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

Electronic supplementary information

Homogeneous doping of entire perovskite solar cells via alkali cation diffusion from hole transport layer

Mengjiong Chen,‡[a] Hong Wei Qiao,‡[a] Ziren Zhou, [a] Bing Ge, [a] Jingjing He, [a] Shuang Yang,*[a] Yu Hou*[a] and Hua Gui Yang [a]

[a]Key Laboratory for Ultrafine Materials of Ministry of Education, Shanghai Engineering Research Center of Hierarchical Nanomaterials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China. Email: syang@ecust.edu.cn and yhou@ecust.edu.cn

‡ These authors contributed equally to this study.

Experimental

Materials

Methylamine solution (33 wt% in absolute ethanol), isopropanol (99.5%) and dimethyl sulfoxide (DMSO, 99.9%) were purchased from Sigma-Aldrich. Lead iodide (PbI_2, 99.9985%), lead bromide ($PbBr_2$, 99.9%), cesium iodide (CsI, 99.9%), N,N-dimethylformamide (DMF, 99%) and 2-methoxyethanol (99%) were purchased from Alfa Aesar. Hydroiodic acid (HI, 57 wt% solution in H_2O) were purchased from J&K Scientific. Rubidium chloride (99.9%) and chlorobenzene (99.5%) was purchased from Aladdin. Ethanol (AR, 99.7%) was purchased from Shanghai Titan Technology Co. LTD. Nickel (II) acetate tetrahydrate and zinc powder were purchased from Sinopharm Chemidical Reagent Co., Ltd. [6,6]-phenyl-C61-butyric acid methyl ester (PCBM, 99.5%) and bathocuproine (BCP, 99%) were purchased from Nichem chemicals. FTO (8 Ω per square) was purchased from Nippon Sheet Glass.

Synthesis of methylammonium iodide (CH_3NH_3I)

CH_3NH_3I was synthesized according to the reported method.[1] In a typical synthesis, 2 mL of HI and 4.8 mL of methylamine solution were dissolved in 20 mL ethanol. The mixture were stirred at 0 °C for 2 h in nitrogen atmosphere. White CH_3NH_3I precipitate was acquired by rotary evaporation of the mixed solution at 45 °C for 1 h, followed by drying at 60 °C in vacuum oven for 12 h. CH_3NH_3I was dissolved in isopropanol with the concentration of 40 mg/ml.

Preparation of NiO_x films

NiO_x solution was prepared by dissolving Nickel (II) acetate tetrahydrate in 2-methoxyethanol with concentration of 0.3 mol/L. For the alkali metal-doped NiO_x, alkali chloride dissolved in 2-methoxyethanol was mixed with the NiO_x solution at different molar ratios (Rb: from 0.1 mol% to 5.0 mol%, Na, K and Cs: 1 mol%). FTO substrate was patterned by etching with Zn powder and 2 M HCl diluted in deionized (DI) water. The etched FTO substrate was then cleaned by ultrasonication with acetone, ethanol and DI water for 20 min, respectively. Then, the substrates were under UV ozone treatment for 15 min before spin coating NiO_x precursor solution. NiO_x solutions were spin-coated onto FTO at 3000 rpm for 30 s, followed by heated at 150 °C for 5min. After cooling to room temperature, the films were annealing at 500 °C for 1 h.

Fabrication of perovskite solar cells

The $CH_3NH_3PbI_3$ was deposited on the NiO_x film using a modified two-step method.[2] The 1.3 M PbI_2 solution was prepared by dissolving 1.1986 g PbI_2 in 2 mL of N,N-dimethylformamide and 185 μL dimethyl sulfoxide, stirring at 45 ºC for 12 h. The solution was spin-coated on the NiO_x films at 3000 rpm for 30 s, and then spinning coating MAI precursor on the top of the PbI_2 film at 5000 rpm for 30 s, followed by annealing at 115 ºC for 10 min. Afterwards, PCBM (20 mg/mL in chlorobenzene) and BCP (0.5 mg/mL in ethanol) was spin-coated on the top of the $MAPbI_3$ films at 2000 rpm for 45 s, and 4000 rpm for 45 s respectively, and then annealed at 70 ºC for 15 min. After cooling to room temperature, 100 nm of Ag was thermally evaporated onto the ETLs as the back electrode. As for $CsPbI_2Br$ PSCs, 277 mg PbI_2, 220 mg $PbBr_2$, and 312 mg CsI were added in 1 mL DMSO, and then heated at 60 °C till completely dissolved. The prepared precursor solution was filtered before utilization. The $CsPbI_2Br$ layer was fabricated by spin-coating the precursor solution on the NiO_x substrate via a two-step process with 500 rpm for 3 s, and 3500 rpm for 30 s. Subsequently, these films were annealed at 43 °C for 2 min, and then at 160 °C for 10 min.[3] Other steps are the same as the $MAPbI_3$ PSCs.

Characterization

Time of flight secondary ion mass spectroscopy (ToF-SIMS VI, IONTOF GmbH, Muenster, Germany) elemental depth profiling was used to probing the distribution of elements. Inductively coupled plasma mass spectrometer (NexION 2000-(A-10)) was carry out to investigating the element components in perovskite solar cells. The morphology and roughness of various NiO_x films and perovskite samples were characterized by field emission scanning electron microscopy (FESEM, HITACHI S4800) and atomic force microscopy (AFM, Veeco/DI). The crystallographic information of various NiO_x films were investigated by powder X-ray diffraction (PXRD, Bruker Advance D8 X-ray diffractometer, Cu Kα radiation, 40kV). X-ray photoelectron spectroscopy (XPS, PHI5300, Mg anode, 250 W, 14 kV) was used to analyze the elemental composition of the various NiO_x films. The transmittance spectra of various NiO_x films and absorption spectra of $MAPbI_3$ perovskite were measured by using a Cary 500 UV-Vis-NIR Spectrophotometer. The solar cells were illuminated by a solar light simulator (Newport, AM 1.5 G) under AM 1.5 G irradiation (at 100 mW cm^{-2}) and the light intensity was calibrated to 100 mW cm^{-2} using a standard Newport calibrated KG5-filtered Si reference cell. *J-V* curves of devices were measured with a Keithley 2400 digital source meter with a scan rate of 0.15 V s^{-1}. Devices were masked with a metal aperture to define the active area to be 0.0625 cm^2. The external quantum efficiency (EQE) was carried out on a Newport-74125 system. The steady state photocurrent output of the best-performing devices was measured by biasing the device at maximum power point for 600 s. Work function of the NiO_x films were measured by ultraviolet photoelectron spectrum (UPS) with He source of incident energy of 21.21 eV (He 1 line). The photoluminescence (PL) measurement was acquired at room temperature using the Fluorolog-3-p spectrophotometer with an excitation wavelength of 460 nm. KPFM (Dimension Icon & FastScan Bio) was used to analyze the surface potential of perovskite films. The electrochemical impedance spectra were measured out using an electrochemical workstation (Parstat 2273, Princeton) in the frequency range of 1.0 MHz and 1.0 Hz at 0.8 V under dark conditions.

Notes and references

1. Y. Hou, X. Chen, S. Yang, Y. L. Zhong, C. Li, H. Zhao and H. G. Yang, *Nano Energy*, 2017, **36**, 102-109.
2. T. Y. Wen, S. Yang, P. F. Liu, L. J. Tang, H. W. Qiao, X. Chen, X. H. Yang, Y. Hou and H. G. Yang, *Adv. Energy Mater.*, 2018, **8**, 1703143.
3. C. Liu, W. Li, C. Zhang, Y. Ma, J. Fan and Y. Mai, *J. Am. Chem. Soc.*, 2018, **140**, 3825-3828.

