Electronic supplementary information (*ESI*)

ZnO as effective hole transport layer for water resistant organic solar cells

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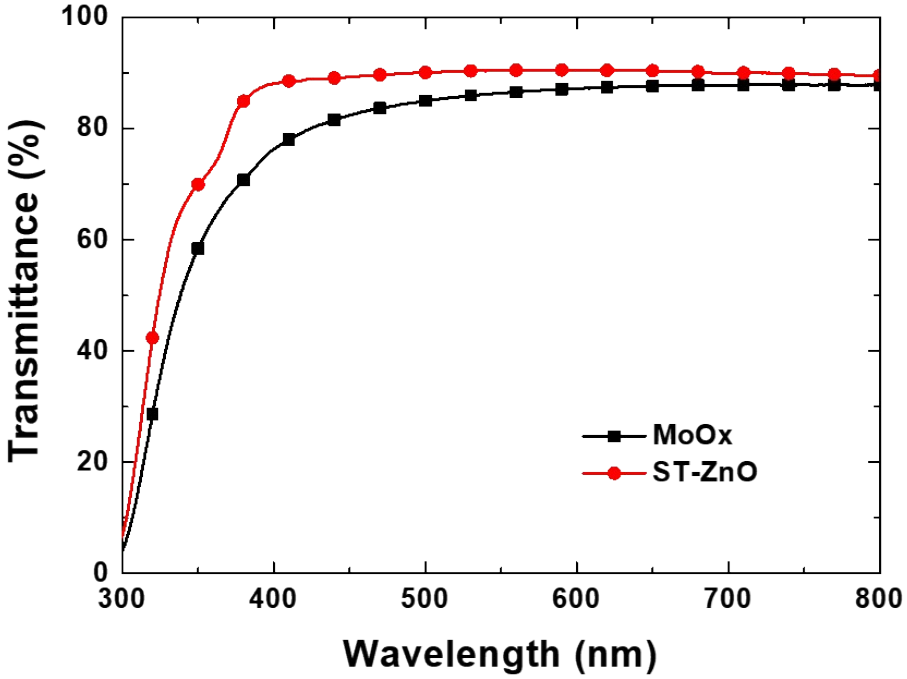


Figure S1: Optical transmission of the MoO_x and ST-ZnO layers with the same thickness.

