

**p-n hybrid bulk heterojunction enables enhanced
photothermoelectric performance with UV-Vis-NIR light**

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Experimental work

1.1 Preparation of ZnO-NWs

The ZnO micro/nanowires used in this work were synthesized via a sample vapor trapping CVD method as previously reported.^{1,2} ZnO powder and graphite powder, as raw materials, were dispersed in ethanol at the weight ratio of 1:1. The mixture was then ground carefully and dried in an oven at 70 °C for 10 h. The resulting source materials was transferred into a ceramic crucible covered with a ceramic lid and then placed in a box furnace, heated at 1000 °C for 120 min. Finally, white-colored products can be collected at the inner surface of the crucible.

1.2 Preparation of PEDOT:PSS/ZnO-NWs hybrid films

To prepare PEDOT:PSS/ZnO-NWs hybrid thin films, ZnO-NWs powders are firstly dispersed into EtOH to obtain the ZnO-NWs/EtOH dispersion (2.7 mg/mL). Simultaneously, 3 mL PEDOT:PSS aqueous solution is dispersed into 22 mL EtOH to obtain PEDOT:PSS/EtOH dispersion (1.6 mg/mL). Then, fully mixing ZnO-NWs/EtOH dispersion with PEDOT:PSS/EtOH dispersion to obtain a uniform dispersion. Finally, the PEDOT:PSS/ZnO-NWs hybrid thin films were prepared via vacuum filtrating dispersion with polyvinylidene fluoride filter membrane (pore size: 0.45 μm) as substrate and then dried at 60 °C for 6 h. Then, the PEDOT:PSS/ZnO-NWs hybrid thin films with different content of ZnO-NWs are prepared via varying the volume ratio of ZnO-NWs/EtOH dispersion and PEDOT:PSS/EtOH dispersion, and the mass for each hybrid thin film is the same as 13.5 mg.

1.3 Instruments and characterizations

The X-ray diffraction (XRD) patterns, morphology, and UV-vis-NIR spectrum absorption of the as-prepared samples are recorded by a DX-2700 B X-ray diffractometer, Quanta 400 FEG scanning electron microscope (SEM, FEI Company, America), and UV-Vis-NIR spectroscopy (Analytikjena Specord 200), respectively. The surface images of the as-prepared films were investigated by atomic force microscopy (AFM, Veeco Multimode, and Plainview, NY) operated in tapping mode. The reflection spectra was measured by a UV-Vis spectrophotometer (Japan SHIMADZU, UV 270).

The electrical conductivity (σ) of the samples is detected using four-point-probe method with Keithley 2700 system, which calculated from $\sigma = L/R \times A$, where the L , R , A are the length, resistance and cross-sectional area of the samples, respectively. The Seebeck coefficient (S) is calculated from $S = -\Delta V/\Delta T$ ($\Delta T = 5 \pm 0.5$ K), where ΔV and ΔT are the TE voltage and temperature difference between the two sides of the samples. Here, ΔT is seted up by heating plate, ΔV and ΔT are monitored with Keithley 2700 system and Pt100 thermocouples, respectively. The carrier concentration and mobility carriers were measured using a high and low temperature Hall effect test system with the equipment model CH-100HL, applying AC magnetic field~500 mT.

In the test of PTE properties, the induced voltage is detected with Keithley 2700 system, the temperature is monitored with Pt100 thermocouples. Herein, to realize an asymmetric light illumination, a shadow mask with different size of aperture (square) is set aside to the sample, and the square part of the sample is illuminated through the aperture. Notably, there is a gap of 0.5 cm between the sample and shadow mask, and

the sample is 50 cm far away the the light source. The induced voltage is detected by attaching Ag electrodes to the sample, and temperature is tested by attaching two Pt100 thermocouples onto the two sides of the sample. A PLS-SXE300+ (PerfectLight Technology Co., Ltd. China) Xenon lamp is used as light source (wavelength: 320-2500 nm). The lasers were purchased from Changchun lei Laser Technology Co. Ltd. Several types of continuous-wave lasers served as the excitation light sources with different wavelengths, including UV (405 nm), visible (532 and 635 nm) and near-infrared (808 and 1064 nm). The incident power at each wavelength was monitored by a calibrated power meter operating in the corresponding waveband.

