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ARTICLE

Lightweight and ultra-flexible perovskite solar cells with "sandwich" perovskite layer based on graphene-carbon nanotube electrodesReceived 00th January 20xx,
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Flexible perovskite solar cells (FPSCs) have fired widespread research enthusiasm due to their great potential in the booming field of flexible electronics and portable devices. A lot of research has been conducted on the performance, flexibility, and stability of FPSCs, but the synergistic improvement between them is still terribly difficult. In this work, we have achieved the lightweight and ultra-flexible perovskite solar cell (LWUF PSC) with high performance and remarkable stability. Specifically, in addition to using a 1.5 μm -thick polyetherimide film as flexible substrate, the improved scheme mainly includes designing a "sandwich" architecture with multifunctionality to take advantage of perovskite quantum dots and polycrystalline perovskite, employing a flexible electrode of graphene-carbon nanotube film, and a hole transport layer of CuCrO_2 nanoparticles containing nickel to facilitate the transfer of photogenerated charge carriers. The resultant device demonstrates a stable power conversion efficiency (PCE) of 17.4% and a power-per-weight of 31.1 W g^{-1} . In particular, after 10,000 bending cycles with a curvature radius of 1 mm, the PCE of the LWUF PSC has sustained at 92.8% of its initial level, and after 32 days in an atmosphere with a relative humidity of 35%, it has remained at 93.0% of its initial level. The unique device's structure design gives the LWUF PSC high PCE, significant power-per-weight, excellent mechanical flexibility and outstanding environmental stability – one of the best performance to date of LWUF PSCs without indium tin oxide electrodes.

1. Introduction

Lightweight and ultra-flexible solar cells have great application potential as flexible and portable photovoltaic power sources, whether in the field of flexible electronics or aerospace.¹⁻³ However, current solar cells based on high power conversion efficiency (PCE), lightweight and flexibility often carry their respective shortcomings and cannot meet the requirements of practical use. For example, although the preparation process of high-performance solar cells based on Si and GaAs is technologically mature, the high-temperature process involved does not match the flexible substrate, so such devices usually form pseudo-flexible ones by integrating rigid structure units into the flexible substrate.^{4,5} Organic solar cells, on the other hand, which are known for their high flexibility, currently have a low reported PCE of 10~15%.⁶⁻⁸ Due to its excellent

photovoltaic properties and compatibility with low temperature solution deposition, organic-inorganic halide perovskite based single-junction flexible perovskite solar cells (FPSCs) can achieve high PCE of 22% on conventional flexible substrates,⁹ and 12 ~ 20.2% PCE and $1.9 \sim 44 \text{ W g}^{-1}$ power-per-weight on ultra-thin substrates.^{1,10-18} The efficiency and power-per-weight significantly outperform other flexible cells, making it an ideal structure for future high-efficiency, lightweight and ultra-flexible solar cells.^{19,20}

More importantly, mechanical robustness is the key criterion for evaluating the performance of FPSCs. Due to their poor flexibility and stability, the reported FPSCs are far from the requirements for practical use in portable devices.²¹ For instance, the actual use of a FPSC will involve some bending, folding, and even slight stretching, which are hardly simulated with its thousands of bending cycles at large bending radius. Moreover, in the previous flexibility experiments, the increased resistance of the flexible electrode and the large number of cracks in the perovskite film led to the rapid degradation of FPSC's performance.²² Thus, there is an urgent need to develop more flexible perovskite solar cells (PSCs) those can withstand the test of mechanical robustness under more demanding experimental conditions.

Various improvement schemes have been proposed to improve the deformation durability of FPSCs, such as reducing

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the substrate thickness,²³ replacing the conventional indium tin oxide (ITO) electrode with a highly flexible nanofilm or a highly conductive polymer electrode,^{16,18,24} and improving the adhesion of each layer through interface engineering.^{21,25,26} All of these strategies contribute to enhancing the mechanical stability of solar cells. Miao et al. prepared the FPSC with a PCE of ~12% on a silver nanowire electrode.^{24,27} After bending 1000 cycles with a curvature radius of 1 mm, the PCE of the device maintained above 99%. Unfortunately, the stability of the device was poor. Their device's PCE had dropped to 81% of the initial value after 100 hours in a nitrogen-filled glove box. Recently, Hu et al.²⁸ fabricated a flexible CsPbI₃ quantum dot (QD) solar cell with a highest PCE of 12.3% assisted by introduction of organic molecule phenyl-C61-butyric acid methyl ester (PCBM) into the CsPbI₃ QD layer to result in the formation of a hybrid heterojunction interfacial connecting layer. It should be noted that the target device is more flexible than the control polycrystalline perovskite cells, but lost 30% of its initial efficiency after storage in the dry air-filled box for 14 days. In fact, poor stability is an obstacle for all PSCs. Particularly, this problem is exacerbated by the fact that the thinner polymer substrates in lightweight ultra-flexible devices have poorer moisture insulation compared to the glass substrates in rigid devices.²² Accordingly, designing high efficiency, lightweight, and ultra-flexible devices must be combined with optimizing device's stability for realizing the real application of FPSCs as flexible and portable photovoltaic power sources. Therefore, how to synergistically improve the efficiency and stability for lightweight, ultra-flexible PSCs (LWUF PSCs) remains a formidable challenge.

In this work, through comprehensively considering several key influencing factors (such as substrate thickness, electrode, and interface), we demonstrate a LWUF PSC with high performance and excellent stability by adopting a collaborative approach to improve the performance of the FPSC. Specifically, a freestanding, super-light, remarkably flexible and high transparent conductive nanofilm of graphene-carbon nanotube (G-CNT) film is selected as electrode to replace the conventional oxide electrode; a ultra-thin (1.5 μm -thick) polyetherimide (PEI) film is used as flexible substrate; the hole transport layer (HTL) is optimized to improve the PCE of FPSC; and the perovskite absorbing layer is designed for the first time to use a "sandwich" architecture formed by CsPbBr₃ QDs/polycrystalline perovskite mixed CsPbBr₃ QDs/CsPbBr₃ QDs. In this "sandwich" layer, the nanoscale perovskite QDs occupy the bulk polycrystalline perovskite grain boundaries and the surfaces to form a multi-scale hybrid interface of QDs wrapped around polycrystalline grains, achieving efficient charge transfer and mechanical flexibility, by combination of the advantages of perovskite's nano-scale QDs and polycrystalline films. As a result, our approach synergistically improves the performance of LWUF PSCs with a high PCE of 17.4% and a power-per-weight of 31.1 W g⁻¹, excellent mechanical stability (maintaining the initial 92.8% PCE after 10,000 bending cycles

with a curvature radius of 1 mm), and marked environmental stability (remaining the initial 93.0% PCE after 32 days in the atmosphere).

