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Enhanced Performance and Flexibility of Perovskite Solar Cells Based on Microstructured Multilayer Transparent Electrodes

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Supporting Information

ABSTRACT: The performance and flexibility of perovskite solar cells (PSCs) have been enhanced by introducing microstructured WO₃/Ag/WO₃ (WAW) multilayer transparent electrodes, which can be fabricated through glancing angle deposition (GLAD) method. The structure and morphology of the second WO₃ layers in WAW films can be altered significantly by changing the deposition angles. A film with porous, oriented WO₃ nanocolumns was obtained at the deposition angle of 75°. The rigid and flexible devices based on this microstructured electrodes show enhanced power conversion efficiencies (PCEs) of 14.91 and 13.79%, respectively, which are increasing by 10.36 and 10.14% in comparison with the devices based on the WAW electrodes with planar structure, respectively. Simultaneously, the bending stability of the flexible PSCs based on the microstructured WAW electrode has been improved significantly, which retains 90.97% of its initial PCE after 1000 times



bending under the maximum strain of 1.3%, compared with the 78.39% of the reference device with the planar WAW electrode. This can be attributed to the unique microstructure of WAW electrodes fabricated by GLAD methods, releasing the mechanical stresses under repeated bending; moreover, the smaller grains induced by this electrode can disperse the stress, which decrease the damage on the perovskite layer; we believe that this work will pave for the way to improve the performance and flexibility of PSCs.

KEYWORDS: perovskite solar cells, multilayer transparent electrodes, glancing angle deposition, microstructure, flexibility

INTRODUCTION

Nowadays, facing with the lack of nonrenewable energy, the research and development of novel applications for renewable energy are of importance. Solar cells based on metal-halide perovskite materials $CH_3NH_3PbX_3$ (MAPbX₃, X = Cl, Br, and I) have been proposed in the past few years,^{1,2} and the power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) have been rapidly boosted from 3.8% to over 22%,³⁻¹⁴ revealing their commercial application prospect and attracting more attention for their correlative devices, such as flexible PSCs.

Compared to the high device efficiencies based on the rigid PSCs, the PCEs of the flexible PSCs have been improved steadily.^{15–17} However, a reliable flexible PSC requests not only high efficiency, but also excellent mechanical flexibility, which is mainly reflected in two aspects, the bending durability of transparent electrodes and active layers. Among the reported flexible transparent electrodes, indium-tin-oxide (ITO) electrodes are popularly used, and a maximum PCE of 16% has been reached based on this electrode.¹⁷ However, because of the brittle nature, ITO electrodes present poor bending resistance, which cause the serious deterioration of flexible device

performance.^{18,19} Additionally, the rising cost and the high-temperature processing of ITO electrodes also hinder their applications on flexible PSCs.

To avoid the negative affection of flexible ITO electrodes, various ITO-free transparent electrodes have been introduced into the flexible PSCs, such as Ag nanowires,²⁰ metal foils,²¹ highly conductive polymer poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS), and graphene.^{22–26} Li et al. demonstrated a flexible PSC with a PCE of 14.0% utilizing an ultrathin silver-mesh/conducting polymer transparent electrode. Importantly, it showed high durability against mechanical bending, which maintained a PCE at 95% of its initial value after 5000 bending cycles with a bending radius of 5 mm.²⁷ Recently, a maximum PCE of 17.3% was reported by using a graphene transparent electrode, and the PCE was maintained at 85% of its initial value after bending 5000 times with a bending radius of 2 mm.²⁶ Although the flexibility of the PSCs based on different transparent electrodes has been

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Figure 1. (a) Schematic diagram of GLAD technology. (b) Average optical transmittance (450–800 nm) of WAW electrodes under various deposition angles. (c) Optimized transmittance spectra and (d) sheet resistance of WAW electrodes deposited at different angles.

improved to different degrees, these transparent electrodes also suffer various issues that degenerated the device performance or hindered themselves to be applied in flexible PSCs, such as poor transmittance or high sheet resistance for metal nanowires and metal foils,²⁸ poor moisture resistance for PEDOT:PSS,²⁹ and troublesome preparation and transfer processing for graphene.³⁰ Therefore, it is important to exploit new transparent electrodes with high transmittance, low sheet resistance, and excellent flexibility for flexible PSCs.

Dielectric-metal-dielectric (DMD) multilayer transparent electrodes, such as $MoO_3/Ag/WO_3$,³¹ NiO/Ag/NiO,³² ZnO/Ag/ZnO,³³ SnO_x/Ag/SnO_x/Bi₂O₃,³⁴ and so on, are competitive alternatives to traditional ITO electrodes because of their low sheet resistance and excellent transmittance, which have been applied in organic light-emitting diodes and polymer photovoltaic cells successfully.^{35,36} In our previous work, WO₃/ Ag/WO₃ (WAW) electrodes have been introduced into PSCs, and a flexible PSC has also been tried and achieved a PCE of 8.04%.³⁷ However, it is found that the performance of flexible devices decreased unexpectedly in the bending test. It is worth mentioning that the WAW electrode possesses excellent flexibility, which has been verified during previous studies.^{38,39} Therefore, the degradation of device performance should be attributed to the perovskite layers, in which large perovskite grains would present after spin-coating and annealing processes. The stress may be mainly concentrated on the larger perovskite grains under repeated bending, resulting in the separation of grains and grains and grains and substrates; also, the large grains are more prone to split into small grains, thus increasing grain boundaries and traps or defects. In contrast, the smaller grains contact with substrates tightly in the process of bending and make the stress more dispersed, reducing the damage on perovskite layer, which will be more stable under plastic deformation.