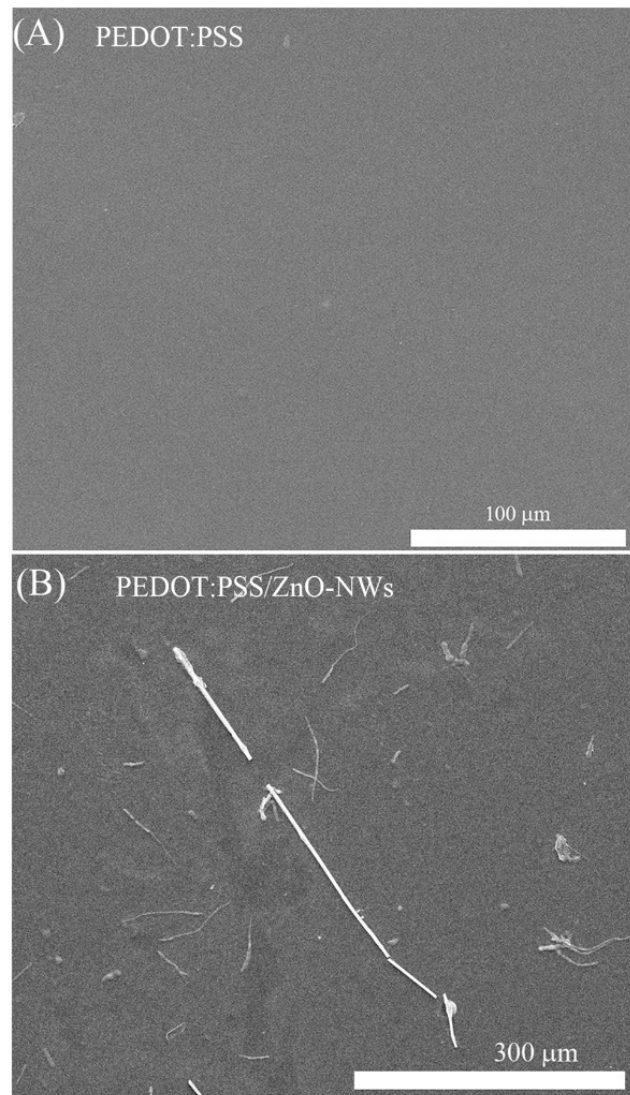


Fig. S1 The SEM images of PEDOT:PSS film (A) and PEDOT:PSS/ZnO-NWs hybrid film with 40 *wt%* content of ZnO-NWs (B).

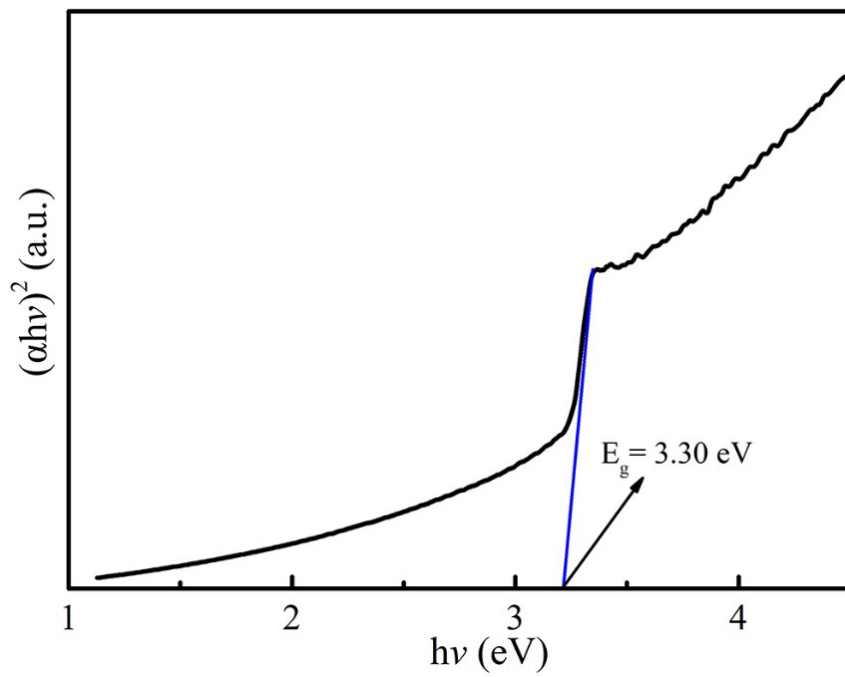


Fig. S2 ZnO-NWs direct band gap is represented by Tauc's plot.

