

Embedded Nickel-Mesh Transparent Electrodes for Highly Efficient and Mechanically Stable Flexible Perovskite Photovoltaics: Toward a Portable Mobile Energy Source

Meng Li, Wei-Wei Zuo, Antonio Gaetano Ricciardulli, Ying-Guo Yang, Yan-Hua Liu,*
 Qiong Wang, Kai-Li Wang, Gui-Xiang Li, Michael Saliba,* Diego Di Girolamo,
 Antonio Abate,* and Zhao-Kui Wang*

The rapid development of Internet of Things mobile terminals has accelerated the market's demand for portable mobile power supplies and flexible wearable devices. Here, an embedded metal-mesh transparent conductive electrode (TCE) is prepared on poly(ethylene terephthalate) (PET) using a novel selective electrodeposition process combined with inverted film-processing methods. This embedded nickel (Ni)-mesh flexible TCE shows excellent photoelectric performance (sheet resistance of $\approx 0.2\text{--}0.5\ \Omega\ \text{sq}^{-1}$ at high transmittance of $\approx 85\text{--}87\%$) and mechanical durability. The PET/Ni-mesh/polymer poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS PH1000) hybrid electrode is used as a transparent electrode for perovskite solar cells (PSCs), which exhibit excellent electric properties and remarkable environmental and mechanical stability. A power conversion efficiency of 17.3% is obtained, which is the highest efficiency for a PSC based on flexible transparent metal electrodes to date. For perovskite crystals that require harsh growth conditions, their mechanical stability and environmental stability on flexible transparent embedded metal substrates are studied and improved. The resulting flexible device retains 76% of the original efficiency after 2000 bending cycles. The results of this work provide a step improvement in flexible PSCs.

Hybrid organic–inorganic perovskite solar cells (PSCs) have attracted enormous research interest and have developed rapidly.^[1–3] In just a few years, the power conversion efficiency (PCE) of PSCs has rapidly increased from the initial 3.8% to the certified 25.2% and has shown great potential for continuous improvement.^[3–7] With the development of Internet of Things (IoT) mobile terminals, flexible and lightweight PSCs have attracted much attention for a wide variety of applications such as portable electronic chargers, flexible display devices, and wearables electronic textiles.^[8–10] As an energy supply device for smart mobile terminals and biomedical devices, in addition to the high efficiency of the device, the mechanical and chemical stability in the long-term operation of the PSC device is also crucial.^[11,12]

To achieve high efficiency and stable photovoltaic devices for IoT, conductive and

Dr. M. Li, K.-L. Wang, Prof. Z.-K. Wang
 Institute of Functional Nano & Soft Materials (FUNSOM)
 Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices
 Soochow University
 Suzhou 215123, China
 E-mail: zkwang@suda.edu.cn

Dr. M. Li, W.-W. Zuo, Dr. Q. Wang, G.-X. Li, Dr. D. Di Girolamo, Prof. A. Abate
 Helmholtz-Zentrum Berlin für Materialien und Energie
 Kekuléstraße 5, Berlin 12489, Germany
 E-mail: antonio.abate@helmholtz-berlin.de

Dr. M. Li
 Laboratory of Advanced Optoelectronic Materials
 College of Chemistry
 Chemical Engineering and Materials Science
 Soochow University
 Suzhou 215123, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202003422>.

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W.-W. Zuo, Dr. A. G. Ricciardulli, Prof. M. Saliba
 Institute of Materials Science
 Technische Universität Darmstadt
 Alarich-Weiss-Straße 2, Darmstadt 64287, Germany
 E-mail: michael.saliba@opto.tu-darmstadt.de

Dr. Y.-G. Yang
 Shanghai Synchrotron Radiation Facility (SSRF)
 Shanghai Advanced Research Institute
 Shanghai Institute of Applied Physics
 Chinese Academy of Sciences
 239 Zhangheng Road, Shanghai 201204, P. R. China

Dr. Y.-H. Liu
 School of Optoelectronic Science and Engineering
 Key Lab of Advanced Optical Manufacturing Technologies
 of Jiangsu Province
 Key Lab of Modern Optical Technologies of Education Ministry of China
 Soochow University
 Suzhou 215123, China
 E-mail: yhliu@suda.edu.cn

Prof. M. Saliba
 Helmholtz Young Investigator Group
 IEK5-Photovoltaik, Forschungszentrum Jülich, Jülich 52425, Germany

transparent electrodes are of primary importance. Also, to match the latest market needs, a high degree of flexibility and excellent chemical/thermal stability is required. To date, transparent conductive metal oxide like indium tin oxide (ITO), fluorine tin oxide, and Al-doped zinc oxide (AZO) are the materials of choice for transparent conductive electrodes (TCEs).^[8,13,14] However, the brittleness of metal oxides limits the mechanical stability of its devices. Alternatively, conductive organic polymers poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS PH1000),^[15] metal nanostructures (metal nanowires, metal grids),^[16–21] and carbon materials (carbon, graphene, carbon nanotube) as TCEs in optoelectronic devices have been demonstrated.^[22–25] Nevertheless, their inherent characteristics like high sheet resistance (R_s) (carbon materials, $R_s \approx 30\text{--}1000\ \Omega\ \text{sq}^{-1}$, conductive polymers, $R_s \approx 100\text{--}450\ \Omega\ \text{sq}^{-1}$), low thermal stability (conductive polymers), and weak mechanical properties (ITO, AZO) limit the performance of photovoltaic devices.

