Electronic Supplementary information for

Redox-active Eu₂O₃ nanoflakes as buffer layer for inverted CsPbI₂Br perovskite solar cells with enhanced performance

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1. Experimental Section

*Preparation of Nano-Eu*₂*O*₃: Lamellar Eu₂O₃ (that is the precursor of Nano-Eu₂O₃) was synthesized using a previously reported hydrothermal method.¹ In a typical synthesis, 0.1 g EuCl₃ (99.9%, Aladdin) and 0.25 g NaHCO₃ were mixed in 18 mL 1,5-pentanediol (98%, Aladdin) and stirred for 30 min at room temperature. Then, the mixture was transferred into a Teflon-lined stainless-steel autoclave (25 mL), and maintained at 90 °C for 10 h. After cooling down, white participate was washed with ethanol, and underwent aging in deionized water for 24 h, followed by a vacuum drying at 50 °C overnight. The as-prepared lamellar Eu₂O₃ (20 mg) was further ball-milled in 4 mL EtOH at 500 rpm for 20 h. The obtained product (Nano-Eu₂O₃; 22 mg) was dispersed in EtOH (10 mL) under sonication and filtered with a 0.4 µm microfiltration membrane for use.

Preparation of perovskite solar cells (PeSCs): ITO glass sheet was cleaned using organic solvents,² followed by a UVO treatment for 15 min. The NiO_x HTL was deposited on an ITO substrate by spin-coating a precursor solution (EtOH) containing 0.25 mol/mL Ni(OCOCH₃)₂·4H₂O and 0.6vol% diethanolamine, followed by a thermal annealing at 325 °C for 1 h. Then, CsPbI₂Br perovskite layer was deposited on the HTL. Briefly, a DMSO precursor solution (500 μ L) containing 110 mg PbBr₂ (99.999%, Alfa Aesar), 139 mg PbI₂ (99.999%, Alfa Aesar), and 156 mg CsI (99.99%, Sigma-Aldrich) was spin-coated at 4000 rpm/45 s, followed by a two-step thermal annealing (43°C for 25 s and 160 °C for 5 min).^{3,4} Subsequently, ETL was deposited by successively spin-coating *Nano*-Eu₂O₃ solution (ca. 0.1 mg/mL in EtOH) at 4000 rpm/40 s, and chlorobenzene solution of PC₆₁BM (20 mg/mL) at 2000 rpm/40 s. Finally, EtOH solution of Bphen (0.5 mg/mL) was spin-coated at 4000 rpm/30 s, then 100 nm Ag electrodes were vacuum deposited with a shadow mask. The device area was defined as 4 mm².

The thickness of Nano-Eu₂O₃ layer can be controlled by changing the number of spin-coating times (i.e., single, double, triple and quadruple spincoating). **Figure S1** presents the J-V characteristics of the devices with Nano-Eu₂O₃ layer with various thicknesses. The extracted parameters are listed in **Table S1**. Obviously, the device with a single spun Eu₂O₃ layer outperforms others.

Physical Characterizations: Electron microscopy was measured with Hitachi instruments (SU8010 for SEM and HT7700 for TEM). High-resolution TEM (HR-TEM) image was taken with a FEI instrument (Tecnai F20). AFM was carried out using a tapping mode with Bruker instrument. The AFM sample was prepared by spin-coating the *Nano*-Eu₂O₃ solution (ca. 0.1 mg/mL in EtOH) on a SiO₂ sheet, similar to that for preparing the perovskite solar cells. X-ray diffraction (XRD) spectra were measured using a Bruker instrument (D8 Advance) with an incident irradiation of λ =0.15406 nm. UPS and XPS were carried out with a Thermo Fisher spectrometer (Escalab 250Xi) with a He irradiation (21.22 eV) and a photon irradiation of 2000 eV, respectively. Absorption spectra were obtained with a Shimadzu spectrometer (UV2600).

Photolumiscence (PL) and transient spectra were measured by an Edinburgh instrument (FLS980) with an excitation wavelength of 468-477 nm and monitored at 760 nm. Non-modulated impedance spectroscopy was performed using an electrochemical workstation (CHI 760E) at various forward biases. A 30 mV voltage perturbation was applied over a constant forward applied bias between 0.2 and 0.8 V in the frequency range between 1.0 KHz and 1.0 MHz.

References in Experimental section.