2. Experimental section

2.1 Materials

Lead (II) iodide (PbI₂, 99.9985%) and copper foil (99.8%) were purchased from Alfa Aesar. Cesium iodide (CsI, 99.999%), lead bromide (PbBr₂, 99.99%), cesium carbonate (Cs₂CO₃, 99%), chromium (III) nitrate nonahydrate (99.99%), copper (II) nitrate trihydrate (99.99%), nickel nitrate (99.99%), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP, 98%), chlorobenzene (CB, 99.8%), n,n-dimethylformamide (DMF, 99.9%), dimethyl sulfoxide (DMSO, 99.9%), 1-Octadecene (90%), methyl acetate (99%), oleic acid (85%), oleylamine (80%-90%) and n-hexane (99%) were purchased from Beijing InnoChem Science & Technology Co., Ltd. in China. Methylamine hydrochloride (MAH, 99%) was purchased from Acros. Formamidinium hydroiodide (FAI, 99.99%), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS, 1.5%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. in China. PCBM (99%) were purchased from Xi'an Polymer Light Technology Corp. in China. PEI was purchased from Suzhou Diamond Electronic Technology Co., Ltd. in China.

2.2 Synthesis of G-CNT films, CuCrO₂(Ni) nanoparticles and CsPbBr₃ QDs

The G-CNT films were synthesized on copper (Cu) foils using a low-pressure chemical vapor deposition system.²⁹ The process steps are as follows: First, the freestanding carbon nanotube (CNT) films were grown directly and continuously by the blown aerosol chemical vapor deposition method, according to our earlier report.³⁰ A piece of freestanding CNT film was first transferred onto a pre-polished Cu foil, then placed in the quartz tube inside a furnace (OTF-1200X). The system was evacuated and then heated to 900°C. After annealing in H₂ for 30 min, the system was heated to 1040°C, and CH₄ (purity: 99.999%) gas at a 1 sccm flow rate was introduced into the system to grow graphene. After 30 min, the system was turned off and cooled to room temperature. Finally, G-CNT/Cu foil was cut into 2.5 cm \times 2.5 cm pieces and dipped into FeCl₃ solution to dissolve the Cu foil, and then rinsed in water and ethanol solution to obtain pure freestanding G-CNT film. Using chromium nitrate, copper nitrate and nickel nitrate as precursors, at a molar ratio of 5:5:1, copper-chromium oxide nanoparticles containing nickel were prepared by a hydrothermal method similar to that reported previously.^{31,32} The structural characterization showed that the synthesized nanoparticles exhibit 2H-CuCrO₂ crystal structure (Fig. S1a), therefore it was labeled as CuCrO₂(Ni). CsPbBr₃ QDs were synthesized by a heat injection method and alternately purified by methyl acetate and n-hexane reported previously.³³

2.3 Fabrication of solar cells



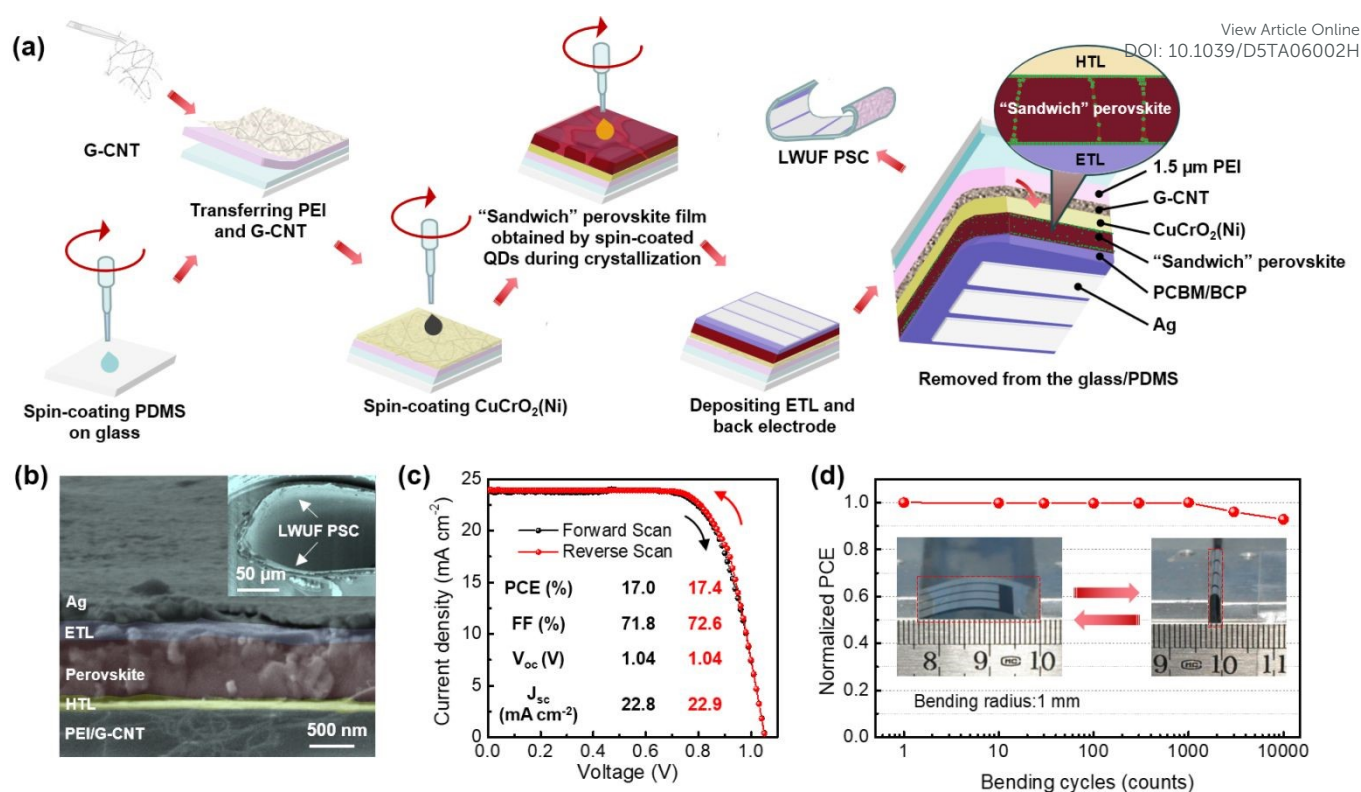


Fig. 1 The process routes and the structural and performance characteristics of the LWUF PSCs. (a) Schematics of the fabrication procedure. (b) Cross-sectional SEM image of the LWUF PSC. The inset shows the SEM image of a LWUF PSC under bending with a curvature radius of 70 μm . (c) J-V curves of the device, recorded in reverse scanning and forward scanning. (d) Mechanical stability of the devices at a bending radius of 1 mm. The inset in (d) shows the digital image of a device under bending cycles.

2.5 cm \times 2.5 cm glass and PEI substrates, as well as glass/ITO electrode substrate were cleaned in an ultrasonic cleaner with detergent, deionized water, acetone, and isopropanol for 20 min each. Before use, the above substrates were dried with air and treated with a plasma cleaner for 5 min. For ultra-thin PEI/G-CNT electrode substrates, poly(dimethylsiloxane) (PDMS, Sylgard 184) and its curing agent (mass ratio 10:1) were spin-coated onto dried glass at 4000 rpm for 1 min and then dried at 80°C for 50 min, then a 1.5 μm -thick PEI film was attached to the glass/PDMS rigid substrate, finally, the pure freestanding G-CNT film obtained in section 2.2 was directly laid out on the PEI film. After further drying, the G-CNT film and PEI film were firmly adhered together under the action of surface van der Waals force. Subsequently, a PEDOT:PSS or $\text{CuCrO}_2(\text{Ni})$ HTL was deposited on this glass/PDMS/PEI/G-CNT structure by spin-coating process. For the PEDOT:PSS HTL devices, by spin-coating PEDOT:PSS at 4000 rpm for 40 s and then annealed at 120°C for 40 min; For $\text{CuCrO}_2(\text{Ni})$ HTL devices, by spin-coating a 5 mg mL^{-1} $\text{CuCrO}_2(\text{Ni})$ nanoparticles colloidal solution at 2000 rpm, followed by annealing at 120°C for 10 min. Afterwards, the aforementioned structure was transferred to an argon glove box for preparation of the perovskite layer and the electron transport layer (ETL).