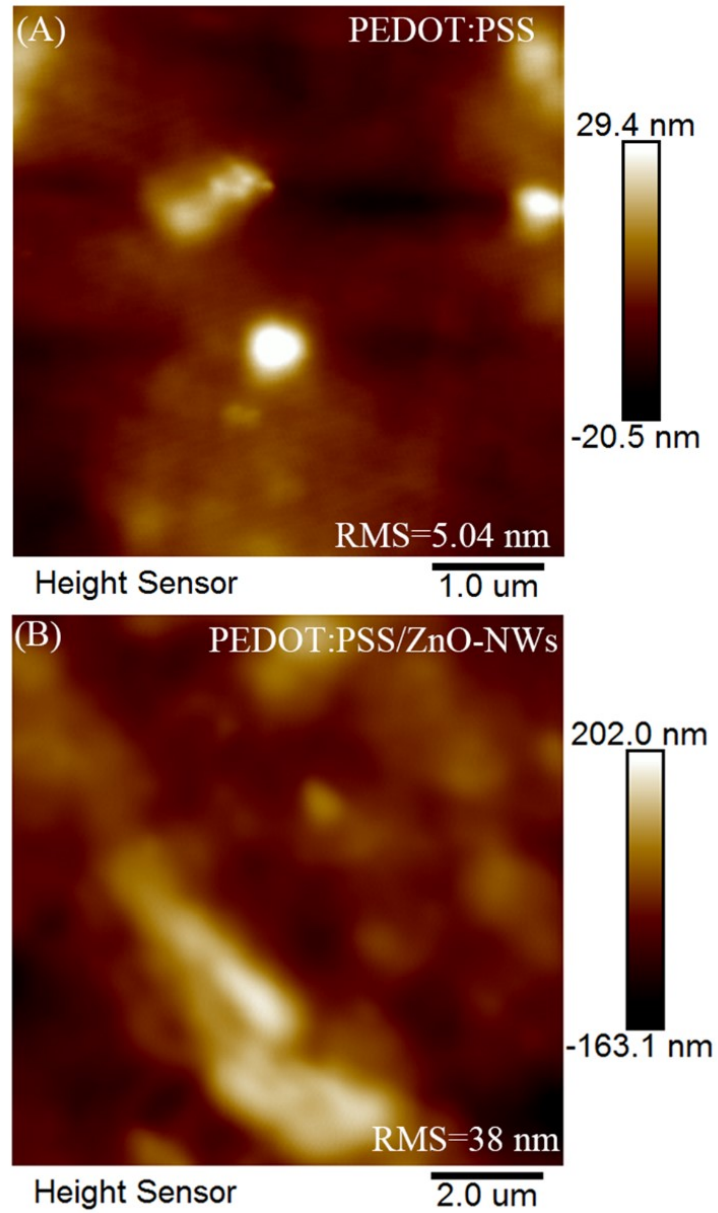


Fig. S3 AFM Height images of PEDOT:PSS film (A) and PEDOT:PSS/ZnO-NWs hybrid film with 40 *wt%* content of ZnO-NWs (B).