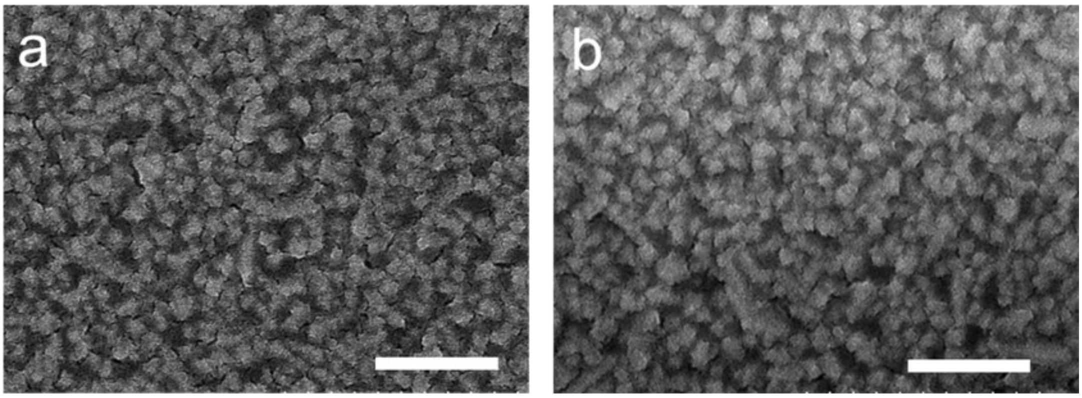

Figure S1. Top-view SEM images of the (a) NiO_x and (b) Rb-NiO_x fresh films, Scale bar is 500 nm.

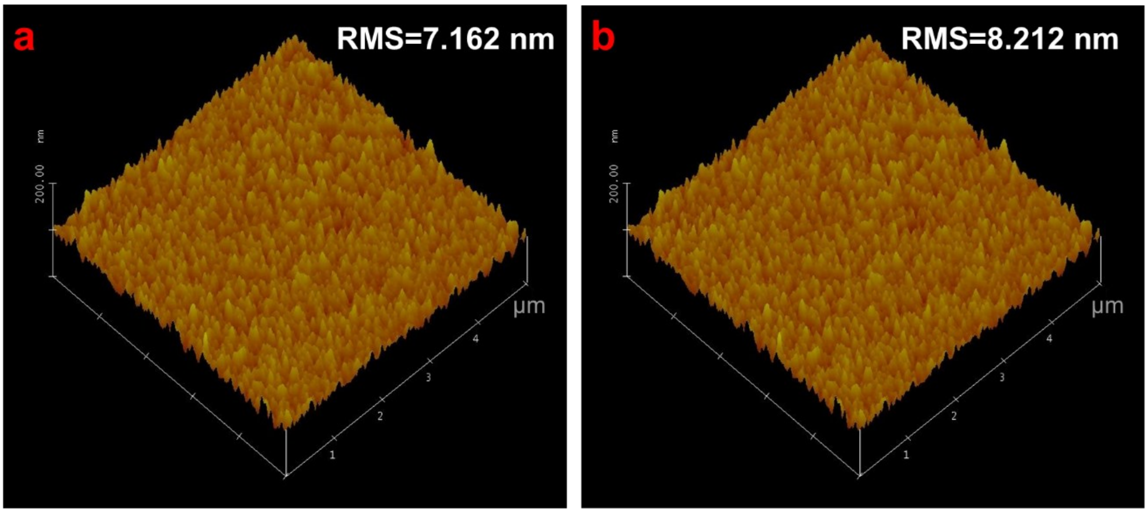

Figure S2. AFM images of (a) NiO_x and (b) Rb-NiO_x fresh films in an area of 5 μm × 5 μm, RMS is the root mean square roughness of the film.

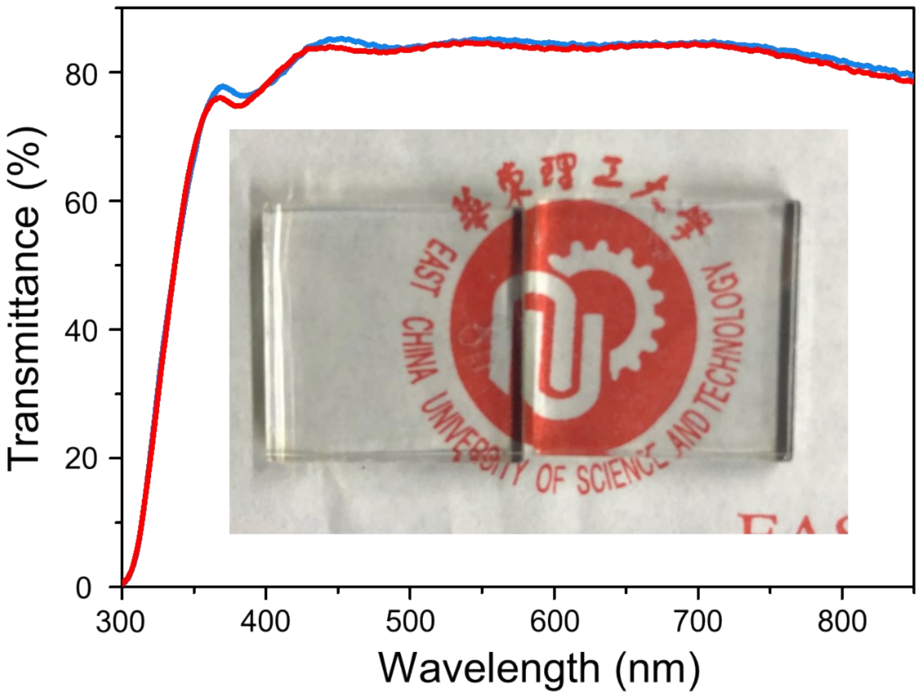

Figure S3. Optical transmission spectra of NiO_x (blue) and Rb-NiO_x fresh (red) films coated on the FTO substrates after thermal annealing. Insets are photographs of the NiO_x films.

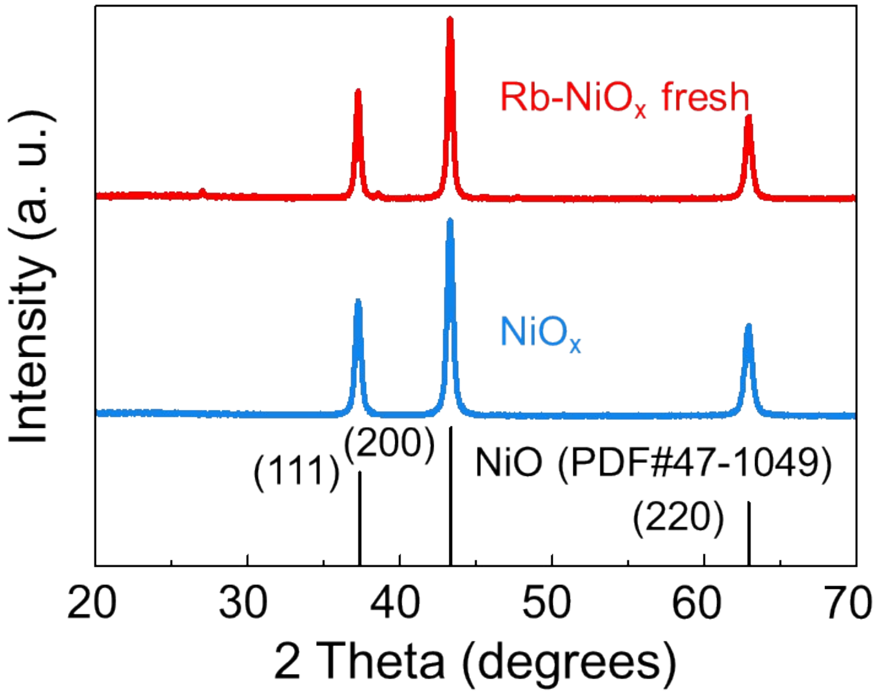

Figure S4. XRD patterns of the NiO_x and Rb-NiO_x fresh.

