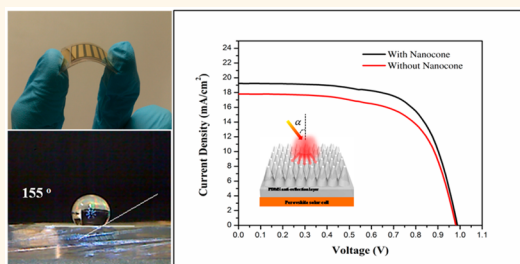


Highly Efficient Flexible Perovskite Solar Cells with Antireflection and Self-Cleaning Nanostructures

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ABSTRACT Flexible thin film solar cells have attracted a great deal of attention as mobile power sources and key components for building-integrated photovoltaics, due to their light weight and flexible features in addition to compatibility with low-cost roll-to-roll fabrication processes. Among many thin film materials, organometallic perovskite materials are emerging as highly promising candidates for high efficiency thin film photovoltaics; however, the performance, scalability, and reliability of the flexible perovskite solar cells still have large room to improve. Herein, we report highly efficient, flexible perovskite solar cells fabricated on ultrathin flexible glasses. In such a device structure, the flexible glass substrate is highly transparent and robust, with low thermal expansion coefficient, and perovskite thin film was deposited with a thermal evaporation method that showed large-scale uniformity. In addition, a nanocone array antireflection film was attached to the front side of the glass substrate in order to improve the optical transmittance and to achieve a water-repelling effect at the same time. It was found that the fabricated solar cells have reasonable bendability, with 96% of the initial value remaining after 200 bending cycles, and the power conversion efficiency was improved from 12.06 to 13.14% by using the antireflection film, which also demonstrated excellent superhydrophobicity.



KEYWORDS: perovskite solar cell · flexible glass · antireflection layer · superhydrophobicity · thermal evaporation

Organohalide perovskite materials have attracted tremendous attention in the past few years for photovoltaic applications due to a number of unique merits including simple and low-cost fabrication methods, excellent optical absorption with tunable band gaps, and long carrier diffusion lengths.^{1–5} To date, both mesoscopic and planar perovskite solar cells have achieved remarkably high efficiencies of more than 19%.^{6–10} In addition to the attractive power conversion efficiency (PCE), utilization of facile and relatively low-temperature fabrication processes to prepare perovskite layers also offers a potentially promising route to realize scalable and cost-effective photovoltaic module production.^{11–17} In order to employ perovskite solar cells for practical applications, including mobile power sources and building-integrated photovoltaics (BIPV), the

PCE needs to be optimized and the portability and flexibility should be taken into consideration in device/module design, as these properties are beneficial for the convenience of practical use and ease of installation. Typically, flexible thin film solar cells are fabricated on plastic substrates. As a matter of fact, there have been a few reports of flexible perovskite solar cells fabricated on polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) plastic substrates with the highest PCE up to 12.2%.^{18–23} In addition, there are also reports on flexible perovskite solar cells on metallic foils, such as titanium, with PCE up to 10.3%.^{24,25} The perovskite solar cell fabrication process typically requires temperatures only up to 100 °C. Thermal expansion of plastic and metallic substrates for this temperature range is still significant. Thus, the thermal process may introduce stress and strain in the perovskite

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films as well as transparent conductive layers of devices, which results in lower PCE as compared with devices fabricated on glass substrates. Also, since metallic foils are not transparent, only a substrate-type device structure can be fabricated on top, whereas the optimized perovskite thin film solar cells typically have superstrate device structure. Therefore, a type of transparent and flexible substrate with high-temperature tolerance and low coefficient of thermal expansion (CTE) is highly desirable for high-performance applications.

In this work, we report fabrication of flexible perovskite solar cells on ultrathin willow glass substrates using a two-step evaporation method. This type of glass is hermetic, highly transparent, mechanically stable, impermeable to water molecules, and suitable for high-temperature processing due to its lower CTE as compared with metal foils and polymer substrates.²⁶ The fabricated solar cell devices on the flexible glass have demonstrated PCE up to 12.06% with reasonable flexibility, retaining more than 96% of the original value after 200 mechanical bending cycles. Furthermore, nanocone array films made of polydimethylsiloxane (PDMS)^{27–31} were attached to the front surface of the devices, which demonstrated dual functions. The nanocone array produces light scattering on the front surface and thus serves as an antireflection (AR) layer, which has further improved device PCE up to 13.14%. Meanwhile, it possesses superhydrophobic property, with a water contact angle of 155°. This

unique property renders the device water repellent feature, which not only can lead to a self-cleaning function, in general, but also is potentially beneficial for device stability since perovskite material can decompose in water quickly without proper passivation.^{6,10}

RESULTS AND DISCUSSION

In this work, perovskite thin film solar cells were fabricated on flexible willow glass (Corning) using a thermal evaporation process, as schematically shown in Figure 1a₁–a₃. The willow glass has a thickness of 50 μm , and it can withstand temperatures up to 500 °C, with a low CTE of $2.5 \times 10^{-6} \text{ K}^{-1}$. Here, we used a sub-100 °C process to fabricate perovskite thin film. Briefly, an indium-doped tin oxide (ITO) layer was sputtered on a flexible glass substrate as the transparent conductive layer, followed by sputtering of zinc oxide (ZnO) as an n-type compact layer. Then, a $\text{CH}_3\text{NH}_3\text{PbI}_3$ film was deposited on the compact layer with sequential thermal evaporation of lead iodide (PbI_2) and methylamine iodide (MAI) in a conventional thermal evaporator, followed by sample annealing at 90 °C for 45 min, in order to complete the reaction and crystallization. Afterward, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) was spin-coated on the perovskite film as a hole transfer layer. Finally, metal gold was thermally evaporated on Spiro-OMeTAD to complete the device as a back contact electrode. Figure 1b shows the cross-sectional SEM image of the