In this work, microstructured WAW multilayer transparent electrodes have been manufactured by the glancing angle deposition (GLAD) method.⁴⁰⁻⁴² As the deposition angle

changes, different structures and morphologies of the second WO_3 layers in WAW films have been observed, and a film with porous, oriented WO_3 nanocolumns is acquired at the deposition angle of 75°. Enhanced device performance has been achieved by using the microstructured WAW transparent electrodes, which shows a PCE of 14.91%, increasing by 10.36% in comparison with the device based on the WAW electrode with planar structure. Correspondingly, the flexible PSC with the microstructured WAW electrode shows a PCE of 13.79%, meanwhile, exhibiting a more excellent bending durability than the reference device. We believe that this work will pave for the way to improve the performance and flexibility of PSCs.

EXPERIMENTAL SECTION

Fabrication of Transparent Electrodes. The WAW electrodes applied in this work were deposited by electron beam evaporation system using GLAD technology, which is schematically represented in Figure 1a. The glass and PET substrates were cleaned with the mixed solvent of ether and ethanol before deposition. SiO₂ (100 nm), WO₃ (35 nm), Ag (10 nm), and WO₃ (*x* nm) were deposited in sequence at room temperature under the pressure of 2×10^{-3} Pa. The evaporation rates of WO₃ and Ag were ~0.1 and ~1 nm s⁻¹, respectively. The thicknesses of the films were monitored by a thin film deposition controller (MDC-360C). Here, the thicknesses of the first WO₃ layer and Ag layer were fixed at 35 and 10 nm, respectively, and the second WO₃ films were deposited through GLAD method with the deposition angles of 0°, 30°, 60°, and 75°, respectively.

Fabrication of PSCs. The PSCs with the structure of WAW/ PEDOT:PSS/MAPbI₃/ C_{60} /Bphen/Ag were manufactured by using the one-step solution deposition. CH₃NH₃I and PbI₂ were dissolved in an hydrous *N*,*N*-dimethylformamide at the molar ratio of 1.04:1 and stirred for several hours in the N₂-filled glovebox. A filtered PEDOT:PSS (Clevios P AI 4083) solution was spin-coated on the substrate at 2000 rpm for 1 min and then dried at 140 °C for 15 min. Afterward, the substrate was transferred into a glovebox, the prepared precursor solution was spin-coated on the substrates, and 300 μ L of chlorobenzene was dropped quickly onto the center of the substrate during the spin-coating processing to promote the formation of perovskite crystals; subsequently, the transparent film changed into

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glossy MAPbI₃ film after the process of annealing at 100 °C for 10 min. C₆₀ (40 nm), Bphen (8 nm), and Ag (100 nm) were deposited successively on substrates at a pressure of 1.0×10^{-4} Pa in a vacuum thermal evaporator. The active area of devices was 0.12 cm². All measurements were conducted in air without encapsulation.

Characterizations. The thicknesses of the deposited films were standardized by a surface profiler (XP-1, Ambios, USA). The transmittance and absorption spectra were obtained using Shimadzu UV-3101PC spectrophotometer. The reflection spectra were carried out with PerkinElmer Lambda 1050 UV-vis-NIR spectrophotometers. The sheet resistance of transparent electrodes was measured by using a four-probe method. Scanning electron microscopy (SEM) images were obtained using a Hitachi S4800 microscope. Atomic force microscopy (AFM) measurements were conducted on a Shimadzu SPM-9700 (Shimadzu Corp., Japan). The optical images were obtained by optical microscopy (BX51TRF, Olympus, Japan). The X-ray diffraction (XRD) patterns were performed on a Rigaku D/Max-2500 diffractometer (Cu K α , λ = 1.54 Å). The current density and voltage (I-V) curves and external quantum efficiency (EQE) were measured using a computer-controlled Keithley 2611 source meter under AM 1.5G illumination from a calibrated solar simulator with an irradiation intensity of 100 mW·cm⁻² and a lock-in amplifier at a chopping frequency of 20 Hz under illumination by a monochromatic light from a xenon lamp, respectively. Electrochemical impedance spectroscopy (EIS) was measured by a CHI 920 electrochemical workstation (Shanghai Chenhua Instruments Inc., China). Timeresolved photoluminescence (PL) was conducted by an Edinburgh FLS920 spectrometer.

RESULTS AND DISCUSSION

To ensure the electrical properties of the WAW electrodes, the first WO₃ layers and Ag layers were deposited as the previous optimized method by electron beam evaporation system, whereas only the second WO₃ layers were deposited using GLAD technology, which has been schematic in Figure 1a. To maximize the transmittance of the WAW electrodes under different deposition angles, WAW electrodes with different thickness of the second WO₃ layer were prepared as shown in Figure S1, and Figure 1b shows the average transmittance (450-800 nm) trends of WAW electrodes as a function of the thickness of the second WO₃ layer deposited at different angles of 0° , 30° , 60° , and 75° , respectively. As the thickness increases, the average transmittance values at different deposition angles all first climb up and then decline. The optimal average transmittance values of various deposition angles are 91.00 (0°-40 nm), 90.61 (30°-42 nm), 91.69 (60°-63 nm), and 90.68% (75°—68 nm), respectively. The corresponding transmittance spectra in the visible range are plotted in Figure 1c, in which it can be found that the optimized transmittance curves with different deposition angles are almost uniform, which would have little affection on the absorption of the active layers of PSCs. Figure 1d shows the sheet resistances of the WAW electrodes with different deposition angles as a function of the second WO₃ layer thickness. Under different deposition angles, all of the sheet resistances increase gradually as the increasing WO₃ thickness, and the sheet resistances (R_{sheet}) of the WAW electrode with the optimal transmittance are 11, 11.3, 11.8, and 12.5 Ω /sq at the different deposition angles of 0° , 30° , 60° , and 75° , respectively.