The perovskite precursor was obtained by dissolving 0.9 mol FAI, 1 mol PbI_2 , 0.1 mol CsI, and 0.2 mol MACI in 1 mL mixture solution of 4:1 V/V DMF/DMSO. The precursor was spin-coated according to a two-step process of 1000 rpm for 6 s

and 3000 rpm for 35 s; 100 μL CB was dropped 5 s before the end of the second step. Then the precursor film was heated at 100°C for 20 min on a hotplate. For "sandwich" perovskite films, a solution of QDs with optimal concentration was pre-spin-coated on the HTL, and then the surface was rinsed sequentially with saturated methyl acetate solution of lead acetate and methyl acetate solution. 70 μL perovskite precursor solution was dropped onto the pre-deposited QDs film, and spin-coated at 1000 rpm for 6 s, followed by 3000 rpm for 35 s. During the last 5 s of the spin-coating process, 100 μL QDs solution with optimal concentration was dropped onto the surface of perovskite precursor during spin-coating. After the spin-coating process, the substrate was transferred to a 100°C hot plate and annealed for 20 min. On top of the perovskite, the ETL of PCBM and BCP was spin-coated at 1500 rpm. Finally, a 100 nm-thick Ag electrode was deposited in a thermal evaporator, and then the LWUF PSC was removed from the glass/PDMS rigid substrate to complete the fabrication process. The LWUF PSC fabrication process is schematically shown in Fig. 1a.

2.4 Characterization of materials and devices

The morphology of the materials was characterized by field-emission scanning electron microscopy (SEM, Hitachi S5200) and high-resolution transmission electron microscopy (HR-TEM). The transmission and absorption spectra of the materials



were measured using an ultraviolet–visible–near infrared spectrophotometer (UV-3600, Shimadzu). Photoluminescence (PL) spectra were recorded by LabRAM HR800 (HORIBA Jobin Yvon Inc.) with an excitation laser of 514 nm wavelength. Transient photocurrent (TPC) decay curves were generated by a microsecond pulse under short circuit conditions (by a very low resistor at 20 Ω). The sheet resistance of the G-CNT film was determined by a handheld four-probe meter (Tonghui, TH2661). The water contact angle was measured by an optical contact angle meter (OCA25, Dataphysics). The phase purity and crystal structure were identified by X-ray diffraction (XRD, Bruker, D8 Advance). Young's modulus of the perovskite films was obtained using an atomic force microscope (AFM, Bruker MultiMode-8 ScanAsyst). Space-charge-limited current (SCLC) and current density-voltage (J-V) performances were measured by a Keithley 4200-SCS. The J-V hysteresis curves were obtained in the reverse scan (from 1.2 V to -0.5 V, step 0.01 V) and forward scan (from -0.5 V to 1.2 V, step 0.01 V) under AM 1.5G (100 mW cm⁻²) irradiation based on a solar simulator (CHF-XM 500, Beijing Trusttech Co. Ltd.). Before J-V measurements, the simulator was cautiously calibrated by using a standard monocrystalline silicon solar cell. To ensure accuracy, a mask with a round aperture (the area is about 0.115 cm²) was employed during the measuring process. The bending cycle test was performed by a stretching machine with a metal stand of specific outside diameter. The environmental stability test was performed at 25°C in the atmosphere, and the relative humidity (RH) was about 35%. And all devices are not encapsulated in any way. The electrochemical impedance spectroscopy (EIS) was carried out on an electrochemical workstation (Zahner, IM6ex). The EIS measurements were performed over a frequency range of 1 MHz to 1 Hz with an applied amplitude of 5 mV. All tests used were conducted at ambient temperature and normal atmosphere.

3. Results and discussion

3.1 The overall excellent performance of the as-designed LWUF PSCs

The LWUF PSC, shown in the schematic diagram in Fig. 1a, results in high performance and excellent stability by adopting a collaborative approach to improve the performance of the FPSC. Specifically, the design scheme mainly includes the following four aspects: (1) Select a freestanding, ultra-light, very flexible and highly transparent conductive G-CNT film as electrode; (2) Use a 1.5 μm -thick PEI film as flexible substrate; (3) Optimize HTL to improve device's efficiency; (4) Design the "sandwich" architecture formed by CsPbBr₃ QDs/polycrystalline perovskite mixed CsPbBr₃ QDs/CsPbBr₃ QDs for the first time as the light-absorbing layer. In this way, while improving the device's PCE, it manages to reduce the weight of the device and improve its mechanical stability and environmental stability.

The entire fabrication process of LWUF PSC is performed on a glass/PDMS rigid substrate, as shown in Fig. 1a. PDMS is used as adhesive nature contact layer between the ultra-thin PEI and the rigid glass substrate to ensure neither wrinkling nor

folding during the fabrication process and to facilitate the removal of the LWUF PSC from the rigid substrate. The detailed process steps are described in the "2.3 Fabrication of solar cells". The entire LWUF PSC is configured as 1.5 μm -thick PEI/G-CNT/CuCrO₂(Ni)/"sandwich" perovskite/PCBM/BCP/Ag, and its SEM image in Fig. 1b shows the cross-sectional structure. The inset shows the device under bending state at about 70 μm radius of curvature, where the device's structure is intact and signifies great flexibility. In contrast, compared to the conventional FPSC prepared on 125 μm -thick PET, the cell structure has been severely disrupted at the same state (Fig. S2).

Figure 1c shows the J-V curves for the forward and reverse scans of the LWUF PSC. The results show that the J-V curves in forward and reverse scans largely overlap, which indicates negligible hysteresis. The short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) of the device in reverse scan are 22.9 mA cm⁻², 1.04 V, and 72.6%, respectively, which results in an optimal PCE of 17.4%. The weight of the 2.5 cm \times 2.5 cm device is only 3.53 mg (areal density of 5.6 g m⁻²), and it's 3.4% and 0.2% of conventional flexible and rigid devices, respectively (Fig. S3), which finally makes the power-per-weight reach 31.1 W g⁻¹. The currently reported FPSCs, fabricated on 1.3-57 μm -thick substrates, have a areal density of 4.4-71 g m⁻² and a power-per-weight of 47.8-1.96 W g⁻¹ (summarized in Table S1).^{1,10-18} It is evident that, under the premise of considering the stability of the devices, the LWUF PSC prepared in this study is one of the few devices that can operate stably in air, and it also leads in terms of lightweight design among such stable devices. The mechanical flexibility of the LWUF PSC was tested by bending cycles with a curvature radius of 1 mm, as shown in Fig. 1d. The results showed that the device's PCE remained 92.8% of the initial value after 10,000 bending cycles, exhibiting extremely mechanical flexibility.

