Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

High-efficiency polymer solar cells employing solution-processible and thickness-independent gallium-doped zinc oxide nanoparticles as a cathode buffer layer

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Table S1. The final Ga/Zn molar ratio with different initial molar ratio of Ga/Zn atom. (detection with ICP-AES)

	Ga^{3+} in ZnO	**Ga^{3+} in ZnO:Ga**	**Ga^{3+} in ZnO**	**Ga^{3+} in ZnO:Ga**	**Ga^{3+} in ZnO:Ga**
Initial ratio	0%	0.5%	1%	3%	5%
Ink	0%	0.31%	0.51%	1.43%	2.48%

Initial ratio: atomic amount ratio in the initial methanol solution

Ink: the atomic amount ratio in the resultant products

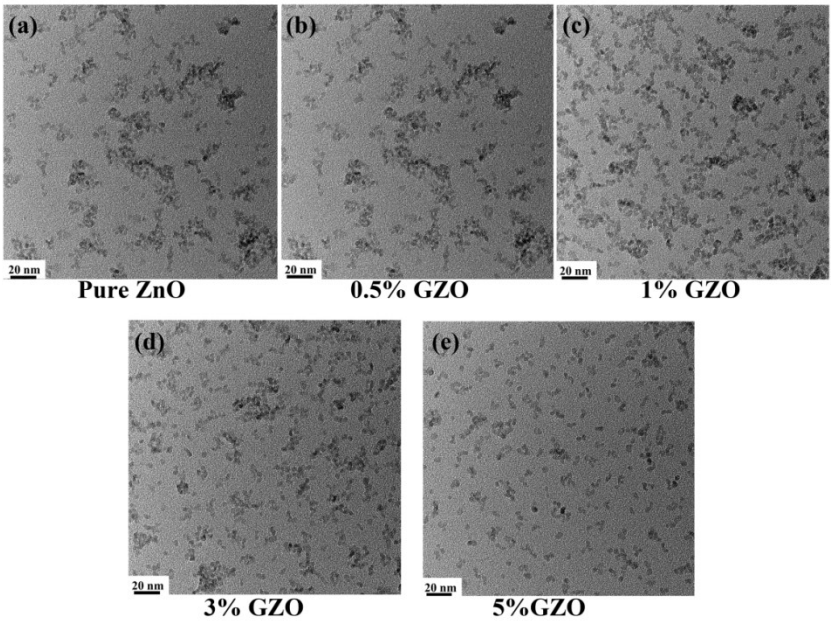

Figure S1. The TEM images of as-prepared pure ZnO NPs and a series of GZO NPs.

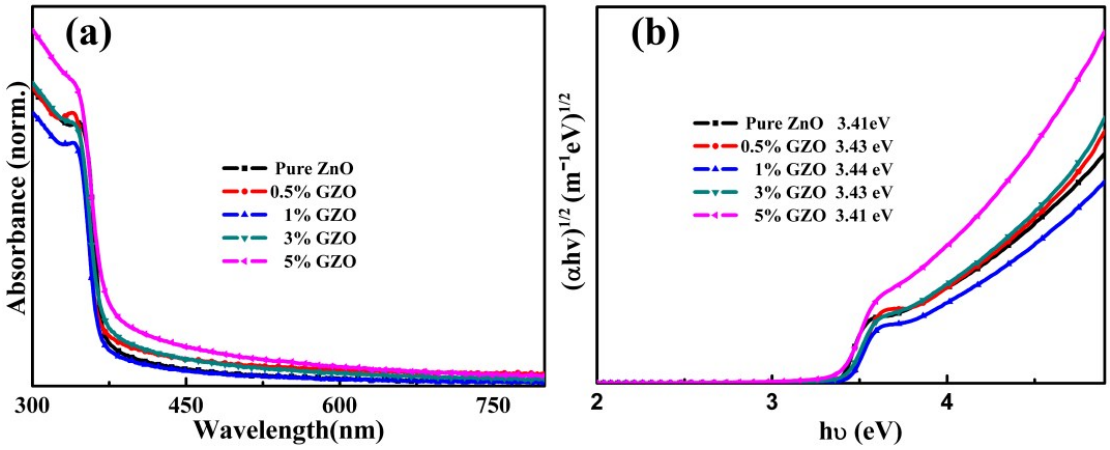

Figure S2. (a) UV-visible absorption spectra of the as-prepared pure ZnO and a series of GZO films. (b) $(\alpha hv)^{1/2}$ verse photon energy (hv) for as-prepared pure ZnO and a series of GZO films. E_g were extracted from corresponding data.