In contrast to the little changes in optical and electrical properties, the structure and morphology of the second WO₃ layers in WAW films have been significantly altered with the change of deposition angles, which can be observed clearly from the SEM and AFM images. Figure 2 shows the cross section and surface SEM images of the WAW electrodes with

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Figure 2. Profile and surface SEM images of WAW electrodes with the second WO₃ layers deposited at various angles. (a,b) 0° , (c,d) 30° , (e,f) 60° , and (g,h) 75° .

the second WO₃ films deposited at different angles. For the WAW -0° film, the film surface is homogeneous, smooth, and dense without cracks (Figure 2b), and the root mean square (RMS) roughness of this film is 1.33 nm, which has been indicated from the AFM measurement shown in Figure S2. When the deposition angle increases to 30°, some small bulges appear on the film surface (Figure 2d), resulting in a slight increase in the RMS roughness (1.38 nm). As the deposition angle increases to 60°, compact WO₃ nanocolumns form and can be observed from the profile SEM image (Figure 2e), the bulges become bigger and some cracks appear on the film surface (Figure 2f), which causes increased RMS roughness of 1.69 nm. When the deposition angle is further increased to 75° (Figure 2g,h), the WO₃ nanocolumns become more tilted, ordered, and scattered in comparison to the WAW-60° film. Furthermore, the cracks on the WAW-75° film surface are much more obvious, and the porous surface leads to larger RMS roughness of 1.98 nm. Hence, the structure and surface morphology of the WAW films can be accurately controlled by adjusting the deposition angle of the second WO₃ layer. The porous WAW-75° films would facilitate the penetration of hole transport material and perovskite layer and effectively increase the contact areas between hole transport layer (HTL) and electrodes, enhancing holes extraction and transportation, thus the PSC performance.

Smooth and dense perovskite films are the prerequisite for achieving excellent photovoltaic performance.⁴³⁻⁴⁵ In our previous investigations, it has been found that the roughness of substrates has significant influence on the morphology of perovskite films as well as the PSC performance. Figure 3a shows the SEM images of MAPbI₃ films prepared on various



Figure 3. (a) SEM images of the MAPbI₃ films prepared on WAW/ PEDOT:PSS substrates with the second WO₃ layers deposited at various angles. (b) Size distribution of the perovskite grains deposited on various substrates.

WAW/PEDOT:PSS substrates, and the corresponding size distribution of these films are plotted in Figure 3b. For the MAPbI₃ films grown on WAW-0°/PEDOT:PSS and WAW-30°/PEDOT:PSS substrates, larger crystals can be seen on the film surface with the main grain size of 240-310 nm. As the deposition angle increases, the grains reduced gradually, and the grain size mainly decreased to 170-240 nm at the deposition angle of 60°, and further decreased to 100-170 nm at the deposition angle of 75°. The change in MAPbI₃ grain size can be attributed to the WAW/PEDOT:PSS substrates with various roughness, which increases from 1.13 nm for WAW-0°/PEDOT:PSS to 1.68 nm for WAW-75°/ PEDOT:PSS (Figure S2), originating from the microstructure of WAW electrodes. It is known that a larger roughness would result in a smaller contact angle for the film with the same material.⁴⁶ Also, the contact angle is related to the surface free energy of the substrate, which has a significant effect on the nucleation and crystallization of the above films, as described in the following equation

$$\Delta G_{\text{heterogeneous}} = \Delta G_{\text{homogeneous}} \times f(\theta) \tag{1}$$

where $f(\theta) = (2 - 3\cos \theta + \cos^3 \theta)/4$, $\Delta G_{\text{heterogeneous}}$ and $\Delta G_{\text{homogeneous}}$ are the free energies needed for heterogeneous and homogeneous nucleation, respectively, and θ is the contact angle between solid and liquid interfaces.⁴⁷ According to this equation, smaller contact angle will reduce $f(\theta)$, which will result in smaller $\Delta G_{\text{heterogeneous}}$ and thus lower the nucleation barrier and promote the nucleation. Therefore, by comparing with the WAW—0°/PEDOT:PSS substrate, the WAW—75°/ PEDOT:PSS substrate possesses larger roughness and thus smaller contact angle, which will be more facilitated to the nucleation and growth of MAPbI₃; thereby, more crystal nucleus and smaller grain size are achieved, as shown in Figure 3. Although the crystalline morphology and grain size of the perovskite films have been obviously implicated by the different WAW/PEDOT:PSS substrates, the crystal nature and absorption characteristics of the $MAPbI_3$ films have little change, as shown in Figure S3.

