Highly Conductive and Homogeneous NiO_x Nanoparticles for Stable and Efficient Flexible Perovskite Solar Cells

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Experimental section

Materials

Ammonium persulphate (APS) and Tetrabutylammonium hydroxide (TBAOH) was purchased from Innochem. Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), Isopropyl alcohol (IPA, 99.7%), anhydrous ethanol (99.5%), toluene and Bathocuproine (BCP, 96%) were obtained from Alfa Aesar. DMF (99.9%), DMSO (99.9%) and chlorobenzene (CB, 99.9%) were purchased from Sigma-Aldrich. Flexible ITO/PET (25-35 Ω/cm^2, 125 μm), Lead iodide (PbI_2, 99.999%), formamidinium iodide (FAI), cesium iodide (CsI), and phenyl-C61-butyric acid methyl ester ($PC_{61}BM$, 99.9%) were bought from Advanced Election Technology. Lead bromide ($PbBr_2$, 99.999%), methylammonium bromide (MABr), and PTAA were purchased from Xi'an Yuri Solar Co., Ltd. All starting materials were obtained from commercial suppliers without further purification.

Synthesis of NiO_x and NiO_x-APS nanoparticles (NPs)

The $Ni(NO_3)_2 \cdot 6H_2O$ (50 mmol) was dissolved in 50 mL deionized water. Subsequently, 50 mL TBAOH was added drop wisely under vigorous stirring. The resulting precipitates were collected by centrifugation and washed with deionized water 4 times to remove residual TBAOH. The washed precipitates were vacuum-dried at 100°C for 12 h, followed by sintering at 270°C for 2 h to obtain NiO_x NPs.

The $Ni(NO_3)_2 \cdot 6H_2O$ (50 mmol) and APS (0.15 mmol (0.3 mol%)) was dissolved in

50 mL deionized water. Subsequently, 50 mL TBAOH was added drop wisely under vigorous stirring. The resulting precipitates were collected by centrifugation and washed with deionized water 4 times to remove residual TBAOH, APS and its by-products. The washed precipitates were vacuum-dried at 100°C for 12 h, followed by sintering at 270°C for 2 h to obtain NiO_x-APS NPs.

Solar cell fabrication

First, the NiO_x NPs or NiO_x-APS NPs were dispersed in deionized water and IPA (4:1) to prepare 5 mg/mL NiO_x or NiO_x-APS solution and filtered with a 0.45 μm nylon filter. The NiO_x or NiO_x-APS solution was spin-coated on the ITO/PET substrates at 4000 rpm for 30 s and annealed on a hotplate at 100°C for 30 min in air. PTAA (0.5 mg/mL in Toluene) was coated on NiO_x or NiO_x-APS films at 6000 rpm for 40 s and then annealed at 100°C for 10 min. For deposition of perovskite layer, The (1.4 M) perovskite precursor solution was constructed by mixing PbI_2, $PbBr_2$, FAI, MABr, and CsI in a mixed solvent (DMF/DMSO=4/1) according to a formula of $Cs_{0.05}(FA_{0.95}MA_{0.05})_{0.95}Pb(I_{0.95}Br_{0.05})_3$. The precursor solution was dripped onto HTL-coated substrates and spin-coated at 5000 rpm for 30 s, 150 μL CB as anti-solvent was dripped on the film at 18 s from the start and then annealed at 100°C for 30 min. After that, the $PC_{61}BM$ (20 mg/mL in CB) was coated on the perovskite surface at 5000 rpm for 30 s and annealed at 100°C for 10 min, then the BCP solution (0.5 mg/mL in IPA) was spin-coated at 4000 rpm for the 30 s on the PCBM layer. Finally, 200 nm thickness of Ag electrode was deposited by thermal evaporation as an electrode using a shadow mask.

Characterizations

The TEM images were taken on JEM-2100 (HR), JEOL Co.Ltd. The XRD patterns were obtained with Smartlab 9kW X-ray diffractometer and with Cu Kα (λ = 1.5406 Å) radiation source. The Raman spectrum was prepared by Raman spectrometer (New Mills, UK). The XPS and UPS characterizations were performed on a Thermo Fisher ESCALAB 250XI (USA), with -5 V bias for UPS measurement. The atomic force microscopy (AFM, Bruker Dimension ICON) instrumented c-AFM and KPFM of NiO_x films. The morphology of samples was acquired by field-emission scanning electron

microscope (FE-SEM, Hitachi SU8010). The UV-Vis absorption spectra were obtained from a UV-2600 spectrophotometer (Shimadzu, Japan). The contact angle of the surface was measured by a video-based automatic contact angle measuring instrument (OCA15, Data Physics). The electrochemical impedance spectra (EIS) were recorded by electrochemical workstation (Zahner, Germany). The current density-voltage (*J-V*) curves of the perovskite solar cells were obtained by a Keithley 2400 source under AM 1.5 G simulated irradiation (100 mW cm^{-2}) from a solar simulator (Newport 94023A) and then obtain the indoor *J-V* curve by altering the illuminance to 1000, 500 and 200 lux using the illuminance meter (ENLITECH) with fluorescent lamps (ILS-30).

