Electronic Supplementary Information

Nanoscale-surface roughness enhances the performance of organic thin-film thermoelectrics

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Experimental Section

Materials: All chemicals were of analytical reagent grade and used as received without further purification. 3,4-Ethylenedioxythiophene (EDOT), anhydrous pyridine, anhydrous 1-butanol, poly(diallyldimethylammonium chloride) (PDAC), and carboxylate-polystyrene nanoparticles (200 nm diameter) (2.5 wt% aqueous suspension) were purchased from Sigma Aldrich, USA. Anhydrous iron (III) tris-p-toluenesulfonate (Fe-Tos) was purchased from Clevios™.

Instrumentation: Field Emission-Scanning electron microscopy (FE-SEM) was performed using a JEOL JSM-7401F electron microscope. Atomic force microscopy (AFM) characterization was carried out using a Veeco Nanoscope IIIaPSIA XE-150 AFM in non-contact mode with a silicon nitride cantilever tip. A Keithley 6514 programmable electrometer and an Omega HH506R digital thermometer were used to measure the Seebeck voltage and the temperature gradient, respectively. A Tekpower TP8236 digital multimeter and a TEKCOPLUS TMTK-173 digital thermometers were utilized to determine the power output and the temperature difference between hot and cold legs from a thermoelectric device, respectively.

Preparation of smooth PEDOT:Tos films: p-toluenesulfonate doped PEDOT (PEDOT:Tos) films were prepared on glass (2.5 cm x 2.5 cm) and polyethylene terephthalate (PET) substrates (2.5 cm x 2.5 cm) as reported in the literature.[1-3] Briefly, 0.5 mL of 40 wt% Fe-Tos solution in 1-butanol was added to a pyridine (20 µL)-EDOT (20 µL) mixture to obtain a pyridine:Fe-Tos:EDOT solution at a ratio of 1.32 : 2.25 : 1.00. Fe-Tos acts as a catalyst for polymerization of the EDOT monomer as well as a dopant for the PEDOT polymer. Pyridine was used to lower the rate of polymerization. The mixed solution of pyridine-(Fe-Tos)-EDOT was then spin-coated at 1000 rpm for 60 seconds on a PET (or glass) substrate. After spin-coating, the spin-coated film on the substrate was heated at 90 °C for 10 minutes to complete the polymerization

process. Finally, the sample was cooled to room temperature and washed with distilled water three times to remove the residual oxidant, non-reacted monomers, and low molecular weight oligomers. The blue PEDOT:Tos films were dried by blowing nitrogen gas.

Preparation of nanorough PEDOT:Tos/PDAC films on PET substrate: The stepwise schematic for the preparation of rough PEDOT:Tos/PDAC film on the PET substrate is provided in **Figure S1**. Firstly, the hydrophobic PET substrate was plasma treated with air at 100 mTorr pressure for 3 minutes to induce the hydroxyl and carboxyl groups on its surface and make it hydrophilic. Then, a very thin layer (few nm) of positively charged PDAC (2 wt% aqueous suspension) was dip-coated on the hydrophilic PET for 5 minutes, washed with deionized water and dried. Negatively charged carboxylate-polystyrene nanobeads (200 nm diameter) were then coated (drop casting) on the positively charged PET surface through electrostatic interaction using 2.5 wt% aqueous suspension of nanobeads. The sample was then washed with deionized water and dried. A mixture of pyridine:Fe-Tos:EDOT at a ratio of 1.32:2.25:1 (prepared as described above) was then spin-coated at 1000 rpm for 60 seconds. The spin-coated film was heated at 90 °C for 10 minutes. The sample was cooled to room temperature and washed in distilled water three times to remove the residual oxidant, non-reacted monomers, and low molecular weight oligomers. The sample was washed also with chloroform vigorously three times (for 10 minutes each) to wash off the polystyrene beads and obtain the nanorough PEDOT:Tos/PDAC on the PET substrate. To make larger films for the fabrication of the complete thermoelectric device, the whole process of chemical polymerization of PEDOT:Tos was simply scaled up by maintaining the molar ratio of pyridine:Fe-Tos:EDOT solution and all the rest steps remained the same to form the nanorough PEDOT:Tos/PDAC on the PET substrate with dimensions 3.2 cm x 6.4 cm.

