Supplementary Information

Self-Assembled Anchoring Shell on NiO_x Nanocrystals Enables Efficient and Stable Wide-Bandgap Perovskite Solar Cells

Sheng Li,[#ab] Chengyue Luo,[#a] Qiuhan Yu,[a] Tianshu Ma,[c] Bowen Deng,[a] Jingxuan Shi,[a] Zhuo Zheng,[a] Xiaodong Wang,[a] and Zhiping Wang*[ab]

Experimental

Materials

All the materials were used as received without further purification. The organic halide salts (FAI, MAI, $PbBr_2$ and GABr with purity of > 99.9%) and (4-(7H-dibenzo[c,g]carbazol-7-yl)butyl)phosphonic acid (4PADCB, 98%) were purchased from Xi'an Yuri Solar. Lead iodide (PbI_2, 98%) were procured from Tokyo Chemical Industry. CsI (99.9%) was purchased from Alfa Aesar. Tin(II) iodide (SnI_2, 99.99%), tin(II) fluoride (SnF_2, 98%), glycine hydrochloride (GlyHCl, 98%), ethylenediamine dihydroiodide ($EDAI_2$, ≥98%), lead thiocyanate ($Pb(SCN)_2$, 99.5%), guanidine thiocyanate (GuaSCN, ≥99%), N,N-dimethylmethanamide (DMF, anhydrous), dimethyl sulfoxide (DMSO, anhydrous) and isopropanol (IPA, anhydrous) were purchased from Sigma-Aldrich. Diethyl ether (DE, HPLC grade) were purchased from Lingfeng Chemical Reagent. Poly(2,3- dihydrothieno- 1,4- dioxin) - poly(styrenesulfonate) (PEDOT:PSS) solution was purchased from Heraeus. Nickel oxide nanoparticles was chemically synthesized as previous report.

Preparation of NiO_x NCs solution

The pristine NiO_x solution was prepared by dissolving 20 mg NiO_x NCs in 1mL deionized water, and then stirred for 30 minutes without heating. The NiO_x NCs solution was sonicated for 30 minutes and then filtered through a 0.22 FTFE filter. The potassium oleate complexed NiO_x NCs solutions were prepared by mixing 0.05-0.4 mg potassium oleate with 20 mg NiO_x NCs before dissolved in 1 mL deionized water, and then stirring for 1 hour. The following steps were the same as pristine NiO_x.

Wide-bandgap perovskite precursor solution

The 1.68 eV FA0.8CS0.2Pb(I0.8Br0.2)3 perovskite precursor solution (1.3M) was prepared by dissolving 0.8 mmol FAI, 0.2 mmol CsI, 0.7 mmol PbI2 and 0.3 mmol PbBr2 in 1 ml mixed solvent of N, N-dimethylmethanamide (DMF, anhydrous, Sigma-Aldrich) and dimethyl sulfoxide (DMSO, anhydrous, Sigma-Aldrich) with a volume ratio of 3:1. Then 6.46 mg (2 mol% in solution) lead thiocyanate (Pb(SCN)2, Sigma-Aldrich, 99.5%) was added into the solution. The perovskite precursor solution was thoroughly mixed and aged for 12 hours before using.

Device fabrication

The Indium-doped tin oxide (ITO)/glass substrates (Advanced Election Technology Co., Ltd) were treated by UV Ozone for 30 min before use. Then the NiOx NCs films were spin-coated at 2000 rpm for 60 s and annealed on a hotplate at 100 °C for 20 min in air. The substrates were transferred to the glove box after cooling. The perovskite films were spin-coated on the NiOx films at 4000 rpm for 60 s with 700 μL diethyl ether (anhydrous, Sigma-Aldrich) dripped on the surface during the spinning. We annealed the as-deposited film at 65 °C for 2 minutes and then 100 °C for 10 minutes. Then we spin-coated 1 mg/mL EDAI2 solution (in IPA) on films and annealed at 65 °C for 5 minutes. Afterwards, the substrates were transferred to the evaporation system. 20 nm C60 and 8 nm BCP were subsequently deposited on top by thermal evaporation. Finally, 100 nm Ag was deposited as cathode by thermal evaporation. For the semitransparent devices, we deposited 20nm SnOx as barrier layer on C60. Then we prepared 100 nm IZO by magnetron sputtering.

Stability testing

The devices were sealed inside a nitrogen-purged glovebox with cover glass and a UV-curable glue (Lumec LT-U001), then transferred to an external stability testing setup for assessment. A broadband LED served as the illumination source, with its intensity adjusted to mimic 1-sun conditions. The device temperature was maintained at 45 °C, and the ambient humidity was kept at 50% relative humidity, the devices were attached to a sample holder.