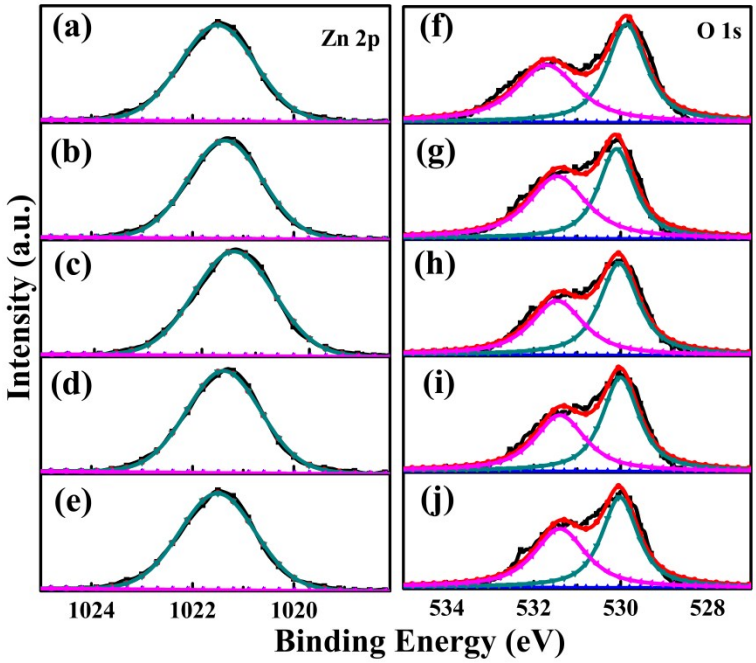

Figure S3. The survey XPS spectra of as-prepared pure ZnO and a series of GZO NPs films. Left panel: Zn $2p_{3/2}$ spectra, (a) pure ZnO, (b) 0.5% GZO, (c) 1% GZO, (d) 3% GZO, (e) 5% GZO. Right panel: O *1s* spectra , (f) pure ZnO, (g) 0.5% GZO, (h) 1% GZO, (i) 3% GZO, (j) 5% GZO.

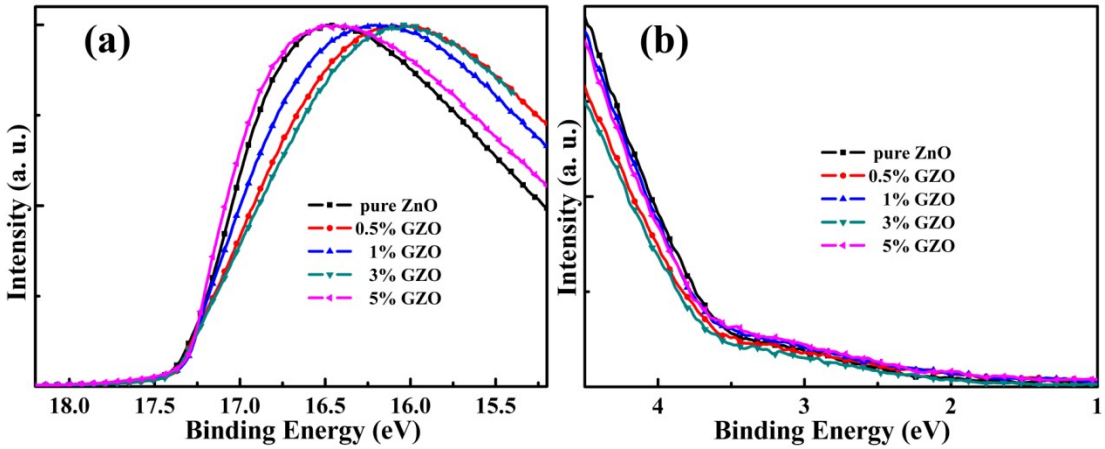

Figure S4. UPS spectra of the pure ZnO and a series of GZO films：(a) secondary electron cut-off region, (b) density of states near the VB edge.