Preparation of smooth PEDOT:Tos/PDAC films on PET: PET film was first plasma treated with air as described above for the preparation of nanorough PEDOT:Tos/PDAC films on PET. Then, a very thin layer (few nm) of positively charged PDAC (2 wt% aqueous suspension) was dip-coated on the hydrophilic PET for 5 minutes, washed with deionized water and dried. A mixture of pyridine:Fe-Tos:EDOT at a ratio of 1.32:2.25:1 (prepared as described above) was then spin-coated at 1000 rpm for 60 seconds. The spin-coated film was heated at 90 °C for 10 minutes. The sample was cooled to room temperature and washed in distilled water three times and dried by blowing nitrogen gas.

Preparation of n-type Bismuth film on PET: Thin bismuth films were deposited on cleaned PET substrates under vacuum (base pressure, around 10^{-6} Torr) by thermal evaporation. The coating rate was set at 10 angstrom/s. The thickness of the thin Bi-film on PET was measured equal to 70±10 nm. The electrical conductivity and Seebeck coefficient of the n-type bismuth film were found to be equal to 3571±12 S/cm and -70.2±1.5 μV/K, respectively.

Thermal conductivity measurements: The cross plane thermal conductivity, $k_{\perp}$, of the smooth and nanorough PEDOT:Tos/PDAC films on PET was measured by fabricating multi-layered composite structures that contain the films (**Fig. S2**) and by using the 3ω method. More specifically, a 200 nm thick heater lines of gold (with width 100 μm or 60 μm) was deposited on a glass substrate and then a 300 nm layer of trichloro(1H, 1H, 2H, 2H-perfluorooctyl)silane (PFOTS) was deposited onto the heater line using vapor deposition. The PEDOT:Tos/PDAC/PET films were then placed and firmly pressed onto the top of the PFOTS coating with constant moderate pressure using a clamping mechanism. Since both of the PEDOT:Tos/PDAC/PET film and the PFOTS film are reasonably pliable, there should be no air gaps between the films and the thermal contact resistance should be negligible.

An alternating current, $I_{1\omega}$, was applied to the heater to generate a line heat source and the resulting third harmonic voltage, $V_{3\omega}$, was measured using a lock-in amplifier. This voltage is proportional to the temperature response of the heater. The temperature response was measured over an applied frequency range of 2-300 Hz using Equation 1. The thermal conductivity of the tested sample was calculated using the "slope" method – Equation 2.[4]

$$\Delta T = 2\frac{dT}{dR}\frac{R}{V_{1\omega}}V_{3\omega} \quad (1)$$

$$k = \frac{V_{1\omega}\ln\left(\frac{f_2}{f_1}\right)}{4\pi R^2 l(V_{3\omega,1} - V_{3\omega,2})}\frac{dR}{dT} \quad (2)$$

where

ΔT is Temperature rise (K); $\frac{dT}{dR}$ is the change in temperature with change in resistance (K/Ω); R is the average resistance of line (Ω); $V_{1\omega}$ is the first harmonic RMS voltage measured across the heater (V); $V_{3\omega}, i$ is the third harmonic in-phase RMS voltage measured across the heater (V); l is the length of heater line (m); f_i is the applied 1ω frequency (Hz).

In this "two sided" system $k_{measured} = k_{sample} + k_{substarte}$ but given that the thermal diffusivities of the substrate SiO_2 and PEDOT-based films are similar, the thermal conductivity of the tested films can be estimated from the difference of the measured thermal conductivity of the composite that contains only the substrate and the composite that contains both the substrate (SiO_2) and tested thin films (**Table S1**). When a 60 μm wide Au line was used, the thermal conductivities of the smooth and nanorough PEDOT:Tos/PDAC films were calculated to be 0.298 and 0.19 W/m K, respectively. These values are close to the values measured when the 100 μm wide Au lines were used (shown in **Table S1)**.

