Supporting Information

Binary treatment of PEDOT:PSS films with nitric acid and imidazolium-based ionic liquids to improve the thermoelectric properties

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Characterization

The thicknesses (*t*) of the PEDOT:PSS films before and after treatment were measured using KLA-Tencor P-10 surface profiler. The minimal detectable film thickness of the KLA-Tencor 10 surface profiler is 100 Å (10 nm). The sheet resistance (*Rs*) of the films was determined by using the four-point probe method (Laresta-GP MCP-T610 from Mitsubishi Chemical) at the room temperature. The Loresta-GP MCP-T610 meter includes standard accessories PSP probe (MCP-TP06P (4-pins, inter-pin distance 1.5 mm, pin points 0.26R, spring pressure 70g/pin is an intelligent)) and probe checker (RMH112 (MCP-TP06P)) with software that measures the resistivity correction factors. The edges of the film were located 10 *mm* from the measurement point. The resistivity (ρ) is a characteristic that quantifies how much a given material opposes the flow of current, and current flows easily when the resistance is low. The σ is the inverse of the ρ . The ρ was calculated using the equation: $\rho = R_s t$.¹ For all synthetic batch, representative current (*I*)-voltage (*V*) measurements were obtained five times at different locations for each

film. The same spot is used for the measurement of sheet resistance and the thickness of the film in order to minimize error from the thickness variation in the film. The samples were kept in the environmental chamber, which is set at the desired humidity level and temperature, for at least two hours before the measurement.

The S was obtained with a homemade setup in a humidity-controlled room with a relative humidity (RH) of 55%. It consists of two stages, which are about 5 mm apart one is integrated with a heater to generate a temperature gradient in the test sample. First, two long and narrow Au electrodes with 20 mm long, 1 mm wide, and 2 mm apart were thermally evaporated on the film. To minimize the experimental errors, the PEDOT: PSS film outside the area of electrodes was also removed. The Au electrodes were connected to a Keithley 2400 source meter through the probes to obtain the voltage difference (ΔV). Simultaneously K-type thermocouples are connected to a data logger (Omron ZR-RX45) at the same time to collect the actual temperatures of the surfaces of the films. The voltage probes and thermocouples were placed at the same temperature zone on each side so that the measured voltage corresponds to the actual thermal gradient between the two voltage probes. The measured thermovoltage was corrected by the thermovoltage of Au wire to obtain the absolute S of the material. The S was evaluated from the slope of the linear relationship between thermoelectric voltage and the temperature difference of the two probes (i.e. $S = -\Delta V / \Delta T$). To calibrate the set up the S of pure Cu and Ni metallic samples were measured. The measured values of S (19.3 μ VK⁻¹ for Ni and 1.9 μ VK⁻¹ for Cu) were similar to the reported values of S (19.5 μ VK⁻¹ for Ni and 1.7 μ VK⁻¹ for Cu) showing the viability of the S measurement system².

The thermal conductivity (κ) was calculated using the equation $\kappa = e^2 / Cp\rho$ where ρ , *e*, *Cp* are density, thermal effusivity, and specific heat capacity respectively. The *e* was measured with Pulsed Light Heating Nano TR (NETZSCH) system with ultrafast pulsed laser flash method using front heating-front detection mode, which is designed for 30 nm-20 μ m thin film analysis. The *Cp* was measured independently using differential scanning calorimeter (DSC) (Mettlier Toledo Q20, TA Instruments, New Castle, DE). The ρ at room temperature was calculated from the mass and volume of the film. The carrier concentration (*n*) and mobility (μ) were measured using a Hall effect measurement system (Ecopia HMS-5000) with a Van der Pauw method. First the Ag electrodes were made-up by depositing Ag metal onto the film layer through a shadow mask. The HMS-5000 measurement system comprises software with an (*I-V*) curve for checking the ohmic contacts. The *n* and μ were calculated using the following equations: $n=I/|R_H| \times e$ and $\mu=|R_H|/\rho$; where *e*, ρ , R_H , are free electron charge, resistivity, and hall coefficient respectively. For all measurements 10 samples for each condition were prepared and

measurements were carried out at least five times for each sample in each synthetic batch to obtain the statistical results. The Raman spectroscopy measurements were obtained using Raman microscopy (Renishaw) with a laser wavelength of 785.5nm, a laser beam spot size of 200 µm and an accumulation time of 30 s. X-ray diffraction (XRD) of the films obtained by a D8 Advance System (Bruker corporation), equipped with Cu K_{α} X-ray source, $\lambda = 0.15406$ nm. Atomic force microscopy (AFM) images were taken on a Bruker Dimension Icon AFM using the tapping mode. Scanning electron microscopy (SEM) photographs were obtained using a JSM -7600F field emission SEM. The PEDOT:PSS films were prepared by drop-casting a filtered PEDOT:PSS solution onto silicon substrates and the samples for the SEM were broken to obtain the cross-section SEM images. The thicknesses provided in the SEM images is not the accurate thicknesses and used only to show the morphology change. The absorption spectra measurement was performed on an UV-Vis-NIR spectrophotometer (Shimadzu UV-Vis spectrophotometer UV-3600). The films were deposited on a quartz substrate by using spin coating method. X-ray Photoelectron Spectrometer (XPS) of the films were obtained by a Theta Probe Angle-Resolved X-ray Photoelectron Spectrometer (ARXPS) System (Thermo Scientific) using monochromated, micro-focused Al K_{α} X-ray photons (*hv* =1486.6 *eV*) at a base pressure of 1×10^{-9} Torr and a step size of 0.1 eV. The curve fitting and linear background subtraction were carried out using the Avantage software.