3.2 Enhancement effect of freestanding and ultra-light G-CNT films on the flexibility and stability of LWUF PSCs

Using carbon nanofilms instead of metal oxides as the electrodes of PSCs can effectively improve the flexibility and stability of the device. G-CNT films were prepared by growing graphene to fill holes in a self-supporting CNT continuous network. So, the G-CNT film combines the self-supporting property of CNT film with the densification of graphene film, which is expected to further improve the FPSC's performance. The SEM and HR-TEM images of the G-CNT film in Fig. 2a show that the pores of the CNT network film formed by the intersection of CNT bundles through "X" and "Y" nodes are filled completely by the grown graphene, which significantly improve the moisture resistance of the G-CNT film. To compare the moisture resistance of CNT and G-CNT films in humid environment, a drop of deionized water was placed on the surface of the copper foils covered with G-CNT and CNT films, respectively, and then heated it to 80°C to accelerate the corrosion of the copper foils below by moisture, as shown in Fig. 2b. After 10 min, red traces were observed in the dripping region on CNT/Cu, while no change was observed in the corresponding position on G-CNT/Cu. Under an optical microscope, patches of red cuprous



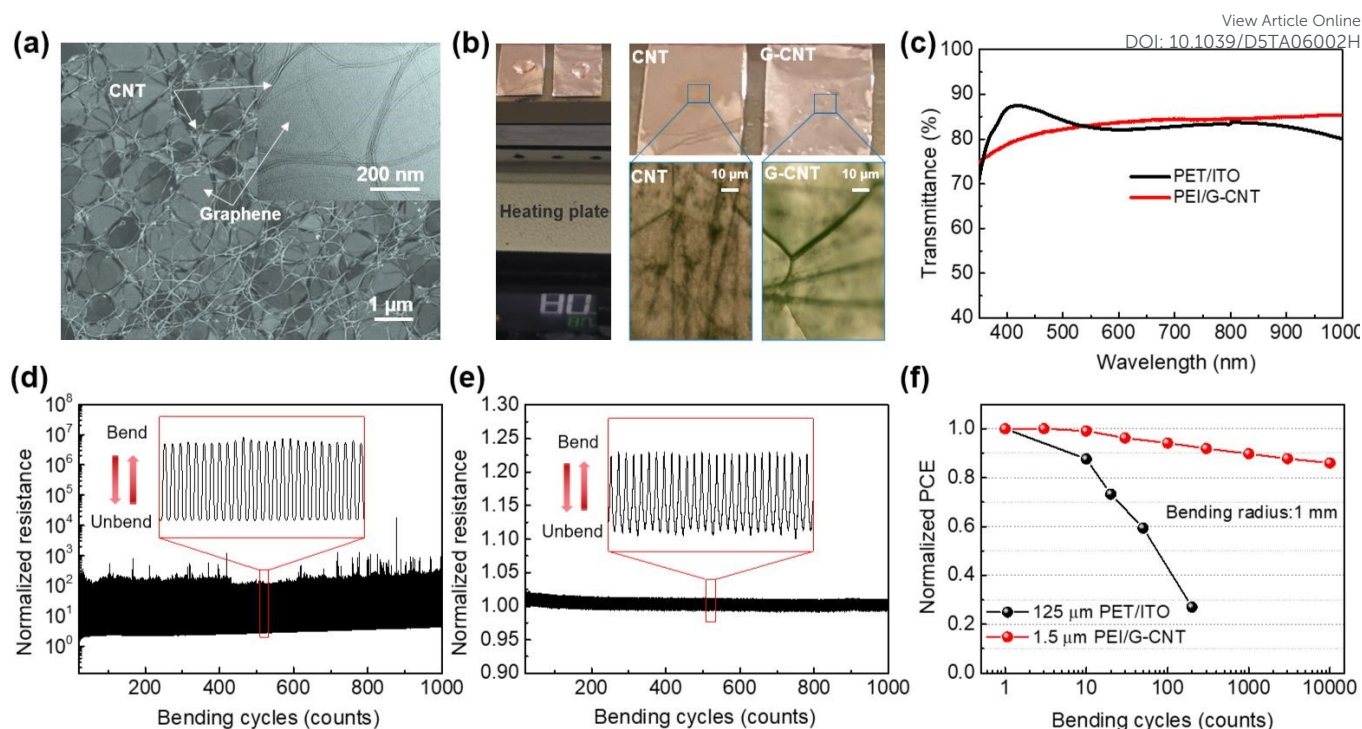


Fig. 2 The microstructure of a G-CNT film and its advantages as a flexible electrode. (a) SEM image of a G-CNT film. The insert is its HR-TEM image. (b) Moisture resistance investigation of CNT and G-CNT films. (c) Transmittance of PEI/G-CNT and PET/ITO electrode substrates. The dynamic resistances of PET/ITO (d) and PEI/G-CNT (e) electrode substrates in real time during bending cycles with a 1 mm bending radius. (f) Normalized PCE of FPSCs based on PET/ITO and PEI/G-CNT electrode substrates as a function of bending cycles with a bending radius of 1 mm.

oxide were observed at the trace site on the CNT/Cu, but almost none on the G-CNT/Cu. In previous reports, CNT film electrodes were considered effective in blocking moisture to improve PSC stability, so the as-grown G-CNT films are undoubtedly more likely to improve device's stability.^{22,34-36} The environmental stability of the device will be discussed at the §3.4 in main text.

In addition, the as-grown G-CNT film presents excellent transparency, high conductivity, and outstanding flexibility.³⁷ In this study, PEI/G-CNT electrode substrates with light transmittance of about 87% shown in Fig. 2c and sheet resistance of about $100 \Omega \text{ sq}^{-1}$ are used. Although the electrical conductivity of the PEI/G-CNT flexible electrode substrate is not as good as that of the current commercial PET/ITO electrode substrate (with a sheet resistance of about $32 \Omega \text{ sq}^{-1}$), the excellent mechanical flexibility of the PEI/G-CNT electrode substrate is something that the PET/ITO electrode substrate cannot match. The dynamic resistances of PET/ITO and PEI/G-CNT electrode substrates were monitored in real time during bending cycles with a bending radius of 1 mm in Figs. 2d and 2e, respectively. The results show that the resistance of a PET/ITO electrode substrate increases by two orders of magnitude from the straightened state to the bent state due to the fragility of ITO, while the increase in resistance of a PEI/G-CNT electrode substrate is negligible. After 1000 bending cycles, the resistance of PET/ITO electrode substrate has increased to 10 times its initial value (from about $32 \Omega \text{ sq}^{-1}$ increase to about $320 \Omega \text{ sq}^{-1}$), while the corresponding change in that of PEI/G-CNT electrode substrate is less than 2% (from about $100 \Omega \text{ sq}^{-1}$

increase to about $102 \Omega \text{ sq}^{-1}$, which is only one-third of that of the PET/ITO electrode, revealing much higher dynamic conductivity). This indicates that the latter exhibits superior mechanical flexibility and excellent stable electrical conductivity during dynamic changes compared to the former.