Herein, we implemented the poly(ethylene terephthalate) (PET)/Nickel (Ni)-mesh flexible TCEs into PSCs and investigated their environmental and mechanical stability. The embedded metal Ni-mesh TCE is prepared on a flexible substrate using a novel selective electrodeposition process combined with inverted film-processing methods. First, metal Ni is filled into randomly distributed micro-grooves in the photoresist layer on the ITO glass substrate generated from laser direct writing lithography by a feasible electrodeposition process. As a result, a freestanding metal mesh is obtained on the ITO glass after removing the photoresist. Then, co-planar and the film inversion process developed ultra-flexible embedded PET/Ni-mesh electrodes.

In contrast to embedded Ag-mesh TCEs, which generally employ soft UV nanoimprinting lithography (UV-NIL) and scraping technique,^[20,26] the dense metal Ni wire dramatically improves the optoelectrical and mechanical properties of the TCE. Indeed, detachment and migration of the metal particles are drastically reduced during the bending process. Not only promotes its mechanical stability but also reduces the reaction with the perovskite film caused by the detachment and migration of metal particles. The PCE of the flexible PSCs can reach 17.3%, which is the highest efficiency reported for devices based on TCE to date.

Moreover, the FET/Ni-mesh-based PCSs retained 76% of its original efficiency even after 2000 bending cycles. Femtosecond transient absorption (fs-TA) spectroscopy has been used to study the charge transfer, and further to determine the effect of the substrate on the degree of film decomposition. Synchrotron-based transmission and grazing-incidence X-ray diffraction (GIXRD) were employed to investigate the crystal quality of the perovskite layers with different bending conditions and different depths (interfaces and inside blocks). Our cost-effective and feasible method of preparing PET/Ni-mesh electrodes provides a new approach for the selection of transparent flexible electrodes for PSCs in wearable electronics.

Different from the traditional preparation of TCEs, our Ni-mesh electrode does not use the methods of thermal evaporation, electron beam evaporation, and magnetron sputtering. Our strategy for manufacturing our freestanding Ni-mesh electrodes, according to our previous works,^[27,28] involves the following steps (Figure S1, Supporting Information): photoresist spin coating, laser direct-writing pattern, Ni metal electrodeposition, UV nanoimprinting, and PET/Ni network peeling. This method is compatible with a cost-effective and straightforward preparation process, which can be scaled to a large area. The substrate consists of periodical randomly distributed Ni meshes (average $\approx 150\ \mu\text{m}$ diagonal, $3\text{--}5\ \mu\text{m}$ wide, and $2\ \mu\text{m}$ high) embedded in UV resin on PET (Figure S2a, Supporting Information). To illustrate the characteristics of the transparent metal mesh electrode, we also prepared the Ag-mesh transparent electrode as a reference by UV-NIL and scraping technique (Figure S2b, Supporting Information). The mesh made of metallic Ni is a relatively dense line, while the Ag lines are formed by the accumulation of some small loose silver particles, which suggests that the Ni-mesh is more stable and mechanically robust. Energy dispersive spectrometry mapping (Figure S3, Supporting Information) shows that each element (C, O, Ni, or Ag) has a uniform distribution throughout the Ni-mesh or Ag-mesh region.

Notably, Ni-mesh and PH1000 are used as electrodes and transmission channels with excellent charge transport characteristics. PH1000 can effectively collect charges from a radius of about $100\ \mu\text{m}$.^[20,29] The highly conductive Ni-mesh provides the longer-range conduction. The PET/Ni-mesh/PH1000 electrode exhibits high optical transparency (85–87% in the visible range), superior to the Ag-mesh counterpart (Figure 1b). Moreover, morphological uniformity is achieved even in large-area PET/Ni-mesh:PH1000 electrodes (Figure 1c).

To evaluate the performance of our TCEs, we embedded them into flexible PSCs with p-i-n architecture. As shown in Figure 1a, the hybrid electrode is used as the anode, i.e., PET/Ni-mesh: highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS PH1000)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (AI 4083)- NiO_x (PEDOT: PSS- NiO_x)/ $\text{CH}_3\text{NH}_3\text{PbI}_3$:C-PCBOD/phenyl- C_{61} -butyric acid methyl ester (PCBM)/BCP/Ag. To evaluate the photovoltaic performance of PSCs based on the Ni-mesh, the devices on PET/Ni-mesh substrate made by PET/Ni-mesh:PH1000/PEDOT:PSS- NiO_x ($\approx 40\ \text{nm}$)/ $\text{CH}_3\text{NH}_3\text{PbI}_3$:C-PCBOD ($\approx 350\ \text{nm}$)/PCBM ($\approx 55\ \text{nm}$)/BCP ($\approx 8\ \text{nm}$)/Ag (100 nm) were fabricated. For the hole transport layer (HTL) of the PSCs, we added the low-temperature-treated NiO_x nanoparticles solution in the PEDOT:PSS solution, which not only ensured the flatness of the HTL but also improved the open-circuit voltage (V_{OC}) of the flexible device (Figure S4 and Table S1, Supporting Information). Figure 2a shows the current density–voltage (J – V) of forward and reverse scan characteristics with negligible hysteresis under AM 1.5G illumination. The performance parameters PCE, V_{OC} , short-circuit current density (J_{SC}), and fill factor (FF) are reported in Table S2 in the Supporting Information.

