrates much lower stress, as seen in Fig. 5b. Specifically, the highest stress in the flat device is 900 Pa; whereas the highest stress in the i-cone device is only 500 Pa.

In addition to the level of stress, the volume of the high stress region in the i-cone device is much smaller than that in the flat device. In other words, the stress is very localized in the i-cone device, particularly only at the valley of the structure in the gold layer. This result suggests that the total strain energy is much lower in the i-cone device than in the flat device, and this attractive stress releasing behavior from the icone device can be rationalized by regarding the i-cone nanostructure as an equivalently folded structure. A folded structure is naturally highly stretchable, as the in-plane stretching of a flat material is converted to local small angle bending at the corners. This stress releasing mechanism significantly improves the device bending cycle life time and durability. It is also worth pointing out that this interesting mechanism can potentially help in improving the device performance/yield when the substrate has a high coefficient of thermal expansion mismatch with the solar cell device layers. In which case, the thermal expansion induced stress can also be released. To further confirm our analysis, SEM images of the flat and i-cone devices after 200 bending cycles were acquired and are shown in Fig. 5c and d. As can be seen, there are many crack lines on the surface of the flat device, while there are only a few sites for crack nucleation on the surface of the i-cone device. Overall, the nanostructure helps dramatically in improving the device flexibility in the current device configuration.

It is noteworthy that as our current fabrication process is not performed inside the glove box, our planar device performance is not on par with the state-of-the-art; however, there is still room to improve the device performance by taking better control of the fabrication environment in the future.

## Conclusions

The imperative demand for high efficiency and flexible solar cells drives continuous innovation in materials and device structures. The low process temperature of the emerging organometallic perovskite materials provides many more choices of substrate materials for high performance solar cells compared to inorganic photovoltaic materials. In addition to the device energy conversion efficiency, the robustness of a flexible device is equally important, and the device mechanical failure mechanism and how to address this issue has rarely been studied before. In this work, we developed a facile process to fabricate a plastic substrate with inverted nanocone structures, and perovskite thin film solar cells were fabricated on this flexible substrate. Owing to the beneficial light trapping effect in the inverted nanocones, the devices demonstrated a power conversion efficiency up to 11.29%. Interestingly, the nanostructured devices were found to be much more robust and durable than a planar reference device during bending cycle tests. Further experiments and mechanical modelling revealed that the three-dimensional nanostructures effectively folded the thin film materials on the surface, thus greatly relaxing the stress and strain between different layers of the device. This intriguing discovery can certainly benefit the design of highly robust and durable flexible thin film solar cells. Together with the attractive light trapping effect, the inverted nanocone structure represents a highly promising substrate to build efficient flexible solar cells based on materials not limited to organometallic perovskites.

## **Experimental**

#### **I-cone fabrication**

Inverted cone nanostructures of alumina with three different aspect ratios (0.25, 05, 1.0) were fabricated by multi-step anodizing using an acidic solution and enough DC voltage, followed by a wet etching process, as reported elsewhere.45,46 Then, 10 nm-thick gold, as an anti-sticking layer, was evaporated on the i-cone array of alumina. Afterwards, PDMS solution (Sylgard 184, Dow Corning, 10:1 ratio with the curing agent) was poured on a Au-coated i-cone template using drop casting, followed by degassing and then a curing process at 80 °C for 2 h. After peeling the products directly off the alumina i-cone templates, PDMS nanocone layers with a thickness of 1 mm and different aspect ratios were obtained. In order to fabricate the plastic i-cone nanostructures, UV curing epoxy (NOA 81, Norland Products) was cast on the PDMS nanocone mold. Thereafter, the epoxy on the template was cured under UV light overnight. Finally, the epoxy i-cone films with different aspect ratios and a thickness of 0.2 mm were peeled off from the PDMS cone template. The i-cone films were then employed as the substrate for flexible perovskite solar cells.

#### **Device fabrication**

Methylamine iodide (MAI) was prepared by the reaction of 24 mL of methylamine (33 wt% in ethanol, Sigma-Aldrich) and 10 mL of hydroiodic acid (57 wt% in water, Sigma-Aldrich) in a 250 mL three-neck flask at 0 °C for 2 h and purified using absolute ethanol and diethyl ether, as reported elsewhere.<sup>1,5</sup>

The epoxy substrates (i-cone and planar samples) were cleaned in several steps by immersion in acetone (Merck) and in deionized (DI) water (Millipore, 18 M  $\Omega$  cm) containing 3 vol% Triton X-100, and sonicated for 30 minutes in each solution. The substrates were then rinsed with DI water and sonicated in isopropanol for 30 min, rinsed with DI water again, sonicated in a DI water bath for another 30 min and finally dried by an air gas flow. Thereafter, 300 nm-thick indiumdoped tin oxide (ITO), followed by 50 nm-thick zinc oxide as