In order to cope with more severe mechanical deformation, the G-CNT electrodes were also tested under winding, twisting, and stretching. The test results are shown in Fig. S4, indicating that this electrode has excellent tolerance to deformation. The weight of the $2.5 \text{ cm} \times 2.5 \text{ cm}$ ultra-thin PEI/G-CNT electrode substrate is only 3.38 mg, and the surface density is less than 0.54 mg cm^{-2} , which is the main reason for making the as-designed LWUF PSC lightweight. The mechanical robustness of the devices with PET/ITO and PEI/G-CNT electrode substrates is compared in Fig. 2f. The device with a $1.5 \mu\text{m}$ -thick PEI/G-CNT electrode substrate is proven to hold about 86.2% of the initial PCE after bending 10,000 times at a curvature radius of 1 mm, while the corresponding device with a $125 \mu\text{m}$ -thick PET/ITO electrode substrate can only maintain 27% of the initial PCE after 200 bends. The improvement in the performance of the G-CNT-based device can be attributed to the superior electrical stability, water vapor barrier property, and mechanical flexibility of the G-CNT electrode, which collectively contribute to a slower rate of performance degradation during operation, thereby providing greater possibilities for large-scale applications. However, despite these advantages, the large-scale fabrication of G-CNT films is still in the development stage, as achieving uniform large-area G-CNT



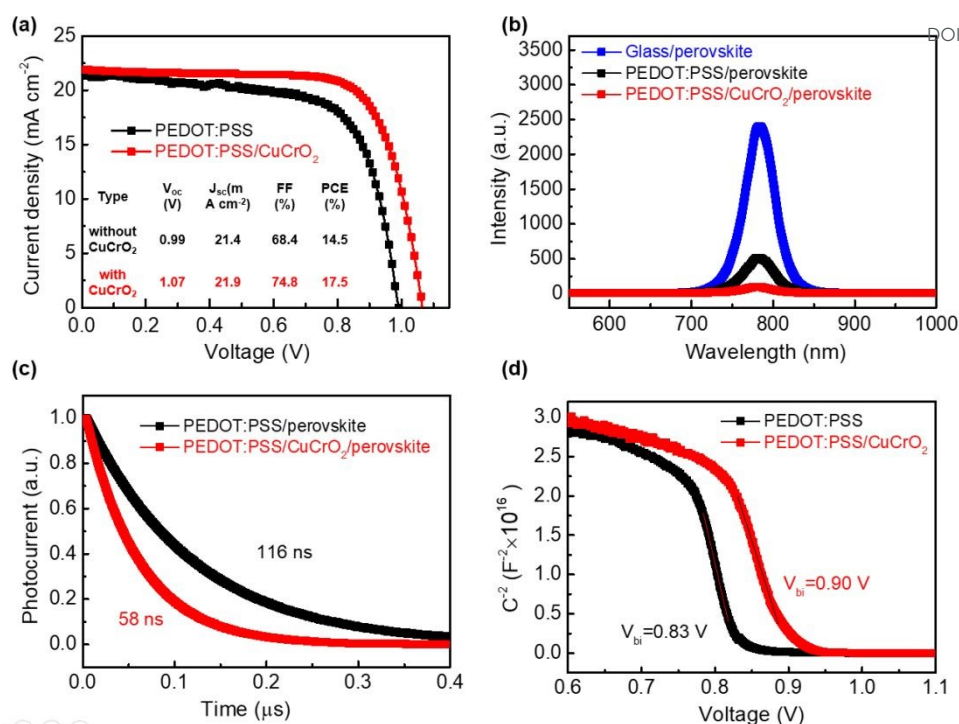


Fig. 3 Optimization of device's efficiency by CuCrO₂(Ni) nanoparticles. (a) J-V curves of the PSCs on rigid glass/G-CNT electrode substrates with different HTLs. (b) PL spectra. (c) TPC curves. (d) The Mott-Schottky analysis plot.

films continues to pose technical challenges that hinder their widespread adoption in FPSCs.

3.3 Optimization of device's efficiency by CuCrO₂(Ni) nanoparticles as HTL

As a high-conductivity organic polymer, PEDOT:PSS can have a synergistic effect with carbon nanofilms to improve the hole collection efficiency of solar cells.³⁸ In inverted PSCs, the balance between the work function and conductivity of PEDOT:PSS, as well as the high hygroscopicity, severely hinder the improvement of the device's PCE and long-term stability.^{39,40} An effective approach involves the doping modification of PEDOT:PSS or identifying novel HTL materials to address the interfacial contact issues with perovskite film. CuCrO₂ nanoparticles, as an inorganic HTL material, exhibit excellent water dispersibility and tunable optoelectronic properties.^{31,41} However, the relatively low crystalline quality of this material limits its direct application in high-efficiency PSCs.^{42,43} In this study, we synthesized a high-quality CuCrO₂(Ni) HTL by introducing nickel into CuCrO₂ nanoparticles. Structural and morphological characterizations (as shown in Fig. S1) confirmed that the material possesses a hexagonal 2H-CuCrO₂ crystal structure with an average grain size of 10–15 nm. Compared with previously the reported CuCrO₂ nanoparticles,^{42,43} the CuCrO₂(Ni) nanoparticles prepared in this work exhibit higher crystallinity (Fig. S1a) and more efficient photogenerated charge extraction and transport capabilities (Fig. S5), which are expected to result in improved performance in PSCs.

Fig. 3a shows the J-V curves of the PSCs on the rigid glass/G-CNT electrode substrates with different HTLs. The results demonstrate that after using CuCrO₂(Ni) HTL, the V_{oc} and FF of the device increase from 1.04 V and 63.9% to 1.09 V and 72.2%, respectively, and the PCE of the cell increased from 15.4% to 18.4%, an increase of 20%. The enhancement of the device's photovoltaic performance is attributed to the improved carrier transport at the interface. To substantiate this, we analyzed the PL spectra of perovskite films deposited on PEDOT:PSS and CuCrO₂(Ni) HTLs. From the PL spectra (Fig. 3b), it can be found that the perovskite on the CuCrO₂(Ni) HTL has a weaker PL peak, which indicates that the photo-quenching is more pronounced than that deposited on PEDOT:PSS HTL.²² TPC is a common technique for analyzing the carrier lifetime of materials, and the carrier lifetime can be directly calculated by fitting the TPC curve with a double exponential function. Fig. 3c shows that the carrier lifetimes of the perovskite on the two HTLs are 116 ns and 57 ns, respectively. The shorter carrier lifetime of the CuCrO₂(Ni) structure represents that the separation and transport efficiency of photogenerated carriers in perovskite are improved, which is also the reason for the more significant PL spectra quenching of this structure. We further performed Mott-Schottky analysis to gain more insight into the effect of the CuCrO₂(Ni) HTL on carrier diffusion and extraction within the perovskite. The built-in potentials (V_{bi}) can be estimated by fitting C⁻²~V linear relationship according to equation (1):⁴⁴