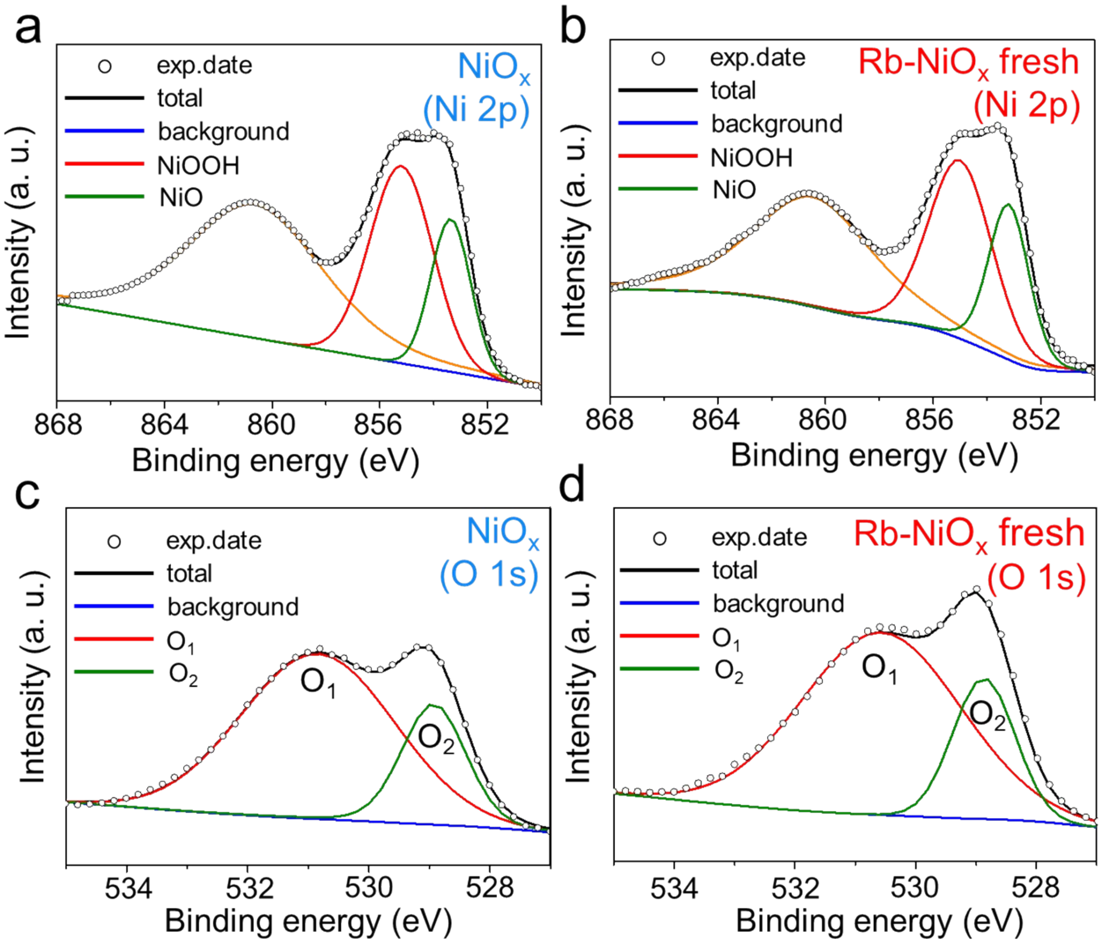

Figure S5. XPS spectra of (a, b) Ni 2p and (c, d) O 1s for NiO$_x$ and Rb-NiO$_x$ fresh films.

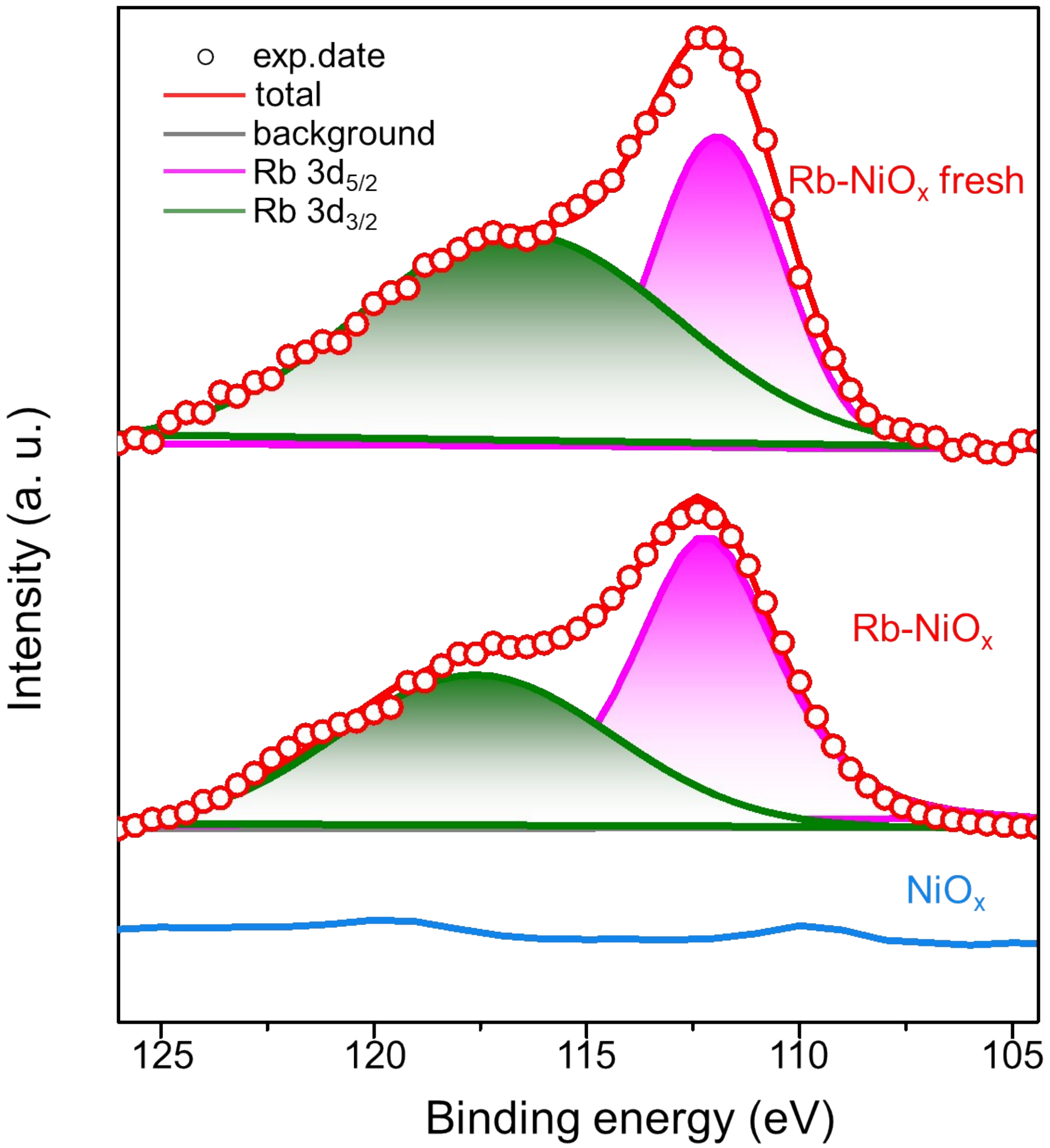

Figure S6. XPS spectra of Rb 3d for NiO_x, Rb-NiO_x and Rb-NiO_x fresh films.