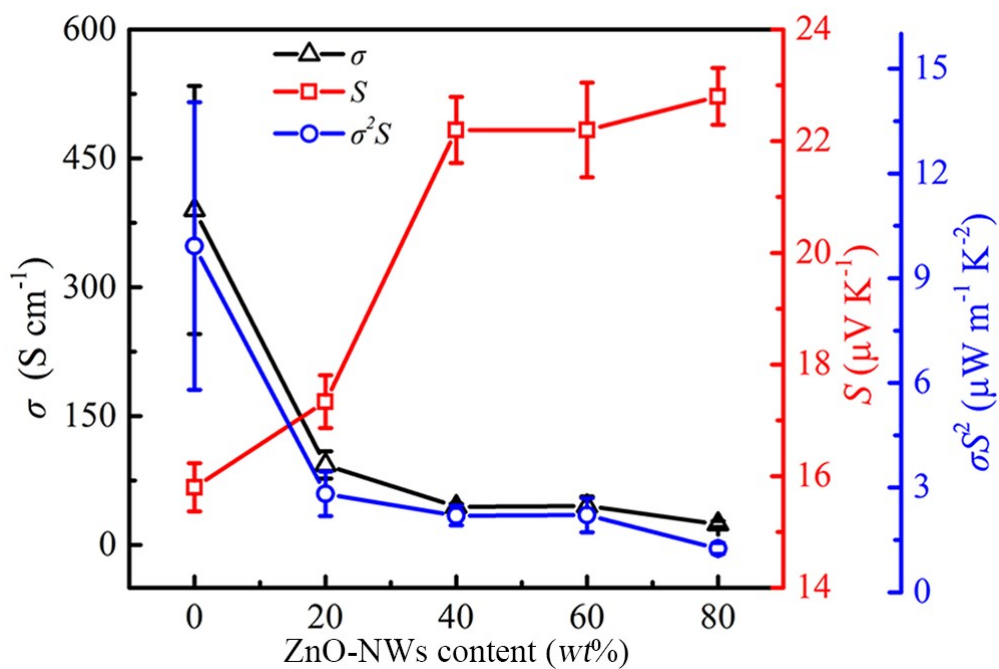


Fig. S4 The electrical conductivity, Seebeck coefficient, and power factor as a function of ZnO-NWs content for the as-fabricated PEDOT:PSS/ZnO-NWs hybrid films.

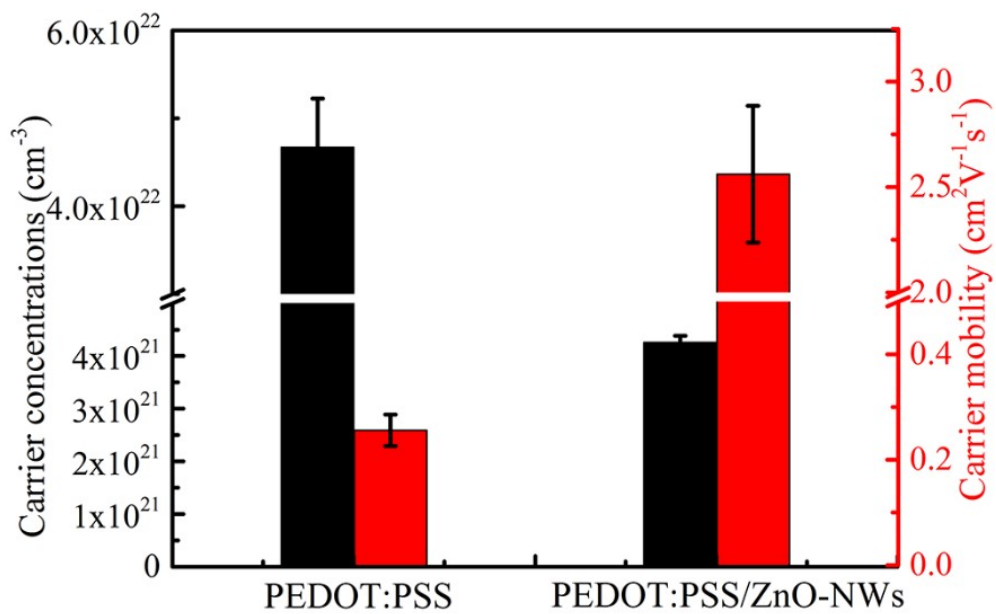


Fig. S5 The carrier concentrations and carrier mobilities of the PEDOT:PSS film and PEDOT:PSS/ZnO-NWs hybrid film with 40 wt% content of ZnO-NWs.