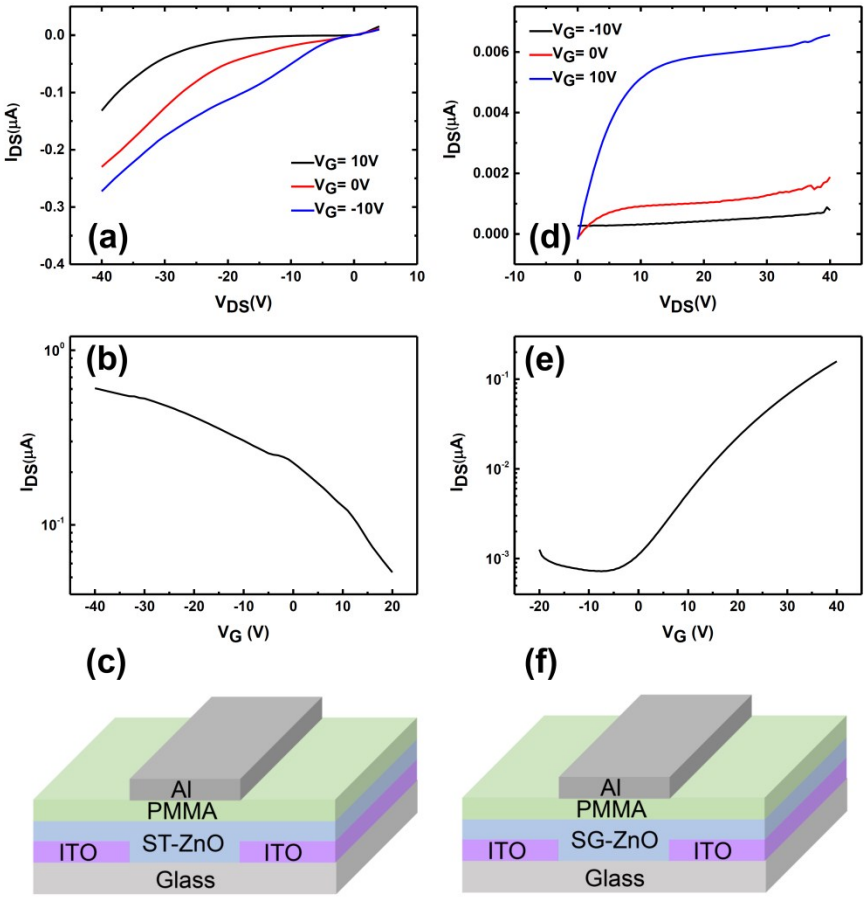


Figure S2: Output characteristics of p-type-like ST-ZnO (a, b) and n-type SG-ZnO (d, e), including the I_{DS} vs V_{DS} (a, d) and I_{DS} vs V_G (b, e) plots, along with the corresponding TFT device structures (c and f). The thicknesses of the ST-ZnO and SG-ZnO layers were 15 nm and 30 nm, respectively, to mimic the thicknesses used in the OSC devices.

Table S1: Charge mobilities of SG-ZnO and ST-ZnO calculated from the TFT output characteristics

	I_{DS} (A) (V_G= 0V)	I_{DS} (A) (V_G=40V)	Mobility (cm^2/Vs)
SG-ZnO	**1.11E-09**	**1.58E-07**	**2.95E-03**
***ST-ZnO**	**2.27E-07**	**6.06E-07**	**4.57E-04**

*These values should only be considered as reference ones, due to the imperfection of the respective TFT device

