

Supporting information for

Cerium oxide as efficient electron extraction layer for p-i-n structured perovskite solar cells

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Experimental Section

Material and preparation: Cerium (III) acetylacetonate hydrate ($\text{Ce}(\text{acac})_3$) was used for the preparation of cerium oxide. Cerium oxide precursor solution was obtained by dissolving cerium (III) acetylacetonate hydrate in chlorobenzene, followed by ultrasonication for 30 min. Cerium oxide was fabricated by spin coating the precursor solution on substrate and being annealed in N_2 at 100 °C for 10 min.

Nickel oxide nanoparticles was prepared according to the literature.¹ First, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5 mol) was dissolved in deionized water (100 mL) to obtain a homogenous and dark green solution. Then NaOH solution (10 mol L⁻¹) was utilized to adjust the pH of the solution to 10. After stirring for 5 min, the colloidal precipitate was separated by centrifugation and was washed twice with deionized water, and dried at 80 °C for 6 h to get green powder. At last, the powder was calcined at 270 °C for 2 h to obtain a dark-black powder. The NiO_x dispersion was prepared by

dispersing NiO_x nanoparticles in deionized water. The concentration of the NiO_x dispersion is 20 mg/ml in this work.

Device fabrication: the inched ITO/glass was cleaned with acetone, detergent, deionized water and isopropyl, and dried by nitrogen flow followed by plasma treatment for 15 minutes. NiO_x nanoparticles were spin-coated on the substrates, followed by annealed in air at 120 °C for 10 min. Perovskite layer was prepared by one step method. PbI₂ (1.3 mmol/ml) and MAI (0.3 mmol/ml) were dissolved in mixed solvent (DMF and DMSO, v/v, 9:1), which was spin coated on top of NiO_x. During the spin coating, MAI solution (35 mg/ml in isopropyl alcohol) was dropped down. After that, the film was annealed at 100 °C for 30 min in N₂. PC₆₁BM and CeO_x was spin coated on top respectively. Finally, 90 nm Ag was deposited by thermal evaporation.

Characterizations

Ultraviolet–visible (UV–vis) absorption spectra and diffuse reflectance spectra were carried out by PerkinElmer Lambda 750 spectrophotometer. Hitachi F-7000 spectrofluorophotometer was applied for the measurements of photoluminescence (PL). The morphologies were measured by an atomic force microscopy (AFM, Digital Instrument Nanoscope 31) and a scanning electron microscopy (SEM, FEI Quanta 200F). Ultraviolet photo-electron spectroscopy (UPS) measurements were carried out by AXIS-ULTRA DLD spectrometer (Kratos Analytical Ltd.) using He (I) (21.2 eV) as monochromatic light source. The thickness of all the layers was measured by surface profilometry (Alpha-Step-IQ). Current-voltage (*J-V*) characteristics were tested using Keithley 2400 Source Meter in the dark and under simulated AM 1.5 G (100 mW·cm⁻²) irradiation (Abet Solar Simulator Sun2000). Incident photon-to-current efficiency (IPCE) were measured under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), while the calibration of the incident light was performed with a monocrystalline silicon diode.