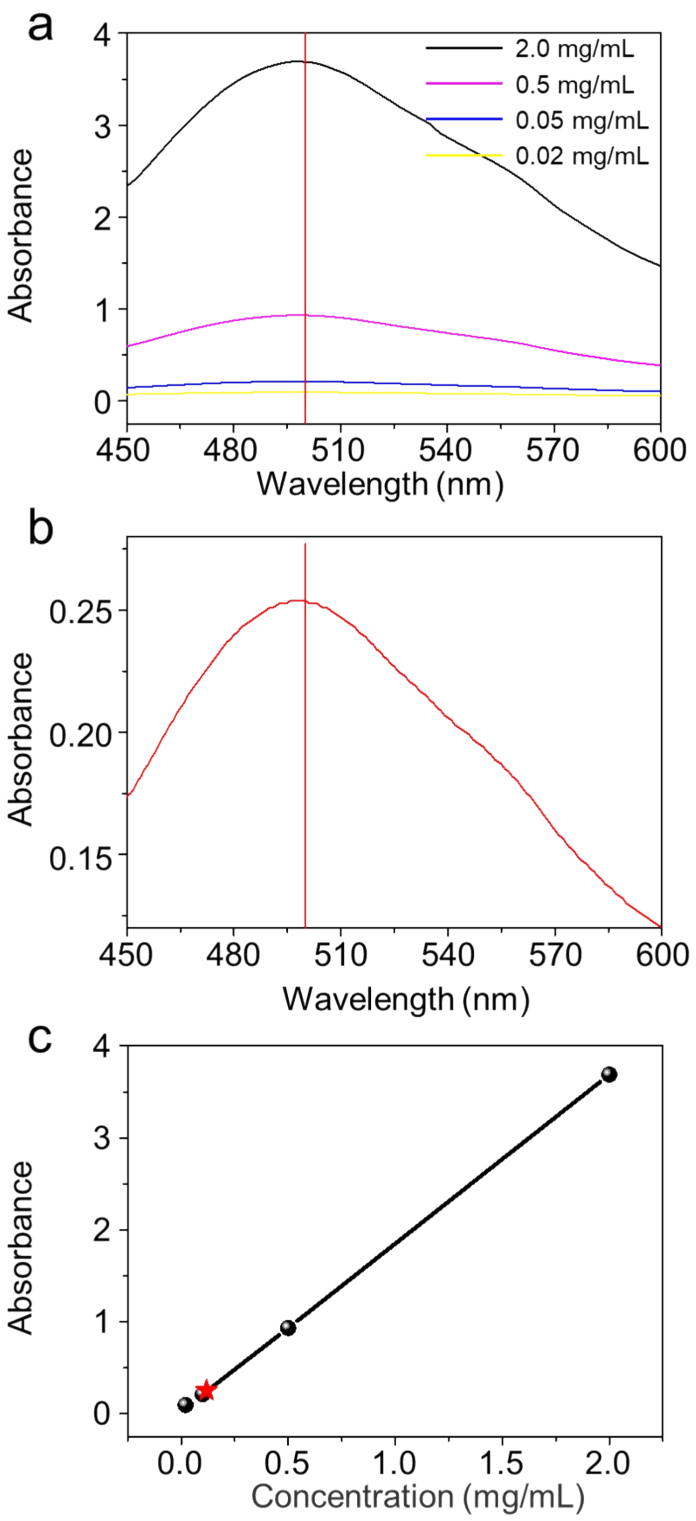

Figure S7. UV-vis absorption spectra of (a) different concentrations PCBM chlorobenzene solution and (b) Experimental solution. (c) The absorption of solution at 500 nm wavelength varies with concentration.

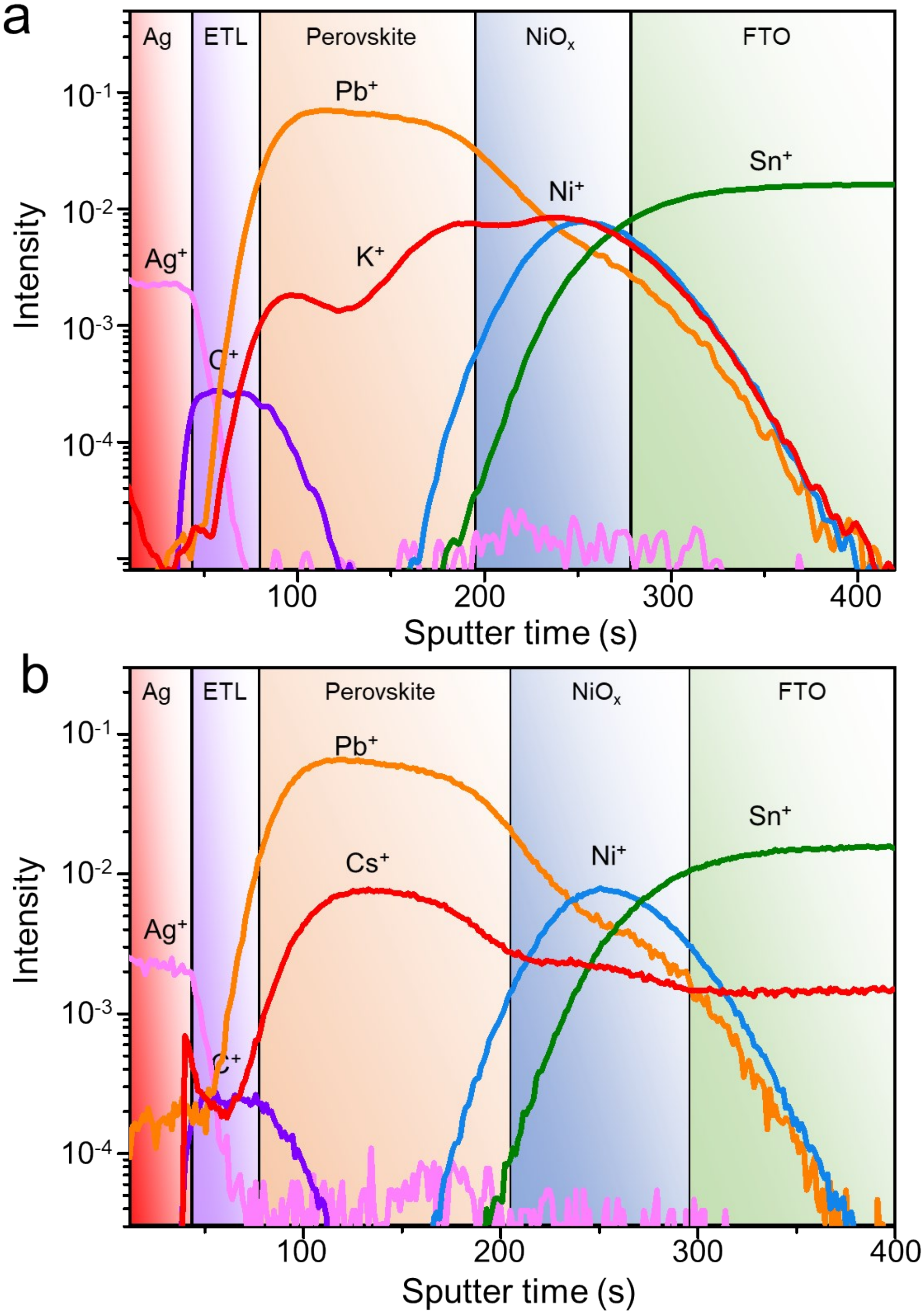

Figure S8. ToF-SIMS image of (a) K-NiO$_x$ and (b) Cs-NiO$_x$ PSCs device.