Film and device characterization

Dynamic light scattering (DLS) measurements were made on a Zetasizer Nano ZSP (Malvern Instruments, Malvern UK) using a detection angle of 173° at a temperature of 25 °C. The Nano ZSP uses a 1 0 mW He-Ne laser operating at a wavelength of 633 nm. Fourier transform infrared (FTIR) spectra of the samples were recorded with a Thermo Fisher Nicolet iS10 spectrometer. XPS on a Thermo Fisher ESCALAB 250Xi used a monochromatic Mg Kα (1.254 keV) source under ultra-high vacuum; binding energies were calibrated to the C 1s peak at 284.8 eV. Scanning electron microscopy (SEM) images were acquired with a TESCAN S9000LMH microscope. AFM height images were attained by a Bruker Multimode 8 in tapping mode. The contact angle was measured with a Dataphysics OCA25 system. XRD patterns were recorded using a Rigaku SmartLab 3 kW diffractometer (Rigaku Ltd.) with Cu Kα radiation (λ = 0.15405 nm). UPS was measured with a monochromatic He I light source (21.2 eV) and a VG Scienta R4000 analyzer. Time-resolved photoluminescence (TRPL) spectra were acquired using a time-correlated single-photon counter (PicoQuant GmbH, TimeHarp 260), pumped by a picosecond diode laser (640 nm, LDH-P-C-640B) operating at a repetition frequency of 125 kHz. Photoluminescence (PL) signals were recorded via a fiber optic spectrometer (Ideaoptics, NOVA2S-EX). J-V curves were measured in air under 100 mW/cm2 AM 1.5G solar irradiation (Newport) with a Keithley 2400 Sourcemeter. The light intensity for J-V measurements was calibrated by a standard silicon (Si) solar cell. EQE spectra were acquired in air using a Zolix SSC600 system. The steady-state efficiencies were obtained by tracking the maximum power point. Electrochemical Impedance Spectroscopy (EIS) was performed on a Keysight E4991B system, offering a frequency resolution of 1 mHz. Scanning electron microscope (SEM) was performed on a TESCAN MIRA3 LMH field emission scanning electron microscope.

Note 1 Synthesis method of PO-NiO$_x$

First, the as-synthesized NiO$_x$ nanocrystals were dispersed in deionized water at a concentration of 20 mg/mL. The dispersion was stirred thoroughly for 12 hours, followed by sonication for 10 minutes, and then filtered through a 0.22 μm PTFE filter to obtain the pristine NiO$_x$ aqueous solution. Separately, PO was dissolved in deionized water at concentrations of 0.5, 1, 2, and 3 mg/mL under stirring for 10 minutes. Each PO solution was then added to the pristine NiO$_x$ solution at a volume ratio of 10%, and the mixture was stirred at room temperature for 12 hours. Subsequently, the mixed solution (including any precipitate) was centrifuged at 6000 rpm for 5 minutes to collect the black precipitate. The precipitate was washed with ethanol and centrifuged again at 6000 rpm for 5 minutes; this washing procedure was repeated three times. Finally, the obtained precipitate was redispersed in deionized water, stirred for 2 hours, sonicated for 20 minutes, and filtered through a 0.22 μm PTFE filter to yield the final PO-NiO$_x$ solution.

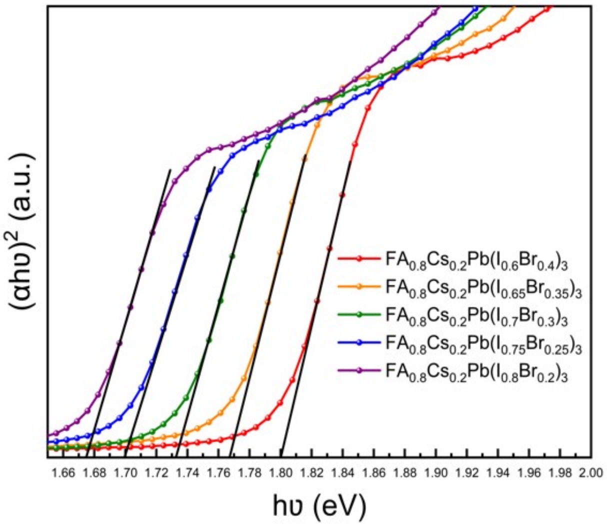

Figure S1. Tauc plots of perovskite with different ratios of I : Br.

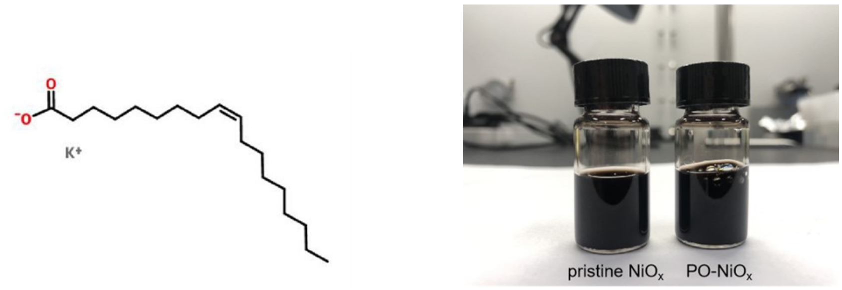

Figure S2. Schematics of the potassium oleate and the real picture of 20 mg/ml pristine NiO$_x$ and PO-treated NiO$_x$ dissolved in deionized water.