To verify the ability of the used approach to get accurate estimates of the thermal conductivity of tested materials we measured the cross plane thermal conductivity of PDMS samples and the measured value ($k_{\perp}$, = 0.18 W/m K) was close to the value ($k_{\perp}$, = 0.15 W/m K) reported in the literature.[5] The cross plane thermal conductivity of the PET substrate was also estimated equal to 0.20 W/mK that is higher but still close to the value reported in the literature ($k_{\perp}$ = 0.15 W/mK). It should be also noted that the estimated $k_{\perp}$ of smooth PEDOT:Tos/PDAC films ($k_{\perp}$= 0.30 W/mK) is close to the value ($k_{\perp}$= 0.33 W/m K) reported by Bubnova et al.[1]

Since measuring the in plane thermal conductivity of very thin films directly is very challenging,[6] previous research studies[1] have prepared 10 times thicker films of the tested material (1.6-1.4 μm) and calculated the in plane thermal conductivity by comparing the heat transport from wide (much wider than the thickness of the film) and narrow (with width similar to the thickness of the film) Au heaters[1]. Unfortunately, this approach cannot be used for the estimation of the in plane thermal conductivity of nanorough PEDOT:Tos/PDAC films as preliminary experiments showed that these films cannot be prepared thicker with the current fabrication method because the dissolution of the polystyrene spheres will be impartial and the produced films not representative to the thinner films. Bubnova et al, however, showed that thin films of PEDOT:Tos are almost isotropic ($k_{\parallel}/k_{\perp}$ = 1.1) when formed using the in situ polymerization approach; in this approach the substrate is spin coated with the monomer solution and then the PEDOT chains are formed, therefore no large thermal anisotropy is expected.[1] By considering that nanorough PEDOT:Tos/PDAC are also almost isotropic and exhibit a similar ratio of $k_{\parallel}/k_{\perp}$= 1.1 then the estimated $k_{\parallel}$ is equal to 0.20 W/m K.

Table S1: Measured cross plane thermal conductivity $k_{\perp}$ of smooth PEDOT:Tos/PDAC and nanorough PEDOT:Tos/PDAC films.

	$k_{measured}$ (W/mK)		
Sample	**Bare Substrate (SiO_2)**	**Substrate w/ Sample**	**Substrate w/ Sample - Bare Substrate**
smooth PEDOT:Tos	1.217	1.513	0.296
nanorough PEDOT:Tos	1.203	1.388	0.185

Table S2: Key parameters of the rough PEDOT:Tos/PDAC/PET films and other PEDOT-based materials reported in the literature.[a]

Sample	Electrical conductivity (S/cm)	Seebeck coefficient (μV/K)	Power factor (μW/mK^2)	Figure of merit (ZT) (T = 310 K)	Output power	Ref.
PEDOT:Tos treated w/ TDAE	67	220	324	0.25	1.13 nW for PEDOT/C ΔT= 1.5°C H = 3 μm	[1]
PEPG:PEDOT:Tos electrochem. treatment	923	117	1270	1.02*	-	[2]
PEDOT:Tos AA treatment	144	110	174.2	0.146	-	[3]
PEDOT:Tos pH treatment			26	-	-	[7]
PEDOT:Tos HI treatment	1690	20.3	69.6	-	-	[8]
PEDOT:Tos H_2SO_4 treatment	1750	14.6	37.3	0.046 (375 K)	-	[9]
PEDOT:Tos $NaBH_4$/DMSO treatment	5.7	143.5	98.1	0.064 at RT	-	[10]
PEDOT:PSS/PANI-CSA multilayer	1680	44	325	-	-	[11]
PEDOT:PSS/ce-MoS_2 assembly	867	21.9	41.6	-	-	[12]
PANi/graphene-PEDOT:PSS/PANi/DWNT-PEDOT:PSS	1900	120	2710	-	8.5 nW, ΔT=5.6 K, 80 QD films (8x15 mm)	[13]
EMIM-DCA/AB-PEDOT:PSS	-	-	754	0.75*		[14]
PEDOT:Tos/glass (untreated)	152	11	-	-		[15,16]
PEDOT:Tos/silicon wafers (untreated)	4398	18.4	148	-		[17]
PEDOT:Tos/glass (untreated)	580	40	-	-		[18]
PEDOT:Tos/glass (untreated)	364	58	122	0.103		[3]
Rough PEDOT:Tos/PDAC/PET	1000	80.1	642	0.99	1.9 nW ΔT = 10 K (2x1 cm)	This work

[a]TDAE: tetrakis(dimethlyamino)ethylene; PEPG: Poly(ethyleneglycol)-block-poly(propyleneglycol)-block-(polyethyleneglycol) triblock copolymer; PANI-CSA: poly aniline-camphor sulfonic acid; ce-MoS_2: chemically exfoliated MoS_2; PANi: polyaniline; DWNT: double-walled nanotube; QD: quadlayer, EMIM-DCA: 1-ethyl-3-methylimidazolium dicyanamide

* Assumed value, not derived from actual thermal conductivity measurements.