To reveal the effect of the electrode morphology on the PSC performance, a series of PSCs based on the various WAW electrodes with different deposition angles have been prepared (Figures S4-S6). The cross-sectional structures and the energy-level diagram of the PSCs are illustrated in Figure 4a,b, respectively. Although the WAW electrode possesses a



Figure 4. (a) Cross-sectional structures of the PSCs based on WAW electrodes. (b) Energy-level diagram of various materials utilized in the PSCs.

high work function of 5.2 eV, matching with the highest occupied molecular orbital level of MAPbI3, a HTL PEDOT:PSS with a work function of 5.1 eV has been inserted between WAW and MAPbI₃ to prevent the possible interfacial reaction and improve perovskite film quality. The wildly used C₆₀ and Bphen are introduced into the PSCs to act as the electron transport layer and the hole blocking layer, respectively. The I-V curves and EQE spectra of PSCs using optimal WAW electrodes with different deposition angles are plotted in Figure 5a,b, respectively, and the detailed device parameters are listed in Table 1. As the deposition angle increases, the open-circuit voltage (V_{OC}) of these devices based on various electrodes stays the same value of 0.98 V, whereas the short-circuit current density (J_{SC}) increases from 19.70 mA/ cm^2 for the device with WAW-0° electrode to 21.13 mA/cm² for the device with WAW— 75° electrode, as well as an enhanced fill factor (FF) from 0.70 to 0.72, which finally provide contributions to the PCE promotion from 13.51 to 14.91%, indicating that the application of microstructured electrode improves charge carriers extracting efficiency and depresses electron-hole recombination probability.

To further understand the origin of enhanced device performance by utilizing WAW— 75° electrode, time-resolved PL has been measured to study the charge carrier transportation and extraction,^{11,48} which is shown in Figure 5c. The PL of the perovskite film deposited on WAW— 75° / PEDOT:PSS substrate shows a faster decay than that on WAW— 0° /PEDOT:PSS substrate (5.2 vs 10.9 ns), demonstrating that the more effective carriers transportation and extraction from the perovskite layer to the microstructured electrode, which is mainly attributed to the enhanced contact ъ



Figure 5. (a) J-V curves and (b) EQE spectra of the PSCs based on various WAW electrodes with the second WO₃ layers deposited at various angles. (c) Time-resolved PL decays of perovskite films on WAW—0°/PEDOT:PSS and WAW—75°/PEDOT:PSS substrates. (d) Nyquist plots of PSCs with WAW—0° and WAW—75° electrodes measured under the dark with a bias voltage of 0.7 V.

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| angle (deg) | $V_{\rm OC}$ (V) | $J_{\rm SC}~({\rm mA/cm}^2)$ | FF | PCE (%) | $J_{\rm EQE}~({\rm mA/cm}^2)$ | $R_{\rm S} (\Omega \cdot {\rm cm}^2)$ |
|-------------|------------------|------------------------------|-----------------|------------------|-------------------------------|---------------------------------------|
| 0 | 0.98 ± 0.01 | 19.70 ± 0.33 | 0.70 ± 0.01 | 13.51 ± 0.57 | 18.19 ± 0.40 | 7.38 |
| 30 | 0.98 ± 0.01 | 20.14 ± 0.36 | 0.71 ± 0.01 | 14.01 ± 0.60 | 18.49 ± 0.39 | 7.49 |
| 60 | 0.98 ± 0.01 | 20.55 ± 0.25 | 0.71 ± 0.01 | 14.30 ± 0.53 | 18.79 ± 0.27 | 6.68 |
| 75 | 0.98 ± 0.01 | 21.13 ± 0.26 | 0.72 ± 0.02 | 14.91 ± 0.76 | 19.36 ± 0.38 | 5.81 |



Figure 6. (a) J-V curves and (b) EQE spectra of PSCs based on PET/WAW—0° and PET/WAW—75° electrodes. The inset is a photograph of the flexible PSC based on PET/WAW—75° electrode.

area of HTL and active layer to the porous WAW—75° electrode. EIS is a valid method to investigate the inner $R_{\rm S}$ of PSCs and the electrical properties of the interfaces can be obtained by EIS analysis. $R_{\rm S}$ is composed of the $R_{\rm sheet}$ of the electrodes and the charge-transfer resistance ($R_{\rm CT}$) at the interfaces between various layers.^{49–51} Figure 5d displays the Nyquist plots of PSCs with WAW—0° and WAW—75° electrode at the same bias of 0.7 V and the $R_{\rm CT}$ values are 685 and 291 Ω for the devices based on WAW—0° and WAW—75° electrodes, respectively. The smaller $R_{\rm CT}$ presented in the WAW—75°-based device demonstrates the more effective hole transportation, which is mainly attributed to its unique microstructured electrode, thus improved $J_{\rm SC}$, FF, and PCE has been realized by utilizing WAW—75° electrode. The hole-

only devices display in Figure S7 also verified that the WAW— 75° electrode could extract the hole more efficiently.

According to our previous studies, WAW electrodes have excellent flexibility, which exhibit advantages in flexible polymer solar cells.³⁸ In this work, WAW electrodes are employed in flexible PSCs. Figure 6 plots the device performance of flexible PSCs based on PET/WAW—0° and PET/WAW—75° electrodes. Because of similar electrode structure and morphologies as the rigid substrates (Figure S8), the characteristics of flexible PSCs based on WAW—0° and WAW—75° electrodes have also shown consistent tendency as the rigid devices. Compared with the flexible WAW—0°-based PSC, the WAW—75°-based PSC shows a higher J_{SC} and FF, resulting in a higher PCE

(13.79 vs 12.52%). Moreover, both of the devices have no obvious hysteresis phenomenon (Figure S9).