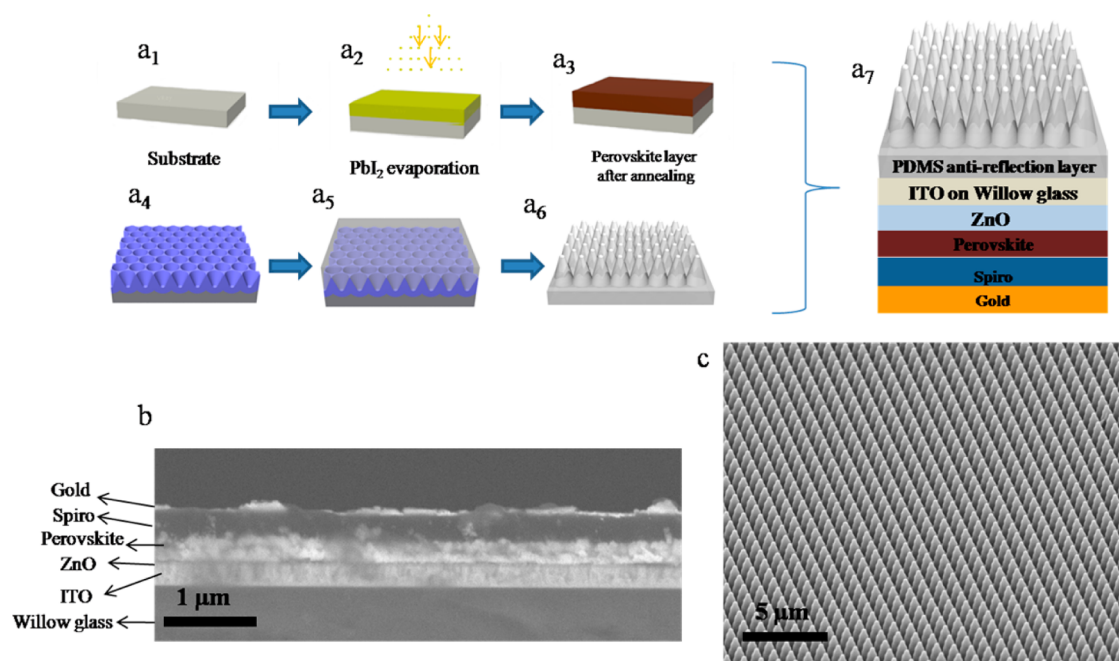


Figure 1. Schematics of perovskite solar cell and nanocone film fabrication. (a₁) Willow glass substrate. (a₂) PbI_2 evaporation. (a₃) MAI evaporation and annealing process at 100 °C for 45 min. (a₄) Inverted cone array fabricated by a multistep anodization and wet etching process on the imprinted Al foil. (a₅) Premixed PDMS poured on a Au-coated template followed by a degassing and curing process. (a₆) Regular nanocone on flexible PDMS after peeling off. (a₇) Schematic structure of the perovskite solar cell device with nanocone PDMS film attached on the top. (b) SEM cross-sectional image of the perovskite solar cell based on a flexible glass substrate. (c) SEM image of PDMS nanocone with 1 μm pitch and 1 μm depth.

completed device with each layer indicated. As the perovskite film is the key active component of the device, its properties have been characterized in detail. Figure S1a,b shows the cross-sectional and top-view SEM images of the perovskite film, suggesting that the thin film is crystalline with uniform surface coverage. Figure S1c,d displays an X-ray diffraction (XRD) pattern and photoluminescence spectrum of the perovskite thin film. The XRD pattern of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite indexed in Figure S1c shows that the perovskite thin film has a tetragonal crystal structure.³² Also, the photoluminescence spectrum of the perovskite film demonstrates a narrow and strong peak at 790 nm under excitation at 405 nm laser, which indicates efficient radiative recombination. In our previous work, various nanostructures have demonstrated promising potential to improve light-harvesting capability^{33–36} and performance of solar cells.^{37–40} In this work, regular nanocone arrays were deployed on the front surface of flexible glass substrates to improve photon-capturing capability of the devices and to achieve water-repellent and self-cleaning functions at the same time. Figure 1a₄–a₆ shows the fabrication process of PDMS nanocone arrays, and Figure 1a₇ shows the final device configuration.

Here, the inverted cone (i-cone) structure achieved by multiple steps of aluminum anodization and etching was employed as the template to fabricate a nanocone PDMS AR film.³³ The tilted angle-view and top-view SEM images of the i-cone template are shown in Figure S2. Note that the evaporation method is capable of depositing uniform perovskite film in a large area, and the nanocone array fabrication is also scalable; a 4 in. willow glass wafer could be deposited with perovskite film, and AR film with the same size has been fabricated, as shown in Figure S3. However, as we have used the spin-coating process to deposit Spiro, our practical devices typically have an area of 0.04 cm².

To investigate the effect of nanocone shape on its AR property, we have fabricated PDMS nanocones with three different aspect ratios (defined by height of nanocones over periodicity) of 0.25, 0.5, and 1.0, using different i-cone templates. Figure 1c illustrates the angular view SEM image of the nanocone film with aspect ratio of 1.0. After the AR films on the solar cell devices were deployed, optical reflectance and absorption measurements were performed and are shown in Figure 2a. It can be seen that the absorption and the