an electron transport layer, were deposited on the epoxy substrates by sputtering. Then an organohalide perovskite film was deposited on the epoxy substrates using a two-step evapormethod. Specifically, methylammonium iodide ation (CH<sub>3</sub>NH<sub>3</sub>I) and lead iodide (PbI<sub>2</sub>) were loaded into two separated quartz crucibles. Then the ZnO-compact-layer-coated ITO epoxy substrates were coated with PbI2 and MAI sequentially, under high vacuum ( $4 \times 10^{-6}$  mbar) after heating the crucible by increasing the current density, which was applied to the tungsten baskets. The film thickness and deposition rate were controlled using a quartz sensor and calibrated after measuring the thickness of the PbI<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I films by FESEM. During evaporation, the distance between the substrate and source was around 20 cm, and the deposition rate was fixed in the range of 0.08-0.15 nm s<sup>-1</sup>. The parameters of the evaporation process were optimized precisely because the relative composition of CH<sub>3</sub>NH<sub>3</sub>I to PbI<sub>2</sub> and the overall deposited thickness are two key factors that improve the device performance. In order to fabricate a high quality perovskite film, a 1 to 1 ratio of CH<sub>3</sub>NH<sub>3</sub>I to PbI<sub>2</sub> and a total thickness of 340 nm were found to be the best conditions. Furthermore, in order to complete the crystallization of the perovskite film, the as-deposited films were annealed at 90 °C for 1 h in an Ar-filled tube furnace. Afterwards, a Spiro-OMeTAD (Lumtec, Taiwan) solution (80 mg per ml chlorobenzene), 17.5 µl Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (500 mg ml<sup>-1</sup>), and 28.5 µl TBP were mixed and 100 µl of this solution was spin coated on the perovskite film (3000 rpm for 40 s). Then, the devices were left in a dry box overnight. Finally, 100 nmthick gold was thermally evaporated (0.08 nm  $s^{-1}$ ) as an electrode. The device area was 0.04 cm<sup>2</sup>.

#### Film characterization

The X-ray diffraction method (Bruker D8 X-ray Diffractometer, USA), utilizing Cu K $\alpha$  radiation, and field-emission scanning electron microscopy (FESEM, JEOL JSM-7100F) were used to study the crystal structure, thickness, and morphology of the films. The optical absorption and steady-state photoluminescence spectra were recorded on a Varian Carry 500 spectrometer (Varian, USA) and an Edinburgh Instruments FLS920P fluorescence spectrometer, respectively.

#### Device characterization

The AM1.5G solar spectrum was simulated by using an Abet Class AAB Sun 2000 simulator with an intensity of 100 mW cm<sup>-2</sup> calibrated with a KG5-filtered Si reference cell. The current-voltage (*I*–*V*) data were measured by using a 2400 Series Source Meter (Keithley, USA) instrument. *I*–*V* sweeps (forward and backward) were performed between -1.2 V and +1.2 V, with a step size of 0.02 V and a delay time of 150 ms at each point. External quantum efficiency (EQE) spectra were recorded *versus* wavelength, with a constant white light bias of nearly 5 mW cm<sup>-2</sup> using an Oriel QE-PV-SI (Newport Corporation).

#### **FDTD optical simulation**

Finite-difference time-domain (FDTD) optical simulations were carried out using a Lumerical FDTD software package, version 8.5. All simulations were performed on a unit cell of the epoxy i-cone with a hexagonal array using periodic boundary conditions in the x and y directions. A broadband (300–900 nm) polarized plane wave source was utilized.

Power absorption was calculated with eqn (1):

$$P_{\rm abs} = -0.5\omega |E|^2 \operatorname{imag}(\varepsilon), \tag{1}$$

where  $P_{abs}$  is the absorbed power per unit volume,  $\omega$  is the angular frequency, *E* is the electrical field, and imag( $\varepsilon$ ) is the imaginary part of the dielectric permittivity. Only  $P_{abs}$  inside the devices was considered.

#### Finite element mechanical simulation

To investigate the device mechanical failure mechanism upon bending, finite element mechanical modeling was carried out using a COMSOL Multiphysics 4.2a finite element code. A device with the dimensions  $10 \times 3 \ \mu m^2$  was modeled using Autodesk AutoCAD 2014 according to FESEM images, and the dimensions were similar to the dimensions of the real device, except that the plastic substrate was set as only 1.5 µm to reduce the simulation time.47 Quadratic Lagrange elements were used for mesh generation. The model used the contact mechanics interface with friction in COMSOL, and the linear elastic material model was employed. This model uses the Green-Lagrange strain tensor and the second Piola-Kirchhoff stress tensor for stress-strain relations considering large deflections. In order to visualize the sliding friction at different stages, parametric stepwise iterative modeling was employed. Also, dynamic effects were neglected due to the low deformation rate. Initially, the device was fixed with a support on the right side and a load was applied to the left side to achieve bending. The material parameters used in the model were the following:

Epoxy: E = 25 GPa,  $\nu = 0.35$ ; ITO: E = 210 GPa,  $\nu = 0.3$ ; ZnO: E = 113 GPa,  $\nu = 0.26$ ; perovskite: E = 60 GPa,  $\nu = 0.24$ ; spiro: E = 15 GPa,  $\nu = 0.36$ ; gold: E = 79 GPa,  $\nu = 0.43$ .

Here *E* represents the Young's modulus, and  $\nu$  represents Poisson's ratio.

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