Bending durability is an important parameter for evaluating the flexible devices. For comparing the effect of different WAW electrodes on device-bending properties, device-bending tests under different bending cycles were performed. Figure 7 shows



Figure 7. (a) Changes of device parameters of J_{SC} , FF, and PCE under various strains. SEM images of MAPbI₃ based on (b) WAW—0° and (c) WAW—75° electrodes after 1000 times bending.

that the device parameters, including J_{SC} , FF, and PCE, changes under various strains. The strain here can be abbreviated as

$$\varepsilon = D/2R$$
 (2)

where D represents the thickness of the flexible devices and R represents bending radius. Compared with the thick PET substrate (130 μ m) used in this work, the thickness of the device fabricated on the PET substrate (~900 nm) can be neglected. Therefore, D in the above equation was set to 130 μ m. After bending 500 times, the performance parameters of the two devices exhibited no significant change under a smaller strain of 0.9%; as the strain increases to 1.3%, the PET/ WAW-75° PSCs still show no appreciable deterioration in device parameters and the J_{SC}, FF, and PCE retain 96.48, 97.90, and 94.36% of their initial values, respectively, whereas the performance parameters of PET/WAW-0° PSCs show an apparent reduction and the J_{SC} , FF, and PCE decrease to 94.27, 94.03, and 88.51%, respectively, of their original values under the same strain. Hereafter, the 1000 consecutive bending tests were further conducted at different strains, surprisingly, under the maximum strain of 1.3%, the PET/WAW— 75° PSCs merely exhibited a slight deterioration and the J_{SC}, FF, and PCE maintain 95.00, 95.71, and 90.97% of their initial values respectively. At the same bending condition, the performance of the device based on PET/WAW-0° electrode degenerated seriously, and the device parameters of J_{SC}, FF, and PCE decrease to 86.70, 90.31, and 78.39% of their original values,

respectively. Meanwhile, in Figure S10, the R_S increased to 2.2 and 1.55 times of their initial R_S for the PET/WAW—0° and PET/WAW—75° devices, respectively. For comparison, the device based on flexible ITO electrode has also been measured at the equal strain of 1.3% and the PCE drops intensely to 35% of its initial value after 1000 times bending, which is mainly attributed to the plenty of cracks on the surface of ITO after repeated bending, as shown in Figure S11.

To explore the reason for better bending durability of the flexible PSC based on WAW-75° electrode compared with WAW -0° electrode, the SEM images of PET/WAW -0° , PET/WAW—75° electrodes, and the perovskite films prepared on the two flexible substrates were carried out after 1000 times bending under the strain of 1.3%, which are shown in Figures S12 and 7b,c, respectively. There is no obvious change for PET/WAW-0° and PET/WAW-75° electrodes, which indicates good bending durability of DMD multilayer transparent electrodes because of the excellent ductility of Ag. Although there are distinct cracks appearing between perovskite grains deposited on PET/WAW-0°/PEDOT:PSS substrate, there is almost no obvious change for the perovskite film prepared on PET/WAW-75°/PEDOT:PSS substrate. For this reason, the WAW-0°-based device under severe bending condition shows the heavily reduced J_{SC} and FF, together with the sharp increased R_{s} , which finally results in the serious deterioration in PCE. In contrast, the WAW-75°-based flexible device exhibits excellent bending stability, which originates mainly from the unique microstructure of WAW-75° surface, dispersing the mechanical stresses under repeated bending, thus reducing the damage on the perovskite layer. In addition, relatively smaller perovskite grains induced by WAW-75° electrode might also reduce the formation of grain boundaries and boundary traps or defects on the perovskite films under the bending tests. This result provides a potential application of microstructured electrodes in flexible PSCs.

Additionally, a Scotch tape test has been conducted to verify the firmness of WAW electrode. As shown in Figure S13, after 20 times taping, the R_{sheet} of both WAW—0° and WAW—75° electrodes are nearly unchanged, indicating that the WAW electrodes are firm enough.

CONCLUSIONS

In this work, the performance and flexibility of PSCs have been improved by introducing the microstructured WAW multilayer transparent electrodes. We obtain tilted, ordered, and porous WO3 nanocolumns by depositing the second WO3 film of WAW electrode using GLAD method at the deposition angle of 75°. Compared with the reference WAW-0° electrode, the microstructured WAW-75° electrode shows comparative photoelectrical properties and an enhanced device performance, resulting from the modified contact between perovskite layer and WAW electrode, which improved carrier extraction and thus increased PCE of 14.91 and 13.79% for rigid and flexible devices, respectively. Simultaneously, the bending stability of the flexible PSC based on the microstructured WAW-75 $^{\circ}$ electrodes has been improved, which retains 90.97% of its initial PCE after bending 1000 times under the maximum strain of 1.3%, increasing by 12.58% compared with the device based on WAW -0° electrode. The unique microstructures of the WAW-75° electrode disperse the stress under repeated bending and induce smaller grains that suppress the boundary traps or defects formation under plastic deformation, reducing

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the damage on the perovskite layer, contributing to the enhanced flexibility of device. The microstructured electrodes proposed in this work exhibit more advantages and greater potential for flexible perovskite photovoltaics, which will pave for the way to improve the performance and flexibility of PSCs.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b03557.