- [1] Y. Zhong, Y. Yang, Y. Ma and J. Yao, Controlled Synthesis of Ultrathin Lamellar Eu₂O₃ Nanocrystals: Self-assembly of 1D Nanowires to 2D Nanosheets, *Chem. Commun.*, 2013, 49, 10355-10357.
- [2] C. Wang, P. Liu, H. Ju, Q. Yuan, D. Han, Y. Wang, D. Y. Zhou and L. Feng, A Simple Perylene Derivative as a Solution-Processable Cathode Interlayer for Perovskite Solar Cells with Enhanced Efficiency and Stability, ACS Appl. Mater. Interfaces, 2018, 10, 15933-15942.
- [3] C. Liu, W. Li, C. Zhang, Y. Ma, J. Fan and Y. Mai, All-Inorganic CsPbI₂Br Perovskite Solar Cells with High Efficiency Exceeding 13%, *J. Am. Chem. Soc.*, 2018, 140, 3825-3828.
- [4] D. Han, Y. Xin, Q. Yuan, Q. Yang, Y. Wang, Y. Yang, S. Yi, D. Zhou, L. Feng and Y. Wang, Solution-Processed 2D Nb₂O₅(001) Nanosheets for Inverted CsPbI₂Br Perovskite Solar Cells: Interfacial and Diffusion Engineering, *Sol. RRL*, 2019, **3**, 1900091.



Figure S1. J-V curves of PeSCs prepared using Nano-Eu₂O₃ with different concentration.



Figure S2. HR-TEM image of as-prepared *Nano*-Eu₂O₃, showing the clear lattice fringe with spacing distance of 0.28 nm. The scale bar is 5 nm.



Figure S3. XRD pattern of the as-prepared *Nano*-Eu₂O₃. The peaks corresponding to the (001), (002), (003) and (004) planes are identified according to the literature (*Chem. Commun.*, 2013, *49*, 10355).



Figure S4. (a,b) AFM height images $(2 \times 2 \ \mu m^2 \text{ and } 5 \times 5 \ \mu m^2)$; (c) Line profiles corresponding to Figure (a).



Figure S5. (a) XPS survey, (b) O1s and (c) Eu 3d spectra of Nano-Eu₂O₃.



Figure S6. Tauc plot of *Nano*-Eu₂O₃ film on glass, from which the optical bandgap of *Nano*-Eu₂O₃ film can be determined to be 3.7 eV.



Figure S7. Cross sectional SEM image of the fabricated CsPbI₂Br solar cell with



inverted configuration.

Figure S8. (Left) SEM image of $ITO/NiO_x/CsPbI_2Br/Nano-Eu_2O_3$ film and (right) corresponding Eu elemental mapping. Note: To highlight film dependent Eu distribution, a scratch was made on the film by knife, as shown in the middle of image.



Figure S9. Histogram of PCE and V_{OC} , J_{SC} , FF of over 20 individual devices with and

without Nano-Eu₂O₃ under 1 sun illumination.



Figure S10. J-V curves of the devices with different ETLs with reverse and forward

scan, respectively.



Figure S11. UV-Vis absorption spectra of the perovskite film with and without Nano-

Eu₂O₃ layer.



Figure S12. Dark *J-V* characteristics of the devices with or without Nano-Eu₂O₃ buffer layer.



Figure S13. Impedance spectra of the PeSCs with and without Nano- Eu_2O_3 buffer layer recorded at different bias voltages in dark. Only fitting data are presented for clarity. Inset is their equivalent circuit.

Table S1.	Photovoltaic	parameters	extracted	from	the	devices	prepared	using	Nano-
Eu ₂ O ₃ with	h different cor	ncentration.							

ETL	V_{OC} (V)	J_{SC} (mA/cm ²)	FF(%)	PCE (%)
Single-spun	1.17	15.50	77.9	14.09
Double-spun	1.08	15.12	75.6	12.38
Triple-spun	1.04	14.41	70.8	10.65
Quadruple-spun	0.99	14.46	65.2	9.33

Table S2. Summary for device performance of lead-based CsPbX₃ perovskite solar cells with inverted configuraion.

