Supporting Information

The Key Mechanism of Conductivity in PEDOT:PSS Thin Films Exposed by Anomalous Conduction Behavior upon Solvent-Doping and Sulfuric Acid Post-Treatment

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Experimental Section

Sample Preparation. Aqueous dispersion (1.3 wt%) of PEDOT:PSS (1:2.5) (Clevios PH1000, Heraeus), first filtered by a 0.45 µm syringe polyvinylidene fluoride (PVDF) filter (Sterlitech), was ultrasonicated for 15 min. Double-side polished 2 by 2 cm^2 silicon wafers (E&M Corp. Ltd., Japan) were pre-washed, ultrasonicated for 30 min and cleaned by acetone, DI water, and isopropanol. After drying, the substrates were UV-Ozone (PSDP Pro, Novascan Technologies Inc., USA) treated for 30 min. The spin coater (WS-650-23, Laurell Technologies Corp., USA) speed was adjusted to 1000 rpm for 30 s. PEDOT:PSS dispersion were mixed with different concentrations (0.2%, 0.5%, 1%, 5%, 8%, and 10%) by volume of a solvent, DMSO or EG (Sigma Aldrich, ≥99.5%,). All samples were annealed inside an oven at 160°C under vacuum for 15 min to remove any residual water left. The samples of pristine and solvent-mixed PEDOT:PSS were then immersed inside sulfuric acid (Sigma Aldrich, 95%), nitric acid, perchloric acid and hydrochloric acid (Sigma Aldrich, ≥ 95%) for 10 min and rinsed with deionized water several times before last-step drying at 120°C for 10 min. All PEDOT:PSS thin films either pristine, doped or post-treated were prepared inside an oven under vacuum, as well as a fume hood and the resulting samples were encapsulated and kept under the vacuum inside the oven to minimize water absorption.

Characterization of the Films. The thickness of the films was determined by variable-angle spectroscopic ellipsometer (J. A. Woollam-M2000, USA). CS-AFM (N9410S, 5500 Keysight Technologies Inc., Canada) data acquisition was conducted using a PtSi coated silicon cantilever in contact mode.[1] The averaged conductivities were measured at 0.1, 2 and 20 mV. The linear four-point probe (Loresta GP, MCP-T610, Mitsubishi Chemical Co., Japan) technique was applied to measure the conductivity of the films at an applied voltage of 10 V. The conductivity of samples post-treated with nitric acid, perchloric acid and hydrochloric acid after initial doping of the polymer with DMSO and EG did not change significantly (Table S6, ESI†). The FTIR (Nicolet iS50, Thermo Fisher Scientific Inc., USA) spectra were collected in the range of 4000−600 cm^{-1} using a mid-IR KBr-DTGS detector and were signal averaged from 32 scans. Raman spectroscopy was performed from 0 to 3700 cm^{-1} on a confocal Raman microscope (WITec alpha 300 R) using a 532 nm laser with the 30−60 s typical integration time of acquisition. XRD (Rigaku ULTIMA III) measurements were performed in conventional theta/2theta geometry with Cu-K α radiation (λ = 1.5406 Å) at 40 kV and 100 mA.

Figures

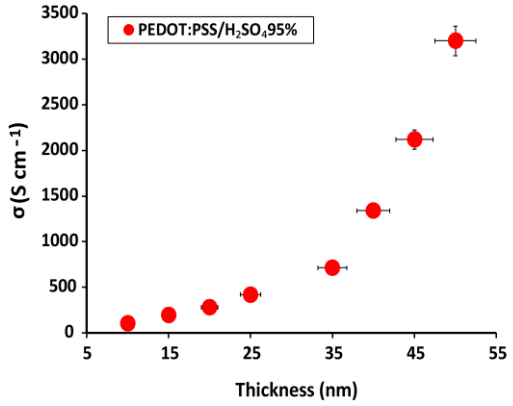

Fig. S1 Conductivity correlation with thickness in PEDOT:PSS thin films treated with H_2SO_4 95%.