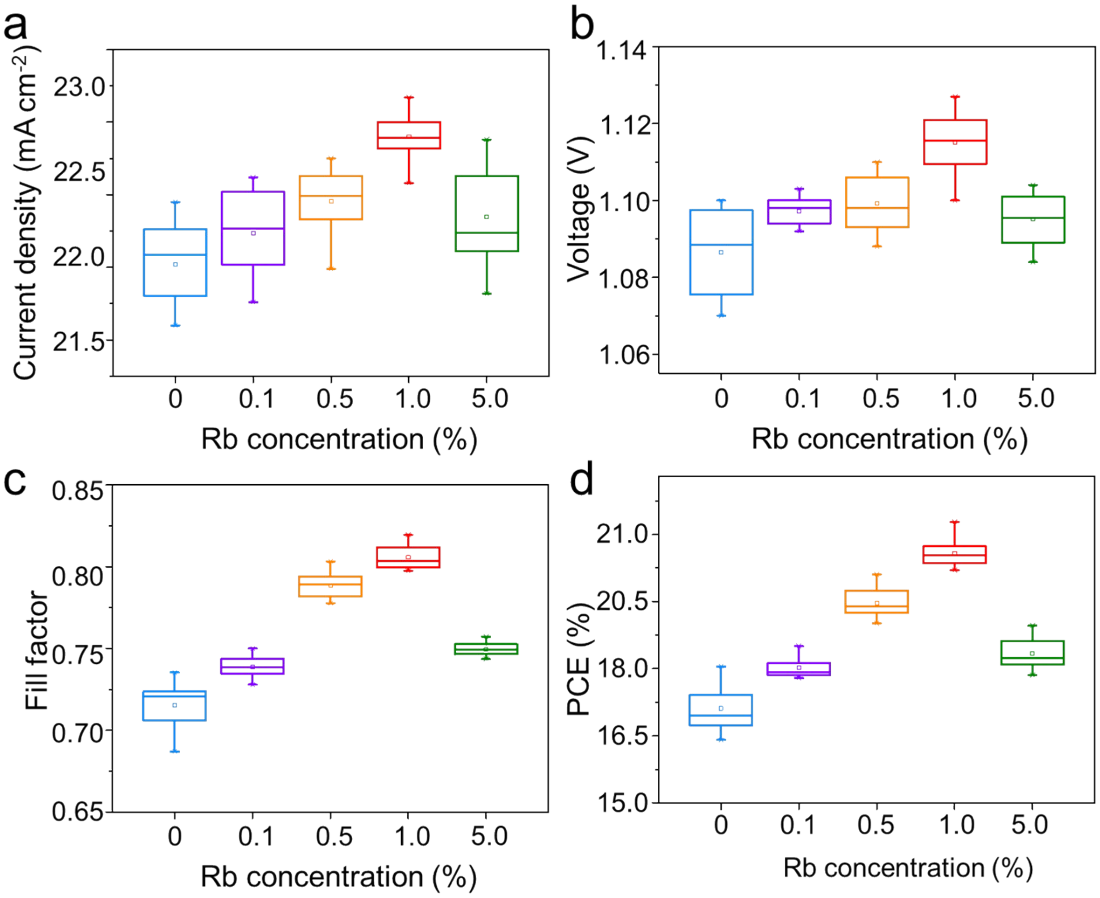

Figure S9. Photovoltaic parameters (a) J_{SC}; (b) V_{OC}; (c) FF; (d) PCE of PSCs with various Rb^+ concentrations.

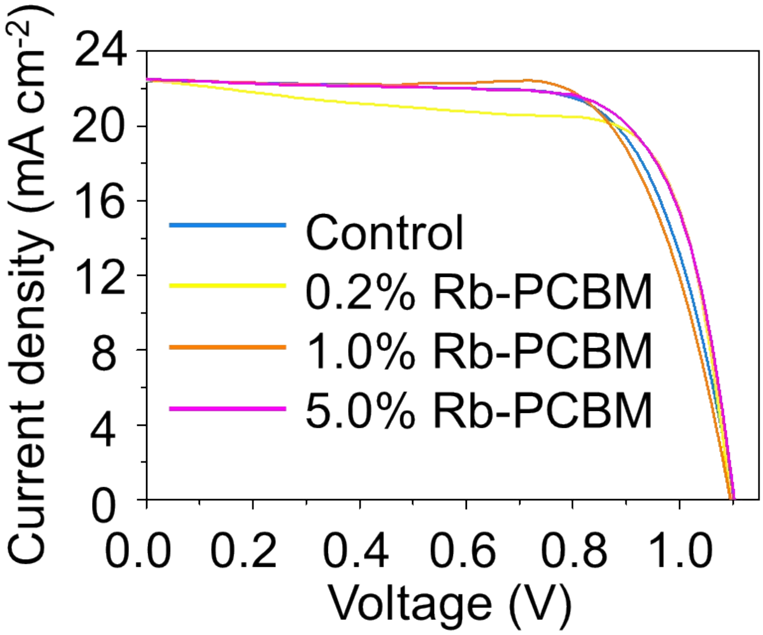

Figure S10. *J*-*V* curves of PSCs based on Rb doped PCBM layers.

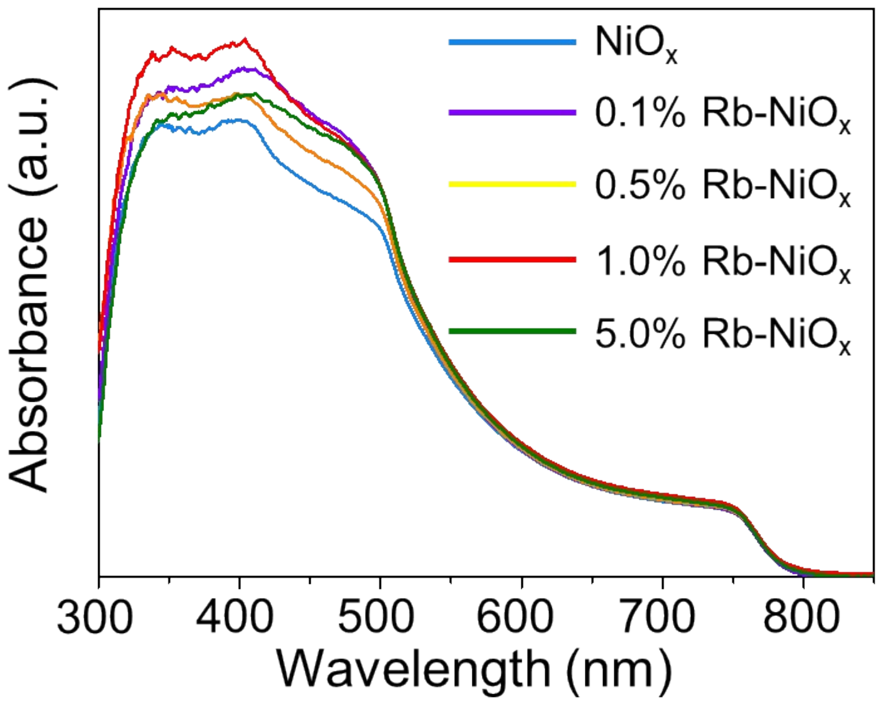

Figure S11. UV-vis absorption spectra of $MAPbI_3$ perovskite films deposited on different NiO_x films.