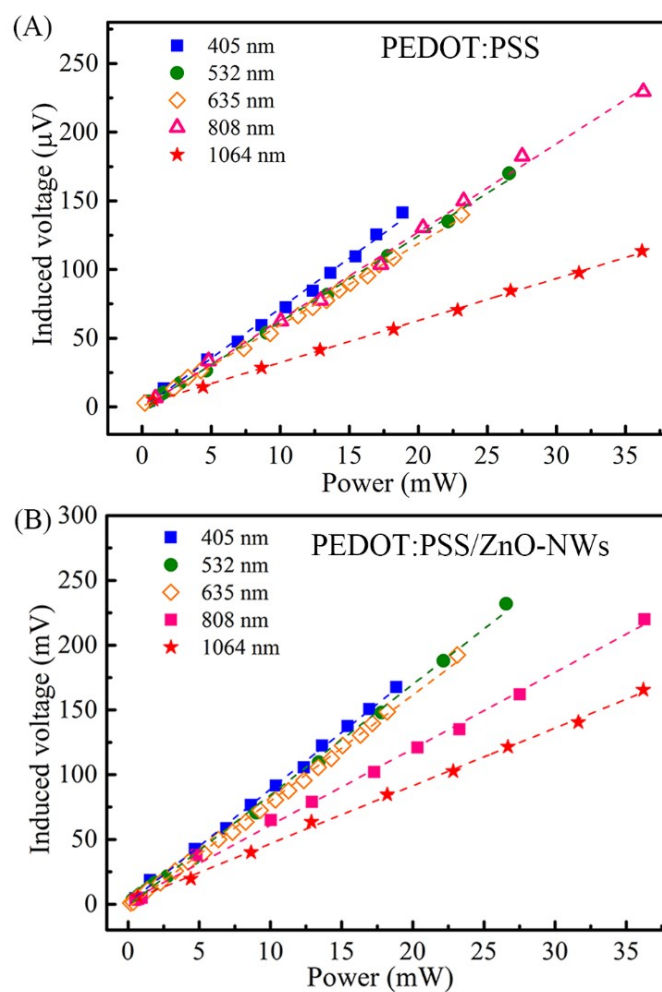


Fig. S6 The relationship between induced voltage of films and laser power: (A) is the PEDOT:PSS film; (B) is the PEDOT:PSS/ZnO-NWs hybrid film.

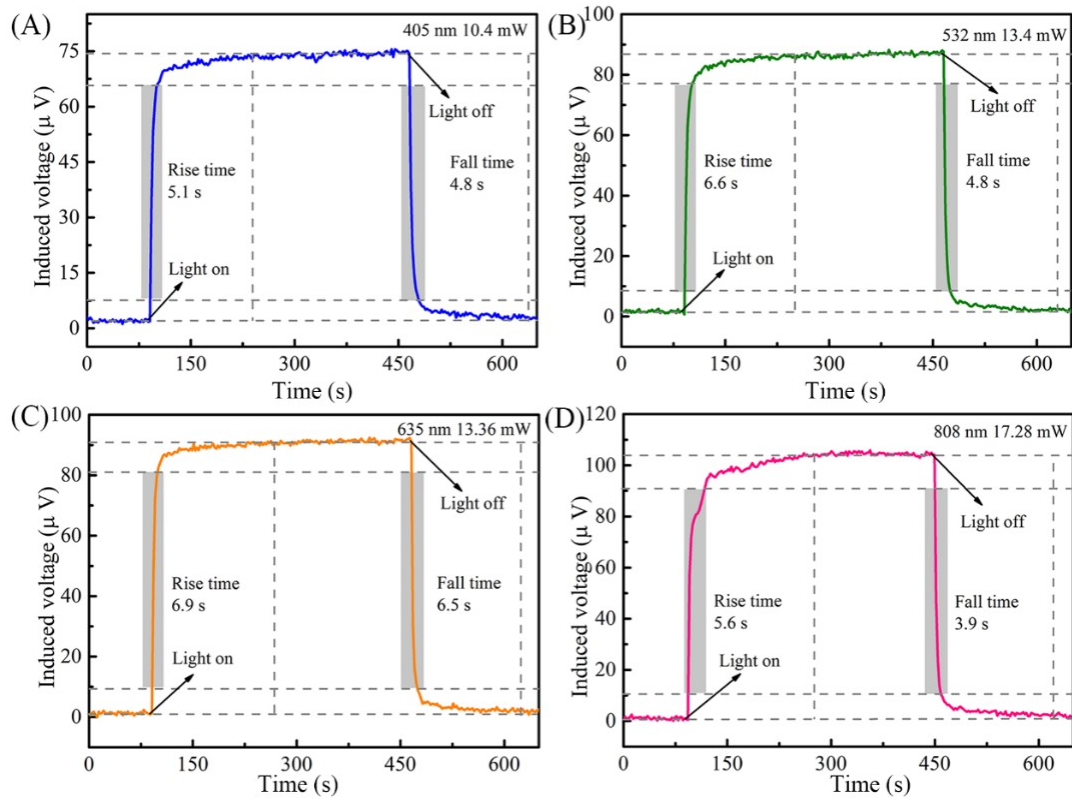


Fig. S7 The induced voltage response velocities of the PEDOT:PSS/ZnO-NWs hybrid film under illumination at (A) 405 nm, (B) 532 nm, (C) 635 nm and (D) 808 nm.