Device structure	Perovskite	PCE _{ave}	PCE _{best}	ref
ITO/PTAA/PVK/PCBM/C ₆₀ /BCP/Cathode	CsPbI ₃		11.4	1
FTO/PTAA/PVK/PCBM/BCP/Ag	CsPbI ₃		13.32	2
FTO/NiMgLiO/PVK/PCBM/BCP/Ag	CsPbI ₂ Br		9.14	3
ITO/NiO _x /PVK/c-Nb ₂ O ₅ /PCBM/Bphen/Ag	CsPbI ₂ Br	11.17	11.74	4
FTO/NiO _x /PVK/ZnO@C ₆₀ /Ag	CsPbI ₂ Br		13.3	5
ITO/P3CT/PVK/PCBM/C ₆₀ /BCP/Ag	CsPbI ₂ Br	12.67	13.88	6
FTO/NiMgLiO/PVK/C-MO _X /Ag	CsPbI ₂ Br	13.71	14.00	7
ITO/NiO _x /PVK/Nb ₂ O ₅ /Ag	CsPbI ₂ Br		14.11	8
FTO/NiO _x /PVK/ZnO@doped C ₆₀ /Ag	CsPbI ₂ Br		15.19	9
ITO/NGO /DV/K/Nano Eu O /DCDM/Drhor/Ac	CaDhi Dr	12 47	14.00	This
$110/100_{x}/r \vee K/10ano-Eu_2O_3/rCBivi/Bpnen/Ag$	USP 012BT	13.47	14.09	work

References in Table S2.

- [1]. Q. Wang, X. Zheng, Y. Deng, J. Zhao, Z. Chen, J. Huang, Joule 2017, 1, 371.
- [2]. T. Wu, Y. Wang, Z. Dai, D. Cui, T. Wang, X. Meng, E. Bi, X. Yang, L. Han, Adv. Mater.
 2019, 31, 1900605.
- [3]. S. Zhang, S. Wu, W. Chen, H. Zhu, Z. Xiong, Z. Yang, C. Chen, R. Chen, L. Han, W. Chen, *Mater. Today Energy* 2018, 8, 125-133.
- [4]. D. Han, Y. Xin, Q. Yuan, Q. Yang, Y. Wang, Y. Yang, S. Yi, D. Zhou, L. Feng, Y. Wang, Sol. RRL 2019, 3, 1900091.
- [5]. C. Liu, W. Li, C. Zhang, Y. Ma, J. Fan, Y. Mai, J. Am. Chem. Soc. 2018, 140, 3825-3828.

- [6]. L. Chen, L. Wan, X. Li, W. Zhang, S. Fu, Y. Wang, S. Li, H. Wang, W. Song, J. Fang, Chem. Mater. 2019, 31, 9032–9039.
- [7]. S. Zhang, W. Chen, S. Wu, R. Chen, Y. Huang, Z. Yang, J. Li, L. Han, W. Chen, J. Mater. Chem. A 2019, 7, 18603-18611.
- [8]. X. Liu, Y. Xiao, Q. Zeng, J. Jiang, Y. Li, J. Phys. Chem. lett. 2019, 10, 6382-6388.
- [9]. C. Liu, Y. Yang, C. Zhang, S. Wu, L. Wei, F. Guo, G. Arumugam, J. Hu, X. Liu, J. Lin, R. Schropp, Y. Mai, *Adv. Mater.* 2020, 32, 1907361.

Table S3. Lifetime data extracted from the TRPL spectra by fitting with biexponential decay function.

Film	$ au_1(ns)$	<i>f</i> ₁ (%)	$ au_2(ns)$	f_2 (%)	$ au_{\mathrm{avg}}(\mathrm{ns})^{\mathrm{a}}$
PVK/PC ₆₁ BM	1.48	39.64	3.66	60.36	2.80
PVK/Nano-Eu ₂ O ₃ /PC ₆₁ BM	1.58	37.34	3.23	62.66	2.61

^a τ_{avg} is calculated from the equation $\tau_{avg} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$

Table S4. Data extracted from the fitting lines in impedance spectra of the PeSCs without and with Nano-Eu₂O₃.

Device	Bias voltage (V)	$R_1(\Omega)$	$R_{rec}^{a}(\Omega)$	CPE1-P	CPE1-T
				S.sec ⁿ /cm ²	S.sec ⁿ /cm ²
w/o	0.2	70.11	398.4	4.0E-9	0.94
	0.5	65.33	225.9	2.0E-9	0.98
	0.8	63.79	135.4	1.3E-9	1.00
w/ Nano-Eu ₂ O ₃	0.2	91.76	1008.0	7.7E-9	0.88
	0.5	77.13	818.3	1.4E-8	0.83
	0.8	69.87	443.5	3.8E-9	0.91

 ${}^{a}R_{rec}$ represents the recombination resistance.