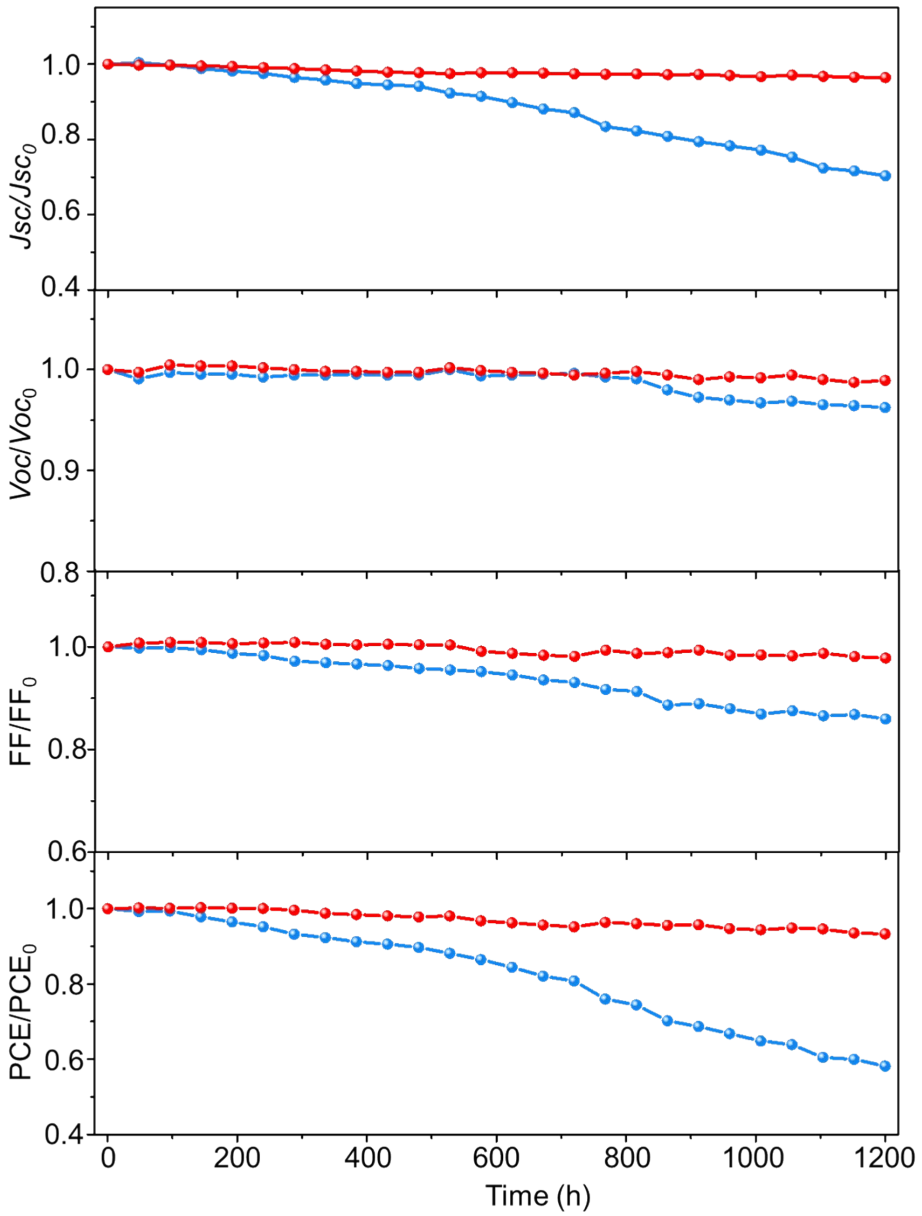

Figure S12. Stability test of unencapsulated solar cells based on the NiO_x (blue) and Rb-NiO_x (red) HTLs.

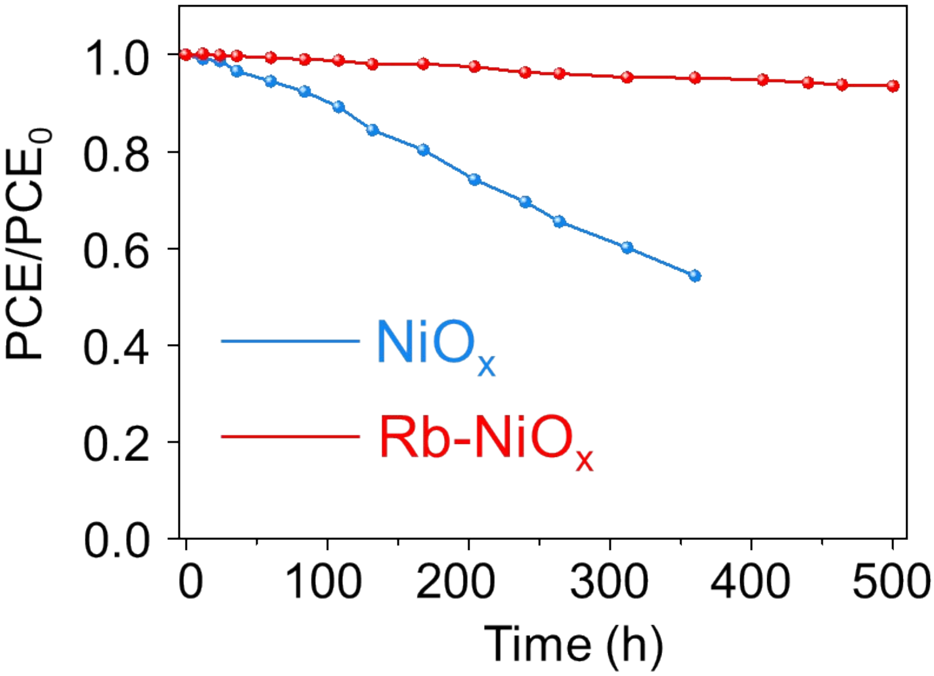

Figure S13. Illumination stability test of unencapsulated solar cells based on the NiO$_x$ and Rb-NiO$_x$ HTLs

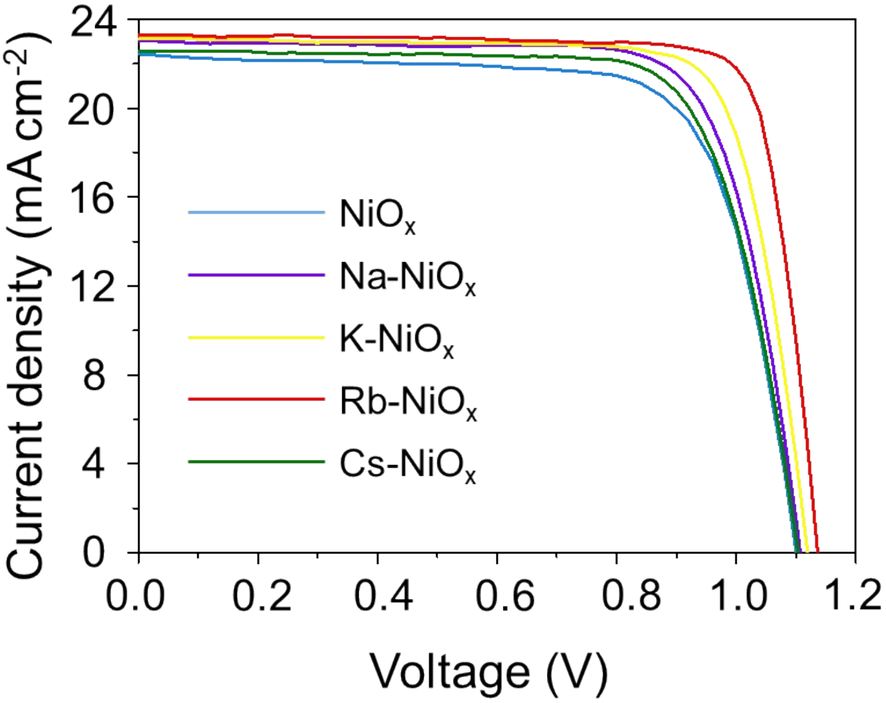

Figure S14. *J-V* curves of PSCs with different alkali metal cation doping NiO$_x$ HTLs under simulated AM 1.5 G of 100 mW cm^{-2} illumination.

