Supplementary Information

Flexible PEDOT electrodes with large thermoelectric power factors to generate electricity by the touch of fingertips

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Experimental Section

Materials: Iron(III) chloride hexahydrate (purity 97 %), p-toluenesulfonic acid monohydrate (purity > 98.5 %), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEPG, weight average molecular weight 2800), 3,4-ethylenedioxythiophene (EDOT) (purity 97 %), pyridine (purity 99.8 %), anhydrous methnol (purity 99.8 %) and n-butanol (purity 99.8 %), tetrabutylammonium perchlorate (purity > 99 %), and propylene carbonate (purity 99.7 %) were purchased from Aldrich Chemicals. The anhydrous n-butanol and propylene carbonate were used after molecular sieve treatment to remove water. Other materials were used without further purification.

Synthesis: Synthesis of iron(III) tris-p-sulfonate was performed following a previous report.[1] Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (30 mmol) was reacted with excess NaOH (100 mmol) in aqueous solution. The precipitate was then filtered through filter paper and washed twice with water. It was then transferred to a 250 mL flask containing 70 mL of methanol. p-Toluenesulfonic acid monohydrate (100 mmol) was added to this solution. After a 3 hour reaction at 45 ˚C, the solution was filtered and evaporated by a rotary evaporator.

The product was finally obtained after further drying in a vacuum oven at 70 ˚C. The solid powder was stored in a desiccator.

Characterization: Electrochemical oxidation control was performed with a CHI624B (CH Instruments, Inc.), using the PP-PEDOT film coated on a slide glass as the working electrode, a platinum wire as the counter electrode at a scan rate of 10 mV/s, and a Ag/Ag^+ reference electrode (0.10 M of $AgNO_3$ in acetonitrile) with the supporting electrolyte of 0.1 M tetrabutylammonium perchlorate (TBAPC)/propylene carbonate (PC). The Seebeck coefficient (S) was measured with a homemade setup (Fig. 1d). This setup consisted of two Peltier devices attached on an aluminum heat sink using a thermal paste to protect against thermal disturbances and to maintain a controlled temperature gradient.[2, 3] Current was controlled using a Keithley 2400 Source meter from +0.5 to -0.5 A, resulting in a temperature gradient. Two T type thermocouples were used to measure the temperature gradient across the samples.[4] These thermocouples were fixed by a plastic holder standing on a stage and the height of stage was controlled automatically by an electronic motor to maintain the pressure applied to the samples. Each end of the thermocouples was attached using a small amount of Ag thermal paste to ensure thermal contact. The average value of the measured temperatures by the two thermocouples from the hot and cold regions was about room temperature. To minimize the error of the measured values, we obtained the voltage difference at the same point of the thermal contact. It was possible due to the low Seebeck coefficient of the Cu wire (1.94 $\mu V\ K^{-1}$) of the T type thermocouple. Typically, 7 points of ΔV and ΔT were obtained 3 times by changing source current for each sample and plotted to calculate the Seebeck coefficient. The same procedures were done for different positions on the sample to obtain the average value of them.

The electrical conductivity (σ) was measured by the standard four-probe method. The thickness of the films was obtained by an Alpha step profilometer (Tencor Instruments,