Transmittance spectra, AFM images, absorbance spectra, and XRD patterns; J-V curves, EQE spectra, and the trend of device parameters; I-V curves of hole-only devices, SEM images of PET/WAW-0°, and PET/ WAW-75°; hysteresis effect measurements of flexible PSCs, R_s changes of the devices based on PET/WAW- 0° , and PET/WAW-75° electrodes; the changes of PCE of the ITO/PET-based device under repeated bending, the reflectance and transmittance spectra of PET/WAW-0°, and PET/WAW-75° electrodes before and after repeated bending; the SEM images of PET/WAW-0° and PET/WAW-75° electrodes after bending test, the sheet resistance of PET/WAW-0°, and $\widetilde{\text{PET}/\text{WAW}}\mbox{--}75^\circ$ electrodes after taping test, device parameters of PSCs based on various rigid WAW electrodes (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) 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.

(2) Im, J.-H.; Lee, C.-R.; Lee, J.-W.; Park, S.-W.; Park, N.-G. 6.5% Efficient Perovskite Quantum-Dot-Sensitized Solar Cell. *Nanoscale* **2011**, *3*, 4088–4093.

(3) Kim, H. S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; Grätzel, M.; Park, N.-G. Lead Iodide Perovskite Sensitized all-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Sci. Rep.* **2012**, *2*, 591. (4) Ball, J. M.; Lee, M. M.; Hey, A.; Snaith, H. J. Low-Temperature Processed Meso-Superstructured to Thin-Film Perovskite Solar Cells. *Energy Environ. Sci.* **2013**, *6*, 1739.

(5) Burschka, J.; Pellet, N.; Moon, S.-J.; 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.

(6) Zhou, H.; Chen, Q.; Li, G.; Luo, S.; Song, T.-b.; Duan, H.-S.; Hong, Z.; You, J.; Liu, Y.; Yang, Y. Interface Engineering of Highly Efficient Perovskite Solar Cells. *Science* **2014**, *345*, 542–546.

(7) Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. High-Performance Photovoltaic Perovskite Layers Fabricated through Intramolecular Exchange. *Science* **2015**, *348*, 1234–1237.

(8) Li, X.; Bi, D.; Yi, C.; Decoppet, J.-D.; Luo, J.; Zakeeruddin, S. M.; Hagfeldt, A.; Grätzel, M. A Vacuum Flash-Assisted Solution Process for High-Efficiency Large-Area Perovskite Solar Cells. *Science* **2016**, 353, 58–62.

(9) Zhao, Y.-C.; Zhou, W.-K.; Zhou, X.; Liu, K.-H.; Yu, D.-P.; Zhao, Q. Quantification of Light-Enhanced Ionic Transport in Lead IodidePerovskite Thin Films and Its Solar Cell Applications. *Light: Sci. Appl.* **2016**, *6*, No. e16243.

(10) Saliba, M.; Matsui, T.; Domanski, K.; Seo, J.-Y.; Ummadisingu, A.; Zakeeruddin, S. M.; Correa-Baena, J.-P.; Tress, W. R.; Abate, A.; Hagfeldt, A.; Grätzel, M. Incorporation of Rubidium Cations into Perovskite Solar Cells Improves Photovoltaic Performance. *Science* **2016**, 354, 206–209.

(11) Tan, H.; Jain, A.; Voznyy, O.; Lan, X.; de Arquer, F. P. G.; Fan, J. Z.; Quintero-Bermudez, R.; Yuan, M.; Zhang, B.; Zhao, Y.; Fan, F.; Li, P.; Quan, L. N.; Zhao, Y.; Lu, Z.-H.; Yang, Z.; Hoogland, S.; Sargent, E. H. Efficient and Stable Solution-Processed Planar Perovskite Solar Cells via Contact Passivation. *Science* **2017**, *355*, 722–726.

(12) Shin, S. S.; Yeom, E. J.; Yang, W. S.; Hur, S.; Kim, M. G.; Im, J.; Seo, J.; Noh, J. H.; Seok, S. I. Colloidally Prepared La-Doped BaSnO3 Electrodes for Efficient, Photostable Perovskite Solar Cells. *Science* **2017**, 356, 167–171.

(13) Yang, W. S.; Park, B.-W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, D. U.; Shin, S. S.; Seo, J.; Kim, E. K.; Noh, J. H.; Seok, S. I. Iodide Management in Formamidinium-Lead-Halide-Based Perovskite Layers for Efficient Solar Cells. *Science* **2017**, *356*, 1376.

(14) Xie, F.; Chen, C.-C.; Wu, Y.; Li, X.; Cai, M.; Liu, X.; Yang, X.; Han, L. Vertical Recrystallization for Highly Efficient and Stable Formamidinium-Based Inverted-structure Perovskite Solar Cells. *Energy Environ. Sci.* **2017**, *10*, 1942–1949.

(15) Chiang, Y.-F.; Jeng, J.-Y.; Lee, M.-H.; Peng, S.-R.; Chen, P.; Guo, T.-F.; Wen, T.-C.; Hsu, Y.-J.; Hsu, C.-M. High Voltage and Efficient Bilayer Heterojunction Solar Cells Based on an Organic-Inorganic Hybrid Perovskite Absorber with a Low-Cost Flexible Substrate. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6033–6040.

(16) Liu, D.; Kelly, T. L. Perovskite Solar Cells with a Planar Heterojunction Structure Prepared using Room-Temperature Solution Processing Techniques. *Nat. Photon.* **2014**, *8*, 133–138.