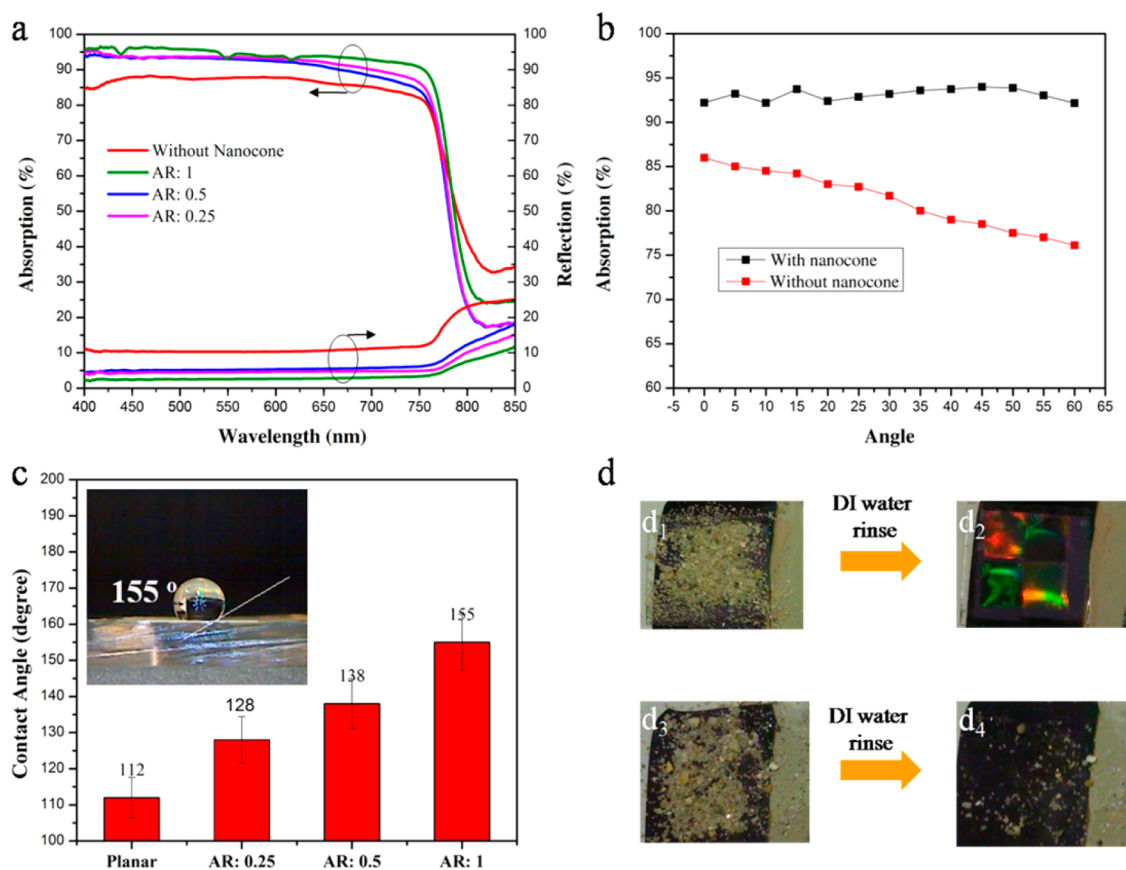


Figure 2. (a) Optical measurements of perovskite solar cell device with and without PDMS nanocone film. (b) Angular absorption of perovskite solar cell with and without PDMS nanocone film. (c) Static contact angles of deionized water on the PDMS layer with different aspect ratios. Inset image is a drop of water on the surface of the nanocone PDMS layer, with AR 1.0 showing a large contact angle of 155°. Self-cleaning experiment of the perovskite solar cell devices with (d₁, d₂) and without (d₃, d₄) a PDMS nanocone layer.

results reflection spectra of perovskite devices with and without AR film using different aspect ratios were acquired in a wavelength range from 400 to 850 nm. A homemade measurement setup equipped with an integrating sphere was used for measurement, and in order to calculate the absorption spectra, the reflectance and transmission were subtracted from unity. Apparently, the reflectance of the device with AR film was significantly reduced as compared with the device without AR film in a broad wavelength range. Particularly, the reflectance reduction is 6% for nanocone aspect ratios of 0.25 and 0.5, and it is close to 8% for nanocones with an aspect ratio of 1.0. The reduction of reflectance is originated by the tapered shape of nanocones, which changes the effective refractive index from the air to the PDMS gradually.³⁰ The higher aspect ratio nanocones on one hand provide a smoother gradient of effective refractive index; on the other hand, a high aspect ratio structure increases light scattering, which further suppresses front side reflectance. Meanwhile, the reflectance at the willow glass/PDMS interface is negligible because of the marginal difference in the refractive index for PDMS and the underneath willow glass. As such, it is important to avoid air bubble trapping at the interface between the AR film and the glass substrate. Otherwise, the reflectance will be adversely increased because of an abrupt change of refractive index. In addition, the optical absorption of solar cell devices with AR layers also demonstrated 6–8% improvement, as shown in Figure 2a, which is consistent with reflectance measurement results, and the absorption spectra also reveal that perovskite solar cells have an optical band gap of ~ 1.55 eV, corresponding to a ~ 795 nm optical wavelength. It is clear that among all the AR films, 1.0 aspect ratio nanocones show the lowest reflection and highest absorption. Therefore, AR films with 1.0 aspect ratio were utilized here for further studies.

It is worth noting that over the time the angle of solar irradiation varies during a day, therefore, omnidirectional light-harvesting capability is important for a solar panel. In this work, optical absorption of perovskite solar cell devices with and without AR films was measured for different angles of the light incidence varying from 0° (normal incidence) to 60° in 10° intervals using a focused halogen light source and an integrating sphere, as shown in Figure 2b. Interestingly, the absorption of the device with AR film remains almost unchanged from 0 to 60° ; however, for the device without AR film, the absorption decreases by $\sim 12\%$ after increasing the incident angle to 60° . These results indicate that the nanocone-based AR film helps the device capture light with both a broad wavelength range and a broad incident angle range.

It is known that organometallic perovskite materials decompose quickly in water.⁶ Therefore, a water proof

passivation/protection packaging layer for the device is crucial from a practical standpoint. In our superstrate device structure, willow glass on the front side is dense and water impermeable; in addition, the nanocone AR films also have a unique water-repellent and superhydrophobic property. This interesting property can avoid water accumulation on solar panels and reduce potential risk of damaging the perovskite layer. Also, PDMS has a strong van der Waals interaction with glass, and as a result, PDMS can be easily attached to the willow glass.³⁰ The static contact angles of deionized (DI) water on the nanocone PDMS layer with different nanocone aspect ratios are shown in Figure 2c. In order to measure the contact angles, $2\ \mu\text{L}$ of DI water was used. It is interesting to see that a planar PDMS substrate is hydrophobic, with a water contact angle of 112° , and the contact angle increases monotonically with nanocone aspect ratio with AR 1.0 nanocones showing a contact angle up to 155° , which satisfies the critical condition of superhydrophobicity (Figure 2c). The reason that the contact angle increases with aspect ratio rests in the fact that a higher aspect ratio structure traps more air inside and typically provides less contact area to the water droplet on the top of nanocones.⁴¹ Besides water contact angle, roll-off angle is also an important parameter. In reality, there is always dust accumulation on the surface of a solar panel, which hurts panel performance dramatically. When the panel surface has nanostructures, the dust will be floating on the nanostructures, and if the water roll-off angle is small, the dust can be easily carried away by the water droplets upon rain fall. This will lead to a self-cleaning effect. Figure S4 shows the water roll-off angle on different AR films. It can be seen that the roll-off angle decreases monotonically with an increase of nanocone aspect ratio. Aspect ratio 1.0 nanocones can achieve a 13° roll-off angle. This small roll-off angle indicates that the AR film may have a dust self-cleaning function. To verify this, dust self-cleaning experiments were carried out and are shown in Figure 2d₁–d₄. In this process, the dust/sand particles can be easily moved by rolling a water droplet across the surface and removed from the device. In order to maintain the solar panel performance for long term, a self-cleaning property is highly desirable.