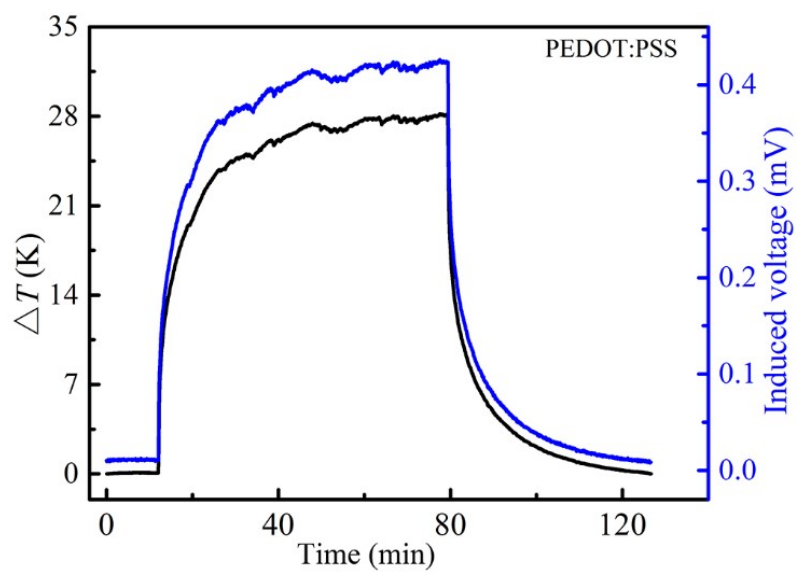


Fig. S8 The ΔT and induced voltage of the PEDOT:PSS film under light on and off.

Here is the xenon lamp lighting.

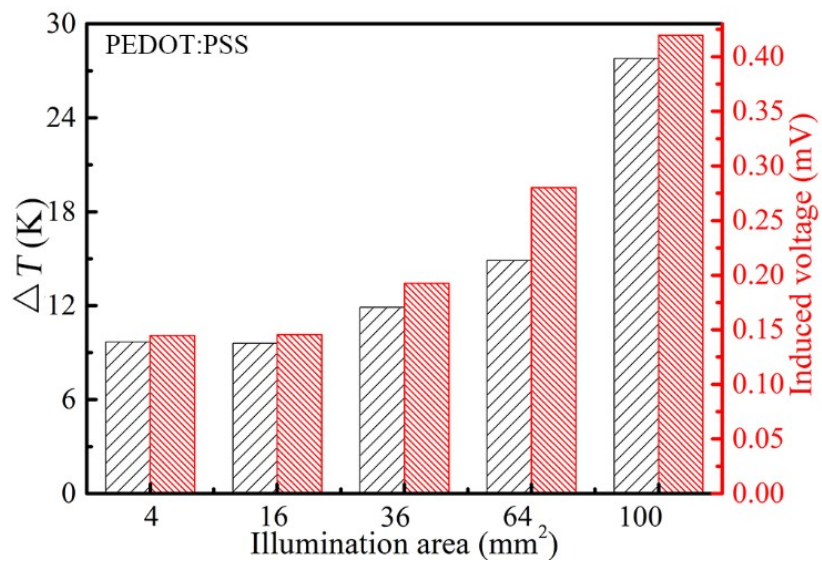


Fig. S9 The ΔT and induced voltage for PEDOT:PSS film at different illumination area.

Here is the xenon lamp lighting.

