High Work Function with Reduced Phase Separation of PSS in Metal Oxide Modified PEDOT:PSS Interlayers for Organic Photovoltaic

Anil Kanwat, and Jin Jang*

Department of information Display, Advanced Display Research Center (ADRC), Kyung Hee University, Dongdaemun-ku, Seoul 130-171, South Korea

E-mail: jjang@khu.ac.kr

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(a) Fabrication of Organic Photovoltaics

Seven different HTLs, PEDOT:PSS (PP), PP:WO_x (20:1, 10:1, 1:1, 1:3), PP:VO_x(1:1), and $PP:NiO_x$ (5:1), were utilized to make regular OPVs for three different bulk heterojunctions, PTB7 : PC₇₀BM, PBDT-TTT:EFT : PC₇₀BM, and P3HT IC₆₀BA. The regular geometry has the structure, ITO / HTL_i / BHJ_i / LiF / Al, where, i represents the seven different HTLs and j represents three different bulk heterojunctions. In the similar fashion, 7 different HTLs were used in the inverted OPVs utilizing P3HT IC₆₀BA BHJ of a structure, ITO / LZO / P3HT:IC₆₀BA / HTL_i / Al. The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol. The pre-cleaned ITO substrate was treated in an ultraviolet-ozone chamber for 15 min. PEDOT:PSS and/or metal oxide mixed PEDOT:PSS aqueous solutions were spin-coated at 4000 rpm for 25 s on the ITO in a regular OPVs and on BHJ in the inverted OPVs. PEDOT: PSS mixture with metal oxide thin films has thickness of 40, 28, 36, 34 nm for PEDOT:PSS (PP), PP:WO_x, PP:VO_x, and PP:NiO_x respectively. The metal oxide doped PEDOT:PSS thin films were baked at 130 °C for 20 min in a glove box. For photoactive layers, PTB7:PC₇₀BM, PBDT-TTT:EFT : PC₇₀BM, and P3HT IC₆₀BA solutions were prepared in the 1,2-dichlorobenzene solvent of w/w of 1:1.5, 1:1.5, and 1:1 respectively. Only P3HT and fullerene derivative (IC₆₀BA) films were annealed at 130 °C for 20 in the glove box, other two films were keep it for one hour to dry in a glove box. All the three layers have optimized thickness of ~ 100 nm. In the inverted OPVs, lithium zinc oxide (LZO) cathode buffer layer was spin-coated at 700 rpm for 25 s on the ITO electrode. Then, P3HT and a fullerene derivative (IC₆₀BA) (1:1 w/w) were coated on the LZO thin film for 25 s, then baked at 130 °C for 30 min. Subsequently, metal oxide doped

PEDOT:PSS were coated on BHJ and annealed in air at 120 °C for 20 min. Finally, the substrate was transferred to a vacuum chamber and 100 nm of Al were thermally deposited on the photoactive layer under a base pressure of 1 x 10^{-7} Torr. The active area of the device was 0.04 cm².

(b) Raman phase imaging of pristine PEDOT:PSS and after metal oxide mixture.



Fig. S1. Raman phase mapping of PEDOT:PSS (a,b,c,d), PEDOT:PSS:WOx (e,f,g,h), PEDOT:PSS:VOx (i,j,k,l) and PEDOT:PSS:NiOx (m,n,o,p) at for different peak intensity. The first column (a,e,i,m) depicts the C α -C α band in pristine PEDOT and after metal oxide injection, followed by C $_{\beta}$ -C $_{\beta}$ band phase (b,f,i,n), and asymmetric peak of C α =C $_{\beta}$ phase (e,g,k,o and d,h,l,p).

(c) AFM images of (a) neat PEDOT:PSS, PEDOT:PSS doped (b) WO_x, (c) VO_x, and (d) NiO_x.



Fig S2. (a) AFM topography images of metal oxide doped PEDOT:PSS thin films; (a) PEDOT:PSS and metal oxide doped (b) WO_x , (c) VO_x , and (d) NiO_x thin films.

The roughness values of PEDOT:PSS is 2.08 nm. After WO_x , VO_x and NiO_x oxide doping roughness slightly decreases to 1.70, 1.74 and 1.95 respectively. PSS in PEDOT:PSS is presented in PSS-Na⁺, PSS-H⁺ or PSS-PEDOT⁺. PSS-H, or PSS-Na chains are neutral and do not have any Columbic interaction. In our previous study on time of flight-secondary ion electron mass spectroscopy (TOF-SIMS) shows that WO_x are presents in negative ions.^[1] Therefore, some of PSS⁻ ions are replaced with MO⁻ ions as the counter anions for PEDOT are possible. This implies that that phase separation occurs between the hydrophilic PSS-H, PSS-Na and hydrophobic PEDOT chains. Moreover, the replacement of PSS⁻ with MO⁻ can result in the conformational change of the conjugated PEDOT chains. PEDOT has a coil conformation, the coil conformation causes the localization of the positive charges on the PEDOT chains. As a results of positive charge localization there is a Columbic repulsion between PEDOT and PSS-H/PSS-Na and thus induce the conformational change of PEDOT. (d) XPS full scan binding spectra of metal oxide doped PEDOT:PSS thin films, and individual XPS spectra of (b) WO_x, (c) VO_x, and (d) NiO_x.