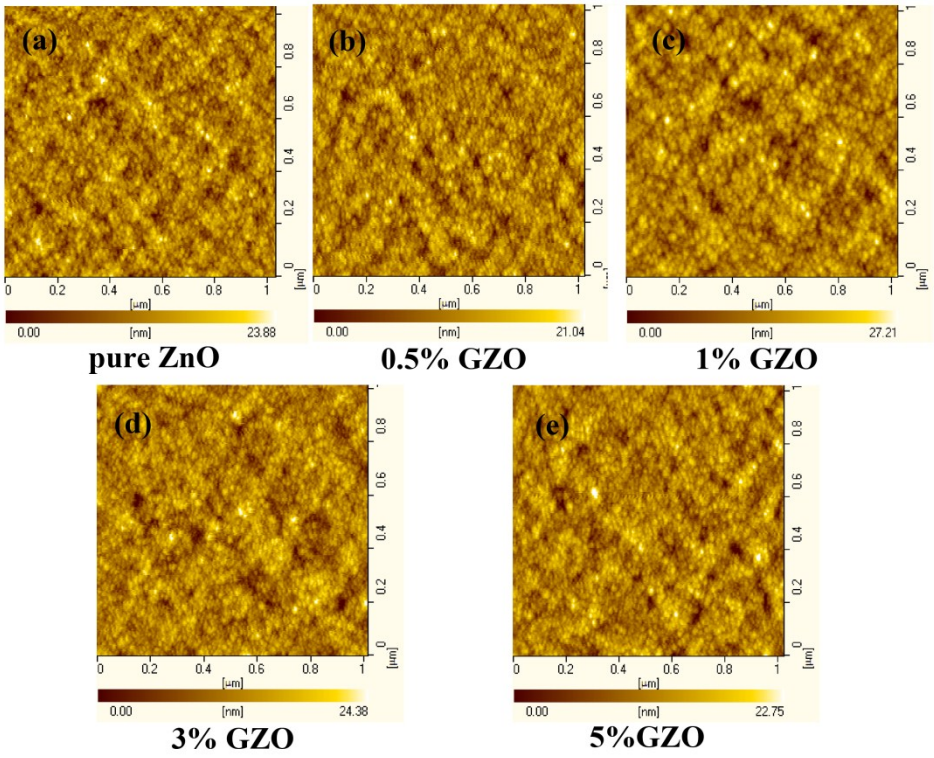

Figure S5. AFM images of the as-prepared pure ZnO NPs and a series of GZO NPs films.

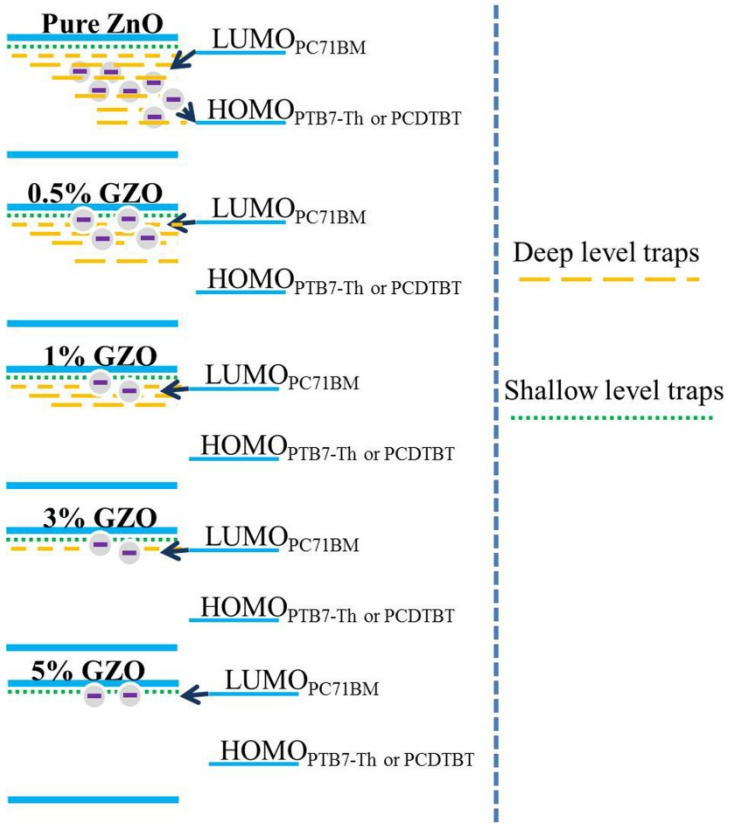

Figure S6. Illustration of surface trap distribution in pure ZnO and a series of GZO NPs films and enhanced charge extraction at the interfaces.

