

Electronic Support Information

Highly Electrical Conductive Polyethylenedioxythiophene Thin Films for Thermoelectrics Applications

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1. Fitting of X-ray photoemission spectroscopy (XPS)

Fitting of XPS spectra of the PP-modified PEDOT:Tos thin films with and without protonic acids treatment are processed on XPSPEAK41 developed by Dr. Raymond W.M. Kwok in the Department of Chemistry, The Chinese University of Hong Kong. The fitting processes are under following routes: the spin-split core levels feature originating from the sulfurs (S^*) in PEDOT chain have peaks from 160-164 eV, then, the contributions from S^* in the doped PEDOT chains are labelled as $S^1 p$, which have spin-split signals from $S^1 p_{1/2}$ and $S^1 p_{3/2}$. The signals from S^* in the neutral PEDOT chains are labelled as $S^2 p$, which also have spin-split signals from $S^2 p_{1/2}$ and $S^2 p_{3/2}$. The spin-split peak to peak distance (s. o. s) is set to 1.0 eV and the full width at half maximum (FWHM) is set to 0.85 eV. The spin-split signals from sulfonate group in Tos^- are labelled as $S^3 p$. The spin-split signals from sulfonate group in $HTos^-$ are labelled as $S^4 p$. The s.o.s and FWHM are set to 1.2 eV and 1.2 eV. And the spin-split signals from sulfonate group in the SO_4^{2-} and HSO_4^- are labelled as $S^5 p$ and $S^6 p$, correspondingly. The s. o. s and FWHM are also set to 1.2 eV and 1.2 eV, respectively. Then, the spin-split signals from Cl^- , HCl , ClO_4^- and $HClO_4^-$ are assigned as $Cl^1 p$, $Cl^2 p$, $Cl^3 p$ and $Cl^4 p$, respectively. The s. o. s and FWHM of Cl^1 and Cl^2 are set to 1.65 eV and 1.2 eV, respectively. The s. o. s and FWHM of Cl^3 and Cl^4 are set to 1.67 eV and 1.2 eV, respectively. By calculating the area under the fitted curves from the above assigned elements, the ratios between acid counter-ions, acid ions and S^* in the PEDOT chains could be calculated. Then the doping level of the PEDOT chain could be estimated by these ratios. The fitted XPS spectra and raw XPS spectra of the PP-modified PEDOT:Tos thin films are shown in Fig. S1.

2. Reduced thin film thickness

The XPS spectra of O_{1s} observed from the PP-modified PEDOT:Tos thin films with and without protonic acids treatment are shown in Fig. S2. Shifts of O_{1s} signals (O atom in the main chain of PP) are observed when the PP-modified PEDOT:Tos thin films are treated with various protonic acids. As discussed in the manuscript, for the PP-modified PEDOT:Tos thin treated with HCl, Tos^- is replaced by Cl^- . Moreover, only HCl^- is introduced into the thin film. Thus, the O_{1s} peaks from the PP-modified PEDOT:Tos thin film treated with HCl are only attributed to the O atom in the PEDOT chains; by another way, it suggests that the electrically insulating PP is completely removed. Thus, the reduced film thickness after HCl treatment is originated from the removal of the PP. The thickness of the PP-modified PEDOT:Tos thin film without protonic acid treatment is 165 ± 5 nm. The thickness of the PP-modified PEDOT:Tos thin films treated with HCl are 130 ± 5 nm. Thus, the reduction in the film thickness is due to complete removal of PP. Since the thicknesses of all the PP-modified PEDOT:Tos thin films are reduced from 165 ± 5 nm to 130 ± 5 nm, the PP additives are also completely removed from of the PP-modified PEDOT:Tos thin films treated with other protonic acids.