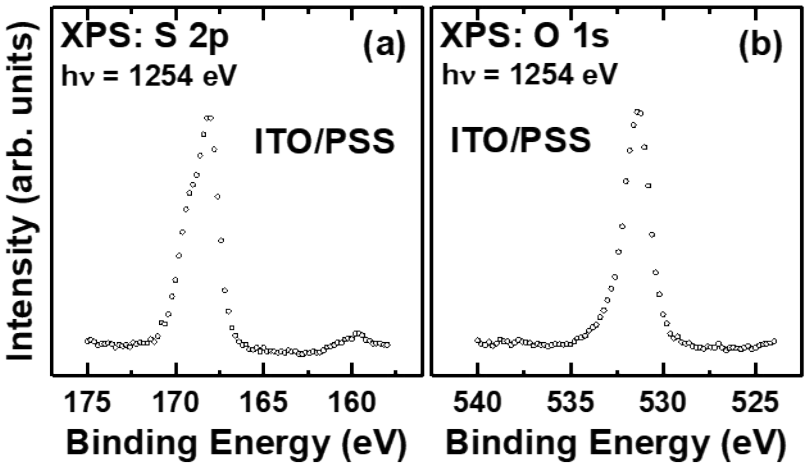


Figure S3: S 2p (a) and O 1s (b) XPS spectra of ITO/PSS

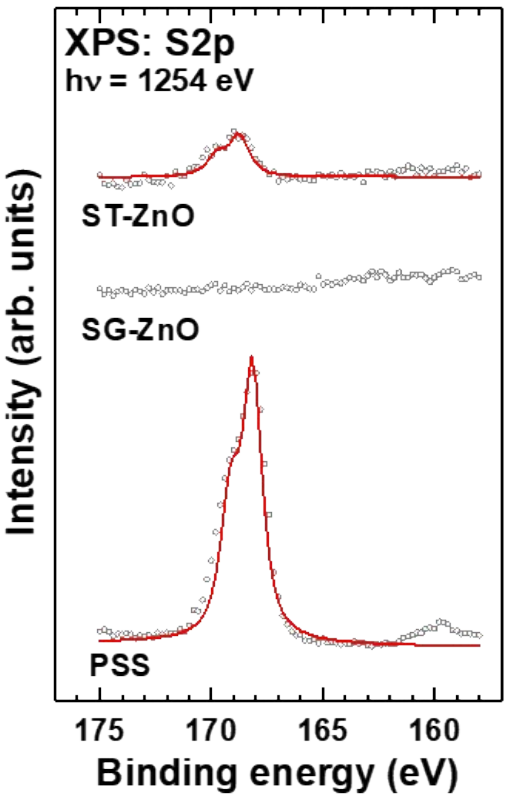
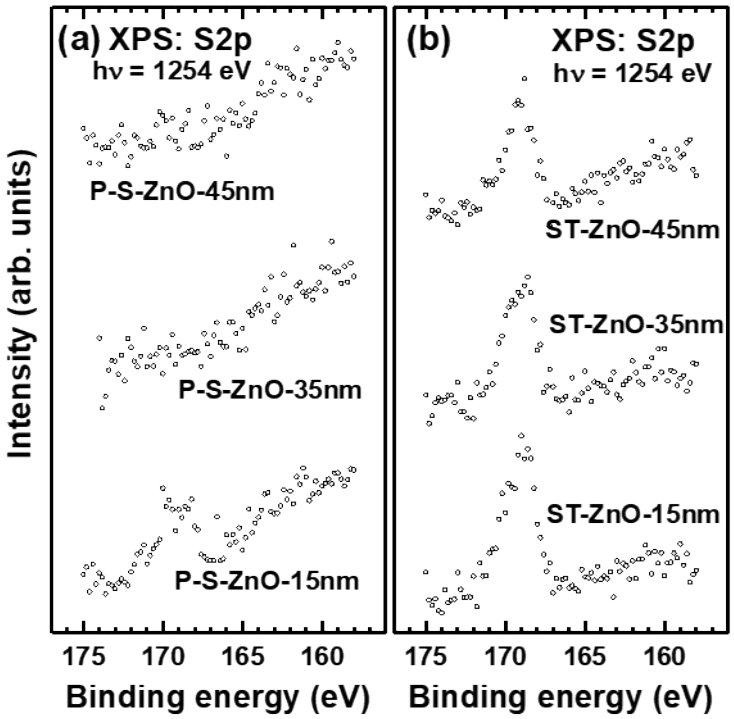
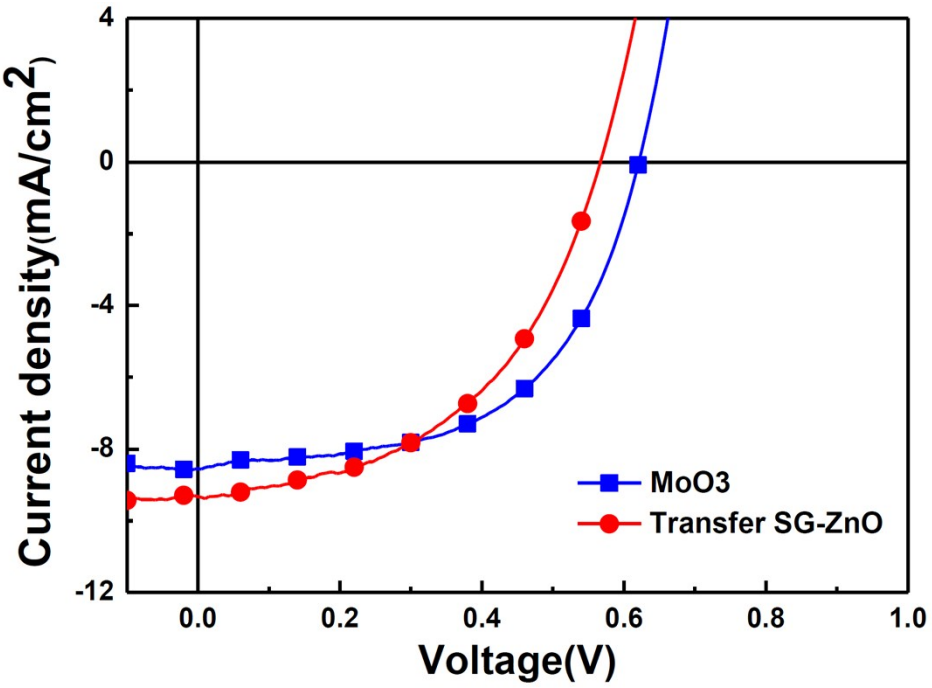


Figure S4: S 2p XPS spectra of ST-ZnO, SG-ZnO and PSS (reference).