Table S3: Maximum power output of the nanorough PEDOT:Tos/PDAC/PET strips of various dimensions (each sample was measured three times at five different points).

Sample	Distance between electrodes on strips (cm)	Width of strip (cm)	Maximum power output at ΔT = 10 K (nW)
1.	1	1	2.17±0.07
2.	2	1	1.92±0.06
3.	4	1	0.63±0.09
4.	6	1	0.25±0.10
5.	2	0.5	1.52±0.09
6.	2	1.5	2.05±0.03
7.	2	2	2.04±0.05

Table S4: Maximum power output of the rough PEDOT:Tos/PDAC/PET strips (width = 1 cm, length between electrodes = 2 cm) as a function of load resistance (each sample was measured three times at five different points).

Sample	Load Resistance (Ω)	Maximum power output at ΔT = 10 K (nW)
1.	10	0.73±0.09
2.	30	1.31±0.05
3.	60	1.92±0.06
4.	100	1.55±0.04
5.	500	0.91±0.07

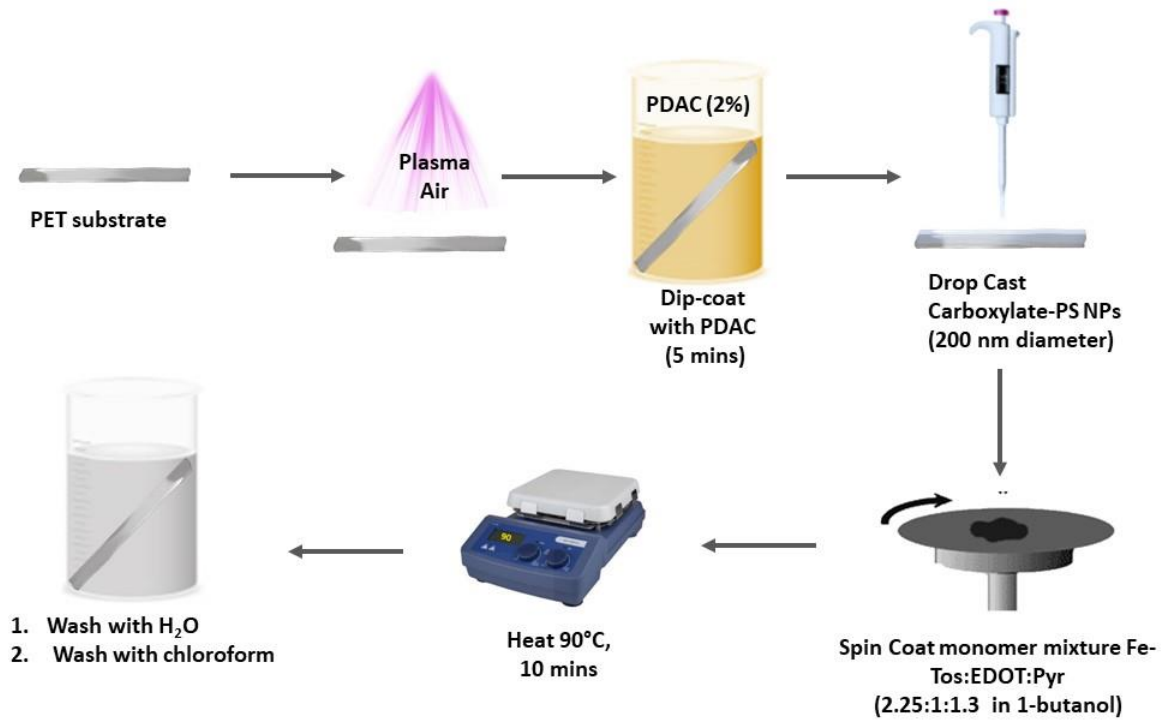

Fig. S1. Stepwise schematic for the preparation of the nanorough PEDOT:Tos/PDAC/PET film.