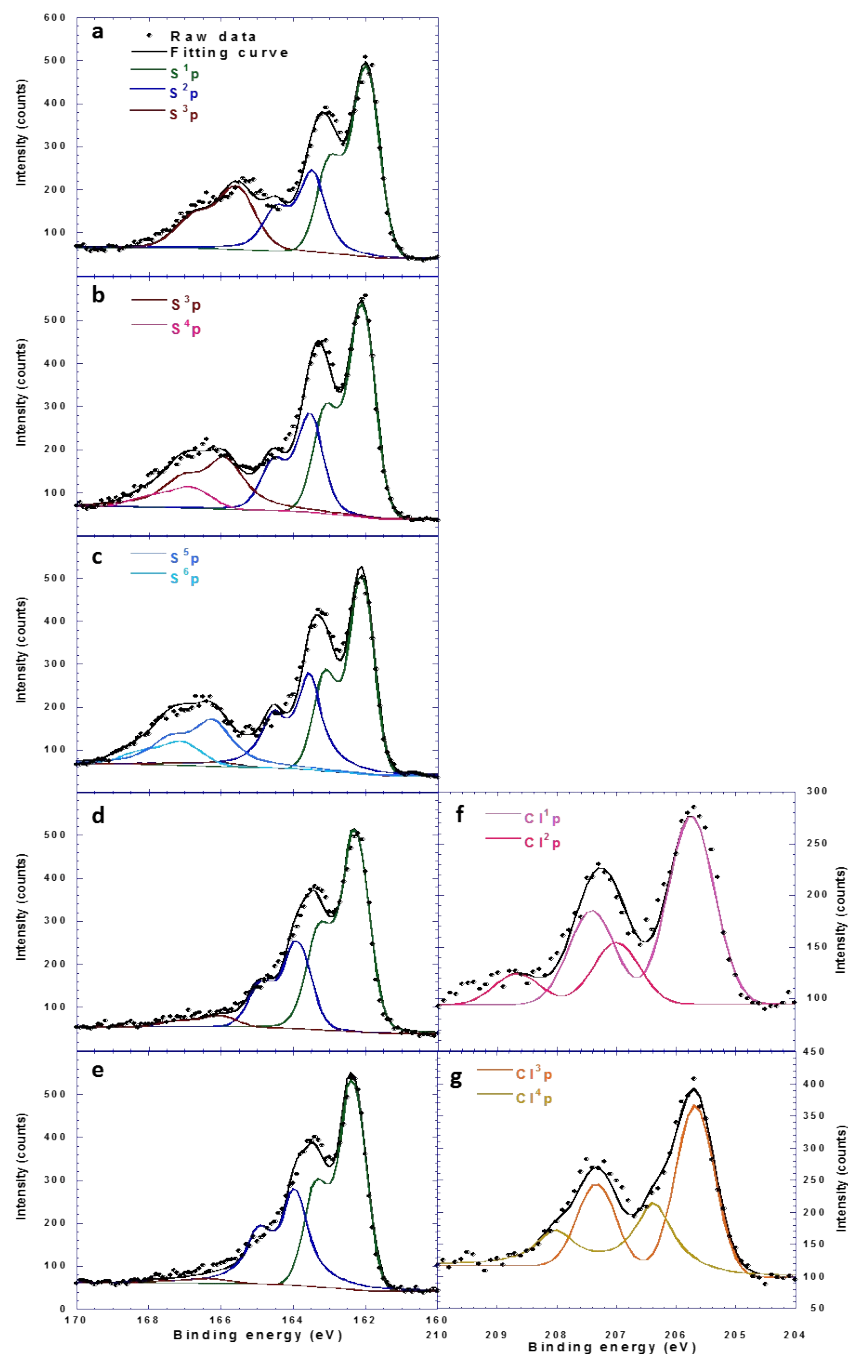


Fig. S1. Fitted S_{2p} XPS spectra of (a) the PP-modified PEDOT:Tos thin film without protonic acid treatment; and the PP-modified PEDOT:Tos thin films treated with (b) p-tos; (c) H₂SO₄; (d) HCl; (e) HClO₄; Fitted Cl_{2p} XPS spectra of the PP modified PEDOT:Tos thin films treated with (f) HCl and (g) HClO₄.

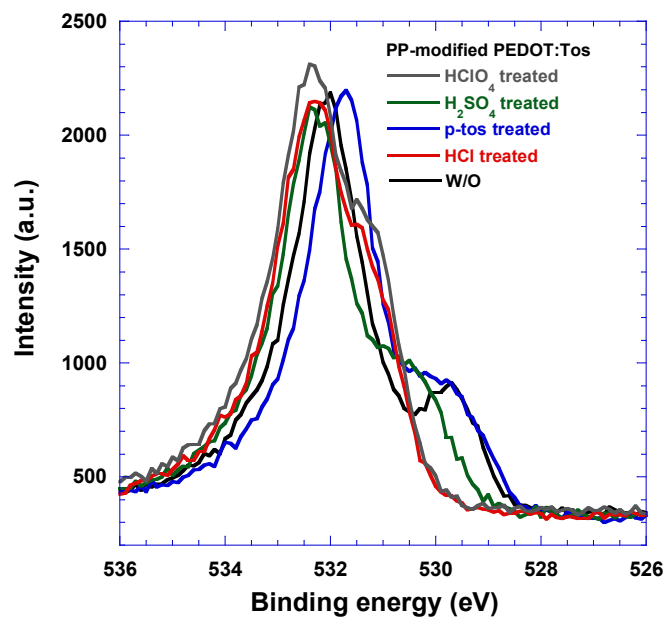


Fig. S2. High resolution XPS spectra of O_{1s} observed from the PP-modified PEDOT:Tos thin films with and without (W/O) protonic acids treatment.