Fig S3. (a) XPS full scan binding spectra of metal oxide doped PEDOT:PSS thin films, and XPS binding energy of (b) WO_x, (c) VO_x, and (d) NiO_x in PEDOT:PSS incorporated thin films.

We report the XPS binding energy of WO_x , VO_x , and NiO_x . The WO_x , VO_x , and NiO_x peaks are in doublet as we can see in Fig. S4(b,c,d). W4f peaks can be noted at 34.6/36.7 and 35.5/37.1 eV. V2p peaks found to be at 517.9 and 524.7 eV. The peaks of NiO_x are in doublet Ni2p(3/2,1/2)and occurred at 882.3/875.6 and 862.4/857.3 eV respectively. (e) XPS binding energy spectra for C1s, O1s, S2p, and Na1s in neat PEDOT:PSS and after metal oxide mixture.



Fig. S4. XPS binding energy for (a) C1s, (b) O1s, (c) S2p, and (d) Na1s in metal oxide (WO_x, VO_x , NiO_x) incorporated PEDOT:PSS thin films. Thin films were coated on the glass substrate.

The XPS peak intensity and binding energy shift indicates the modification of chemical bonds in presence of metal oxide in PEDOT:PSS thin films. C1s occurred in doublets and O1s, S2p, Na1s are found less intensity after WO_x incorporation. The binding energy shifts have been demonstrated in next Fig. S3. The high intensity S2p peak at high binding energy and low intensity S2p peak at low binding energy observed on surface of pristine PEDOT:PSS and metal oxide doped PEDOT:PSS thin films The high intensity S2p peak at high binding energy and low intensity S2p peak at low binding energy observed on surface of pristine PEDOT:PSS and metal oxide doped PEDOT:PSS thin films. For Sulphur only in Fig. S3 (c), the higher binding energy component with the S(2p3/2) peak at 168.8 \pm 0.2 and 168.4 \pm eV is associated with PSSH and PSSNa respectively. The lower binding energy S2p peak at 164 \pm 0.2 eV indicates the presence of PEDOT⁺. Therefore, high intensity S2p (PSS) indicates the presence of PSS on the interface. We further elaborate the XPS peak intensity via sputtering though depth profile binding energy spectra in Fig. S5.

(f) XPS elemental composition of C1s, O1s, S2p, Na1s and wt. % of metal oxide in PEDOT:PSS : metal oxide mixture.

Table S1: XPS elemental composition of C1s, O1s, S2p, and Na1s and metal oxide wt. % in a neat PEDOT:PSS and metal oxide PEDOT:PSS mixture.

	РР	PP:WOx	PP:VOx	PP:NiOx
C1s	69.9	63.7	68.9	65.3
Ols	19.7	26.9	16.6	27.6
S2p	8.60	5.72	6.77	5.45
Nals	1.45	1.14	1.46	1.28
W4f	-	1.11	-	-
V2p	-	-	4.99	-
Ni2p	-	-	-	2.46

PEDOT:PSS has no doping element initially shows initial concentration of present elements in black column. Elements concentration (C, O, S, Na) altered after metal oxide mixture are marked in red (WO_x), blue (VO_x) and green (NiO_x). The histogram on the right side depicts the metal oxide concentrations, of 0 (PEDOT:PSS), 1.11% (PEDOT:PSS:WO_x), 4.99 (PEDOT:PSS:VO_x), and 0.42 (PEDOT:PSS:NiO_x) in weight%.



(g) Deconvolution of S2p (PEDOT and PSS) with and w/o metal oxide mixture.

Figure S5. S2p binding energy of PEDOT:PSS and metal oxide doped PEDOT:PSS, including Gaussian fit (red). a-d depicts S2p in PSS and e-f shows S2p in PEDOT.



(h) XPS depth profile of PEDOT:PSS and PEDOT:PSS:WO_x thin films.

Fig. S6. XPS depth profile for PEDOT:PSS and PEDOT:PSS:WO_x mixture films for (a,e) C1s,
(b, f) O1s, (c,g) S2p, (d,h) Na1s and (i) W4f.

Neat PEDOT:PSS and after WO_x mixture (1:1) thin films coated on bare glass, characterized by XPS. Chemical binding energy of C1s, O1s, S2p, Na1s and W4f at the interface and after 10nm of sputtering reveals reduction in C1s, O1sm S2p, and Na1s chemical intensity. The optimized thickness of PEDOT:PSS and thin films were 40nm and 28 nm respectively. The surprising

increment in O1s peak intensity at 45nm (PEDOT:PSS), and 30nm (PEDOT:PSS:WO_x) contribute O1s from the ITO. Interesting observation is the presence of C1s, Na1s specifically S2p in neat PEDOT:PSS films coated on ITO, diffused in ITO. Along with that, C1s, Na1s and S2p after WO_x mixture are less intensive in comparison to neat PEDOT:PSS but WO_x itself diffuse in ITO (Fig.S5i).