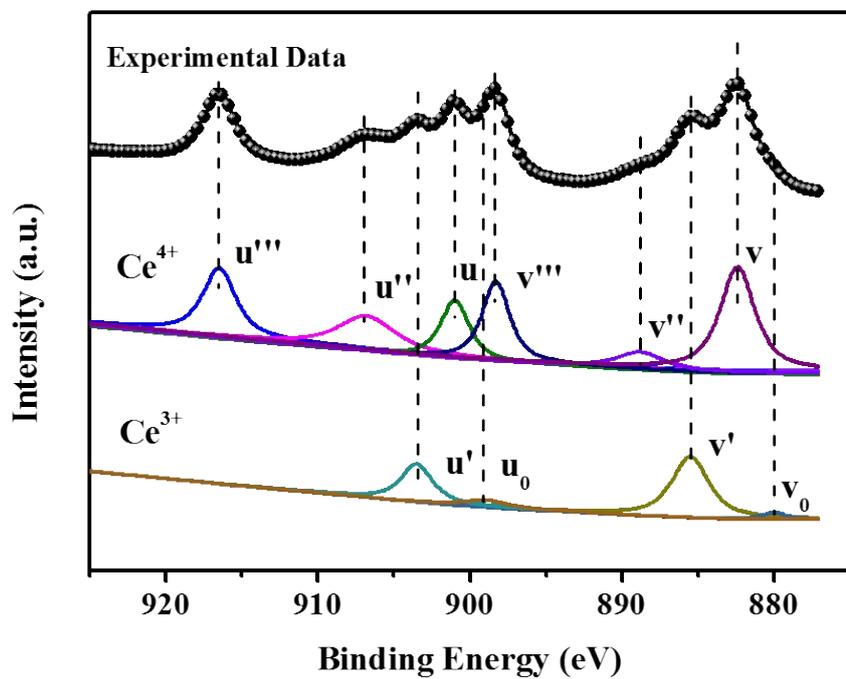


Figure S1. Decomposition of the Ce 3d core level XPS spectra into Ce⁴⁺ and Ce³⁺ emissions.

$$c_{Ce^{3+}} = \frac{v_0 + v' + u_0 + u'}{\sum (v + u)}$$

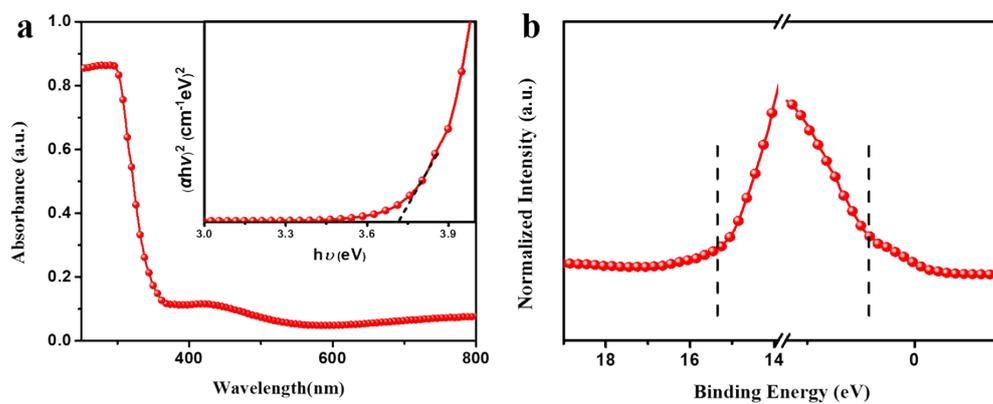


Figure S2. (a) UV–vis absorbance spectra (the inset is plots of $(\alpha h\nu)^2$ versus energy) of CeO_x and (b) UPS spectra of the CeO_x film.

Table S1. Energy levels and band gap of CeO_x .