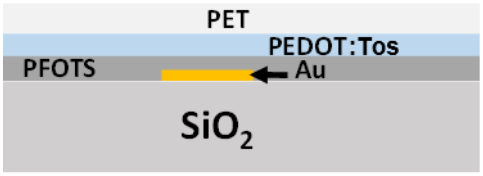

Fig. S2. Schematic diagram for the measurement of thermal conductivity.

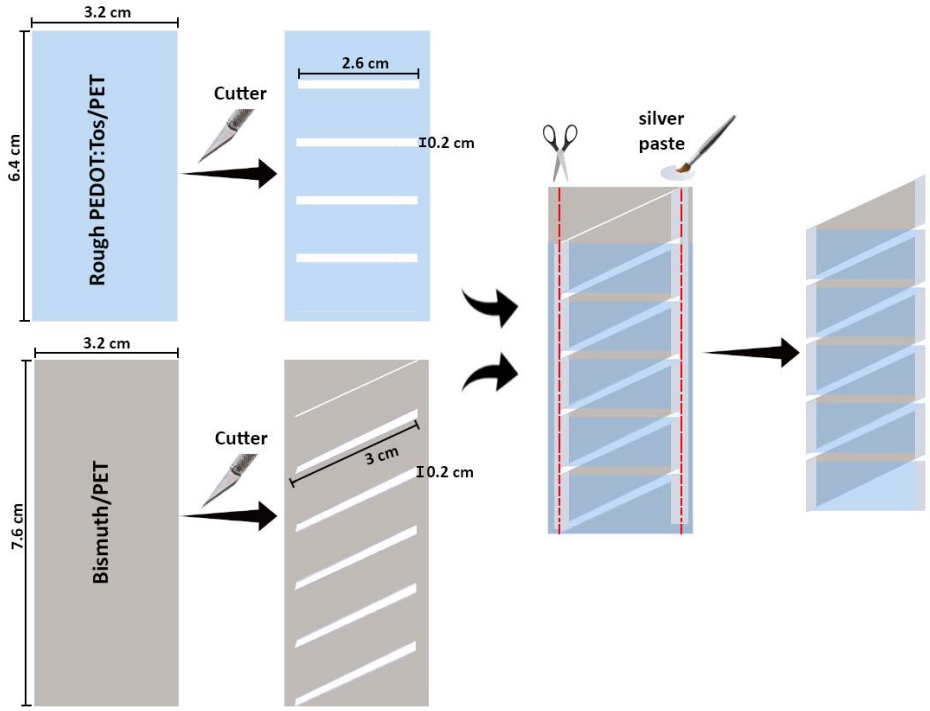

Fig. S3. Schematic representation of the design of the complete thermoelectric device.

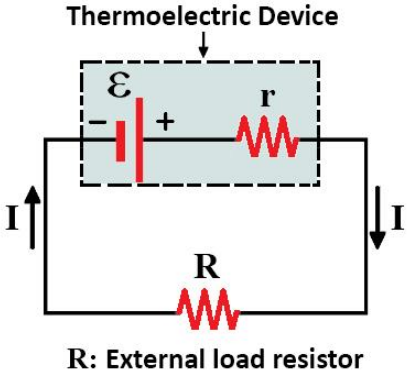

Fig. S4. Schematic diagram for the power measurement set up.