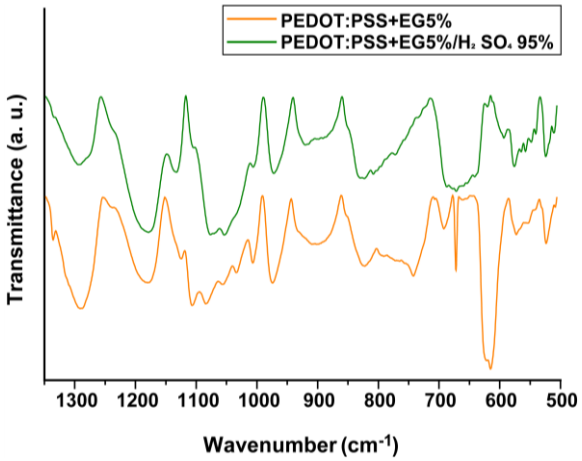

Fig. S2 Transmission FTIR spectra of EG-doped, and sulfuric acid post-treated PEDOT:PSS thin films. The spectra are similar to the DMSO-doped samples.

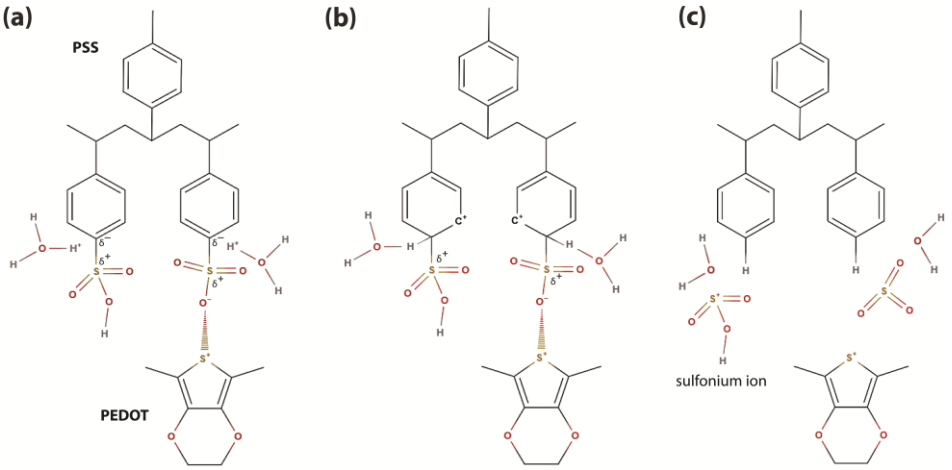

Fig. S3 Cartoon depiction of PSS desulfonation by sulfuric acid hydronium ion.

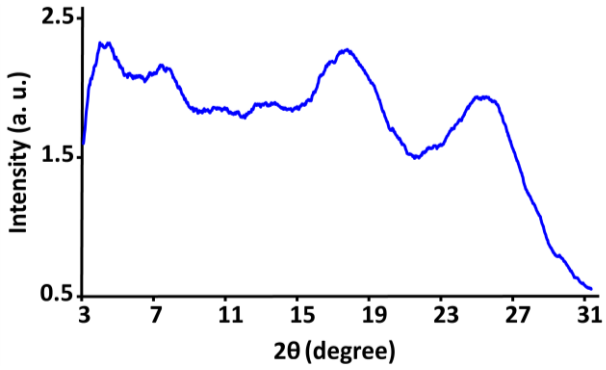

Fig. S4 XRD pattern of amorphous pristine PEDOT:PSS film showing some degree of crystallinity.

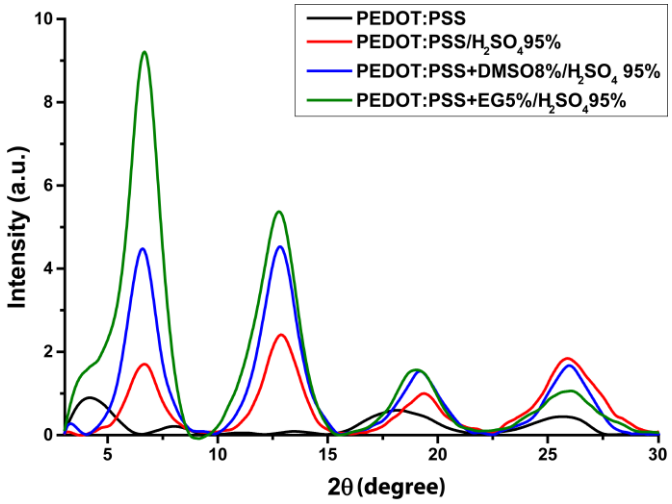

Fig. S5 XRD diffractograms of pristine, solvent-doped, acid post-treated and solvent-doped/acid post-treated PEDOT:PSS films.