Buffer layer	E_g (eV)	HOMO (UPS) (eV)	LUMO (eV)
CeO_x	3.70	7.69	3.99

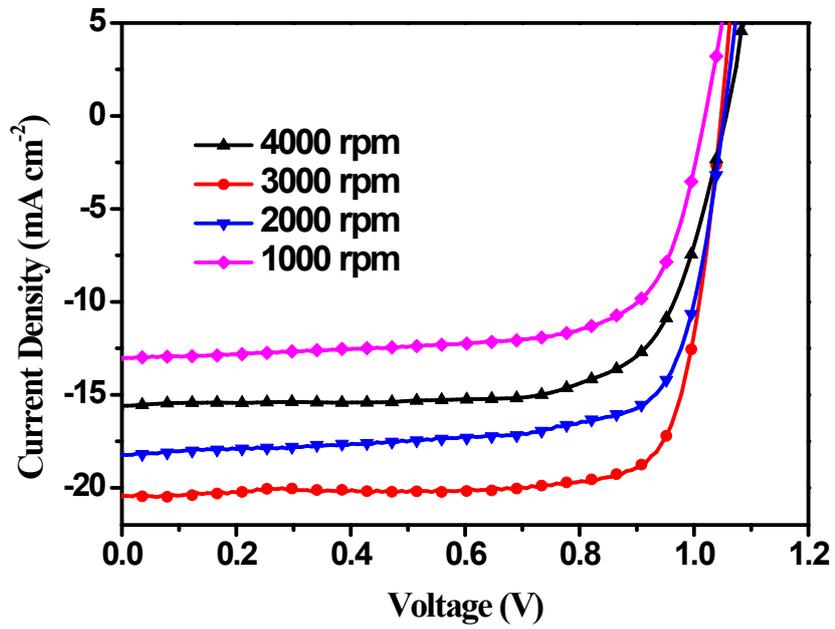


Figure S3. Current–voltage characteristics of PVSCs based on CeO_x EEL with different spin speed.

Table S2. Performance parameters for PVSCs based on CeO_x EEL with different spin speed.

Spin speed (rpm)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
4000	15.54	1.056	71.7	11.8
3000	20.43	1.047	76.5	16.4
2000	18.18	1.042	74.0	14.0
1000	13.02	1.019	70.3	9.3

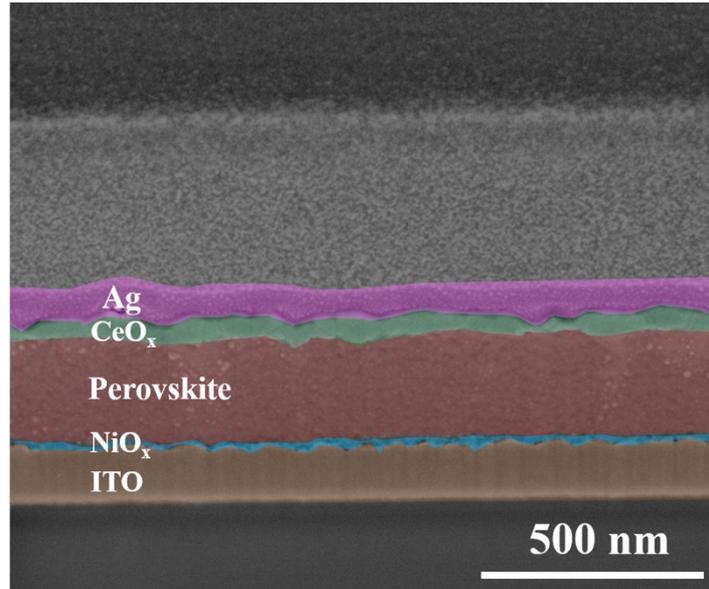


Figure S4. Cross-sectional scanning electron micrograph of the optimized PVSC with CeO_x as EEL.