To verify the experimental results, finite-difference time domain (FDTD) simulations were carried out on the devices with and without AR layers. As shown in Figure 3a, the simulated absorption spectra show a consistent trend with the experimental ones for different aspect ratios of AR films. As can be seen, the AR film has a clear effect on improving the overall absorption. In order to identify the optimal aspect ratio of PDMS AR films, the absorption spectra of the devices with different aspect ratios were integrated with an AM1.5G solar spectrum (Figure 3b). The results illustrate that AR films improve the integrated absorption by

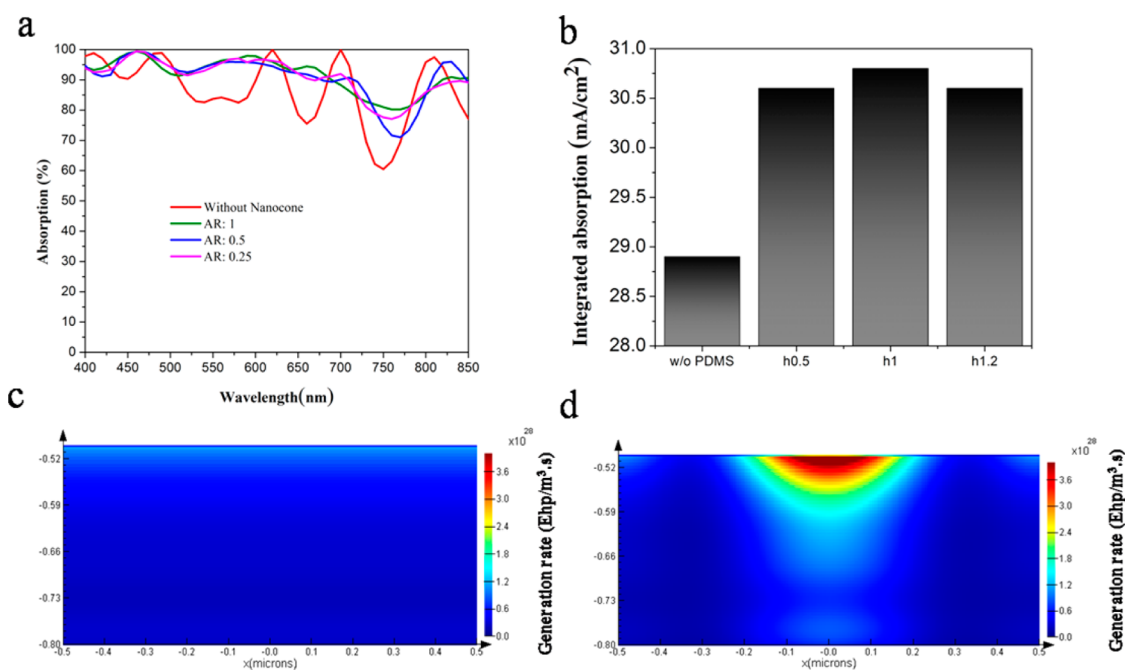


Figure 3. FDTD simulation. (a) Absorption spectra and (b) integrated absorption of perovskite thin film integrated with nanocone PDMS films with different aspect ratios. Integrated absorption is calculated by integrating absorption spectra with an AM1.5G solar spectrum. Generation rate (number of absorbed photons/m³/s) in the perovskite layer (c) without and (d) with PDMS nanocone film with AR 1.0. The maximum values of the color bars are both 2×10^{28} photons/m³/s, with red showing a high generation rate and blue showing a low generation rate.

around 1 mA/cm², and the 1.0 aspect ratio shows the best absorption, which agrees well with experimental results. To shed more light on the detailed absorption situation inside the perovskite layer, the generation rate profiles for devices with and without AR films are shown in Figure 3c,d. When the two profiles are compared, the absorption of the device with AR film shows a clear focusing effect inside the perovskite layer, leading to significant absorption enhancement in the perovskite solar cell. Interestingly, the hot spot of generation was found right below the nanocone structure, inside the active perovskite layer, as shown in Figure S5. This clearly indicates the benefit of introducing the nanocone structure on top of the device.

Figure 4a shows the photograph of a nanocone AR film attached on the perovskite solar cell based on flexible glass. The performance of the same device with and without AR films has been characterized systematically. Figure 4b presents current density–voltage (*J*–*V*) characteristics of a representative device under 1 sun simulated illumination. The figures of merit for this device together with average performance of multiple devices are summarized in Table 1. The *J*–*V* curves show that the *J*_{sc} increases from 17.7 to 19.3 mA/cm² after attaching the nanocone AR film on the top side of the solar cell device, which results in an enhancement in the PCE from 12.06 to 13.14%, corresponding to a ~9% increment. This can be clearly attributed to the enhancement of light absorption using AR film, as shown in Figure 2a. As presented in Table 1,

this conclusion is consistent for 10 devices with an average PCE of 10.6 and 11.7%, without and with AR film, respectively. This improvement can also be confirmed with external quantum efficiency measurements, as shown in Figure 4c. As it can be seen, the AR effect contributes to the entire wavelength range, which proves that the AR film is effective enough to harness visible light. In order to study the effect of scan direction, the forward and reverse scan direction were performed as shown in Figure S6. The results show that there is nearly no significant change in the *J*–*V* curves. In addition, *J*_{sc} and PCE of the devices with and without AR film were measured at different incident angles, as shown in Figure 4d. Note that both *J*_{sc} and PCE are normalized with the horizontal light projection area on the device when it is inclined under the collimated irradiation, in order to have a fair comparison with the condition where the device is not inclined with normal light incidence. Because the AR film can be easily attached and detached, the same device was also used for the measurements. Apparently, the absolute enhancement of *J*_{sc} and PCE for devices with AR film is nearly 1.5–2.5 mA/cm² and 1–1.75%, respectively. More interestingly, with increasing light incident angle, both *J*_{sc} and PCE drop more rapidly without AR film, as compared to the case with AR film. Particularly, the efficiency of the device with AR film for a 60° incident angle is improved by 20% as compared with the reference sample. This confirms the observation from Figure 2b, where the nanocones have omnidirectional light-harvesting capability. This property is highly attractive

