Electronic Supplementary Information

Crystallinity-modulated hollow CeO_{2-x} nanorods as free radical scavengers for long-term photostability in organic photovoltaics

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Supplementary Tables S1 to S2

State	Peak position	CeO ₂ NP		CeO _{2-x} S-hNR		CeO _{2-x} P-hNR	
		FWHM	Area	FWHM	Area	FWHM	Area
Ce ³⁺	v ⁰ (880.9 eV)	3.9	8.3%	2.6	4.0%	2.9	6.7%
	u ⁰ (899.1 eV)	3.0	6.6%	2.7	4.3%	2.1	3.3%
	v' (885.2 eV)	3.1	7.8%	2.4	6.7%	3.7	11.6%
	u' (903.4 eV)	3.1	2.8%	4.8	7.0%	4.9	6.3%
Ce ⁴⁺	v (882.7 eV)	2.8	16.4%	2.5	18.9%	2.8	16.1%
	u (901.3 eV)	2.4	7.5%	2.4	9.8%	2.8	9.3%
	v" (888.5 eV)	4.0	10.5%	4.3	13.9%	4.3	10.5%
	u" (907.3 eV)	7.1	9.3%	3.5	6.4%	5.0	6.3%
	v''' (898.3 eV)	3.3	17.0%	2.7	15.7%	3.4	17.5%
	u''' (916.9 eV)	3.3	13.8%	2.8	13.4%	3.3	12.3%
Ce ³⁺ /(Ce ³⁺ + Ce ⁴⁺)		25.5%		21.9%		28.0%	

 Table S1. Deconvolution fitting parameters for Ce 3d XPS spectra

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Device Condition	V _{oc} [V]	J _{SC} [mA cm ⁻²]	Int. <i>J_{SC}</i> [mA cm ⁻²]	FF [%]	PCE [%]
ZnO	0.837 (0.836 ± 0.002)	$24.47 \\ (24.18 \pm 0.42)$	23.49	$73.49 (73.55 \pm 0.98)$	$15.05 \\ (14.73 \pm 0.42)$
ZnO/NP	$\begin{array}{c} 0.835 \\ (0.836 \pm 0.002) \end{array}$	$24.54 \\ (24.22 \pm 0.48)$	22.98	$74.12 (73.38 \pm 1.24)$	$15.19 \\ (14.76 \pm 0.35)$
ZnO/S-hNR	$\begin{array}{c} 0.836 \\ (0.835 \pm 0.002) \end{array}$	$24.39 \\ (24.08 \pm 0.45)$	23.84	$74.24 \\ (73.41 \pm 1.05)$	$15.14 \\ (14.77 \pm 0.44)$
ZnO/P-hNR	$0.836 \\ (0.836 \pm 0.002)$	$24.50 \\ (24.23 \pm 0.55)$	22.99	$73.55 (73.25 \pm 0.82)$	$15.06 \\ (14.80 \pm 0.29)$

Table S2. Photovoltaic parameters of OPV cells with various types of CeO₂-based interfacial layers showed in Figure 4b. Int. J_{SC} indicates the J_{SC} values calculated from external quantum efficiency (EQE) spectra. The average and standard deviation values of each photovoltaic parameter in parentheses were obtained from 10 independent OPV devices.

Supplementary Figures S1 to S9



Figure S1. (a) Transmission electron microscope (TEM) image of CeO_{2-x} nanorods (NRs). (b) Size distribution histograms on the length and diameter of the CeO_{2-x} NRs measured from the TEM image.



Figure S2. (a) TEM image of CeO_{2-x} S-hNR. (b) Size distribution histograms on the length and diameter of the CeO_{2-x} S-hNRs measured from the TEM image. (c) TEM image of CeO_{2-x} P-hNR. (d) Size distribution histograms on the length and diameter of the CeO_{2-x} P-hNRs measured from the TEM image.



Figure S3. (a) TEM image of commercial CeO_2 NPs (Aldrich). (b) Size distribution histogram of CeO_2 NPs measured from the TEM image.