The champion flexible device based on PET/Ni-mesh substrate gave the best PCE of 17.3%, with J_{SC} of $21.78\ \text{mA cm}^{-2}$, V_{OC} of 1.02 V, and FF of 0.78. In Figure S5 in the Supporting Information, we show the J – V curves of the Glass/ITO-based

Dr. D. Di Girolamo, Prof. A. Abate
Department of Chemical
Materials and Production Engineering
University of Naples Federico II
Piazzale Tecchio 80, Fuorigrotta, Naples 80125, Italy

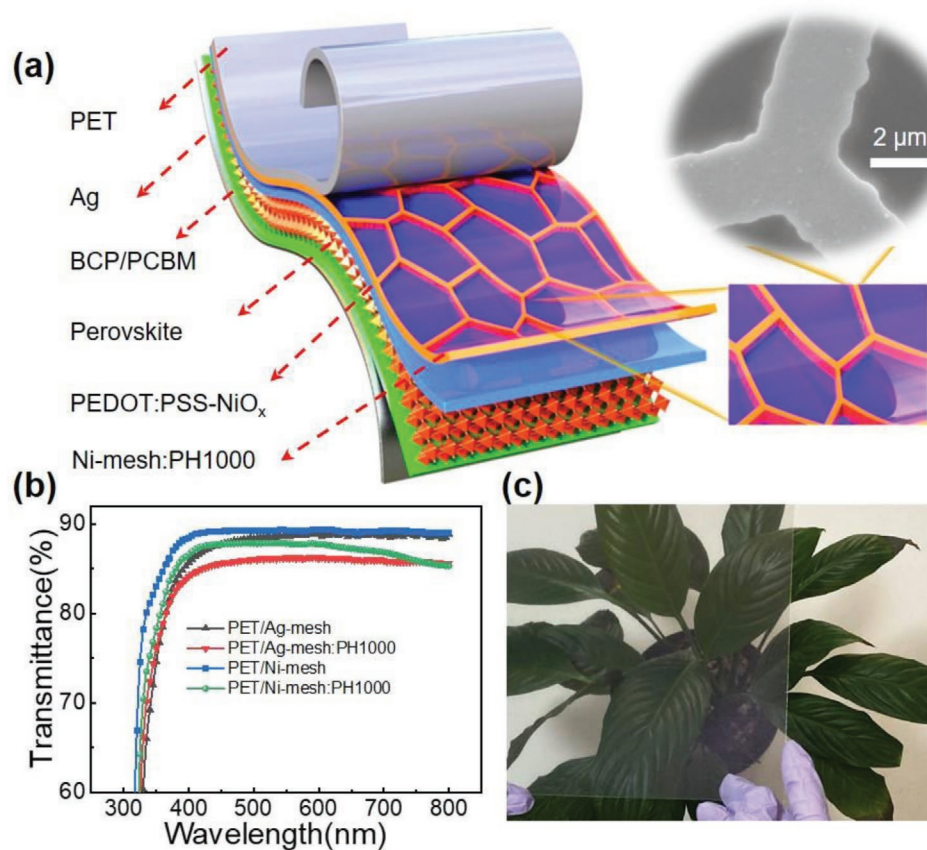


Figure 1. Characteristics of the PET/Ni-mesh substrate and hybrid electrode. a) Schematic illustration of the PET/Ni-mesh substrate, Ni-mesh:PH1000 hybrid electrode, and perovskite device; the top right image shows the high-magnification SEM images of Ni-mesh. b) Transmittance spectra of PET/Ag-mesh, PET/Ag-mesh:PH1000-based, PET/Ni-mesh, and PET/Ni-mesh:PH1000-based substrates. c) Optical image of the large-area PET/Ni-mesh substrate.

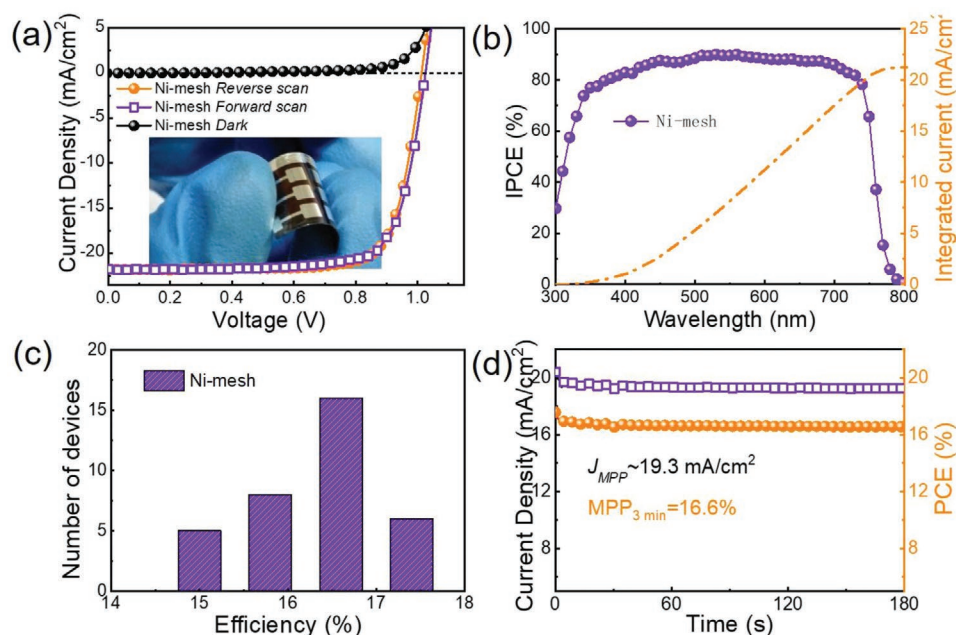


Figure 2. Photovoltaic performance of PSCs on the PET/Ni-mesh substrate. a) J - V curves of the champion device measured under AM 1.5 irradiation with the intensity of 100 mW cm^{-2} . b) IPCE spectra, c) efficiency histogram of PCEs, and d) steady-state photocurrent and PCE at the maximum power point of 0.85 V of the PET/Ni-mesh-based PSCs.