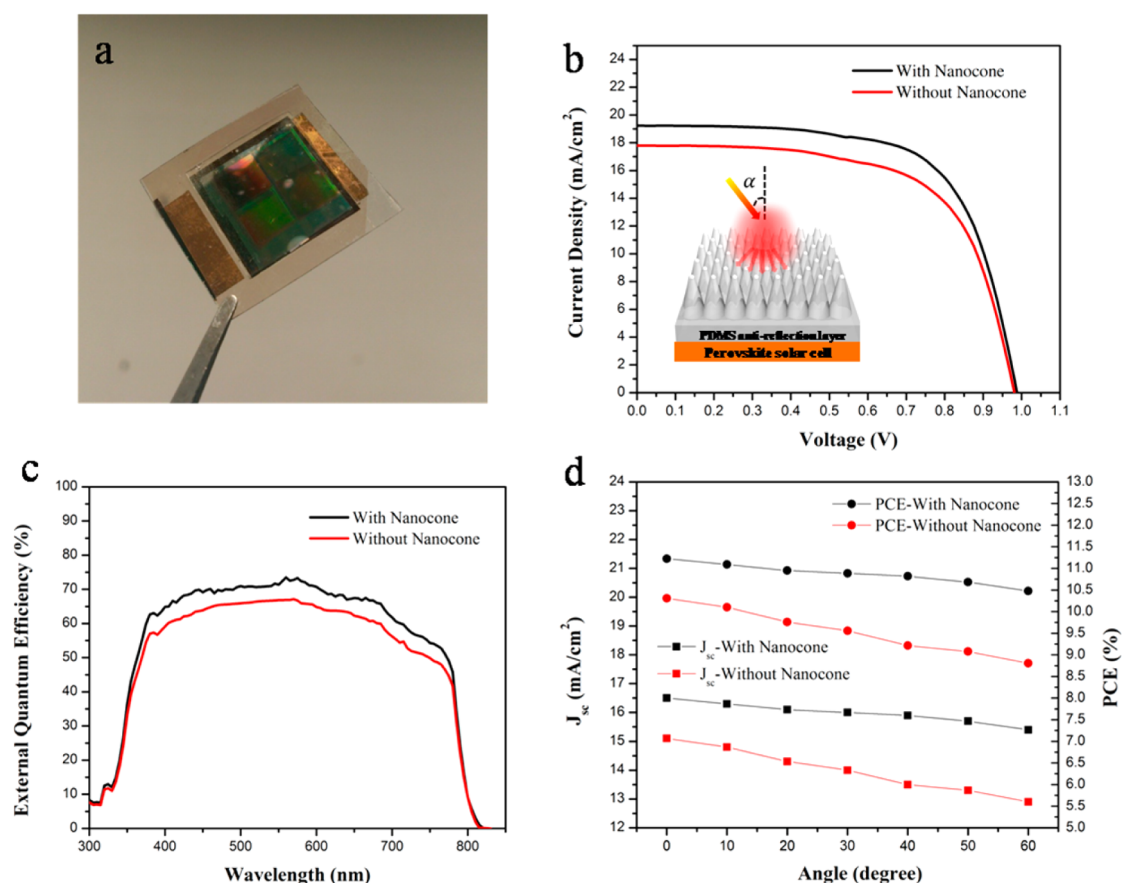


Figure 4. (a) Photograph of perovskite solar cell based on flexible willow glass integrated with a nanocone PDMS layer. (b) J - V measurements of perovskite solar cell devices with and without PDMS nanocone film (inset image is the schematic of light scattering in the device with a nanocone layer). (c) QE measurement of perovskite devices with and without a PDMS nanocone film. (d) J_{sc} and PCE of a perovskite solar cell device with and without a PDMS nanocone film obtained at different incident angles of light.

TABLE 1. Figures of Merit for the Solar Cell Devices with and without AR Films

devices	V_{oc} (V)	J_{sc} (mA/cm^2)	fill factor (%)	efficiency (%)	average of PCE (%)
without nanocone	0.97	17.7	70	12.06	10.6
with nanocone	0.98	19.3	69	13.14	11.7

for solar panels without a mechanical solar tracking system.

Flexibility is a desirable feature of solar cells for many applications, such as mobile power sources and BIPV. In this work, 50 μm thickness renders willow glass and our perovskite solar cells with respectable flexibility. Figure 5a shows a photograph of a flexible device. The variation of PCE *versus* bending angle for a willow-glass-based perovskite solar cell is shown in Figure S7. Note that the change of light projection area on the device during a bending process is considered when calculating the power conversion efficiency. To examine the bendability of the devices, we used a solar cell with a length of 3 cm and bent it to a radius of 4 cm by applying mechanical force up to 200 cycles, then after

each cycle, the device performance was measured repetitively. The maximum bending angle of a flexible device was found to be 90° , beyond that, the flexible glass substrate is prone to break. The effect of the bending cycles on the photovoltaic parameters of the device is presented in Figure 5b. The results show that J_{sc} , open-circuit voltage (V_{oc}), and fill factor (FF) were only marginally reduced through the bending tests. Specifically, J_{sc} , V_{oc} , and FF of the flexible device were reduced from 18.3 to 18.11 mA/cm^2 , from 0.98 to 0.97 V, and from 0.65 to 0.64, respectively. As a result, the PCE of the device is decreased from 11.7 to 11.24% after 200 bending cycles. As shown in Figure S8, during bending cycles, microcracks and delamination could be produced at the interfaces between different layers of the perovskite solar cells, which would deteriorate the device and increase the series resistance of devices. It is noteworthy that in the current device structure there is no backside passivation, and the entire device is not packaged; thus the active layer is not in the mechanical neutral plane during bending. With proper packaging and placement of the films in the mechanical neutral plane, the bending side effects can be minimized and performance degradation upon bending is expected to be much less.

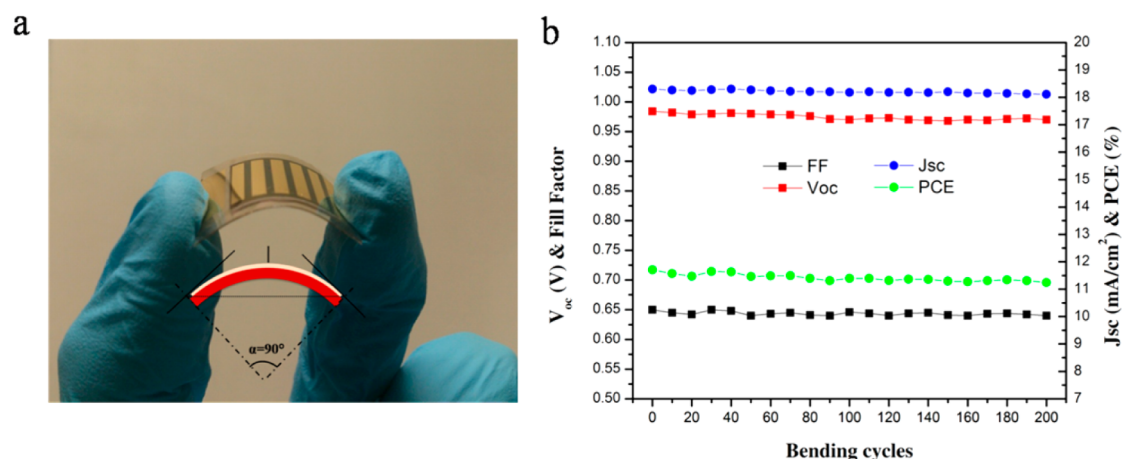


Figure 5. (a) Photograph of perovskite solar-cell-based flexible willow glass. (b) Efficiency stability depending on bending cycle in perovskite solar cells based on a willow glass substrate.

