Electronic Supplementary Information

Enhancement in the Thermoelectric Properties of PEDOT:PSS via One-step Treatment with Cosolvents or Their Solutions of Organic Salts

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1. Characterizations

Electrical conductivities of the PEDOT:PSS films were measured by the van der Pauw four probe technique using a Keithley 2400 source/meter. The electrical contacts were made by pressing indium on the four corners of each PEDOT:PSS thin film on glass substrate. Seebeck coefficients of the PEDOT:PSS films were measured in ambient environment using a home-built system, which consisted of two Peltier devices (TEC1-19906 by Beijing Geshang Electronic Pte. Ltd.) affixed on an alumina heat sink. The temperature difference (ΔT) ranging from 0 to 8 K across the film was detected with two T-type thermocouples (Omega, US) which have a diameter of 25 μm, and the thermal voltage output (ΔV) was measured with a Keithley 2000 multimeter. For each sample, the ΔV values were measured at 7 different ΔT values. At least 3 different Peltier heating rates were adopted for each ΔT value. The Seebeck coefficient of each film was derived through the best linear fitting of the ΔV–ΔT plots. The Seebeck measurement system was calibrated with a pure nickel foil, and the accuracy was within 10%. Through-plane thermal conductivities of the PEDOT:PSS films were measured by the time-domain thermoreflectance (TDTR) method[1]. The PEDOT:PSS films were coated with ~100 nm Al by thermal evaporation. Thermoreflectance data were collected for at least 3 times at one point, and the averaged TDTR signals were used for fitting.

UV-vis absorption spectra of PEDOT:PSS films were taken with a Shimadzu-1800 spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were collected with an Axis Ultra DLD XPS equipped with an Al K_α X-ray source (1486.6 eV). Atomic force microscopic (AFM) images were obtained using a Veeco NanoScope IV Multi-Mode AFM with the tapping mode. Thickness of the PEDOT:PSS films was determined by an Alpha 500 step profiler. Temperature dependences of the resistivities of the untreated and treated films were tested using a Janis Research VPF-475 dewar with liquid nitrogen as the coolant and a Conductus LTC-11 temperature controller. Cyclic voltammograms (CVs) were acquired with an ECO CHEMIE AUTOLAB PGSTAT 302N + FRA2 system in 0.1 M NaCl solution. The working electrode was a gold disc coated with PEDOT:PSS film, the counter electrode a Pt wire, and the reference electrode a Ag/AgCl (3 M NaCl).

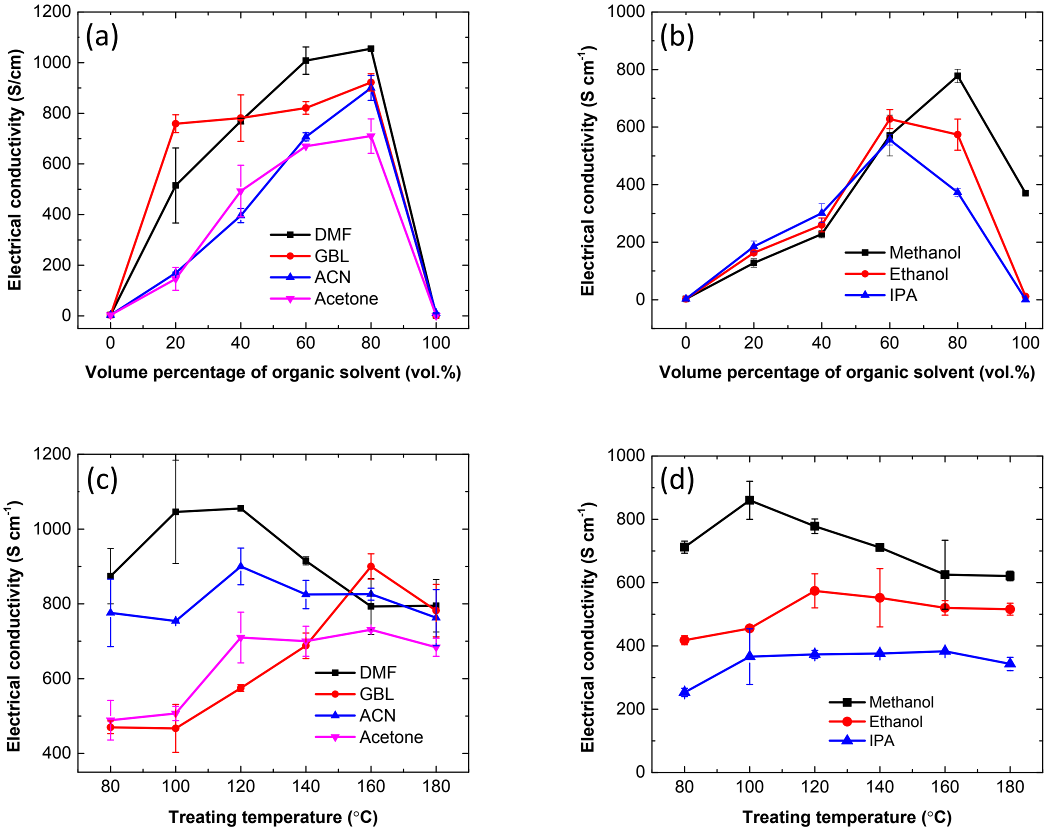

Fig. S1 Dependences of the electrical conductivities of the PEDOT:PSS films treated with cosolvents on (a, b) the volume percentage of organic solvent and (c, d) the treating temperature.

Table S1 Comparison of the electrical conductivities of the PEDOT:PSS films treated with cosolvents, neat solvents, solutions of MAI in cosolvents and solutions of MAI in neat organic solvents.

Solvent	**Electrical conductivities of PEDOT:PSS (S cm^{-1})**			
	Cosolvents	Neat solvents	Solutions of MAI in cosolvents	Solutions of MAI in neat solvents
DMF	1055	1.2	1866	1660
GBL	922	0.87	1643	1640
Acetone	710	0.24	1018	740
ACN	900	10	1002	Poor solubility
Methanol	778	370	1153	1370
Ethanol	574	0.35	1074	853
IPA	373	0.5	1004	227
H_2O	-	3	-	970

Table S2 The through-plane thermal conductivities of PEDOT:PSS films measured by a TDTR method at room temperature.

	Measurement 1	Measurement 2	Measurement 3	Measurement 4	Thermal conductivity (W m^{-1} K^{-1})
Untreated	0.260	0.344	0.335	0.292	0.307 ± 0.039
Cosolvent-treated	0.301	0.330	0.231	0.286	0.287 ± 0.042
Cosolvent solution-treated	0.305	0.259	0.312	0.299	0.294 ± 0.024

Table S3 Comparison of energy barriers T_0 for the PEDOT:PSS films treated by different methods.

Treatment	$\boldsymbol{T_0}$ **(K)**	**References**
0.1 M MAI in DMF	92	[2]
0.1 M $ZnCl_2$ in DMF	128	[3]
HFA·$3H_2O$	99	[4]
H_2SO_4 three times	29	[5]
80% DMF-20% water, water rinsing	100	**This work**
0.1 M MAI in 80% DMF-20% water	67.2	**This work**

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