Tables

Table S1 FTIR band assignments of the pristine, solvent-doped, acid post-treated and solvent-doped/acid post-treated PEDOT:PSS films, colored for the red and blue shifts related to each moiety

Moiety	ν [cm^{-1}] PEDOT:PSS	ν [cm^{-1}] PEDOT:PSS /H_2SO_4 95%	ν [cm^{-1}] PEDOT:PSS +DMSO 8%	ν [cm^{-1}] PEDOT:PSS+DMSO 8% /H_2SO_4 95%
C_α – S	818	822	898	829
	910	883	973	916
	968	968	1003	967
C_β – O – C	1070	1042	1107	1073
	1128	1132	1123	1137
	1181	1192	1177	1180
C_β – C_β	1294	1301	1290	1292

Table S2 Raman peak assignments of the pristine, solvent-doped and solvent-doped/acid post-treated PEDOT:PSS thin films, colored for the red and blue shifts related to each moiety

Moiety	ν [cm^{-1}] PEDOT:PSS	ν [cm^{-1}] PEDOT:PSS +DMSO 8%	ν [cm^{-1}] PEDOT:PSS+DMSO 8% /H_2SO_4 95%
EDO[a] ring	582	577	585
	996	988	993
$C_\alpha - S - C_\alpha$	707	705	710
$C_\beta - O - C$	1127	1115	1132
$C_\alpha - C_\alpha$	1262	1257	1267
$C_\beta - C_\beta$	1370	1363	1373
$C_\alpha = C_\beta$	1438[b]	1432	1443
	1547	1531	1542
	1573	1560	1566

[a] ethylenedioxy; [b] the main PEDOT:PSS Raman peak

Table S3 XRD peak results for the pristine, solvent-doped, acid post-treated and solvent-doped/acid post-treated samples of PEDOT:PSS

Index	PEDOT:PSS		PEDOT:PSS /H_2SO_4 95%		PEDOT:PSS +DMSO 8%		PEDOT:PSS +EG 5%		PEDOT:PSS +DMSO 8% /H_2SO_4 95%		PEDOT:PSS +EG 5% /H_2SO_4 95%	
hkl	2θ°	d [Å]	2θ°	d [Å]	2θ°	d [Å]	2θ°	d [Å]	2θ°	d [Å]	2θ°	d [Å]
d_{100}	4.1	21.8	6.7	13.2	4	22.1	4	22.1	6.7	13.3	6.7	13.3
d_{200}	8.1	10.97	12.8	6.95	7.8	11.3	7.7	11.5	12.9	6.9	12.7	7
d_{100}	11.2	7.94			10.9	8.2	10.6	8.4				
d_{100}	13.84	6.44			13.79	6.46	13.77	6.47				
d_{001}	18.2	4.93	19.5	4.62	18.45	4.87	18.52	4.85	19.3	4.66	18.96	4.74
d_{010}	25.54	3.57	26.2	3.49	26.63	3.44	26.63	3.44	25.9	3.53	26	3.51

Table S4 Average conductivity data of DMSO- and EG-doped samples of PEDOT:PSS thin films post-treated with nitric acid, perchloric acid and hydrochloric acid

Sample	σ [S cm^{-1}]
PEDOT:PSS + DMSO	1980
PEDOT:PSS + EG	1000
PEDOT:PSS + DMSO/HNO_3	1965
PEDOT:PSS + EG/HNO_3	966
PEDOT:PSS + DMSO/HCl	1955
PEDOT:PSS + EG/HCl	983
PEDOT:PSS + DMSO/$HClO_4$	1972
PEDOT:PSS + EG/$HClO_4$	992

References

1. V. Ozhukil Kollath, M. Arjmand, P. Egberts, U. Sundararaj, K. Karan, *RSC Adv.*, 2017, **7**, 32564.