Alpha-step IQ). UV-Vis-NIR absorption spectroscopy was performed using PerkinElmer Lambda 750. To calculate the density of the PEDOT films, a microbalance (Sartorius CPA2P, resolution of 0.001 mg) was used. To minimize the error, all samples were cut to the same size. The density of the film was calculated by measuring the mass and volume. The morphology of the film was determined using atomic force microscopy (AFM) and scanning electron microscopy (SEM). AFM measurements were carried out with a Multimode (Veeco Instruments) in tapping mode using a Si cantilever tip. SEM was performed using JEOL-JSM-6700F with thin Pt coating (<10 nm). All X-ray photoelectron spectroscopy (XPS) measurements were carried out using a VG Scientific Instrument model ESCALAB 220i-XL with Mg Kα / AI Kα dual source and monochromator. The XPS spectra of the PP-PEDOT films (Fig. S2) showed eight different peaks including four spin orbit splitting peaks of sulfur (S) were observed as reported before,[5] indicating the presence of sulfur atoms with different oxidation states. The lower binding energy peaks at 163.4 and 164.58 eV are assigned to the neutral sulfur atoms of the PEDOT backbone, S ($2p_{3/2}$), which showed doublets due to spin orbit splitting.[5c, 6] The peaks at the higher binding energies of 164.7 and 165.88 eV characterized the partially charged sulfur in the PEDOT backbone. The binding energy of the sulfur atom from the doped PEDOT ($PEDOT^{+}$-Tos^{-}) appeared higher due to the highly charged sulfur atoms in Tos^{-} as previously reported.[5a, 5b, 6-7] After deconvolution of the peaks, the ratios of the areas for each peak were calculated and the oxidation level of the pristine PP-PEDOT was determined as 24.1 %, which is lower than the determined 28.1 % for the prepared Py-PEDOT sample (PEDOT-Tos) shown in Fig. S2.