$$C^{-2} = \frac{2}{NA^2 q \epsilon \epsilon_0} (V_{bi} - V) \quad (1)$$



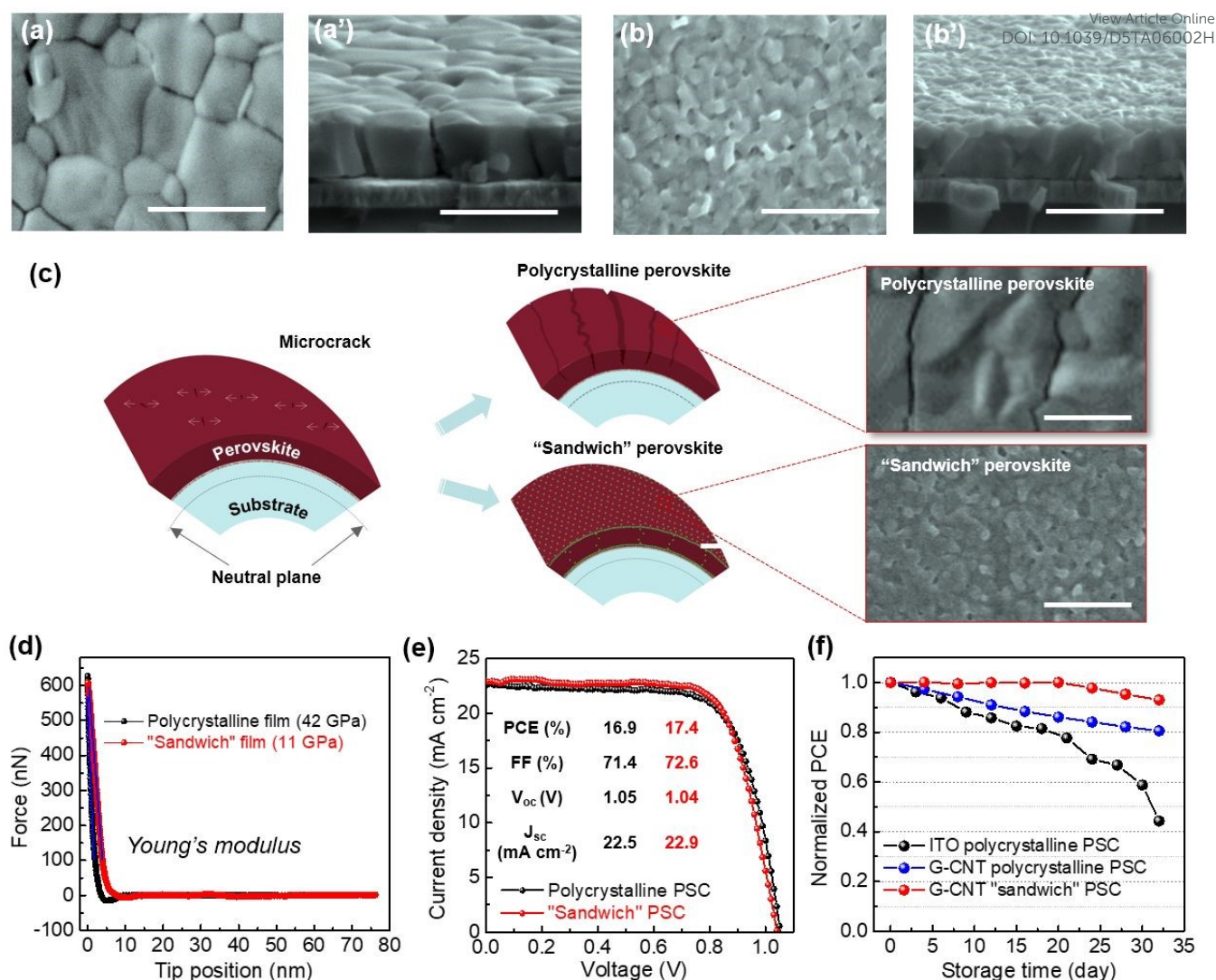


Fig. 4 Improvement of device's performance by the as-designed "sandwich" perovskite architecture. The SEM images of top and cross-section of polycrystalline perovskite film (a, a') and the "sandwich" perovskite film (b, b'). (c) Schematic representation of the relationship between the perovskite structure and the cracks generated during bending. The inset shows SEM images of two kinds of perovskite films after 1000 bending cycles at a curvature radius of 4 mm. (d) Young's modulus of polycrystalline and "sandwich" films. (e) J-V curves of LWUF PSCs. (f) environmental stability of the PSCs. The scale bar is 1 μ m.

where C is the capacitance, V is the applied voltage, N is the defect density, A is the device's area, q is the elementary charge, ε is the relative dielectric constant of the perovskite material ($\varepsilon = 46.9$ for FAPbI_3),⁴⁵ and ε_0 is the vacuum permittivity ($8.8542 \times 10^{-12} \text{ F} \cdot \text{m}^{-1}$). As shown in Fig. 3d, the V_{bi} for the PSC with $\text{CuCrO}_2(\text{Ni})$ HTL is 0.91, significantly higher than that of the PSC with PEDOT:PSS HTL. A higher V_{bi} signifies the formation of a stronger electric field in the PSC, which favors carrier transfer.⁴⁶ Furthermore, the corresponding carrier density at the perovskite interface is inversely proportional to the slope of the C^2 - V fitted line.⁹ The lower line slope of the device based on $\text{CuCrO}_2(\text{Ni})$ HTL refers to the higher interfacial carrier density, which suggests that more carrier in the perovskite of the device has been separated and transported. This is in good agreement with the weak PL intensity and the short carrier lifetime of the composite HTL structure.

3.4 Excellent flexibility, marked stability and high PCE of LWUF PSC enabled by the "sandwich" perovskite

It is noted that in recent years, perovskite QDs (such as CsPbBr_3 QDs) have been applied to interface modification materials and light absorption materials in PSC,^{28,47} effectively improving the flexibility of PSC, although its PCE is much lower than that of rigid PSC. In this study, we intend to combine the advantages of perovskite QDs and polycrystalline perovskite, and try to adopt a scheme to refine polycrystalline perovskite grains, to jointly improve the flexibility and PCE of PSC.

We design a "sandwich" perovskite architecture as a light absorption layer for the first time. The grain size of the as-synthesized CsPbBr_3 QDs is about 20 nm. Their structural characterizations by HR-TEM and XRD are shown in Fig. S6. A "sandwich" perovskite layers were prepared by burying bottom QDs before crystallization, and then spin-coating QDs on the upper surface of polycrystalline perovskite during



crystallization. The SEM images in Figs. 4a and 4b show that the polycrystalline perovskite consists of uneven and large grains with diameters ranging from 200 nm to 1000 nm (Figs. 4a and 4a'), with gaps and pinholes at the wider grain boundaries, while the "sandwich" perovskite consists of small grains with diameters of 100-200 nm (Figs. 4b and 4b') packed to form a dense structure. The smaller grain size and denser structure of the "sandwich" film compared to the polycrystalline film are attributed to the modulation effect of QDs. The SEM images of the "sandwich" perovskite films with different QDs are shown in Figs. S7 and S8. The film with 5 mg mL⁻¹ QDs exhibits a relatively uniform grain shapes and sizes and a dense structure, so we use this concentration to regulate the formation of perovskite. The QDs incorporated during the crystallization process act as nucleation sites for perovskite crystallization and promote grain refinement. Comparing Figs. 4a', 4b' and S7, it can be seen that when the QDs first buried at the bottom the perovskite crystal particles on HTL tend to be smaller and more dense than those without adding QDs, and this modulation effect is more obvious in the crystallization process of the middle layer of the "sandwich" and the addition of quantum dots at the top. If only QDs is laid on HTL, but no QDs is added in the subsequent perovskite crystallization, the particles on the upper surface of the perovskite layer are still uneven and large in size, as shown in Fig. S9.