CONCLUSIONS

In summary, we demonstrated flexible $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells fabricated on ultrathin willow glasses using an evaporation method. A willow glass substrate is transparent, waterproof, and compatible with high-temperature processes with a low thermal expansion coefficient. These attractive properties make flexible glass a suitable replacement for flexible polymer substrates. On this type of flexible substrate, we have achieved device performance up to 12.06%. Meanwhile, the device performance was further improved to 13.14% by adding a layer of nanocone AR film on the front surface of willow glass to enhance light absorption. In addition, the AR film also

demonstrated a water-repellent feature with a water contact angle up to 155° and a low roll-off angle of 13° . These properties lead to an interesting dust self-cleaning function which helps to maintain solar panel cleanliness and stable power output. In the end, the flexibility of the devices has been evaluated with 200 bending cycles. It was found that device performance was not significantly affected by repetitive bending. Overall, to our best knowledge, the device performance reported here is among the best for flexible perovskite solar cells. The processes developed here open up a promising route for large-scale and cost-effective production of high-performance thin film photovoltaics, which are not limited to organometallic perovskite materials.

METHODS

Preparation of Nanocone AR and SC Layer. Aluminum foil (0.25 mm thick, 99.99% purity, Alfa Aesar) was polished electrochemically and imprinted using a hexagonally ordered nanopillar silicon stamp with a pitch of $1\ \mu\text{m}$ and a height of 200 nm in order to create nanostructured indentation on the Al foil. The i-cone pattern was fabricated on the imprinted Al foil by multistep anodization using an acidic solution and proper DC voltage, followed by a wet etching processes.^{30,33,34} Afterward, 50 nm thick gold was thermally evaporated on the i-cone array as an antisticking layer. Then, the PDMS solution (Sylgard 184, Dow Corning, 10:1 ratio with the curing agent) was drop-cast on the Au-coated i-cone template followed by a degassing process and then cured at 80°C for 2 h. Finally, PDMS nanocone films with a thickness of 0.2 mm and different nanocone heights were peeled off directly from the i-cone template.

Methylamine Iodide Preparation. Methylamine (27.8 mL, 33 wt % in ethanol, Sigma-Aldrich) was added dropwise to 30 mL of hydroiodic acid (57 wt % in water, Sigma-Aldrich) in a 250 mL three-neck flask and mixed at 0°C for 2 h to complete the reaction. The MAI powder was recovered from the solution using a rotary evaporator at 50°C followed by dissolving in absolute ethanol and precipitating by adding diethyl ether to the solution. Finally, the MAI powder was dried at 60°C overnight in a vacuum oven.

Device Fabrication. The $50\ \mu\text{m}$ thick willow glass pieces were purchased from Corning Company (USA) and cleaned prior to use by the following procedure. First, they were immersed in acetone (Merck) and then DI water (Milipore, $18\ \text{M}\Omega\cdot\text{cm}$)

containing 3 vol % of Triton X-100 and sonicated for 30 min for each solution. The specimens were then rinsed with DI water and sonicated in isopropyl alcohol for 30 min, rinsed with DI water again, sonicated in a DI water batch for another 30 min, and finally dried by blowing with air. Thereafter, they were coated with 300 nm thick ITO followed by 50 nm thick zinc oxide as an electron transport layer using sputtering. Then, a two-step thermal evaporation method was employed to deposit the organohalide perovskite film on the substrates. Specifically, the PbI_2 and MAI ($\text{CH}_3\text{NH}_3\text{I}$) were loaded onto two different quartz crucibles and then evaporated sequentially onto the ZnO compact-layer-coated ITO willow glass substrates under high vacuum (4×10^{-6} mbar) with a deposition rate of $0.1\text{--}0.2\ \text{nm/s}$. The vapor deposition rate was controlled using a quartz sensor and calibrated after measuring the thickness of PbI_2 and $\text{CH}_3\text{NH}_3\text{I}$ films. The sources were located at the bottom of the chamber with an angle of 90° with respect to the substrates. The distance between source and substrate was 20 cm. We fixed the evaporation rate in a range of $0.08\text{--}0.15\ \text{nm/s}$. Since the relative composition of $\text{CH}_3\text{NH}_3\text{I}$ to PbI_2 and the overall deposited thickness are two key parameters to improve the device performance, we optimized them for evaporation method. Finally, we found that a 1:1 ratio of $\text{CH}_3\text{NH}_3\text{I}$ to PbI_2 and a thickness of 340 nm of the perovskite film were the best conditions in order to achieve optimal device performance. The as-deposited films were annealed at 90°C for 45 min in the Ar-filled tube furnace. Thereafter, Spiro-OMeTAD (Lumtec, Taiwan) solution (80 mg/mL chlorobenzene) with 17.5 mL of Li-bis(trifluoromethanesulfonyl)imide (Li-TFSI)/acetonitrile

(500 mg/mL) and 28.5 mL of TBP as additives was deposited on the perovskite film by a spin-coating process (3000 rpm for 40 s). Then the devices were left in a desiccator overnight, and finally, 100 nm thick gold was deposited by thermal evaporation (0.08 nm/s) as an electrode. The device area was 0.04 cm².

Film Characterization. Field-emission scanning electron microscopy (JEOL JSM-7100F) and X-ray diffraction method (Bruker D8 X-ray diffractometer, USA) utilizing Cu K α radiation were used to study the thickness, morphology, roughness of the films, and phase characterization. The optical absorption and steady-state photoluminescence spectra were recorded on a Varian Cary 500 spectrometer (Varian, USA) and an Edinburgh Instruments FLS920P fluorescence spectrometer, respectively.

Device Characterization. The AM1.5G solar spectrum was simulated by an Abet Class AAB Sun 2000 simulator with an intensity of 100 mW cm⁻² calibrated with a KG5-filtered Si reference cell. The current–voltage (*I*–*V*) data were measured using a 2400 series sourcemeter (Keithley, USA). *I*–*V* sweeps (forward and backward) were performed between –1.2 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 spectra were recorded versus wavelength with a constant white light bias of nearly 5 mW cm⁻² using an Oriel QE-PV-SI (Newport Corporation).