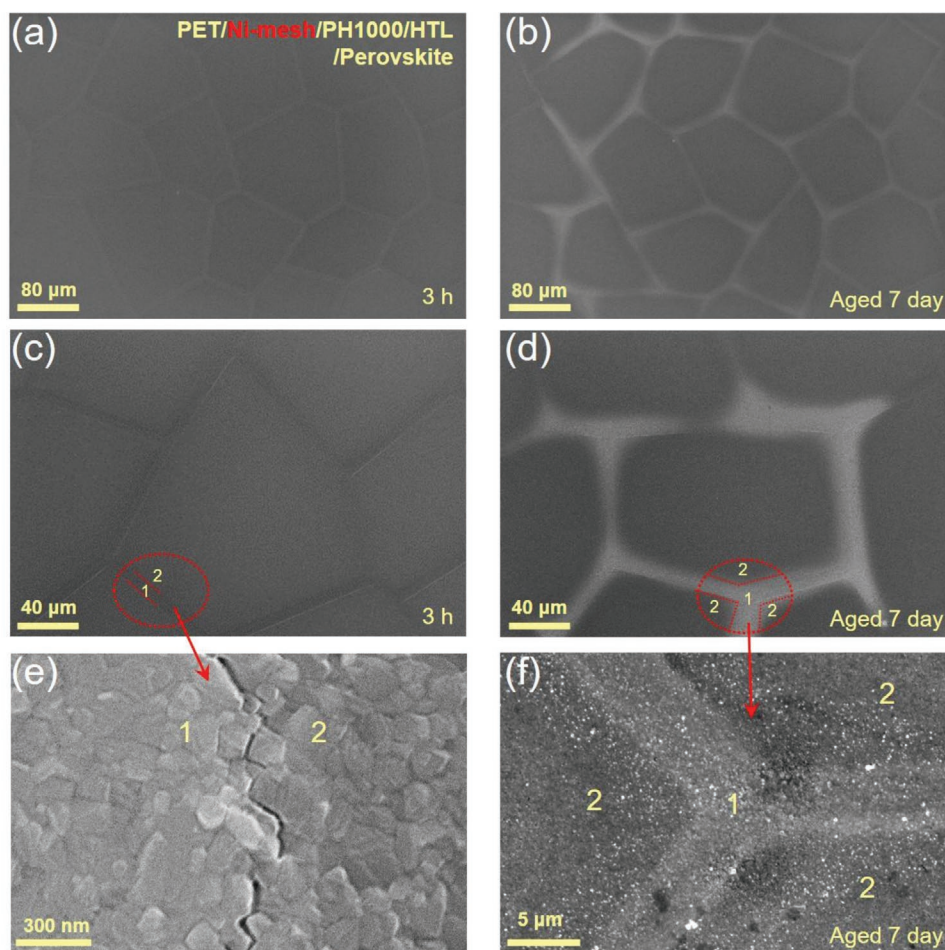


Figure 3. Environmental stability of the perovskite films. a–f) Top-view SEM images of the perovskite films coated on PET/Ni-mesh:PH1000/PEDOT:PSS-NiO_x (HTL) and stored in the air under room temperature and with a relative humidity of 25% with 3 h (a,c,e) and aged 7 days (b,d,f).

and PET/Ag-mesh-based PSCs under the same device fabrication process. The PET/Ni-mesh outperformed the PET/Ag-mesh-based devices, which delivered the best efficiency of 17.3%. Compared with the rigid (Glass/ITO based) devices, the lower PCE of flexible devices is mainly attributed to the lower J_{sc} . The incident photon-to-current efficiency (IPCE) spectra of the PET/Ni-mesh-based device show an excellent IPCE over the whole spectral range (Figure 2b).

Moreover, our PSCs exhibit excellent reproducibility based on the statistical evaluation of the PCE values (Figure 2c). Figure 2d displays the steady-state photocurrent and efficiency measured at the maximum power point of 0.85 V for 3 min. The PCE of the PET/Ni-mesh-based device stabilizes at 16.6%, which is close to the value obtained from the $J-V$ measurement, confirming the negligible hysteresis of the devices.

Further, we have studied the environmental stability of perovskite-based on the PET/Ni-mesh. A scanning electron microscope (SEM) analysis highlights that the morphology evolution of the perovskite films grown on the PET/Ni-mesh substrate as the storage time in ambient air increases, as shown in **Figure 3**. First, we show the topography on the Ni wire, which suggests that the area of the perovskite above the Ni wire is more conductive and quickly collect charges. By further comparing

the characteristics of the perovskite crystals in the area above the Ni wire (Region 1 of Figure 3c,e) and the surrounding area (Region 2 of Figure 3c,e), it is found that the morphology of the perovskite crystals upon the Ni wire and the surroundings is not different. However, due to the stress of the substrate, a crack was formed between the two regions, as shown in Figure 3e.