Stability of PEDOT:PSS films

PEDOT:PSS thin films treated with HNO₃ and then further dedoped with ionic liquids are compared to the pristine polymer regarding their response to high temperature (70°C) and high humidity (75%) conditions using temperature-test humidity chamber. PEDOT:PSS films were placed in a humidity controlled chamber and their TE performance was measured at varied temperature and humidity conditions in order to study the effect of humidity on TE properties of PEDOT:PSS films ³. In this study, the stability study was conducted using a constant climate chamber (Memmert HPP 110) in the temperature range from +0 °C to +70 °C, as well as the active humidification and dehumidification from 10% to 90% RH.



Figure S1. The digital photos of pristine (a) treated PEDOT:PSS films (b) and gold deposited PEDOT:PSS films for TE characterisation (c)



Figure S2. Illustrative diagrams of the four-point probe method. Two probes are used to measure the *I* passing through the film, and the other two probes are used to measure the V (left) and a hypothetical PEDOT:PSS film showing five different locations used for *I-V* measurements using the four-point probe (right). Each location is 6 mm wide; *a* is the width of the film and/or substrate, *b* is the length of the film and/or substrate and *t* is the thickness of the PEDOT:PSS film.



Figure S3. TE characterization of the PEDOT:PSS films. Schematic illustration of the *S* measurement setup (left) and detailed electrode geometry (right).



Figure S4. The curve fitting XPS spectra using Origin-Pro Software: (a) pristine PEDOT:PSS, (b) HNO₃-treated PEDOT:PSS and (c) [bmim][OTf]-N-PEDOT:PSS films



Figure S5. Raman spectra of the untreated, N-PEDOT:PSS, [bmim][OTf]-N-PEDOT:PSS and [bmim][BF4]-N-PEDOT:PSS films in the range of from 1050 to 1200 cm⁻¹.



Figure S6. The surface/ top-view SEM photographs of (a) pristine (b) HNO₃ treated (c) [bmim][BF₄]-N-PEDOT:PSS and (d) [bmim][OTf]-N-PEDOT:PSS films. The cross-section SEM photographs of (e) Pristine (f) HNO₃ treated (g) [bmim][BF₄]-N treated (h) [bmim][OTf]-N treated PEDOT:PSS films on the silicon substrate. Image of the close-up of the crack formed during sample preparation. All images captured an area of $1 \times 1 \ \mu m^2$.



Figure S7. The normalized thermalreflectacne signals of the pristine (a) and HNO₃ treated (b) [bmim][OTf]-N-PEDOT:PSS films coated with 100 nm-thick-Al after the nanosecond-pulse heating. The solid red lines represent the fitted temperature response curve that is used to extract the thermal effusivity of the PEDOT:PSS films. (The inset shows the front heating, front detecting configuration used in the measurement).

Table S1. Thermoelectric properties of the pristine and surface treated PEDOT:PSS films

Post-treatment process	σ (Scm ⁻¹)	S (µVK ⁻¹)	$PF(\mu Wm^{-1}K^{-2})$
Untreated	0.03 ± 0.003	17.5 ± 1.6	0.01 ± 0.001
HNO ₃ treated	3200 ± 89	16 ± 1.2	76 ± 5.3
[bmim][OTf]-N-PEDOT:PSS	1260 ± 61	34.8 ± 1.8	152 ± 11.2
[bmim-BF ₄]-N-PEDOT:PSS	1188 ± 45	33.9 ± 1.9	137 ± 12.5

Table S2. Comparison of this work with previous reports in literature on some typical sequential treated PEDOT based TE materials.

Post-treatment Process	σ	S	PF	к	ZT	Referenc
	(S/cm)	(µV/K)	(µW/mK ²)	(W/mK)		e
PEDOT:PSS treated with p- toluenesulfonic acid monohydrate, then hydrazine /DMSO solution	~1300	~50	318.4	0.3	0.31	4
Addition of DMSO in to PEDOT:PSS and then teated with Poly(ethylene oxide)	1061	38.4	157.35	-	-	5
PEDOT:PSS treated with DMSO, then DMSO and hydrazine	677	41	115.48	0.17	0.2	6
PEDOT:PSS treated with sulfuric acid, then NaOH	2170	39.2	334	-	-	7
PEDOT:PSS treated with DMSO/NaBH ₄	~580	~40	98.1	0.451	0.064	8
PEDOT:PSS treated with Nitric acid (HNO ₃) and then [bmim][OTf]	1260	34.8	152.7	~0.3	~0.12	This work

Post-treatment Process	σ Reduction	S Reduction	к Reduction	Reference
PEDOT:PSS treated with sorbitol	~ 5% at 30% RH	-	-	9
Neutralization of acidic PEDOT:PSS with imidazole	~12% at 85 °C and 85% RH	-	-	10
PEDOT:PSS Treated with formic Acid	~30% at 75% RH	-	-	11
PEDOT:PSS treated with methanol and formic acid.	~20% at 75% RH	-	-	12
PEDOT:PSS treated with methanol	~20% at 75% RH	-	-	13
PEDOT:PSS treated with nitric acid and then [bmim][OTf]	~14% at 70 °C and 75% RH	~13%	~13%	This work

Table S3. Comparison of the long-term stability of tretaed PEDOT:PSS in this work with previous reports in literature.

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