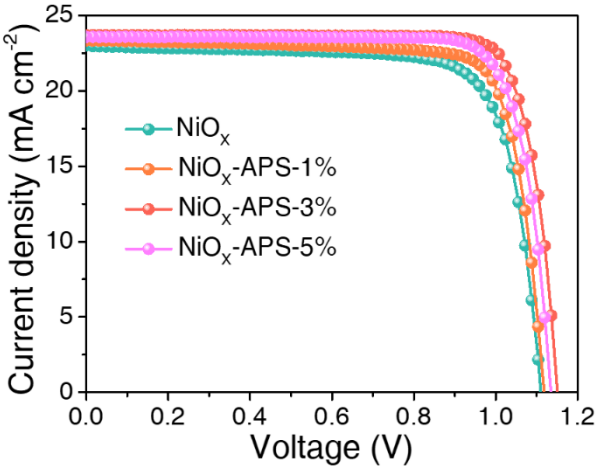

Figure S1. *J-V* curves of F-PSCs based on different concentrations of APS assisted synthesized NiO_x-APS.

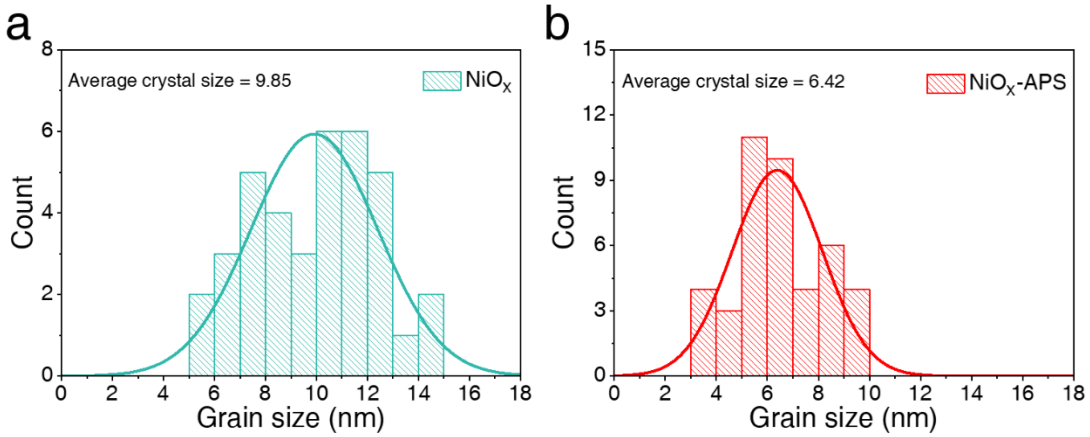

Figure S2. The statistical crystal grain size distribution of NiO_x (a) and NiO_x-APS (b).

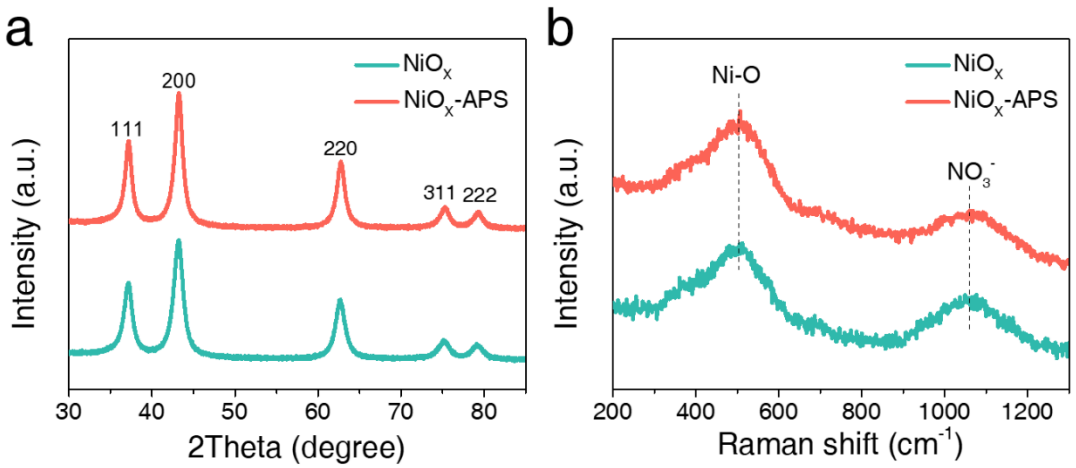

Figure S3. XRD patterns (a) and Raman spectrum (b) of the NiO_x and NiO_x-APS NPs.