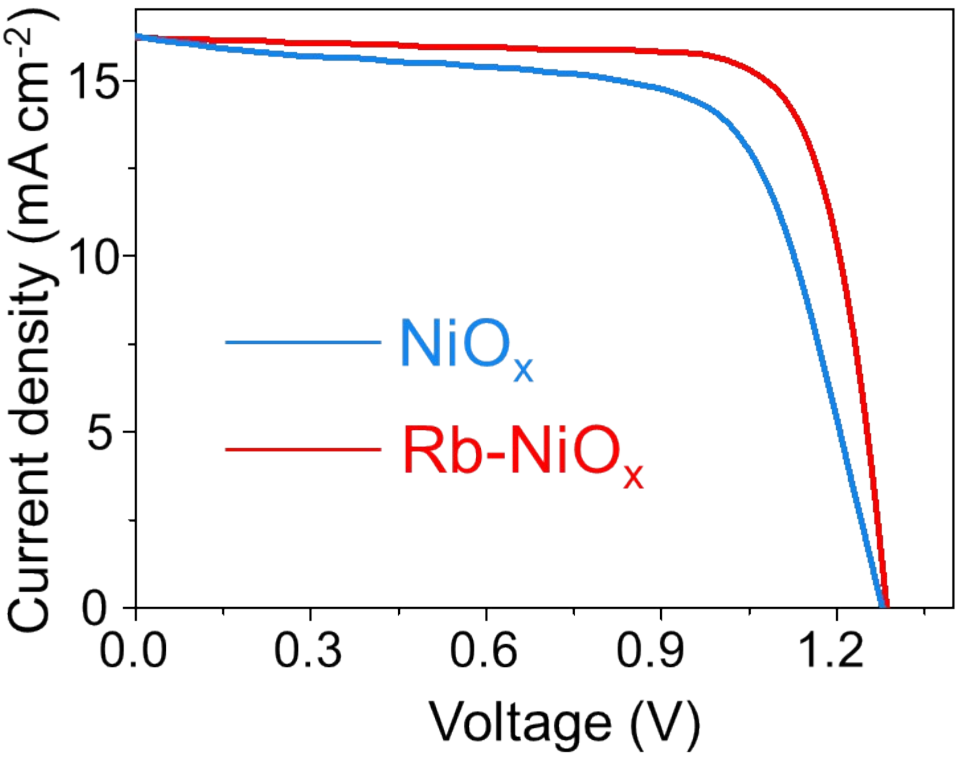

Figure S15. *J-V* curves of $CsPbI_2Br$ PSCs with NiO_x and Rb-NiO_x under simulated AM 1.5 G of 100 mW cm^{-2} illumination.

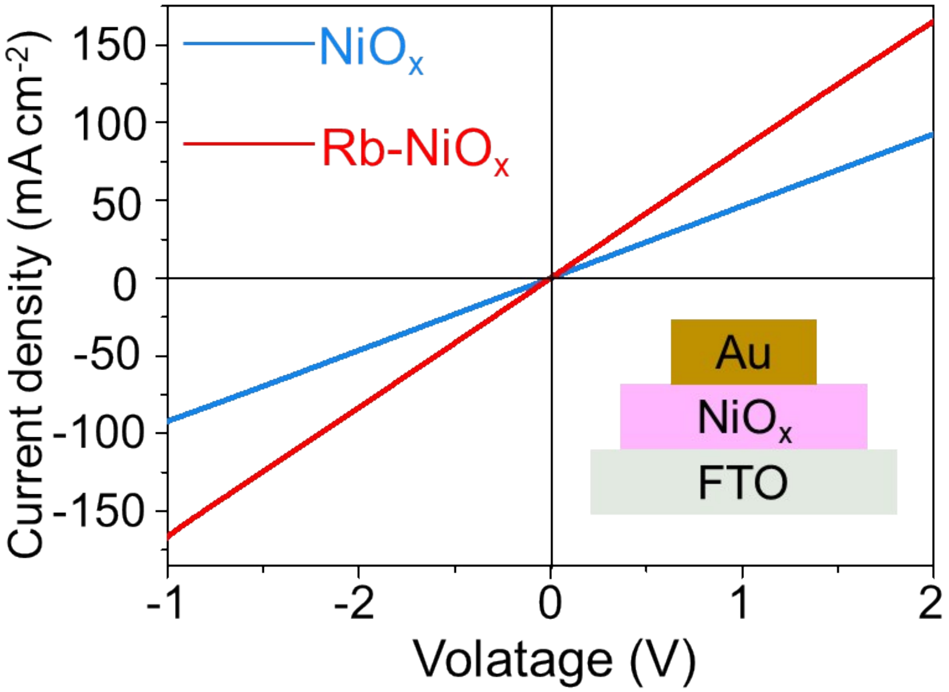

Figure S16. *J*-*V* curves of NiO$_x$ films deposited on FTO glass, the device structure is FTO/NiO$_x$/Au. The thickness was ~120 nm for all metal oxide films.

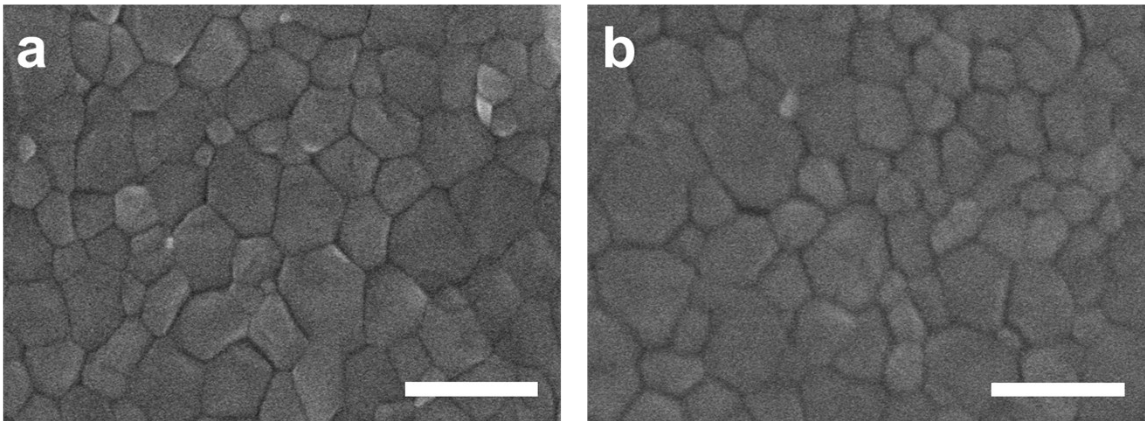

Figure S17. Top-view SEM images of $MAPbI_3$ perovskite films deposited on a) NiO_x and b) Rb-NiO_x thin films, Scale bar is 500 nm.