When the perovskite film is left in the air for 7 days, the morphology of the perovskite degrades starting from Ni wires and expanding toward the center of the mesh (Figure 3f), suggesting that the substrate plays a role in the environmental stability of the perovskite film. We further compared the decay of the perovskite films based on the PET/Ag-mesh and the PET/Ni-mesh in the air under room temperature and with a relative humidity of 25% (Figure S6, Supporting Information). Perovskite films with different substrates were left in the air for 3 h, 3 days, and 7 days. For new films, the morphology of perovskite layers with different substrates does not show any apparent change. The XRD of the corresponding films also shows similar crystallinity (Figure S7, Supporting Information). With the increase of time, the perovskite above the Ag wire showed noticeable decomposition when it was left for 3 days and continued to expand to the surroundings. However, the perovskite on the PET/Ni-mesh is relatively more stable. As the placement time

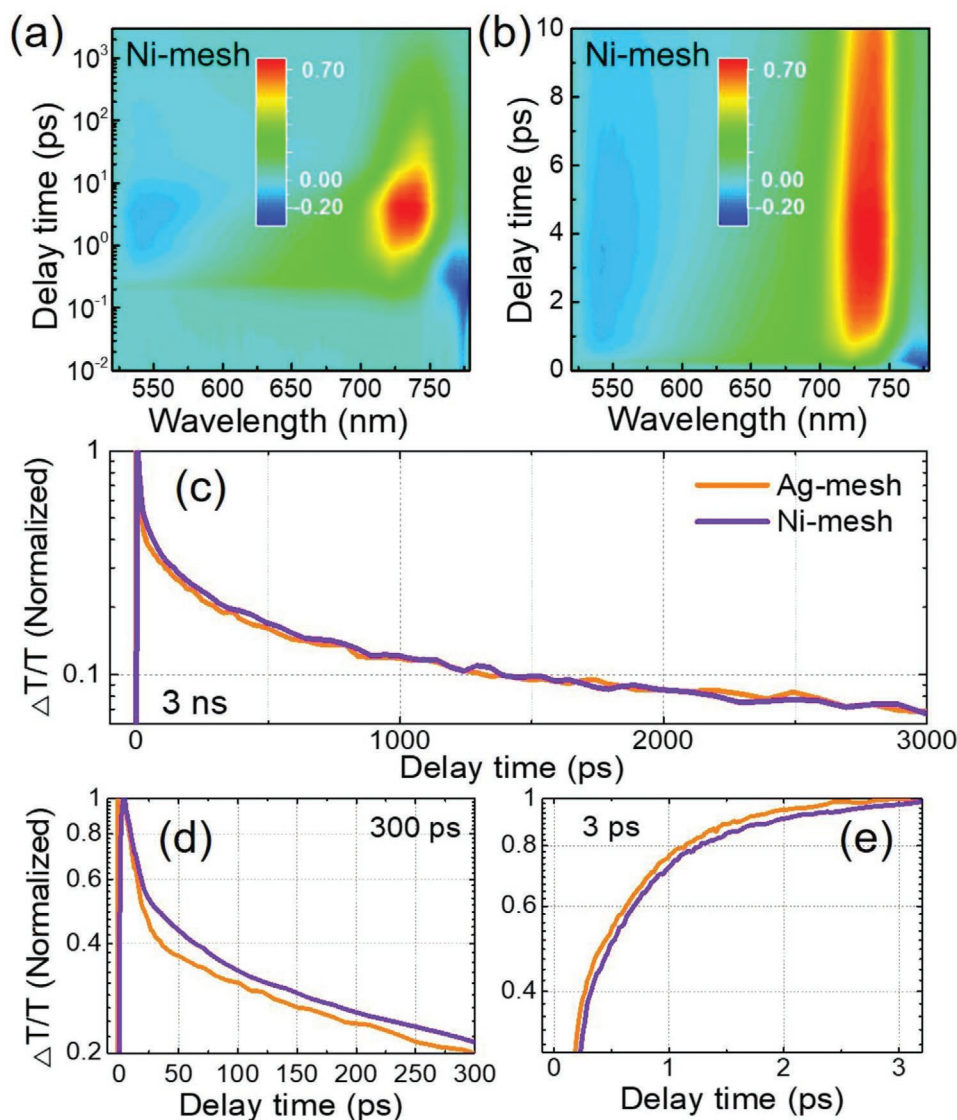


Figure 4. fs-TA spectroscopies of the perovskite films. a,b) Pseudocolor images of the fs-TA spectra for PET/Ni-mesh:PH1000/PEDOT:PSS-NiO_x/perovskite films up to 3 ns (a) and up to 10 ps (b). The vertical and horizontal axes represent the pump–probe delay and probe wavelength, respectively. The inset image is a color scale indicating the amplitude of the signal. c–e) The fs-TA dynamics of neat perovskite based on PET/Ni-mesh:PH1000/PEDOT:PSS-NiO_x and PET/Ag-mesh:PH1000/PEDOT:PSS-NiO_x. Normalized dynamics extracted at the bleaching peak (732 nm) after photoexcitation at 560 nm show kinetics in different time scales (3 ns, 300 ps, and 3 ps).

increased, only the topography appeared bright on the Ni wire, and the perovskite film remains in its original state. It can be explained that Ag particles in PET/Ag mesh electrode can easily fall off and migrate to combine with iodine in perovskite film to form AgI, thereby this accelerating the decomposition of the perovskite film. Simultaneously, as a dense nickel oxide film is easily formed on the surface of the Ni-mesh, to a certain extent, the nickel oxide hinders further decomposition of the Ni-mesh, and the self-oxidation of the surface of the Ni-mesh effectively improves the stability of the device. At the same times, we recorded the device efficiency as a function of time in the air under room temperature and with a relative humidity of 25%, as illustrated in Figure S8 in the Supporting Information. The degradation of device efficiency is consistent with the changes

in film morphology. With the increase of time, the efficiency of the Ni-mesh-based PSC still maintains the initial 86% after 192 h storage, while the Ag-mesh-based PSC has decayed to the initial 59%. This trend suggests that the Ni-mesh-based PSC device has better air stability than Ag-mesh-based PSC device.