FDTD Simulation. The FDTD simulation was conducted with the Lumerical FDTD software package. Plane waves with wavelengths ranging from 300 to 900 nm were utilized. A unit cell of the PDMS nanocone hexagonal array was studied, and a periodic boundary condition was utilized.⁴² Power absorption was calculated with eq 1:

$$P_{\text{abs}} = -0.5\omega|E|^2\text{imag}(\epsilon) \quad (1)$$

where P_{abs} is the absorbed power per unit volume, ω is the angular frequency, E is the electrical field, and $\text{imag}(\epsilon)$ is the imaginary part of the dielectric permittivity. Only P_{abs} inside the perovskite layer was considered. Furthermore, the absorption spectrum can be integrated with the AM1.5G solar spectrum to obtain the integrated absorption. If the internal quantum efficiency is assumed to be 100%, then the integrated absorption will be equal to the generation rate, namely, generated electron–hole pairs per unit volume per second. In order to model the antireflection films on a perovskite solar cell, a 5 μ m thick layer of PDMS on top of FTO glass was employed.

Conflict of Interest: The authors declare no competing financial interest.

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Characterization of perovskite materials, SEM images of AAO template, photographs of large-scale flexible perovskite solar cell and antireflection film, roll-off angles of DI water on the surface of the nanocone PDMS film, models of FDTD simulation, and *J*–*V* measurement of the device with different scan direction, variation of PCE versus bending angle of flexible device, and top-view SEM image of perovskite solar cell after 200 bending cycles (PDF)

REFERENCES AND NOTES

- Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Low-Temperature Solution-Processed Perovskite Solar

- Cells with High Efficiency and Flexibility. *Science* **2013**, *342*, 341–344.
- Nie, W.; Tsai, H.; Asadpour, R.; Blancon, J. C.; Neukirch, A. J.; Gupta, G.; Crochet, J. J.; Chhowalla, M.; Tretiak, S.; Alam, M. A.; et al. High-Efficiency Solution-Processed Perovskite Solar Cells with Millimeter-Scale Grains. *Science* **2015**, *347*, 522–525.
- Tavakoli, M. M.; Gu, L.; Gao, Y.; Reckmeier, C.; He, J.; Rogach, A. L.; Yao, Y.; Fan, Z. Fabrication of Efficient Planar Perovskite Solar Cells Using a One-Step Chemical Vapor Deposition Method. *Sci. Rep.* **2015**, DOI:10.1038/srep14083.
- Dong, Q.; Fang, Y.; Shao, Y.; Mulligan, P.; Qiu, J.; Cao, L.; Huang, J. Electron-Hole Diffusion Lengths > 175 μ m in Solution-Grown CH₃NH₃PbI₃ Single Crystals. *Science* **2015**, *347*, 967–970.
- Kazim, S.; Nazeeruddin, M. K.; Grätzel, M.; Ahmad, S. Perovskite as Light Harvester: A Game Changer in Photovoltaics. *Angew. Chem., Int. Ed.* **2014**, *53*, 2812–2824.
- Stoumpos, C. C.; Malliakas, C. D.; Kanatzidis, M. G. Semiconducting Tin and Lead Iodide Perovskites with Organic Cations: Phase Transitions, High Mobilities, and Near-Infrared Photoluminescent Properties. *Inorg. Chem.* **2013**, *52*, 9019–9038.
- Rong, Y.; Tang, Z.; Zhao, Y.; Zhong, X.; Venkatesan, S.; Graham, H.; Patton, M.; Jing, Y.; Guloy, A. M.; Yao, Y. Solvent Engineering Towards Controlled Grain Growth in Perovskite Planar Heterojunction Solar Cells. *Nanoscale* **2015**, *7*, 10595.
- Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* **2012**, *338*, 643–647.
- Liu, M.; Johnston, M. B.; Snaith, H. J. Efficient Planar Heterojunction Perovskite Solar Cells by Vapour Deposition. *Nature* **2013**, *501*, 395–398.
- National Renewable Energy Laboratory. Best Research-Cell Efficiencies; http://www.nrel.gov/ncpv/images/efficiency_chart.jpg (accessed March 20, 2015).
- Tavakoli, M. M.; Aashuri, H.; Simchi, A.; Kalytchuk, S.; Fan, Z. Quasi Core/Shell Lead Sulfide/Graphene Quantum Dots for Bulk Heterojunction Solar Cells. *J. Phys. Chem. C* **2015**, *10.1021/acs.jpcc.5b04195*.
- Liu, D.; Kelly, T. L. Perovskite Solar Cells with a Planar Heterojunction Structure Prepared Using Room-Temperature Solution Processing Techniques. *Nat. Photonics* **2014**, *8*, 133–138.
- Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131*, 6050–6051.
- Hodes, G. Perovskite-Based Solar Cells. *Science* **2013**, *342*, 317–318.
- Tavakoli, M. M.; Simchi, A.; Aashuri, H. Supercritical Synthesis and *In Situ* Deposition of PbS Nanocrystals with Oleic Acid Passivation for Quantum Dot Solar Cells. *Mater. Chem. Phys.* **2015**, *156*, 163–169.
- Burschka, J.; Pellet, N.; Moon, S.; Humphry-Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. Sequential Deposition as a Route to High-Performance Perovskite-Sensitized Solar Cells. *Nature* **2013**, *499*, 316–319.
- Tavakoli, M. M.; Tayyebi, A.; Simchi, A.; Aashuri, H.; Outokesh, M.; Fan, Z. Physicochemical Properties of Hybrid Graphene–Lead Sulfide Quantum Dots Prepared by Supercritical Ethanol. *J. Nanopart. Res.* **2015**, *17*, 1–13.
- Wang, X.; Li, Z.; Xu, W.; Kulkarni, S. A.; Batabyal, S. K.; Zhang, S.; Cao, A.; Wong, L. H. TiO₂ Nanotube Arrays Based Flexible Perovskite Solar Cells with Transparent Carbon Nanotube Electrode. *Nano Energy* **2015**, *11*, 728–735.
- Kumar, M. H.; Yantara, N.; Dharani, S.; Graetzel, M.; Mhaisalkar, S.; Boix, P. P.; Mathews, N. Flexible, Low-Temperature, Solution Processed ZnO-Based Perovskite Solid State Solar Cells. *Chem. Commun.* **2013**, *49*, 11089–11091.
- You, J.; Hong, Z.; Yang, Y. M.; Chen, Q.; Cai, M.; Song, T.; Chen, C.; Lu, S.; Liu, Y.; Zhou, H. Low-Temperature Solution-Processed Perovskite Solar Cells with High Efficiency and Flexibility. *ACS Nano* **2014**, *8*, 1674–1680.