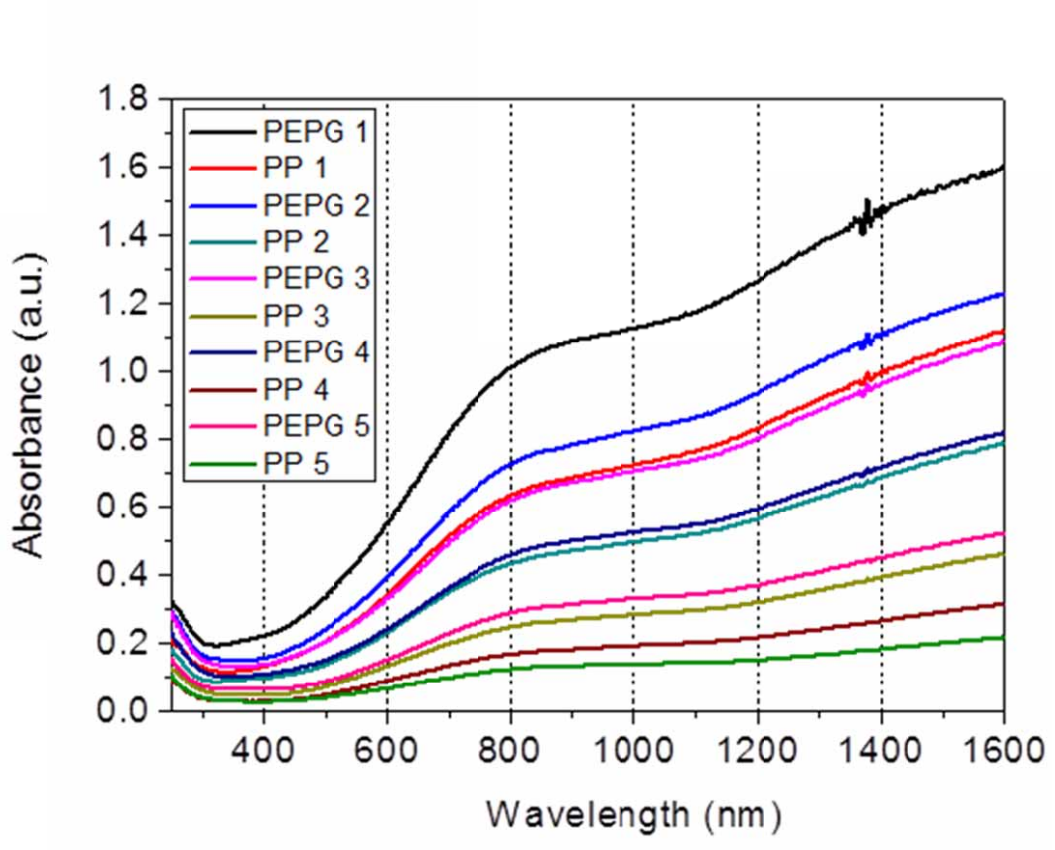

Fig. S1. UV-Vis-NIR spectra of PEG-PPG-PEG PEDOT (PEPG-PEDOT) and PP-PEDOT films with different composition of oxidation solution. As the ratio of PEPG was increased, the thickness of PEDOT films was decreased. After the pyridine was added and polymerized, the thickness of PP-PEDOT films was reduced compared to the PEPG-PEDOT without pyridine addition.

Table S1. Conductivity of PEDOT films under different composition.

Sample code	Additives (wt %)		wt ratio bet.		Thickness	Conductivity	Description
	Pyridine	PEPG	Pyr/ox	PEPG/ox	(nm)	(S cm^{-1})	
Py-1	1.34	0	0.03		230	357	Ref
Py-2	2.67	0	0.07		160	1060	Py-PEDOT
PEPG-1	0	9.1		0.25	252	568	
PEPG-2	0	16.6		0.5	225	874	
PEPG-3	0	23.1		0.75	183	1015	
PEPG-4	0	28.6		1	175	762	
PEPG-5	0	33.3		1.25	115	753	
PP-1	1.22	9.0	0.03	0.25	193	1031	
PP-2	1.12	16.5	0.03	0.5	122	1362	PP-PEDOT
PP-3	1.03	22.8	0.03	0.75	88	1253	
PP-4	0.96	28.3	0.03	1	69	1045	
PP-5	0.90	33.0	0.03	1.25	47	969	

Sample code PP-2 is the optimized condition of oxidation solution for PP-PEDOT polymerization. (ox: iron(III) tosylate)

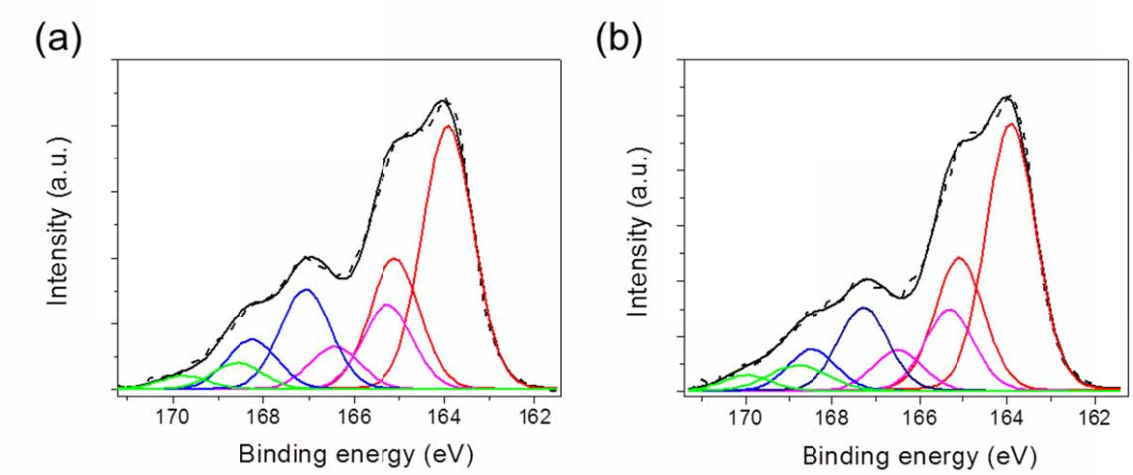

Fig. S2. S(2p) XPS spectra of polymerized PEDOT film by solution casting polymerization method. Spectrum (a) is for the pristine PEDOT polymerized by pyridine added oxidative solution with molar ration of pyridine: iron(III) tosylate: monomer was fixed as 1.1: 2.25: 1 (sample code Py-2 in Table S1). The oxidation level is 28.8 %. (b) is for the pristine PEDOT film polymerized by using oxidative solution containing pyridine and PEPG copolymer as mediators (sample code PP-2 in Table S1). The oxidation level is 24.1 %.