The XRD diffraction pattern in Fig. S10 shows that the "sandwich" perovskite synthesized by adding QDs retain the crystal structure of the polycrystalline perovskite film, which may be related to the position of QDs in the polycrystalline film. According to the EDS mapping (Fig. S11), cesium is mainly distributed around the grain. Since cesium atoms mainly exist in QDs, it can be concluded that QDs occupies the grain boundary of the polycrystalline film, which may also be the reason for retaining the crystal structure of the polycrystalline film. The QDs entering the grain boundaries of the polycrystalline films will also fill the voids and pinholes, leading to densification of the films.

In order to verify the flexibility of the two perovskites (i.e., the polycrystalline perovskite and the "sandwich" perovskite), they were deposited onto a normal 125 μm -thick PET, respectively. Their surface morphologies were compared after bending 1000 times with a curvature radius of 4 mm. As shown in Fig. 4c, the "sandwich" perovskite layer did not exhibit some cracks as the polycrystalline perovskite layer did. To figure out why "sandwich" perovskite doesn't crack, the Young's modulus of two perovskite and QDs films was measured at the peak-force model of AFM as shown in Figs. 4d and S12.⁴⁸ The results show that the Young's modulus of the "sandwich" perovskite is 11 GPa, higher than 8 GPa of QDs and lower than 42 GPa of polycrystalline film. The lowest Young's modulus of QDs can be attributed to their small particle size and the soft surface ligands between particles,²⁸ which may facilitate interparticle motion and thus contribute to the excellent flexibility of QDs. These results allow us to conclude that the QDs filled at grain boundaries act as a "roller" during the bending process, effectively promoting the inter-grain sliding and preventing the micro-cracks after deformation. Similarly, the "sandwich"

perovskite has a significantly lower Young's modulus than polycrystalline film, meaning that it may be able to withstand more elastic deformation to release stress under the same pressure, which helps stabilize the crystal structure under deformation to prevent cracking.

Naturally, LWUF PSCs were further prepared on ultra-thin PEI/G-CNT electrode substrates using polycrystalline and "sandwich" perovskite, respectively. The J-V curves and performance parameters of the two devices are shown in Fig. 4e. The PCE of the "sandwich" device increases to 17.4%, compared to 16.9% for the polycrystalline LWUF PSC. The reproducibility of the study results shows that the arithmetic mean (*M*) of the PCE of the "sandwich" device group increases to 17.1% from 16.5% of the control group, and the standard deviation (σ) decreases to 0.269 from 0.302 of the control group (Fig. S13), indicating that the "sandwich" LWUF PSC has higher PCE and repeatability. The mechanical robustness of the resultant devices can be seen in Fig. S14. After 10,000 bending cycles with a curvature radius of 1 mm, the "sandwich" perovskite-based LWUF PSC retain 92.8% of initial PCE, while the polycrystalline perovskite LWUF PSC sustains 86.2% of original PCE. Thus, thanks to the structural design of the "sandwich" perovskite layer combined with the G-CNT flexible electrode, the "sandwich" perovskite LWUF PSC exhibits superior efficiency and excellent mechanical stability.

As another key indicator for evaluating the device's performance, the environmental stability was measured in a dark environment with 35% RH and 25°C, as shown in Fig. 4f. For polycrystalline PSC fabricated with G-CNT instead of ITO electrode, the PCE retention rate increased from 44.3% to 80.6% after 32 days. This remarkable improvement is attributed to the excellent moisture resistance of the G-CNT films (Fig. S15). Moreover, the environmental stability of the "sandwich" perovskite-based PSC is significantly superior to that of the polycrystalline perovskite-based PSC, further indicating that QD passivation can also improve the environmental stability of PSCs. This is because the surface coordination of QDs contains a large number of alkane functional groups.⁴⁹ When they are anchored at the grain boundaries and the surface of perovskite, a non-polar molecular hydrophobic layer will be formed on its surface (Fig. S16). Ultimately, the as-designed "sandwich" perovskite-based LWUF PSC with G-CNT electrodes presented the best environmental stability, as the device maintained 93.0% of the initial PCE after 32 days.

The "sandwich" devices on flexible PEI/G-CNT electrode substrates demonstrate effective performance enhancement, which should be related to the carrier behavior in "sandwich" perovskite layer. Then, PL, SCLC and EIS tests were carried out to investigate the carrier recombination dynamics. The PL intensity of "sandwich" perovskite film is slightly higher than that of the polycrystalline film (Figure 5a), implying that the QD-based passivation process in "sandwich" perovskite does not lead to an increase in defect density despite grain refinement. This highlights the effectiveness of QDs in passivating perovskite defects, which is similar with the findings reported in reference,⁴⁹ where post-treatment of crystallized perovskite surfaces with QDs was demonstrated to reduce defect density