Figure S4. N₂-isotherm curves of CeO_{2-x} NR (Figure S1), S-hNR (Figure 1a), and P-hNR (Figure 1c) and the calculated BET surface area of the samples (inset).



Figure S5. Radical scavenging activity of the CeO_{2} based radical scavengers. Change in UVvisible absorption spectra of the aqueous solution containing MV dye, H_2O_2 , $FeSO_4$, and radical scavenger dispersion over 90 min: (a) Without CeO_{2-x} , (b) commercial CeO_2 NP, (c) CeO_{2-x} ShNR, and (d) CeO_{2-x} P-hNR. The change in the intensity maximum absorption peak at 575 nm was used to evaluate the hydroxyl radical scavenging activity of the radical scavengers.



Figure S6. Scanning electron microscope (SEM) images of (a) $CeO_2 NP$, (b) $CeO_{2-x} S-hNR$, and (c) $CeO_{2-x} P-hNR$ on ZnO films. Lower images are magnified results from white box in the upper images and the scale bar is 20 μ m.



Figure S7. The SEM-energy dispersive spectroscopy (EDS) elemental mapping images of (a) $CeO_2 NP$, (b) $CeO_{2-x} S$ -hNR, and (c) $CeO_{2-x} P$ -hNR on ZnO films for Ce element. The scale bar is 10 μ m.



Figure S8. (a-d) The AFM topography images (top, $4 \ \mu m \times 4 \ \mu m$) and 3D images (bottom) of pristine ZnO film (a), CeO₂ NP on ZnO (b), CeO_{2-x} P-hNR on ZnO (c), and CeO₂ S-hNR on ZnO films (d).



Figure S9. The (top) AFM topography (10 μ m × 4 μ m) and (bottom) line profiles of (a) CeO₂ NP, (b) CeO_{2-x} P-hNR, and (c) CeO_{2-x} S-hNR films on ZnO layer at corresponding red solid lines. The scale bar is 2 μ m.



Figure S10. Linear *I-V* plots of ITO/ZnO/Al and ITO/ZnO/CeO_{2-x} S-hNR/Al sandwiched devices with CeO_{2-x} S-hNR layer thicknesses of 10 nm and 50 nm.



Figure S11. The evolution of *J-V* characteristics of OPVs over light soaking time: (a) ZnO-based, (b) ZnO/CeO_2 NP-based, (c) ZnO/CeO_{2-x} S-hNR-based, and (d) ZnO/CeO_{2-x} P-hNR-based.



Figure S12. The dependency of normalized (a) J_{SC} , (b) V_{OC} and (c) FF of OPV cells with various cerium oxide-based interlayers on light soaking time under 1 sun condition.



Figure S13. (a) The transmittance spectrum of a polyimide film and (b) the PCE dependence of ZnO- and ZnO/CeO_{2-x} S-hNR-based OPVs on light soaking time. Polyimide films were attached to the backside of the OPV cells to filter the UV light (inset of **Figure S13a**).



Figure S14. The time-dependent UV-visible absorption spectra of thin PM6:N3 blend films on (a) ZnO, (b) $CeO_2 NP/ZnO$, (c) CeO_{2-x} S-hNR/ZnO, and (d) CeO_{2-x} P-hNR/ZnO films under various UV exposure times.



Figure S15. The absorption spectra of pristine PM6 and N3 films.



Figure S16. Surface regeneration properties of CeO₂ NP, CeO_{2-x} S-hNR, and CeO_{2-x} P-hNR samples. (a-c) The time-dependent UV-visible absorption spectra of the aqueous dispersion (695 mM) of (a) CeO₂ NP, (b) CeO_{2-x} S-hNR, and (c) CeO_{2-x} P-hNR after injection of H₂O₂ (5 μ mol). (d) Change in absorbance wavelength at the optical density 0.30 after injection of H₂O₂, which is a marker of the catalytic activity of CeO_{2-x} nanostructures.