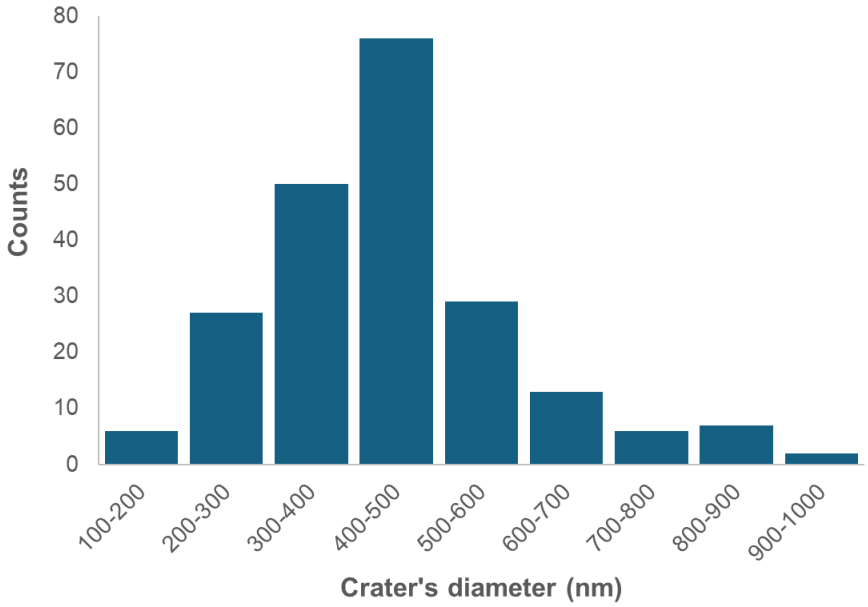

Fig. S5. Histogram that shows the distribution of the diameter of the craters on the surface of nanorough PEDOT:Tos/PDAC/PET film

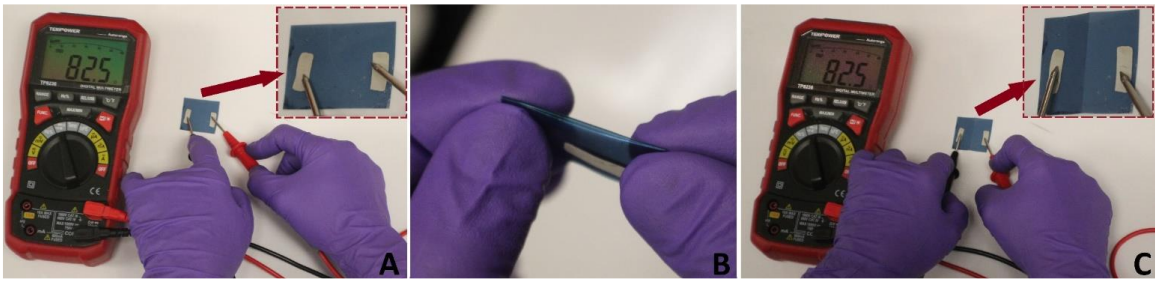

Fig. S6. (A) Measuring the electrical resistance of the nanorough PEDOT:Tos/PDAC/PET film. (B) Creasing of the rough film. (C) Measuring the electrical resistance after creasing the rough film.

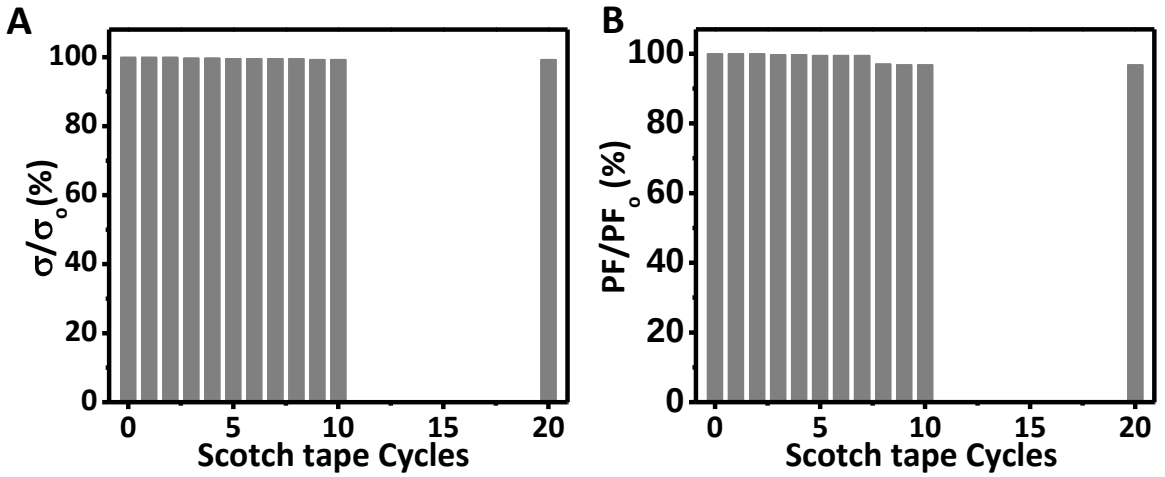

Fig. S7. (A) Relative electrical conductivity and (B) relative power factor of a nanorough PEDOT:Tos/PDAC/PET film before and after the Scotch tape test as a function of the test cycles.