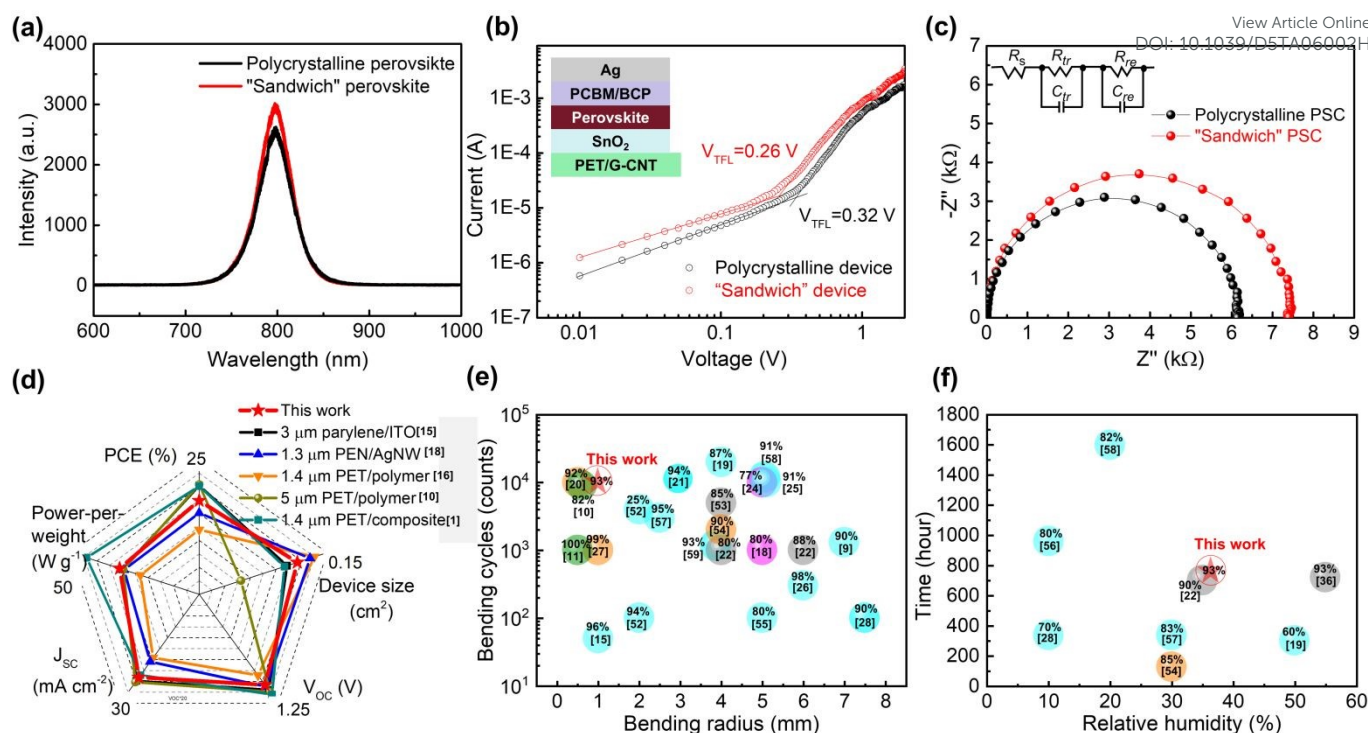


Fig. 5 Performance of LWUF PSCs based on polycrystalline and "sandwich" perovskite films. (a) PL spectra of perovskite films. (b) SCLC measurements. (c) Nyquist plots. The insets in (b) and (c) show the electron-only device's architecture and equivalent circuit model, respectively. (d) Comparison of the performance of the LWUF PSC in this work with that of FPSCs reported so far. (e) Mechanical stability of the FPSCs reported so far. (f) Environmental stability of the FPSCs reported so far. Light blue, magenta, gray, and saffron yellow bubbles in (e) and (f) represent ITO electrodes, Ag nanowire electrodes, carbon nanofilm electrodes, and composite electrode-based FPSCs in that order, and the percentages on the bubbles represent the maintenance rate of PCE after bending or aging.

and enhance PL emission. According to the SCLC results in Fig. 5b, the trap-filled limit voltages (V_{TFL}) of the "sandwich" perovskite-based device and the polycrystalline perovskite-based device are 0.26 V and 0.32 V, respectively. The trap states density (n_t) used to quantify the concentration of defects can be calculated according to equation (2):⁵⁰

$$n_t = \frac{2\epsilon\epsilon_0 V_{TFL}}{qd^2} \quad (1)$$

where d is the film thickness. Compared with the polycrystalline perovskite-based device, the n_t of the "sandwich" perovskite device slightly decreases from $7.67 \times 10^{21} \text{ m}^{-3}$ to $6.23 \times 10^{21} \text{ m}^{-3}$ (as shown in Table S2), indicating that the defect density in "sandwich" perovskite is not higher or even lower than that of polycrystalline perovskite. Based on previous findings, the weak interaction between the carbonyl group on the QDs ligand and Pb allows the QDs to be chemically anchored at the grain boundaries.^{47,51} A similar phenomenon is observed that "sandwich" perovskites have been shown to have a unique structure of QDs into the pinholes and grain boundaries of polycrystalline perovskites (Figs. S10 and S11). Therefore, the experimental results suggest that the QDs entering pinholes and grain boundaries of the "sandwich" perovskite may also be able to passivate defects.

Figure 5c presents the Nyquist plot of devices with polycrystalline perovskite and "sandwich" perovskite under dark condition. The inset shows the equivalent circuit model, composed of series resistance (R_s), transfer resistance (R_{tr}), recombination resistance (R_{re}), and parallel capacitance.⁴⁴ The

fitting parameters are shown in Table S3. Compared to the polycrystalline perovskite-based device, R_{re} of the "sandwich" perovskite-based device increases from 5644Ω to 6917Ω and R_{tr} decreases from 295Ω to 242Ω (R_s change can be neglected), which shows that the carrier recombination in the device is effectively suppressed due to defect passivation, thereby increasing V_{OC} and FF of devices.

In addition, our work provides an effective approach to fabricate LWUF PSCs on an ultra-thin PEI/G-CNT electrode substrate. Among these LWUF PSCs, as-designed "sandwich" perovskite exhibits three functions in improving the device's performance: ① By forming uniform and fine grains on the surface of the perovskite, it enhances the flexibility of the perovskite film and thereby improves the device's mechanical stability. ② By passivating the interface defects of the perovskite with QDs, it is conducive to increasing the PCE of the device. ③ Meanwhile, due to the passivation effect of QDs, by forming hydrophobic layers at the grain boundaries and on the surface, it undoubtedly helps to enhance the environmental stability of LWUF PSCs.⁴⁹ Thus, the resultant device contributes a high efficiency of 17.4% and a power-per-weight of 31.1 W g^{-1} , which is also the highest performance reported so far for LWUF PSCs with inorganic nanofilm electrodes, as shown in Fig. 5d (detailed results are summarized in Table S1). Furthermore, the mechanical flexibility and environmental stability of the resultant device are at the top level among the FPSC devices reported previously, as shown in Figs. 5e and 5f (detailed results are summarized in Tables S4 and S5). These



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results will further promote the application of FPSC in the field such as wearable devices, flexible electronics, artificial intelligence robot, aerospace and so forth.

4. Conclusions

In this study, a LWUF PSC with high performance and excellent stability has been fabricated by adopting a collaborative approach in terms of four aspects. First, selecting a freestanding, ultra-light, very flexible and highly transparent conductive G-CNT film as electrode, instead of the conventional oxide electrode, has improved flexibility, mechanical stability and environmental stability of PSCs. Second, using a 1.5 μm -thick PEI film as flexibility substrate has increased flexibility and reduced weight of the device greatly. Third, optimizing the transfer of photogenerated charge carriers by employed $\text{CuCrO}_2(\text{Ni})$ nanoparticles as a novel HTL, which has boosted the PCE of PSCs. Fourth, a "sandwich" perovskite layer of CsPbBr_3 QDs wrapped around the compact perovskite grains is designed as a light absorption layer with synergistic effects for the first time, giving LWUF PSC excellent flexibility, remarkable stability and high PCE. As a result, the resultant device records a PCE of 17.4% and a power-per-weight of 31.1 W g^{-1} , which is the best performance of LWUF PSCs with nanofilm electrodes to date. In addition, the formation of sandwich-structured perovskite films through QD passivation effectively addresses the issue of deteriorated interfacial contact behavior resulting from the limited mechanical supportability of ultrathin substrates. The grain size of the "sandwich" perovskite decreased from random 200–1000 nm to uniform 100–200 nm. Moreover, the QDs introduced at the grain boundaries and surfaces acted as rollers for grain sliding during deformation, effectively suppressing the cracking problem after bending. As a result, the LWUF PSCs sustained 92.8% of the initial PCE after 10,000 bending cycles with a curvature radius of 1 mm. Due to the use of an impermeable "sandwich" perovskite absorption layer and a G-CNT electrode, LWUF PSC maintains 93.0% of its initial PCE after 32 days in the atmosphere of 35% RH, presenting excellent environmental stability. Given the high PCE, power-per-weight, outstanding mechanical flexibility, and marked environmental stability of this LWUF PSC, it's expected to meet a wider range of needs and applications, such as wearable devices, flexible electronics, and aerospace applications.

Conflicts of interest

There are no conflicts to declare.

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Data availability

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The data supporting this article have been included as part of the Supplementary Information.