The nature of the substrate influences the crystal properties of perovskite. Hence, to investigate the carrier and charge extraction dynamics in the perovskite films based on different substrates, femtosecond transient absorption (fs-TA) spectroscopy was employed.^[30–34] The fs-TA 2D maps obtained by using different delay for PET/Ni-mesh:PH1000/PEDOT:PSS-NiO_x/perovskite and PET/Ag-mesh:PH1000/PEDOT:PSS-NiO_x/perovskite systems are shown in Figure 4a,b and Figure S9a,b in the Supporting Information, respectively. The fs laser excitation produces a ground

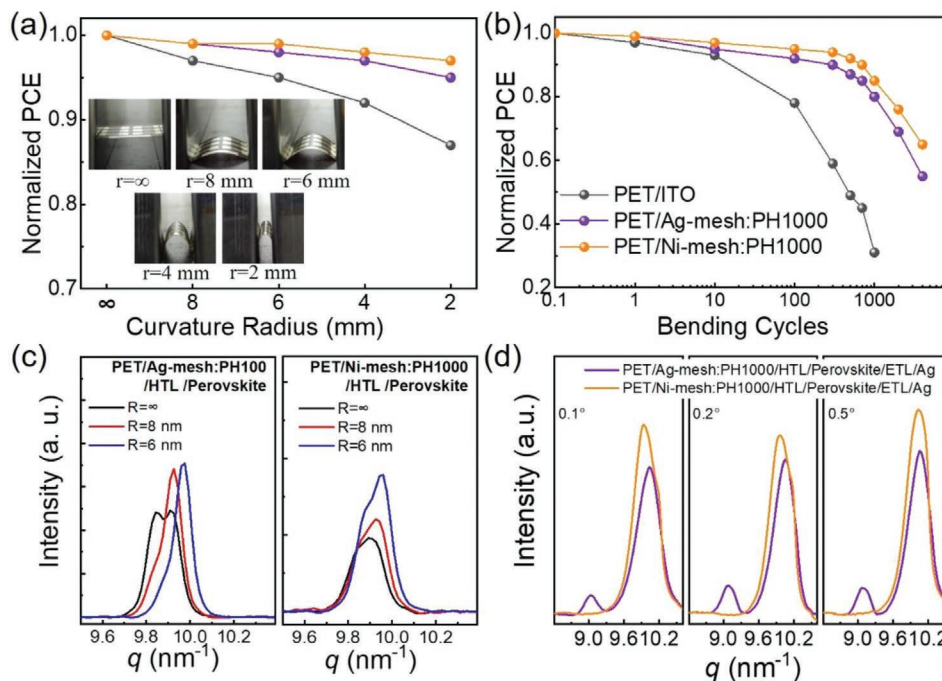


Figure 5. Mechanical durability of flexible PSCs. a) PCEs measured after bending PET/Ni-mesh:PH1000-based flexible PSCs within a specified radius of ∞ , 8, 6, 4, and 2 mm. The inset shows the photos of the corresponding bending radius, respectively. b) PCEs of flexible PSCs based on different electrodes as a function of bending cycles at a radius of 4 mm. c) The intensity of the diffraction peaks of perovskite films based on different electrodes under different bending radii with transmission mode on synchrotron-based XRD. d) The intensity of the diffraction peaks of perovskite films based on different PSCs by grazing-incidence mode of synchrotron radiation with different angles of incidence (0.1°, 0.2°, 0.5°).

state bleaching band at 625–775 nm for both the samples, which is related to the fluorescent emission from perovskite. The comparative analysis of the 2D maps does not show any apparent difference, indicating a similar behavior for both PET/Ni-mesh and PET/Ag-mesh-based films. Our findings are confirmed by the normalized TA dynamics (Figure 4c), which exhibit similar amplitudes for the two TCE substrates, suggesting the same charge transport character. The long decay component corresponds to the exciton recovery to the ground state. In contrast, the analysis of the fast decay kinetics (Figure 4d) within 300 ps exhibits a slower decay of the signal for PET/Ni-mesh:PH1000/PEDOT: PSS-NiO_x/perovskite than PET/Ag-mesh:PH1000/PEDOT:PSS-NiO_x/perovskites. It is observed that the fast decay component with a small amplitude at the beginning, related to extra cooling of the electrons to the PEDOT:PSS-NiO_x valance band edge, is different between the two TCEs. The decay kinetics further evidences this behavior within 300 ps (Figure 4d). The decay kinetics can be understood as an interplay process which is a combination of the electron-hole recombination and the charge extraction into the electron acceptor.^[35] In the process of hot-carrier cooling, Ag has a faster response to exchange electrons with PEDOT:PSS-NiO_x. Hence, Ag-mesh-based TCE undergoes to a quicker degradation than Ni-mesh TCE upon perovskite coating. Moreover, Ag tends to spread into the perovskite layer what makes hot-carrier annihilation when they arrive in the interface. Further, the kinetics in the first 3 ps (Figure 4e) reveal a higher density of hot carrier at early times for the PET/Ag-mesh-based device than PET/Ni-mesh systems.