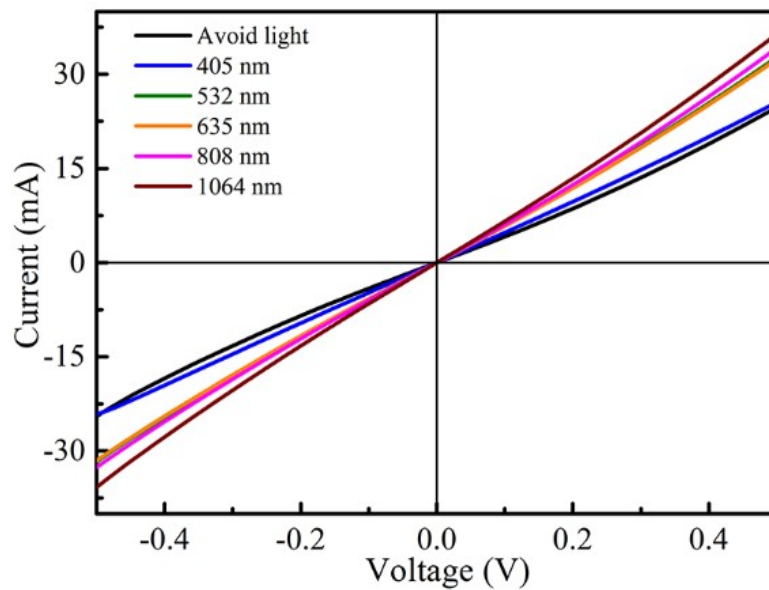


Fig. S10 The $I-V$ curves of PEDOT:PSS film illuminated with lasers of different wavelength. The illumination area is 100 mm².

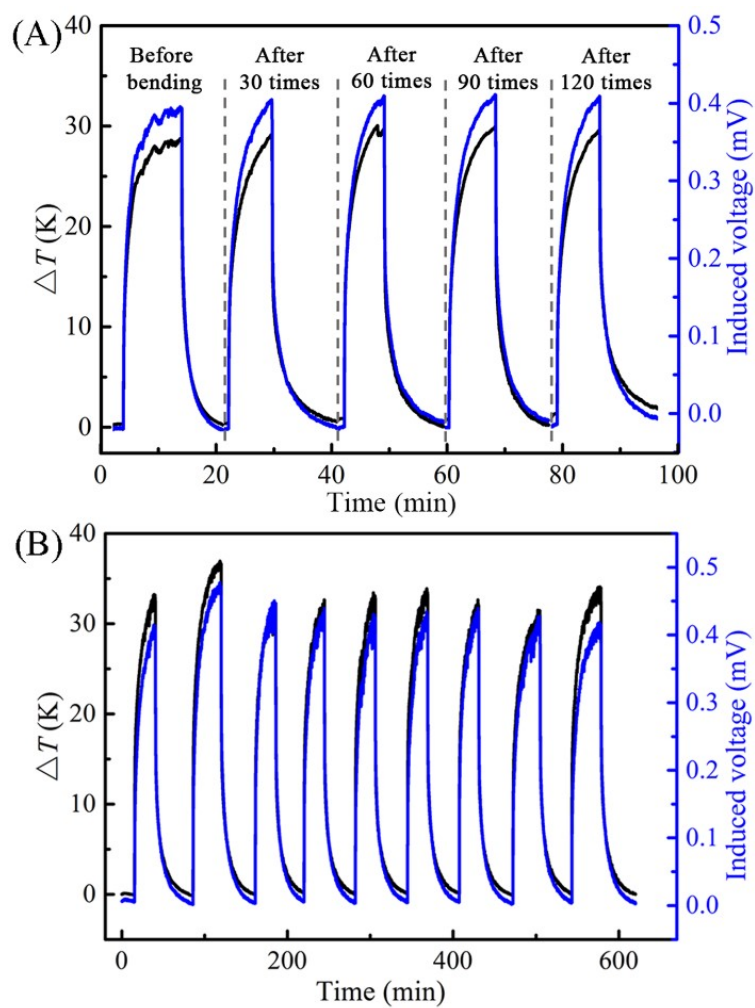


Fig. S11 The continuous ΔT and induced voltage under different bending times for PEDOT:PSS film (A); the ΔT and induced voltage as an function of illumination time within 9 cycles light on and off for PEDOT:PSS film (B). Here is the xenon lamp lighting and the illumination area is 100 mm².

References

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- [2] X. Yang, G. Hu, G. Gao, X. Chen, J. Sun, B. Wan, Q. Zhang, S. Qin, W. Zhang, C. Pan, Q. Sun, Z.L. Wang, *Adv. Funct. Mater.*, 2019, **29**.