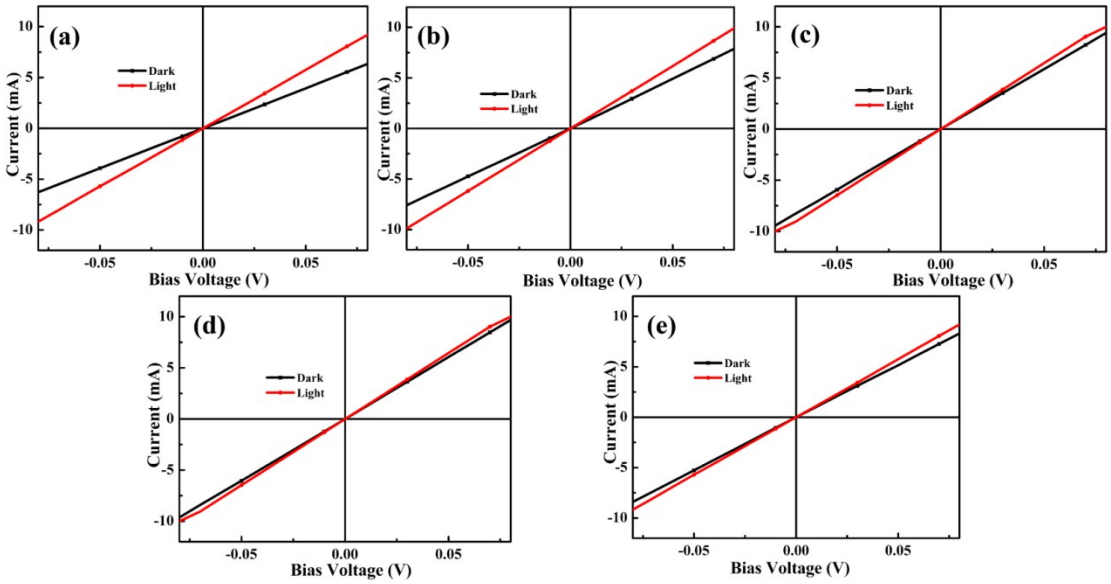

Figure S7. *I-V* curves of the electron-only transfer devices under dark and illuminated conditions. (a) pure ZnO, (b) 0.5% GZO, (c) 1% GZO, (d) 3% GZO, (e) 5% GZO.

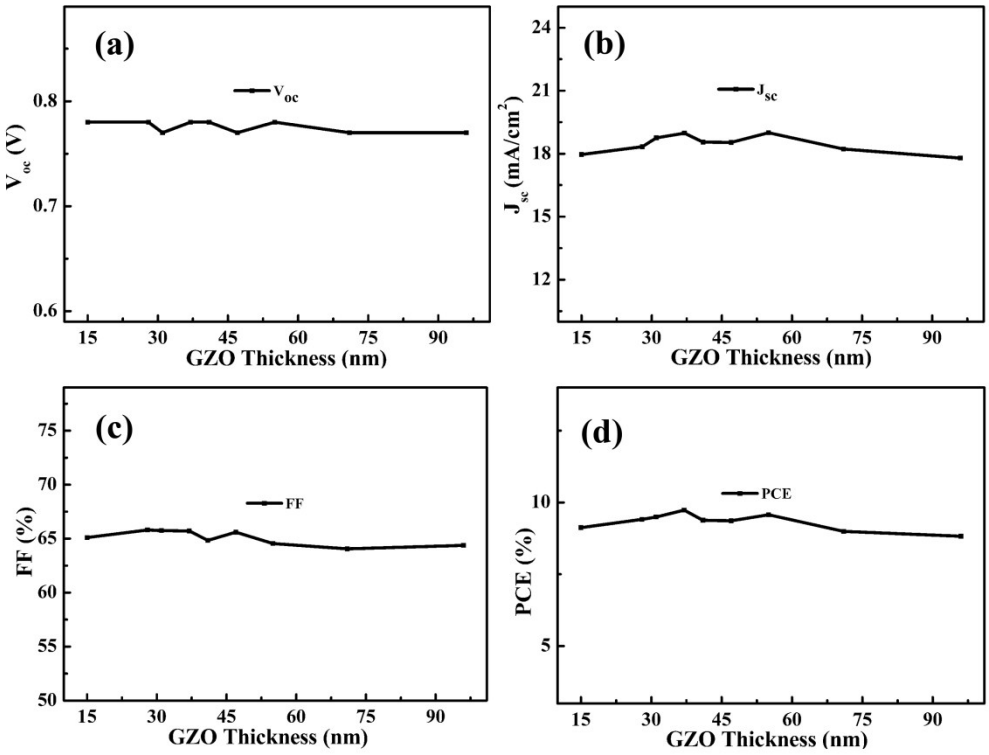

Figure S8. Device parameters of the PTB7-Th:$PC_{71}BM$ PSCs employing 3% GZO buffer layer with its thickness varying from 15 nm to 96 nm. (a) V_{OC}, (b) J_{SC}, (c) FF, and (d) PCE.

Table S2. Summarized photovoltaic parameters of the PCDTBT:$PC_{71}BM$ PSCs with pure ZnO or a series of GZO interfacial layers.

PCDTBT:$P_{71}CBM$	V_{OC} (V)	J_{SC} (mA cm^{-2})		FF (%)	PCE (%)	
		Measured	Calculated		Measured	Calculated
Pure ZnO	0.90	13.05	12.79	54.27	6.37	6.25
0.5% GZO	0.91	13.49	13.25	59.20	7.27	7.14
1% GZO	0.90	13.56	13.33	59.47	7.26	7.13
3% GZO	0.91	13.68	13.42	58.93	7.34	7.20
5% GZO	0.91	13.62	13.38	59.20	7.33	7.21