The mechanical stability of the device is a critical factor for flexible PSCs. To further study the mechanical stability of flexible PSCs based on PET/Ni-mesh, we compared device performance based on flexible PET/ITO, PET/Ag-mesh, and PET/Ni-mesh. **Figure 5a** shows the characteristics of the device under different bending curvatures. Flexible PSCs based on various substrates are bent with five different radii of curvature ($r = \infty$, 8, 6, 4, and 2 mm). As the degree of bending increases, the performance of devices based on different substrates decreases. Among them, the performance degradation of PET/ITO-based flexible devices is the largest, while PET/Ni-mesh-based devices are relatively the most stable. Even with a bending radius of 2 mm, the efficiency of the PCE is minimally reduced, conserving 97% of the original PCE value. Devices based on PET/Ag-mesh and PET/ITO substrates retain only 95% and 87% of their initial PCE values. This result indicates that PET/Ni-mesh electrode and perovskite film have high flexibility. We further evaluated the effects of mechanical bending on different flexible electrodes through a multicycle bending test. The PCE of PSCs on different flexible electrodes was compared. A total of 5000 continuous bending cycles were performed with a radius of 4 mm. As shown in Figure 5b, the flexible PSCs based on PET/Ni-mesh electrode exhibit very promising mechanical bending stability. Even after 500 cycles of bending, the value of PCE remained above 92% of the original value. The PET/ITO-based devices retained only 78% of the original PCE when it is bent 100 times. We further increased to 2000 cycles, and the PET/Ni-mesh based device still retained 76% of its initial PCE.

This result suggests great competitiveness of the PET/Ni-mesh-based devices in the field of flexible photovoltaics.

In addition to the variation in PCE, we further studied the changes in the crystalline structure of the perovskite films on different flexible substrates under different curvatures, employing synchrotron-based transmission and GIXRD. As shown in Figure 5c, under different bending radii of PET/Ag-mesh-based perovskite crystals, the peak width and peak position of (110) has changed significantly. In contrast, PET/Ni-mesh-based perovskite crystals are relatively stable. This finding suggests that perovskite on PET/Ni-mesh has more stable mechanical properties under bending, and it also affects the change of perovskite crystal to a small extent. The 2D GIXRD profiles of the MAPbI₃:C-PCBOD PSCs based on PET/Ni-mesh and PET/Ag-mesh substrate after exposing to air (relative humidity 25%) for 3 days (Figure S10, Supporting Information). The PSCs structure are PET/Ni-mesh:PH1000/PEDOT:PSS-NiO_x/perovskite/PCBM/BCP/Ag (10 nm) and PET/Ag-mesh:PH1000/PEDOT:PSS-NiO_x/perovskite/PCBM/BCP/Ag (10 nm). We used different angles of incidence (0.1°, 0.2°, 0.5°) to probe the crystal structure of perovskite at different depths. As shown in Figure 5d, the plots of the azimuthally (90°) integrated intensities of PbI₂ (001) and perovskite (110) planes in both samples reflected this feature more clearly. The perovskite in the PET/Ni-mesh-based device is very stable.

In contrast, the perovskite film in the PET/Ag-mesh-based device has the precipitation of lead iodide (PbI₂), and PbI₂ has been precipitated in perovskites of different depths, suggesting that the Ag-mesh prepared by the UV-NIL and scraping technique has a severe impact on the stability of perovskite. Loose silver particles can easily affect the stability of the entire perovskite crystal, not just at the interface. Our novel method of preparing PET/Ni-mesh is an ideal choice for flexible perovskite devices in both mechanical and chemical stability.

The mechanical stability of transparent electrodes is critical for flexible optoelectronic devices. In this work, we showed the first application of a PET/Ni-mesh flexible TCE to PSCs and investigated their environmental and mechanical stability. The effect of PET/Ni-mesh on the growth of perovskite crystals was studied. Through synchrotron-based transmission and GIXRD, we explored in detail the characteristics of perovskite thin-film crystals grown on different metal grids. The synchrotron-based XRD pattern of perovskite growth on the PET/Ni-mesh showed better stability toward the substrate bending and exposure to moisture. This behavior is in line with the stability of the flexible PSCs. PET/Ni-mesh-based devices remain 76% of the original efficiency after 2000 fully bending cycles. This result, combined with the excellent PCE of 17.3%, confirms the optimal quality of the PET/Ni-mesh as a substrate for flexible photovoltaics. Our strategy provides novel ideas for the preparation of efficient and stable flex-resistant flexible optoelectronic devices.

Experimental Section

Fabrication of the Embedded Metallic Mesh: The fabrication process for the embedded Ni metallic mesh is described as follows. First, a photoresist was spin coated (RZJ-390PG, Ruihong Electronic Chemical Co., Ltd.) on a pre-cleaned ITO substrate conductive substrate, and TCE micro trench clusters were designed by laser-writing techniques. Then,

the metal in the microgrooves was selectively electrodeposited to form a uniform Ni metallic mesh structure. After the photoresist was removed, a dispersed UV-curable resin (D10, Philchem) was drop-casted onto the substrate. Then a flexible PET (thickness of 175 μm, transmittance of 92%, the maximum working temperature was 150 °C) was fixed onto the UV resin through a roll-to-roll process. Then, the UV resin was cured by being exposed to UV light (1000 mW cm⁻², light-emitting diode tube). After the curing step, the PET structure was peeled from the Ni substrate to obtain a flexible and transparent embedded Ni-mesh.

The fabrication process for the embedded Ag metallic mesh is described as follows. First, the photoresist (RZJ-390PG, Ruihong Electronic Chemical Co., Ltd.) layer on the pre-cleaned glass substrate was patterned into randomly distributed grooves structure by laser direct-writing techniques. Then the patterned microgroove structure on the glass was replicated to a soft polyurethane acrylate (PUA) mold, and the microgroove structure was transferred to PET substrate through soft nanoimprinting techniques using the PUA as a template. Finally, the Ag nanoparticles ink (concentration of 70%, a viscosity of 25 cps, and particle diameter in the range of 200–300 nm) (Figure S11, Supporting Information) was filled into the microgrooves through the scraping technique. After 20 min sintering at 80 °C, the embedded Ag-mesh could be formed in the UV resin.