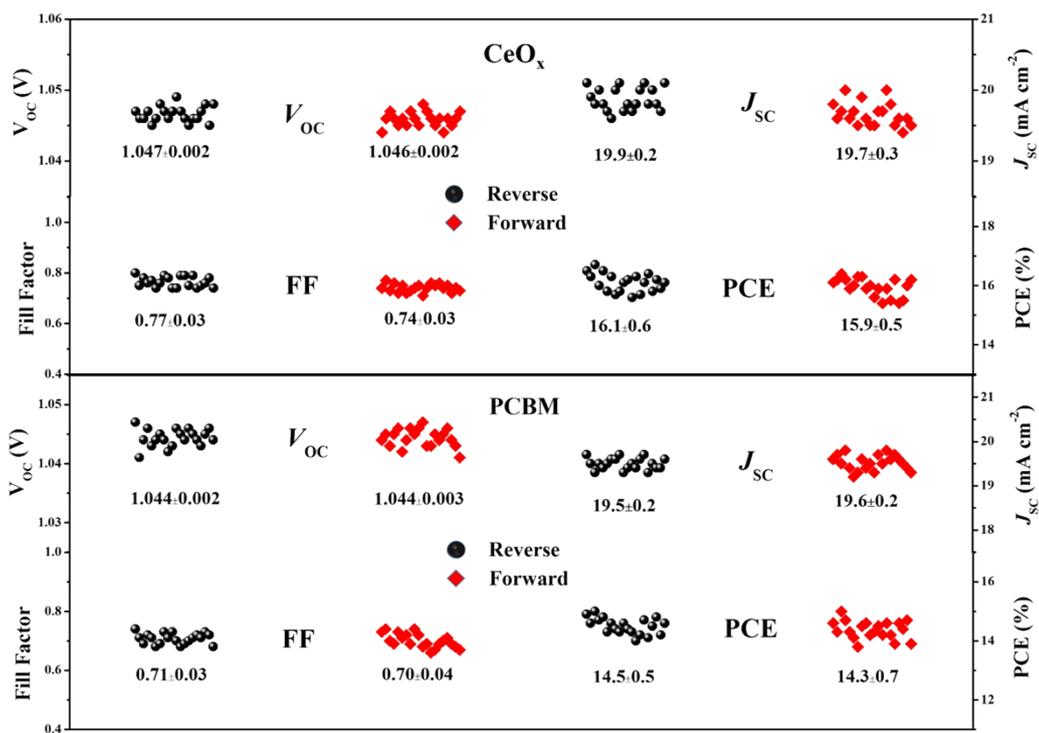


Figure S5. A graphical representation of the device characteristics of cells based on CeO_x and PCBM as EEL. Mean values and standard deviation were obtained from 20 devices for each EEL configuration.

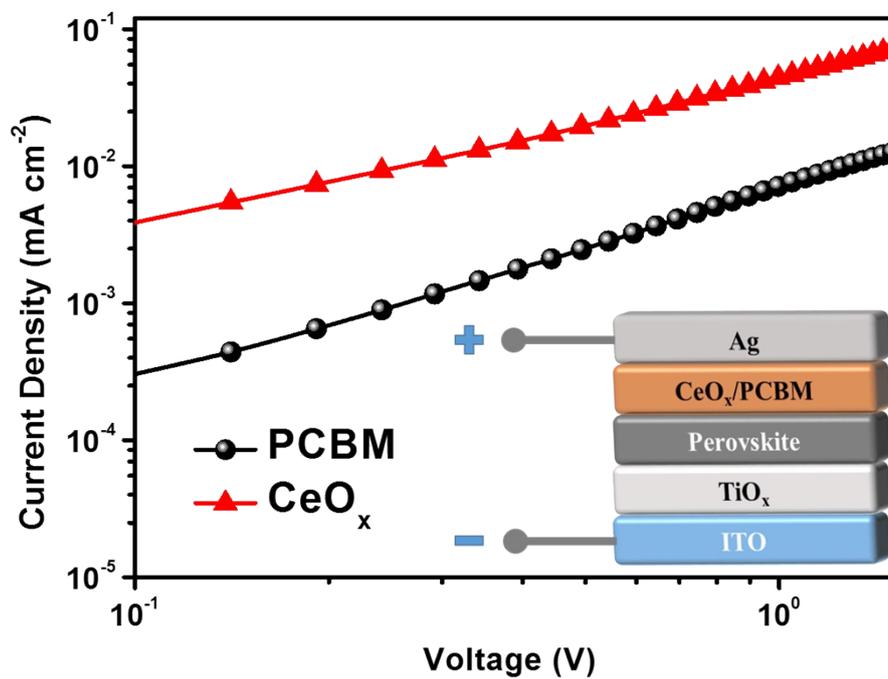


Figure S6. J - V curves in dark of the electron-only devices based on CeO_x and PCBM as EEL. The insert is the architecture of the electron-only devices.