As it is mentioned before in Fig. S3, and here, it is very much visible in Fig S5 (c&g) that the PSS (S2p) signal dominated at the top interface (BHJ side) of the interlayers where PEDOT (S2p) has very low intensity. But, XPS sputtering from the top interface (BHJ side) to the bottom interface (ITO side), it reveals that in the bulk of PEDOT:PSS after 10nm sputtering, the 'S2p' peak for PSS and PEDOT interchanges. Thus, it could be said that the insulating PSS dominate between BHJ and PEDOT after phase separation.

(i) UPS full scan spectra of neat PEDOT:PSS and after metal oxide mixture.



Fig. S7. UPS full scan spectra of neat PEDOT:PSS and after metal oxide mixture, WO_x mixture (10:1, 1:1) and optimized wt.% of VO_x and NiO_x has depicted. ITO, of having work function of 4.52, were used for the reference. Work function calculated from the high binding energy of the UPS spectra and, HOMO and E_F shift measured from the low binding energy UPS spectra has been elaborated in the main text (Fig. 4, Table 1).



(j) Cyclic voltammetry of neat PEDOT:PSS and after metal oxide mixture.

Fig. S8. (a) Cyclic voltammetry of PEDOT:PSS and WO_x : PEDOT:PSS mixture. Interpretation of current-voltage plots to find the exact HOMO level in PEDOT:PSS and PEDOT:PSS:WO_x (1:1) films. (c) HOMO level shift with WOx doping in PEDOT:PSS.





Fig. S9. Current - voltage characteristics of the following geometry, ITO/HTL/Al. In HTL, (a) WO_x mixture with PEDOT:PSS and (b) optimized WO_x , VO_x , and NiO_x concentration in PEDOT:PSS.



Fig. S10. External quantum efficiency of regular OPVs of pristine PEDOT:PSS device and after WO_x mixture in the following ratio, 20:1, 10:1, 1:1, and 1:3. WO_x mixed PEDOT:PSS was examined through three different active layers, (a) PTB7:PC₇₀BM, (b) PBDTTT-EFT:PC₇₀BM, (c) P3HT:IC₆₀BA in a regular OPV. EQE of the regular OPVs with (d) pristine PEDOT:PSS hole transport materials and optimized metal oxides (WO_x , VO_x , and NiO_x) doped PEDOT:PSS interlayers utilizing P3HT:IC₆₀BA as the active layer.

(m) Leakage currents density, J_L, utilizing PTB7:PC₇₀BM, PBDTTT:EFT:PC₇₀BM, and P3HT:IC₆₀BA BHJ.

Table S2. Leakage currents density, J_L , utilizing PTB7:PC₇₀BM, PBDTTT:EFT:PC₇₀BM, and P3HT:IC₆₀BA bulk heterojunctions with neat PEDOT:PSS (PP) and metal oxide doped PEDOT:PSS hole transport interlayers. WOx doping concentration is varied as PEDOT:PSS:WOx, 1:0, 20:1, 10:1, 1:1 and 1:3.

J _L (mA/cm ²)*10 ⁻⁴	1:0 (PP)	20:1	10:1	1:1	1:3	PP:VO _x	PP:NiO _x
BHJ1	2.91	0.86	0.77	0.43	0.17		
BHJ2	4.00	3.56	0.90	0.54	2.26		
BHJ3	4.66	2.44	1.23	0.96	8.37	2.19	1.97

(n) Power conversion efficiency table of regular geometry, utilizing PTB7:PC₇₀BM, PBDTTT:EFT:PC₇₀BM, and P3HT:IC₆₀BA BHJ.

Table S3: Power conversion efficiency (PCE) of regular geometry OPVs under light illumination, utilizing PTB7:PC₇₀BM, PBDTTT:EFT:PC₇₀BM, and P3HT:IC₆₀BA BHJ. Voc, Jsc, and FF depict open circuit voltage short current density, and fill factor, respectively.

J-V	V _{oc} (mV)	J _{sc} (mA/cm2)	FF(%)	PCE(%)		
PTB7:PC ₇₀ BM						
(PP:WOx) 1 : 0	745	15.24	56.80	6.45		
20:1	744	15.52	61.25	7.08		
10:1	746	15.23	62.63	7.11		
1:1	751	15.46	62.86	7.30		
1:3	746	15.32	59.39	6.79		
PBDTTT:EFT:PC ₇₀ BM						
(PP:WOx) 1 : 0	790	13.51	57.33	6.12		
20:1	788	13.66	61.54	6.63		
10:1	805	13.45	62.86	6.81		
1:1	806	13.70	63.09	6.97		
1:3	765	13.81	60.46	6.34		
P3HT:IC _{co} BA						
1:0 (PP:WOx)	844	8.28	53.55	3.75		
20:1	839	8.97	54.82	4.12		
10:1	839	8.97	56.51	4.24		
1:1	844	8.89	57.89	4.35		
1:3	837	8.46	52.26	3.70		
PP:VO _x	839	9.28	53.78	4.18		
PP:NiO _x	855	8.57	57.79	4.19		