21. Roldán-Carmona, C.; Malinkiewicz, O.; Soriano, A.; Espallargas, G. M.; Garcia, A.; Reinecke, P.; Kroyer, T.; Dar, M. I.; Nazeeruddin, M. K.; Bolink, H. J. Flexible High Efficiency Perovskite Solar Cells. *Energy Environ. Sci.* **2014**, *7*, 994–997.
22. Kim, B. J.; Kim, D. H.; Lee, Y.-Y.; Shin, H.-W.; Han, G. S.; Hong, J. S.; Mahmood, K.; Ahn, T. K.; Joo, Y.-C.; Hong, K. S.; et al. Highly Efficient and Bending Durable Perovskite Solar Cells: Toward a Wearable Power Source. *Energy Environ. Sci.* **2015**, *8*, 916–921.
23. Docampo, P.; Ball, J. M.; Darwich, M.; Eperon, G. E.; Snaith, H. J. Efficient Organometal Trihalide Perovskite Planar-Heterojunction Solar Cells on Flexible Polymer Substrates. *Nat. Commun.* **2013**, *4*, 1–6.
24. Jung, H. S.; Park, N. G. Perovskite Solar Cells: From Materials to Devices. *Small* **2015**, *11*, 10–25.
25. Troughton, J.; Bryant, D.; Wojciechowski, K.; Carnie, M. J.; Snaith, H.; Worsley, D. A.; Watson, T. M. Highly Efficient, Flexible, Indium-Free Perovskite Solar Cells Employing Metallic Substrates. *J. Mater. Chem. A* **2015**, *3*, 9141–9145.
26. Rance, W. L.; Burst, J. M.; Meysing, D. M.; Wolden, C. A.; Reese, M. O.; Gessert, T. A.; Metzger, W. K.; Garner, S.; Cimo, P.; Barnes, T. M. 14%-Efficient Flexible CdTe Solar Cells on Ultra-Thin Glass Substrates. *Appl. Phys. Lett.* **2014**, *104*, 143903.
27. Raut, H. K.; Ganesh, V. A.; Nair, A. S.; Ramakrishna, S. Anti-Reflective Coatings: A Critical, in Depth Review. *Energy Environ. Sci.* **2011**, *4*, 3779–3804.
28. Leung, S. F.; Yu, M.; Lin, Q.; Kwon, K.; Ching, K. L.; Gu, L.; Yu, K.; Fan, Z. Efficient Photon Capturing with Ordered Three-Dimensional Nanowell Arrays. *Nano Lett.* **2012**, *12*, 3682–3689.
29. Guldin, S.; Kohn, P.; Stefk, M.; Song, J.; Divitini, G.; Ecarla, F.; Ducati, C.; Wiesner, U.; Steiner, U. Self-Cleaning Antireflective Optical Coatings. *Nano Lett.* **2013**, *13*, 5329–5335.
30. Chen, J.; Chang, W.; Huang, C.; Sun, K. Biomimetic Nanostructured Antireflection Coating and Its Application on Crystalline Silicon Solar Cells. *Opt. Express* **2011**, *19*, 14411–14419.
31. Tsui, K. H.; Lin, Q.; Chou, H.; Zhang, Q.; Fu, H.; Qi, P.; Fan, Z. Low-Cost, Flexible, and Self-Cleaning 3D Nanocone Anti-Reflection Films for High-Efficiency Photovoltaics. *Adv. Mater.* **2014**, *26*, 2805–2811.
32. Baikie, T.; Fang, Y.; Kadro, J. M.; Schreyer, M.; Wei, F.; Mhaisalkar, S. G.; Graetzel, M.; White, T. J. Synthesis and Crystal Chemistry of the Hybrid Perovskite (CH₃NH₃)PbI₃ for Solid-State Sensitized Solar Cell Applications. *J. Mater. Chem. A* **2013**, *1*, 5628–5641.
33. Lin, Q.; Leung, S.; Lu, L.; Chen, X.; Chen, Z.; Tang, H.; Su, W.; Li, D.; Fan, Z. Inverted Nanocone-Based Thin Film Photovoltaics with Omnidirectionally Enhanced Performance. *ACS Nano* **2014**, *8*, 6484–6490.
34. Gao, Y.; Jin, H.; Lin, Q.; Li, X.; Tavakoli, M. M.; Leung, S.; Tang, W. M.; Zhou, L.; Chan, H. L. W.; Fan, Z. Highly Flexible and Transferable Supercapacitors with Ordered Three-Dimensional MnO₂/Au/MnO₂ Nanospoke Arrays. *J. Mater. Chem. A* **2015**, *3*, 10199–10204.
35. Qiu, Y.; Leung, S. F.; Zhang, Q.; Hua, B.; Lin, Q.; Wei, Z.; Tsui, K. H.; Zhang, Y.; Yang, S.; Fan, Z. Efficient Photoelectrochemical Water Splitting with Ultrathin Films of Hematite on Three-Dimensional Nanophotonic Structures. *Nano Lett.* **2014**, *14*, 2123–2129.
36. Kapadia, R.; Fan, Z.; Takei, K.; Javey, A. Nanopillar Photovoltaics: Materials, Processes, and Devices. *Nano Energy* **2012**, *1*, 132–144.
37. Kapadia, R.; Fan, Z.; Javey, A. Design Constraints and Guidelines for CdS/CdTe Nanopillar Based Photovoltaics. *Appl. Phys. Lett.* **2010**, *96*, 103116.
38. Lin, Q.; Hua, B.; Leung, S. F.; Duan, X.; Fan, Z. Efficient Light Absorption with Integrated Nanopillar/Nanowell Arrays for Three-Dimensional Thin-Film Photovoltaic Applications. *ACS Nano* **2013**, *7*, 2725–2732.
39. Yu, R.; Ching, K. L.; Lin, Q.; Leung, S. F.; Arcrossito, D.; Fan, Z. Strong Light Absorption of Self-Organized 3-D Nanospoke Arrays for Photovoltaic Applications. *ACS Nano* **2011**, *5*, 9291–9298.
40. Leung, S. F.; Gu, L.; Zhang, Q.; Tsui, K. H.; Shieh, J. M.; Shen, C. H.; Hsiao, T. H.; Hsu, C. H.; Lu, L.; Li, D.; et al. Roll-to-Roll Fabrication of Large Scale and Regular Arrays of Three-Dimensional Nanospikes for High Efficiency and Flexible Photovoltaics. *Sci. Rep.* **2014**, *4*, 4243.
41. Choi, W.; Tuteja, A.; Mabry, J. M.; Cohen, R. E.; McKinley, G. H. A Modified Cassie–Baxter Relationship to Explain Contact Angle Hysteresis and Anisotropy on Non-Wetting Textured Surfaces. *J. Colloid Interface Sci.* **2009**, *339*, 208–216.
42. Tavakoli, M. M.; Tavakoli, R.; Davami, P.; Aashuri, H. A Quantitative Approach to Study Solid State Phase Coarsening in Solder Alloys Using Combined Phase-Field Modeling and Experimental Observation. *J. Comput. Electron.* **2014**, *13*, 425–431.