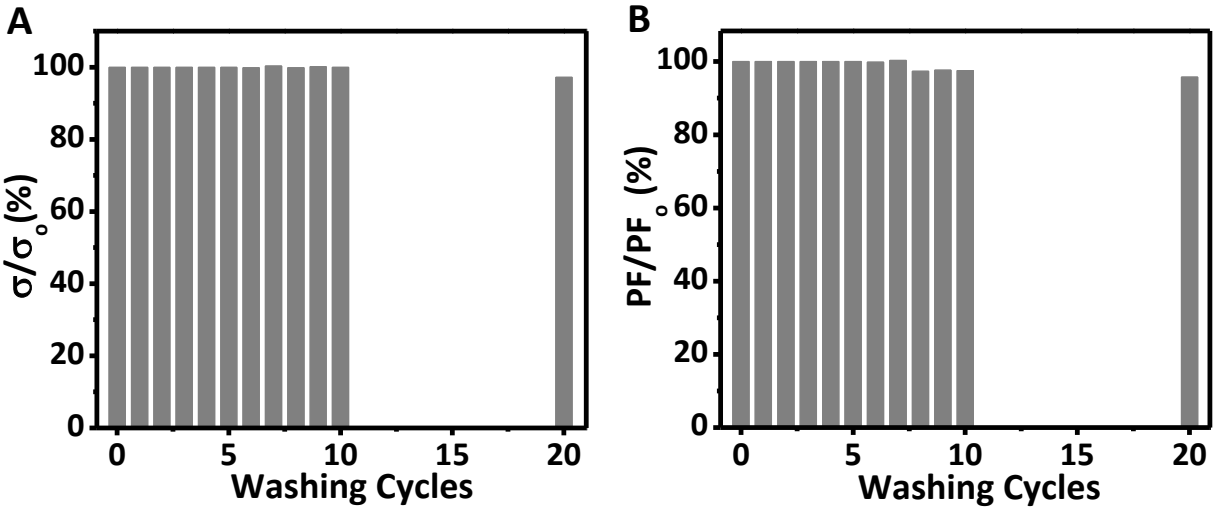

Fig. S8. (A) Relative electrical conductivity and (B) relative power factor of a nanorough PEDOT:Tos/PDAC/PET film before and after washing test as a function of washing cycles.

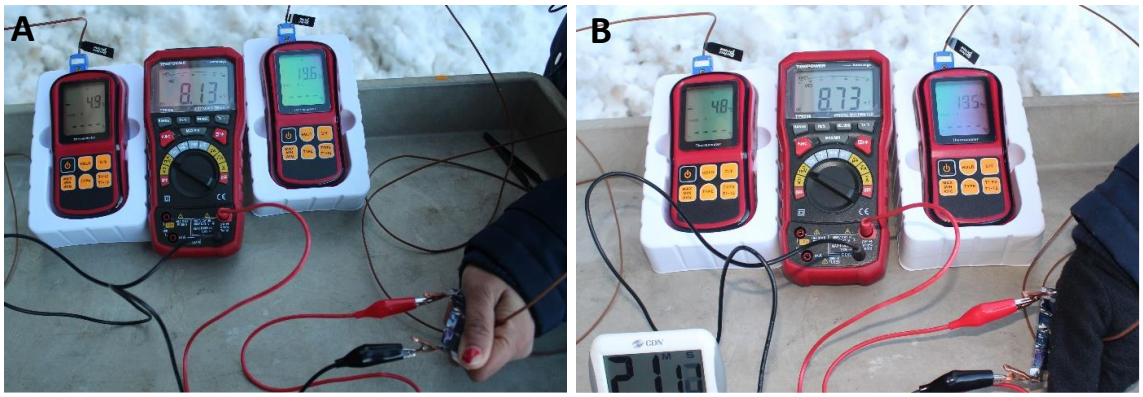

Fig. S9. Potential readings when a bare hand holds the device (A) and when a gloved hand holds the device (B) on a cold day (-4.9 °C)**.**

Video: Potential readings when a gloved hand holds the device on a cold day (-0.6 °C). The video was recorded for 20 minutes and then edited to be displayed in 4x speed.

Video link: https://youtu.be/EyskuJ8Y_ac

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