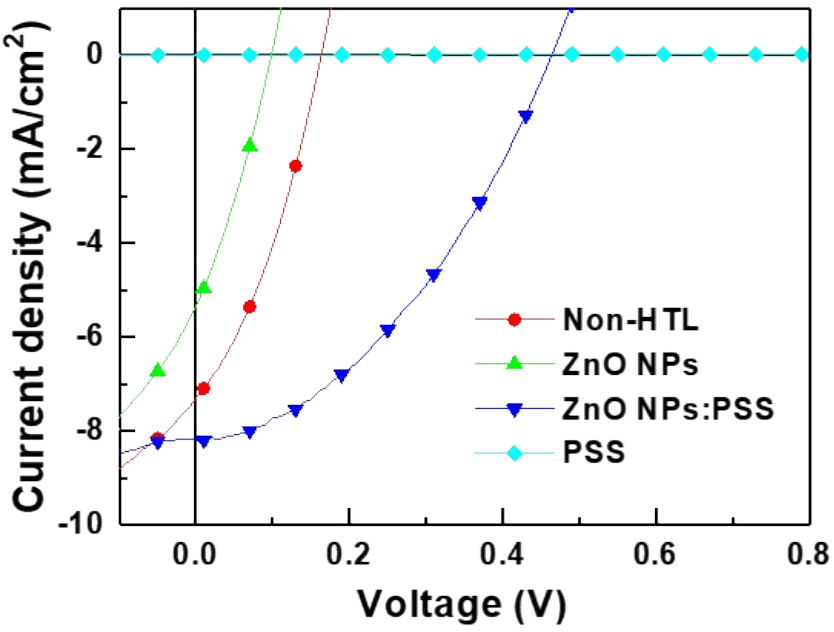
Before transfer			After transfer		
Sample	Structure	ZnO(nm)	Sample	Structure	ZnO (nm)
Spray-ZnO-45nm	ITO/PSS/Spray-ZnO	45	ST-ZnO-45nm	ITO/Spray-Transfer-ZnO	45
Spray-ZnO-35nm	ITO/PSS/Spray-ZnO	35	ST-ZnO-35nm	ITO/Spray-Transfer-ZnO	35
Spray-ZnO-15nm	ITO/PSS/Spray-ZnO	15	ST-ZnO-15nm	ITO/Spray-Transfer-ZnO	15

Figure S5: S 2p XPS spectra of sprayed ZnO on the PSS surface (before the transfer) and ST-ZnO (after the transfer to another ITO substrate and dissolving of the PSS layer). Note that the thickness of all the films exceeded the sampling depth of XPS at the given kinetic energy (~8 nm), so that the spectra are exclusively representative of the ZnO films.



HTL	Jsc (mA)	Voc (V)	η (%)	FF (%)
MoO3	8.55	0.61	2.92	55.00
Transfer SG-ZnO	9.41	0.55	2.48	48.02

Figure S6 and Table S1: I-V characteristics and parameters of OSCs with MoO_x and PSS-transferred SG-ZnO as HTLs. The legend is given in the plot.



HTL	Jsc (mA)	Voc (V)	η (%)	FF (%)
Non-HTL	7.29	0.16	0.41	34.18
ZnO NPs	5.35	0.10	0.15	29.28
ZnO NPs:PSS	8.20	0.46	1.48	39.00
PSS	0.01	0.31	0.00	25.61

Figure S7 and Table S2: I-V characteristics and parameters of OSCs without HTL (non-HTL), PSS as HTL, and with HTL based on non-doped and PSS-doped ZnO NPs. The legend is given in the plot.

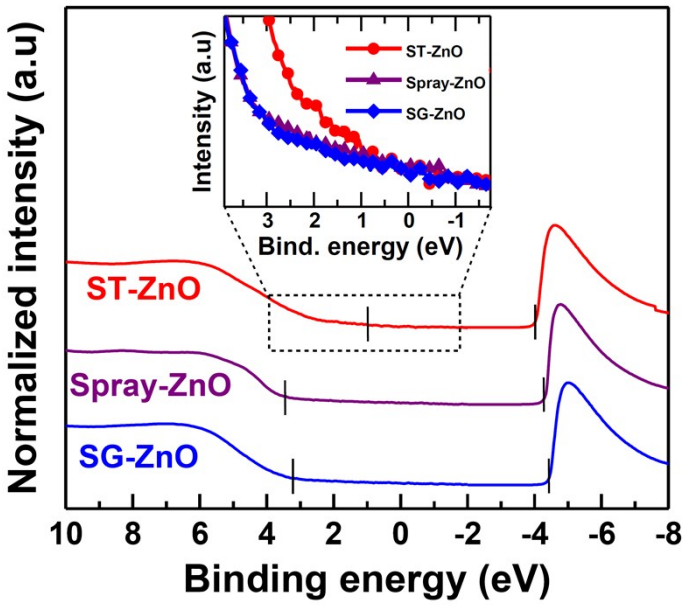
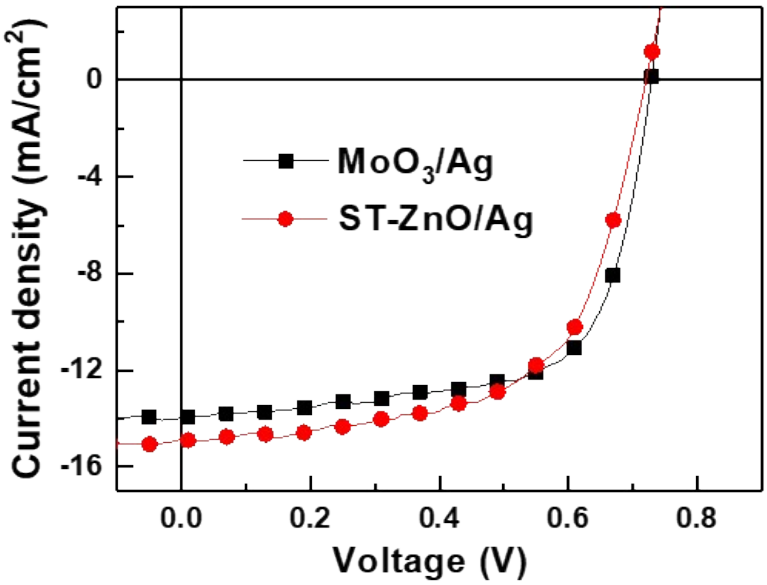