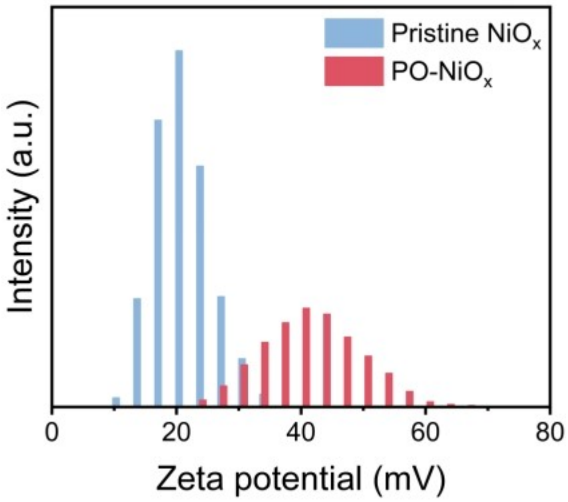

Figure S3. The zeta potential distribution of pristine NiOx and PO-NiOx solutions after one week storage. We extracted the supernatants as the test samples.

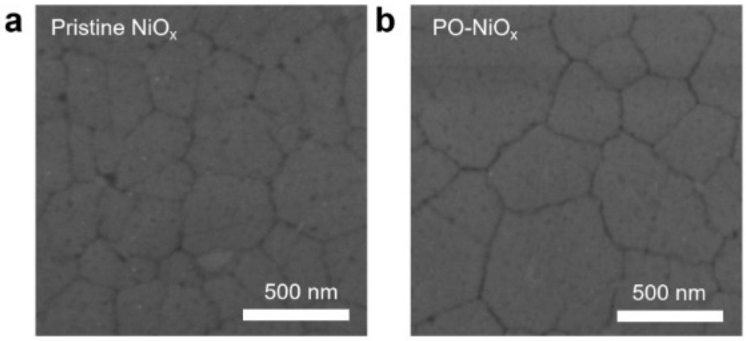

Figure S4. The SEM images of WBG perovskite buried interfaces based on pristine NiO$_x$ and PO-NiO$_x$.

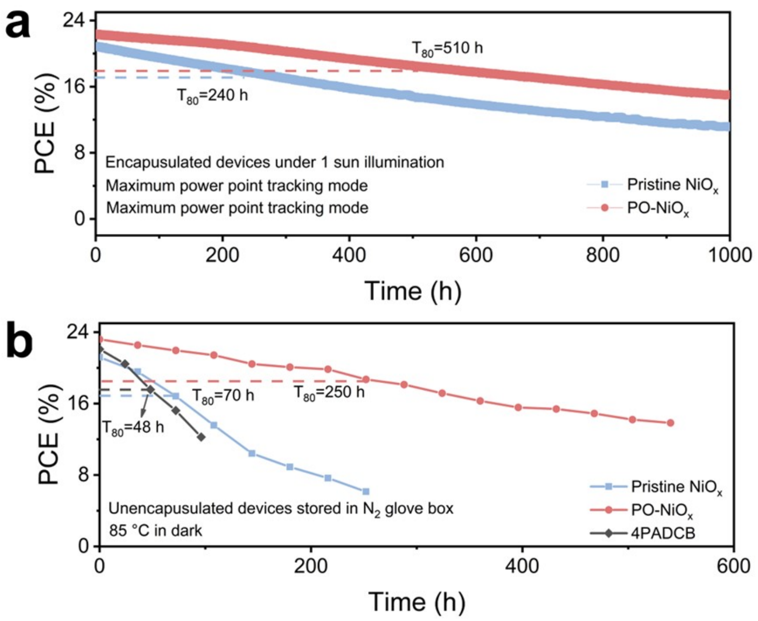

Figure S5. (a) The operational stablity test of encapusulated devices under 1Sun illumination wtih pristine NiO$_x$,4PADCB and PO-NiO$_x$ HTL. (b) The 85 °C thermal steady test.

Table S1. The binding energy values of pristine NiO_x and PO-NiO_x Ni2P.

	Pristine NiO_x	PO-NiO_x
Ni_2P_3 Ni^{2+}	853.63 eV	853.73 eV
Ni_2P_3 Ni^{3+}	855.42 eV	855.54 eV
Ni_2P_3 Sat1	860.81 eV	860.89 eV
Ni_2P_3 Sat2	865.62 eV	865.61 eV

Table S2. Parameters of the TRPL spectra of perovskite films deposited on different substrates (Excitation intensity 0.3 μJ/cm^2)

samples	τ_1 (ns)	A_1 (%)	τ_2 (ns)	A_2 (%)	Mean τ (ns)
ITO/PVK	79.9	52	155.9	48	128.8
ITO/Pristine NiO_x/PVK	19.2	20	61.2	80	58.1
ITO/PO NiO_x/PVK	44.2	34	109.8	66	98.5

Table S3. Parameters of the champion devices based on pristine NiO_x and PO-NiO_x.

	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF*	PCE (%)
Pristine NiO_x (reverse scan)	1.24	22.2	0.846	23.3
Pristine NiO_x (forward scan)	1.24	22.1	0.832	22.8
PO-NiO_x (reverse scan)	1.17	21.9	0.821	21.2
PO-NiOx (forward scan)	1.17	21.8	0.816	20.7