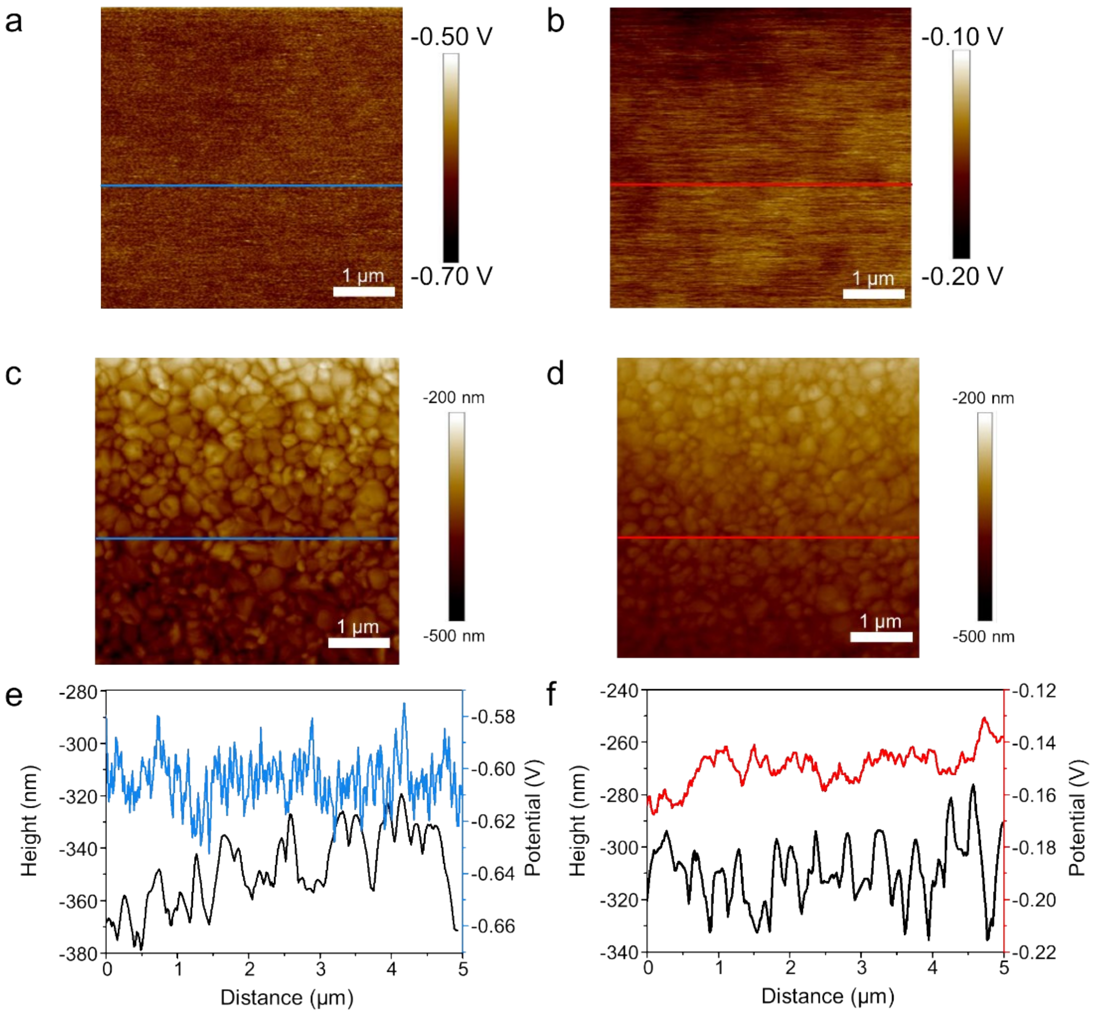

Figure S18. Surface potential maps (KPFM) of $MAPbI_3$ films deposited on (a) NiO_x and (b) Rb-NiO_x, the blue and red lines across the images mark the locations to extract the potential profiles in e, f. AFM images of $MAPbI_3$ films deposited on (c) NiO_x and (d) Rb-NiO_x thin film. (e) and (f) height and potential profiles of the corresponding perovskite films.

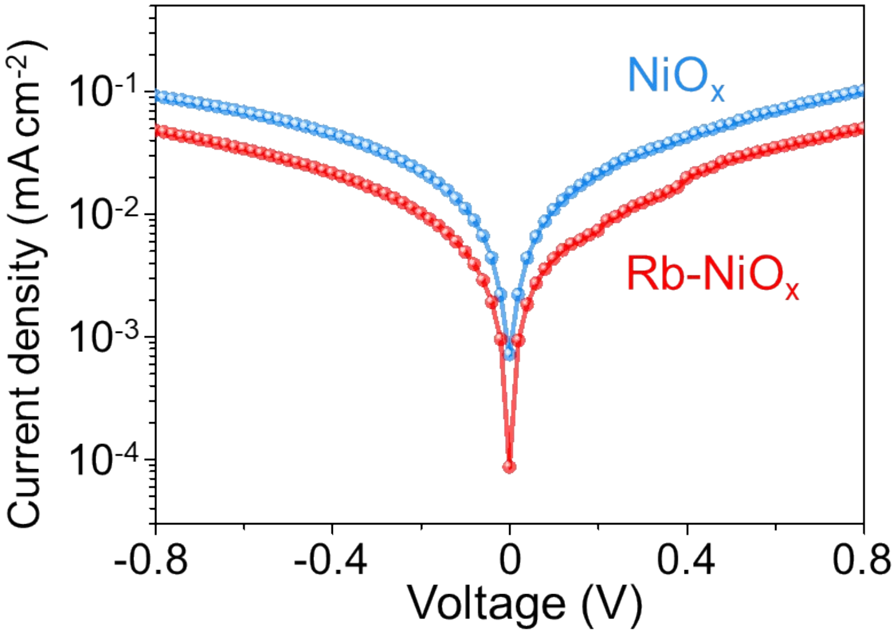

Figure S19. Dark current of PSCs device based on the NiO$_x$ and Rb-NiO$_x$.

Table S1. Summary of ICP-OES results

Samples	Element	Concentration (mg/mL)	Mol%
Rb-NiO$_x$ fresh	Rb	0.86	0.984
	Ni	60	
Rb-NiO$_x$	Rb	0.24	0.549
	Ni	30	
MAPbI$_3$	Rb	0.05	0.186
	Pb	65	
ETL	Rb	0.001	8.986
	PCBM	0.1186	

Table S2. Photovoltaic parameters of PSCs with various Rb^+ concentrations, measured by reverse scan under simulated AM 1.5 G solar irradiation.

HTLs		J_{SC}/(mA/cm^2)	V_{OC}/V	FF	PCE/%
NiO_x	Average	22.02 ± 0.26	1.087 ± 0.012	0.715 ± 0.014	17.11 ± 0.49
	Highest	22.45	1.100	0.731	18.04
0.1% Rb-NiO_x	Average	22.24 ± 0.29	1.097 ± 0.004	0.739 ± 0.006	18.03 ± 0.23
	Highest	22.61	1.100	0.744	18.50
0.5% Rb-NiO_x	Average	22.46 ± 0.22	1.099 ± 0.007	0.788 ± 0.008	19.46 ± 0.33
	Highest	22.75	1.106	0.799	20.10
1.0% Rb-NiO_x	Average	22.90 ± 0.16	1.115 ± 0.007	0.806 ± 0.007	20.58 ± 0.29
	Highest	23.35	1.133	0.824	21.80
5.0% Rb-NiO_x	Average	22.35 ± 0.33	1.095 ± 0.007	0.749 ± 0.004	18.34 ± 0.31
	Highest	22.72	1.104	0.756	18.96

Table S3. Photovoltaic parameters of PSCs with various Rb^+ doping methods, measured by reverse scan under simulated AM 1.5 G solar irradiation.

	J_{SC}/(mA/cm^2)	V_{OC}/V	FF	PCE/%
NiO_x	22.45	1.100	0.731	18.04
Rb-NiO_x	23.35	1.133	0.824	21.80
Rb-NiO_x-$MAPbI_3$	23.15	1.118	0.799	20.69
Rb-$MAPbI_3$	23.11	1.104	0.752	19.19

Table S4. Photovoltaic parameters of PSCs measured at simulated AM 1.5G solar irradiation.

	J_{SC} (mA/cm^2)	V_{OC} (V)	FF	PCE (%)
Control	22.42	1.102	0.727	17.96
0.2% Rb-PCBM	22.47	1.098	0.722	17.82
1.0% Rb-PCBM	22.50	1.096	0.717	17.67
5.0% Rb-PCBM	22.48	1.103	0.731	18.13

Table S5. Photovoltaic parameters of the champion NiO_x and Rb-NiO_x PSCs in forward and reverse scan.

HTLs	Scan direction	$J_{SC}/(mA/cm^2)$	V_{OC}/V	FF	PCE/%
NiO_x	FB-SC	22.45	1.100	0.731	18.04
	SC-FB	22.42	1.095	0.729	17.91
Rb-NiO_x	FB-SC	23.35	1.133	0.824	21.80
	SC-FB	23.22	1.133	0.816	21.46

Table S6. Photovoltaic parameters of PSCs with different NiO_x HTLs, measured by reverse scan under simulated AM 1.5 G solar irradiation.

HTLs	$J_{SC}/(mA/cm^2)$	V_{OC}/V	FF	$PCE/\%$
NiO_x	22.45	1.100	0.731	18.04
Na-NiO_x	22.87	1.107	0.782	19.78
K-NiO_x	23.05	1.118	0.794	20.45
Rb-NiO_x	23.35	1.133	0.824	21.80
Cs-NiO_x	23.03	1.106	0.767	19.54