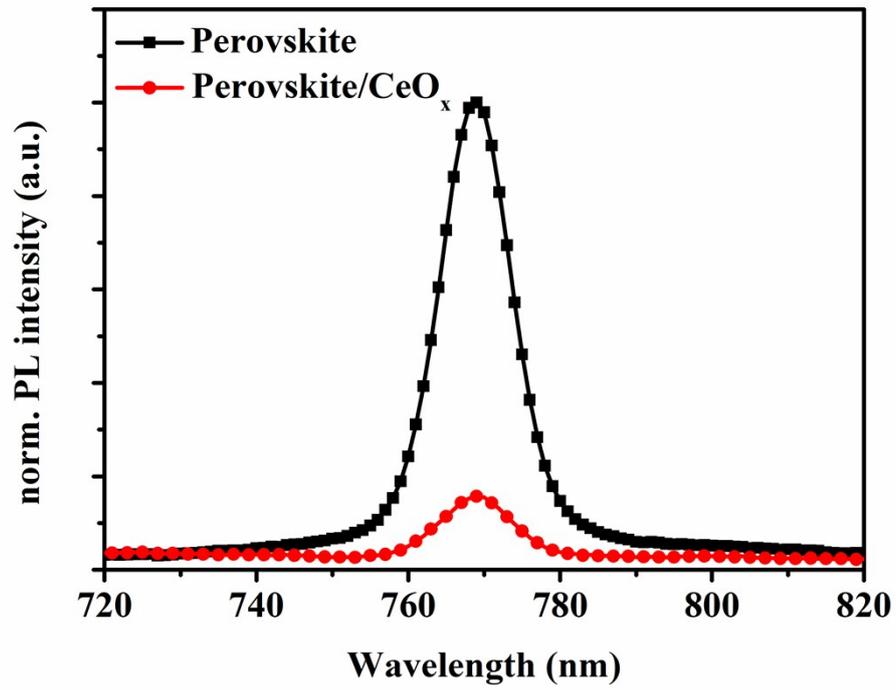


Figure. S7 Normalized photoluminescence (PL) spectra of pristine perovskite layer and perovskite layer/CeO_x on glass substrate.

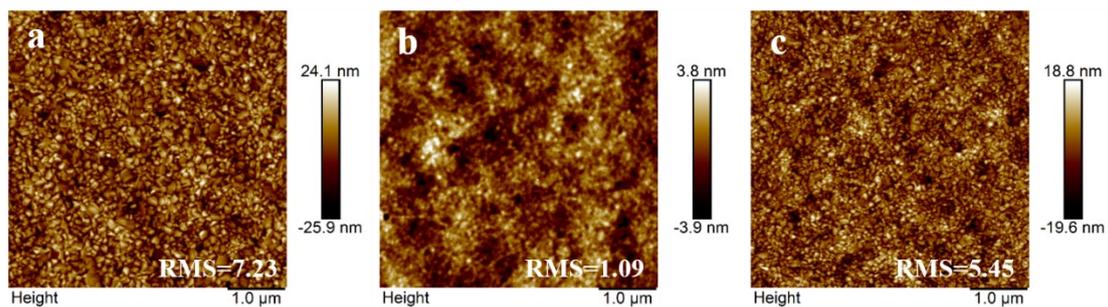


Figure S8. AFM height images (5 × 5 μm) of (a) perovskite film, (b) PCBM on the perovskite film, (c) CeO_x on the perovskite film. All of the films were spin coated on ITO glass and (d) SEM images of CeO_x on the ITO glass.

Reference

1. F. Jiang, W. C. Choy, X. Li, D. Zhang and J. Cheng, *Adv. Mater.*, 2015, **27**, 2930-2937.