(17) Yoon, H.; Kang, S. M.; Lee, J.-K.; Choi, M. Hysteresis-Free Low-Temperature-Processed Planar Perovskite Solar Cells with 19.1% Efficiency. *Energy Environ. Sci.* **2016**, *9*, 2262–2266.

(18) Das, S.; Yang, B.; Gu, G.; Joshi, P. C.; Ivanov, I. N.; Rouleau, C. M.; Aytug, T.; Geohegan, D. B.; Xiao, K. High-Performance Flexible Perovskite Solar Cells by Using a Combination of Ultrasonic Spray-Coating and Low Thermal Budget Photonic Curing. *ACS Photonics* **2015**, *2*, 680–686.

(19) 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.; Park, N.-G.; Lee, S.; Jung, H. S. Highly Efficient and Bending Durable Perovskite Solar Cells: Toward a Wearable Power Source. *Energy Environ. Sci.* **2015**, *8*, 916–921.

(20) Han, J.; Yuan, S.; Liu, L.; Qiu, X.; Gong, H.; Yang, X.; Li, C.; Hao, Y.; Cao, B. Fully Indium-Free Flexible Ag Nanowires/ZnO: F

ACS Applied Materials & Interfaces

Composite Transparent Conductive Electrodes with High Haze. J. Mater. Chem. A 2015, 3, 5375–5384.

(21) Lee, M.; Jo, Y.; Kim, D. S.; Jun, Y. Flexible Organo-Metal Halide Perovskite Solar Cells on a Ti Metal Substrate. *J. Mater. Chem. A* **2015**, *3*, 4129–4133.

(22) Sun, K.; Li, P.; Xia, Y.; Chang, J.; Ouyang, J. Transparent Conductive Oxide-Free Perovskite Solar Cells with PEDOT: PSS as Transparent Electrode. *ACS Appl. Mater. Interfaces* **2015**, *7*, 15314– 15320.

(23) Bao, C.; Zhu, W.; Yang, J.; Li, F.; Gu, S.; Wang, Y.; Yu, T.; Zhu, J.; Zhou, Y.; Zou, Z. Highly Flexible Self-Powered Organolead Trihalide Perovskite Photodetectors with Gold Nanowire Networks as Transparent Electrodes. *ACS Appl. Mater. Interfaces* **2016**, *8*, 23868–23875.

(24) Chen, L.; Xie, X.; Liu, Z.; Lee, E.-C. A Transparent Poly(3,4ethylenedioxylenethiophene):Poly(styrene sulfonate) Cathode for Low Temperature Processed, Metal-Oxide Free Perovskite Solar Cells. J. Mater. Chem. A 2017, 5, 6974–6980.

(25) Liu, Z.; You, P.; Xie, C.; Tang, G.; Yan, F. Ultrathin and Flexible Perovskite Solar Cells with Graphene Transparent Electrodes. *Nano Energy* **2016**, *28*, 151–157.

(26) Yoon, J.; Sung, H.; Lee, G.; Cho, W.; Ahn, N.; Jung, H. S.; Choi, M. Superflexible, High-Efficiency Perovskite Solar Cells Utilizing Graphene Electrodes: towards Future Foldable Power Sources. *Energy Environ. Sci.* **2017**, *10*, 337–345.

(27) Li, Y.; Meng, L.; Yang, Y. M.; Xu, G.; Hong, Z.; Chen, Q.; You, J.; Li, G.; Yang, Y.; Li, Y. High-Efficiency Robust Perovskite Solar Cells on Ultrathin Flexible Substrates. *Nat. Commun.* **2016**, *7*, 10214.

(28) 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.

(29) Kim, Y. H.; Sachse, C.; Machala, M. L.; May, C.; Müller-Meskamp, L.; Leo, K. Highly Conductive PEDOT: PSS Electrode with Optimized Solvent and Thermal Post-Treatment for ITO-Free Organic Solar Cells. *Adv. Funct. Mater.* **2011**, *21*, 1076–1081.

(30) De, S.; Coleman, J. N. Are There Fundamental Limitations on the Sheet Resistance and Transmittance of Thin Graphene Films. *ACS Nano* **2010**, *4*, 2713–2720.

(31) Li, F.; Ruan, S.; Xu, Y.; Meng, F.; Wang, J.; Chen, W.; Shen, L. Semitransparent Inverted Polymer Solar Cells Using MoO₃/Ag/WO₃ as Highly Transparent Anodes. *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 877–880.

(32) Xue, Z.; Liu, X.; Zhang, N.; Chen, H.; Zheng, X.; Wang, H.; Guo, X. High-Performance NiO/Ag/NiO Transparent Electrodes for Flexible Organic Photovoltaic Cells. *ACS Appl. Mater. Interfaces* **2014**, *6*, 16403–16408.

(33) Kim, J. H.; Lee, J. H.; Kim, S.-W.; Yoo, Y.-Z.; Seong, T.-Y. Highly Flexible ZnO/Ag/ZnO Conducting Electrode for Organic Photonic Devices. *Ceram. Int.* **2015**, *41*, 7146–7150.

(34) Xue, Z.; Liu, X.; Lv, Y.; Zhang, N.; Guo, X. Low-Work-Function, ITO-Free Transparent Cathodes for Inverted Polymer Solar Cells. *ACS Appl. Mater. Interfaces* **2015**, *7*, 19960–19965.