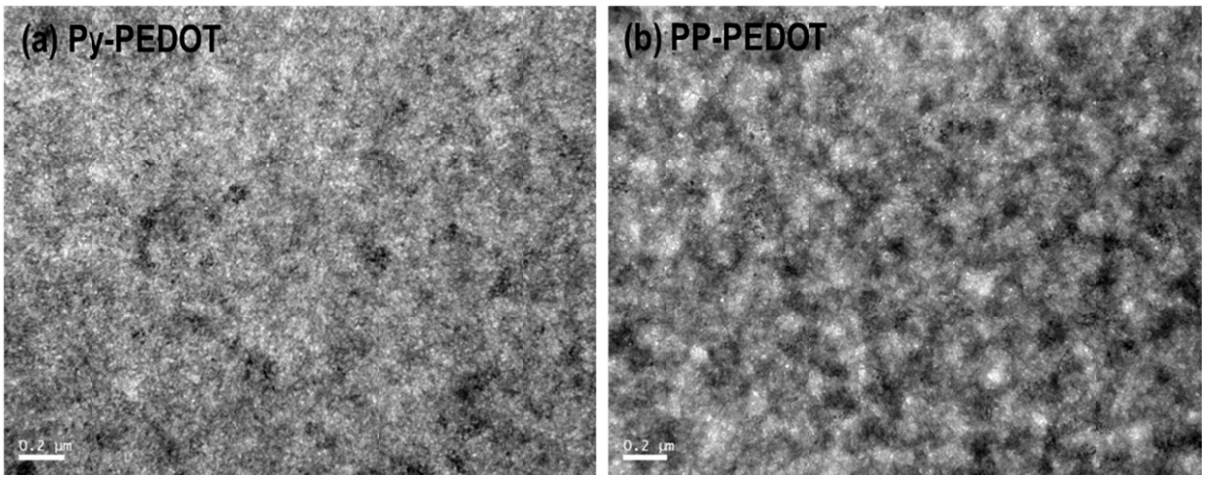

Fig. S3. High contrast TEM images of Py-PEDOT and PP-PEDOT films. (a) The pristine PEDOT polymerized by pyridine added oxidative solution. (b) The pristine PEDOT film polymerized by using oxidative solution containing pyridine and PEPG triblock copolymer as mediators. The morphology of PP-PEDOT film shows larger grain size than Py-PEDOT films.

Table S2. Experimentally measured σ, S, and $S^2 \cdot \sigma$ for PP-PEDOT films and comparison with literature values for PEDOT-based materials and other conductive polymers.[8]

Sample	σ (S cm^{-1})	S (μV K^{-1})	$S^2 \cdot \sigma$ (μW m^{-1} K^{-2})	reference
PP-PEDOT films at 0.1 V	~923	~117	1270	this work
PP-PEDOT films (pristine)	~1354	~79.7	861	this work
PP-PEDOT films at 1.1 V	~2122	~50	531.8	this work
PEDOT-Tos films	~67	~220	324	[7b]
PEDOT nanowire	7-40	33-122	6-12	[8a]
PEDOT films	3.2-18.3	33-57	0.5-4.4	[8a]
PEDOT nanotubes (pellets)	0.64×10^{-3}	-4088	1.07	[9]
PEDOT:PSS/DMSO/EG	220-298	12.5-14.2	3.4-6.0	[10]
PEDOT:PSS/5% DMSO	298.52	12.65	4.78	[11]
PEDOT:PSS/urea	8.16-63.13	14.47-20.70	2.7	[12]
Polymer matrix/PEDOT:PSS/SWCNT	~400	~25	~25	[13]
PEDOT:PSS/Te nanowire	~19.3	~163	70.9	[14]
PA iodine doped	3×10^4-5×10^4	15-20	1200-1500	[15]

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