Figure S8: UPS spectra of SG-ZnO, S-ZnO, and ST-ZnO, including the cutoff region. Inset: The region close to the Fermi energy. The VBM offset and UPS cutoff are shown by the vertical solid lines. The selection of the VBM offset for ST-ZnO is additionally visualized in the inset.

Table S3: Work function (WF), absorption onset (λ_{abs}), band gap (E_g), VBM offset (ΔE_H), and respective VBM (E_{VBM}) and CBM (E_{CBM}) calculated from WF, ΔE_H, λ_{abs}, and E_g for SG-ZnO, S-ZnO, and ST- ZnO.

	WF (eV)	ΔE_H (eV)	E_{VBM}(eV)	λ_{abs} (nm)	E_g (eV)	E_{CBM} (eV)
SG-ZnO	-4.44	-3.17	-7.61	375	3.31	-4.30
Spray-ZnO	-4.29	-3.38	-7.67	391	3.17	-4.50
ST-ZnO	-4.07	-1.01	-5.08	398	3.12	-1.96



HTL	Jsc (mA/cm^2)	Voc (V)	FF (%)	η (%)
MoO_3/Ag	13.97	0.73	66.97	6.82
ST-ZnO/Ag	14.86	0.72	60.90	6.53

Figure S9/Table S4: Illustration of versatility of the spray-transfer process. IV characteristics of model OSCs fabricated using a low band gap chromophore PffBT4T-2OD as the active layer. The OSCs were prepared without HTL (non-HTL) and with MoOx and ST-ZnO. The legend is given in the plot.

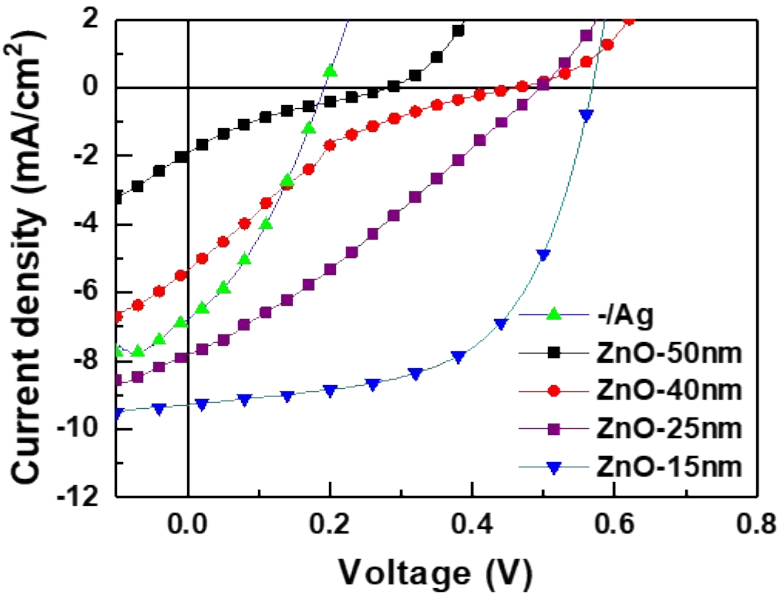


Figure S10: I-V characteristics of model OSC devices with ST-ZnO HTL of different thickness (15, 25, 40, and 50 nm). The performance of the OSCs worsens with increasing ST-ZnO thickness, which suggests that a thick ST-ZnO layer loses its ability to act as a good HTL becoming similar to conventional ZnO. The legend is given in the figure.

Video S1: Video showing water dipping test of model OSCs with ST-ZnO and MoO_x HTL.