(35) Choi, K.-H.; Nam, H.-J.; Jeong, J.-A.; Cho, S.-W.; Kim, H.-K.; Kang, J.-W.; Kim, D.-G.; Cho, W.-J. Highly Flexible and Transparent InZnSnOX/Ag/InZnSnOX Multilayer Electrode for Flexible Organic Light Emitting Diodes. *Appl. Phys. Lett.* **2008**, *92*, 223302.

(36) Shen, L.; Xu, Y.; Meng, F.; Li, F.; Ruan, S.; Chen, W. Semitransparent Polymer Solar Cells Using $V_2O_5/Ag/V_2O_5$ as Transparent Anodes. Org. Electron. 2011, 12, 1223–1226.

(37) Liu, X.; Guo, X.; Gan, Z.; Zhang, N.; Liu, X. Efficient Perovskite Solar Cells Based on Multilayer Transparent Electrodes through Morphology Control. J. Phys. Chem. C 2016, 120, 26703–26709.

(38) Guo, X.; Lin, J.; Chen, H.; Zhang, X.; Fan, Y.; Luo, J.; Liu, X. Ultrathin and Efficient Flexible Polymer Photovoltaic Cells Based on Stable Indium-Free Multilayer Transparent Electrodes. *J. Mater. Chem.* **2012**, *22*, 17176–17182.

(39) Wang, Y.; He, B.; Wang, H.; Xu, J.; Ta, T.; Li, W.; Wang, Q.; Yang, S.; Tang, Y.; Zou, B. Transparent WO₃/Ag/WO₃ Electrode for Flexible Organic Solar Cells. *Mater. Lett.* **2017**, *188*, 107–110.

(40) Deniz, D.; Frankel, D. J.; Lad, R. J. Nanostructured Tungsten and Tungsten Trioxide Films Prepared by Glancing Angle Deposition. *Thin Solid Films* **2010**, *518*, 4095–4099.

(41) Sanchez-Valencia, J. R.; Longtin, R.; Rossell, M. D.; Gröning, P. Growth Assisted by Glancing Angle Deposition: A New Technique to Fabricate Highly Porous Anisotropic Thin Films. *ACS Appl. Mater. Interfaces* **2016**, *8*, 8686–8693.

(42) Trottier-Lapointe, W.; Zabeida, O.; Schmitt, T.; Martinu, L. Ultralow Refractive Index Optical Films with Enhanced Mechanical Performance Obtained by Hybrid Glancing Angle Deposition. *Appl. Opt.* **2016**, *55*, 8796–8805.

(43) Dualeh, A.; Tétreault, N.; Moehl, T.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. Effect of Annealing Temperature on Film Morphology of Organic-Inorganic Hybrid Pervoskite Solid-State Solar Cells. *Adv. Funct. Mater.* **2014**, *24*, 3250–3258.

(44) Eperon, G. E.; Burlakov, V. M.; Docampo, P.; Goriely, A.; Snaith, H. J. Morphological Control for High Performance, Solution-Processed Planar Heterojunction Perovskite Solar Cells. *Adv. Funct. Mater.* **2014**, *24*, 151–157.

(45) Fang, H.-H.; Wang, F.; Adjokatse, S.; Zhao, N.; Even, J.; Loi, M. A. Photoexcitation Dynamics in Solution-Processed Formamidinium Lead Iodide Perovskite Thin Films for Solar Cell Applications. *Light: Sci. Appl.* **2016**, *5*, No. e16056.

(46) Palasantzas, G.; de Hosson, J. T. M. Wetting on Rough Surfaces. *Acta Mater.* **2001**, *49*, 3533–3538.

(47) Salim, T.; Sun, S.; Abe, Y.; Krishna, A.; Grimsdale, A. C.; Lam, Y. M. Perovskite-Based Solar Cells: Impact of Morphology and Device Architecture on Device Performance. *J. Mater. Chem. A* **2015**, *3*, 8943–8969.

(48) Hu, X.; Huang, Z.; Zhou, X.; Li, P.; Wang, Y.; Huang, Z.; Su, M.; Ren, W.; Li, F.; Li, M.; Chen, Y.; Song, Y. Wearable Large-Scale Perovskite Solar-Power Source via Nanocellular Scaffold. *Adv. Mater.* **2017**, *29*, 1703236.

(49) Liu, D.; Li, Y.; Yuan, J.; Hong, Q.; Shi, G.; Yuan, D.; Wei, J.; Huang, C.; Tang, J.; Fung, M.-K. Improved Performance of Inverted Planar Perovskite Solar Cells with F4-TCNQ doped PEDOT: PSS Hole Transport Layers. J. Mater. Chem. A **2017**, *5*, 5701–5708.

(50) Wang, B.; Zhang, Z.-g.; Ye, S.; Gao, L.; Yan, T.; Bian, Z.; Huang, C.; Li, Y. Solution-Processable Cathode Buffer Layer for High-Performance ITO/CuSCN-based Planar Heterojunction Perovskite Solar Cell. *Electrochim. Acta* **2016**, *218*, 263–270.

(51) Huang, X.; Wang, K.; Yi, C.; Meng, T.; Gong, X. Efficient Perovskite Hybrid Solar Cells by Highly Electrical Conductive PEDOT: PSS Hole Transport Layer. *Adv. Energy Mater.* **2016**, *6*, 1501773.