Materials Preparation: Synthesis of nonstoichiometric NiO_x nanoparticles: 1 mol nickel nitrate hexahydrate (Aladdin) was dispersed in 200 mL of deionized water to obtain a dark green solution. And then NaOH solution (10 mol L⁻¹) was added to adjust the pH of the solution to 10. After stirring for 5 min, the precipitate was thoroughly washed twice with deionized water and dried at 80 °C for 6 h. The resulting green powder was then calcined at 270 °C for 2 h. After that, dark black powder was obtained. Finally, the obtained nanoparticles were dispersed in the deionized water to 7 mg mL⁻¹.^[36,37]

Photo crosslinked [6,6]-phenylC₆₁-butyric oxetane dendron ester (PCBOD) was synthesized according to previous reports.^[10,38] Methylamine iodide (MAI, 98%) was purchased from Dyanamo. Lead iodide (PbI₂, 99.999%), dimethyl sulfoxide (DMSO, 99.9%), γ-butyrolactone (GBL, 99%), chlorobenzene (CB, 99.9%), PCBM (99%), and bathocuproine (BCP, 99.9%) were purchased from Sigma-Aldrich. High-conductivity polymer Clevis PH1000 and Clevis VP Al 4083 PEDOT:PSS water dispersion was acquired from Heraeus (Germany).

The perovskite precursor solution was prepared by mixing 1 mmol PbI₂, 1 mmol MAI, PCBOD (15 mg), and diphenyliodonium hexafluoroarsenate (6 wt% to PCBOD) in 1 mL GBL and DMSO (7:3, v/v) with stirring overnight at 60 °C. PCBM was dissolved in chlorobenzene at a concentration of 20 mg mL⁻¹. BCP was dissolved in ethanol at a concentration of 0.5 mg mL⁻¹.

Device Fabrication: Flexible ITO and embedded metallic Ni or Ag mesh substrates were cut into a 15 mm × 13 mm, and then the antistatic protective film was peeled off to directly fabricate a PSC on it. Then, the high conductivity polymer PH1000 was spin-coated on the surface of embedded metallic Ni or Ag mesh substrates under 600 rpm, and then annealed at 100 °C for 15 min in ambient air. An ≈40 nm PEDOT:PSS Al 4083 doping with different volumes of NiO_x solution was then spin-coated at 3000 rpm and annealed at 100 °C for 20 min in ambient air. Subsequently, the perovskite solution was then spin-coated onto the HTL layer by a consecutive two-step spin-coating process at 1000 and 4000 rpm for 20 and 40 s, respectively. During the second spin-coating step, the substrate was treated with a chlorobenzene drop-casting. Subsequently, the as-cast film was treated by UV irradiation in the glovebox for crosslinking. Then the perovskite substrate was heated at 100 °C for 5 min in nitrogen glovebox. After annealing, the PCBM solution was coated onto the perovskite layer at 3000 rpm for 40 s, and the BCP solution was coated onto PCBM layer at 3000 rpm for 30 s. Finally, the device was transferred to a vacuum chamber under 2 × 10⁻⁶ Torr for Ag (100 nm) electrode evaporation. The active area of each device was 7.25 mm² for the flexible devices defined through a shadow mask.

SEM Images: The field-emission SEM images were obtained from a Quanta 200 FEG (FESEM, FEI Co.).

XRD and GIXRD Measurement: XRD measurement was conducted using PANalytical (Empyrean) equipment. The GIXRD measurements were performed at the BL14B1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF) using X-ray with a wavelength of 0.6887 Å. 2D GIXRD patterns were acquired by a MarCCD mounted vertically at a distance ≈ 278 mm from the sample with a grazing-incidence angle of 0.1°, 0.2°, and 0.5°, and an exposure time of 30 s. The in situ bending XRD experimental was measured by the transmission mode, and the flexible PSCs were pasted on the lateral side of the sample holder and placed at the vertical of X-ray incidence direction.

Solar Cell Characterization: J - V characteristics of PSCs under 1 sun illumination were performed using a programmable Keithley 2400 source meter under AM 1.5G solar irradiation at 100 mW cm⁻² (Newport, Class AAA solar simulator, 94023A-U). J - V curves were measured at a scan rate of 0.1 V s⁻¹, and the time interval was 50 ms. IPCE measurement was performed using a system combining a xenon lamp, a monochromator, a chopper, and a lock-in amplifier with a calibrated silicon photodetector.

Transmission Spectroscopy Measurements: The absorbance was measured with a UV-vis spectrophotometer (PerkinElmer Lambda 750).

fs-TA Spectroscopy Measurement: All fs-TA spectroscopy measurements were carried out in the commercial ultrafast spectroscopy (Helios Fire, Ultrafast Systems, Inc.), an automatic femtosecond transient absorption spectrometer. The femtosecond laser amplifier (Astrella, Coherent, Inc.) delivered 800 nm laser pulse with a pulse duration of ≈ 35 fs. Part energy of the laser pulse was guided into the optical parametric amplifier (TOPAS, Coherent, Inc.), finally delivering the pump pulse with a wavelength of 500 nm. The other part of the femtosecond laser entered the Helios spectrometer, which implemented the scanning of the pump-probe delay time, the supercontinuum white generation, and the collection of the spectral signal.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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