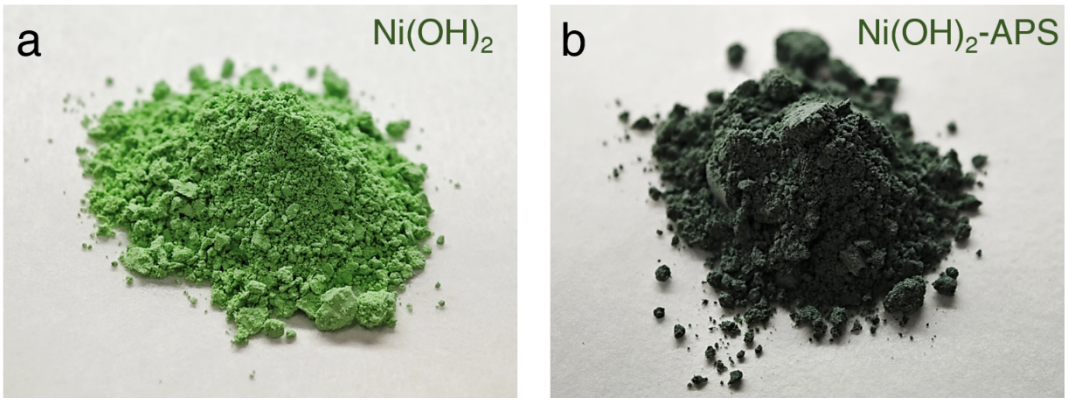

Figure S4. Photographs of $Ni(OH)_2$ (a) and $Ni(OH)_2$-APS (b).

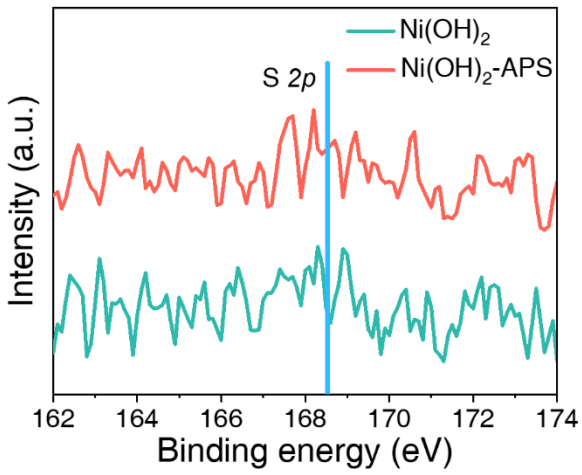

Figure S5. XPS S *2P* spectra of $Ni(OH)_2$-APS NPs.

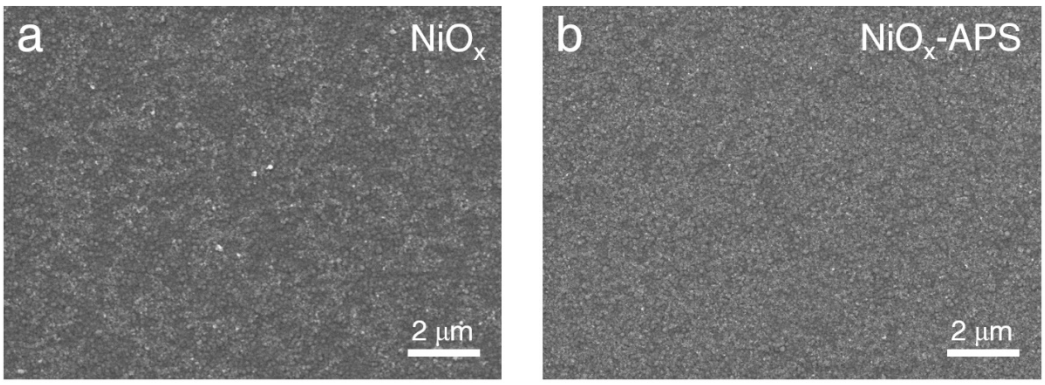

Figure S6. SEM images of NiO_x (a) and NiO_x-APS (b) films.

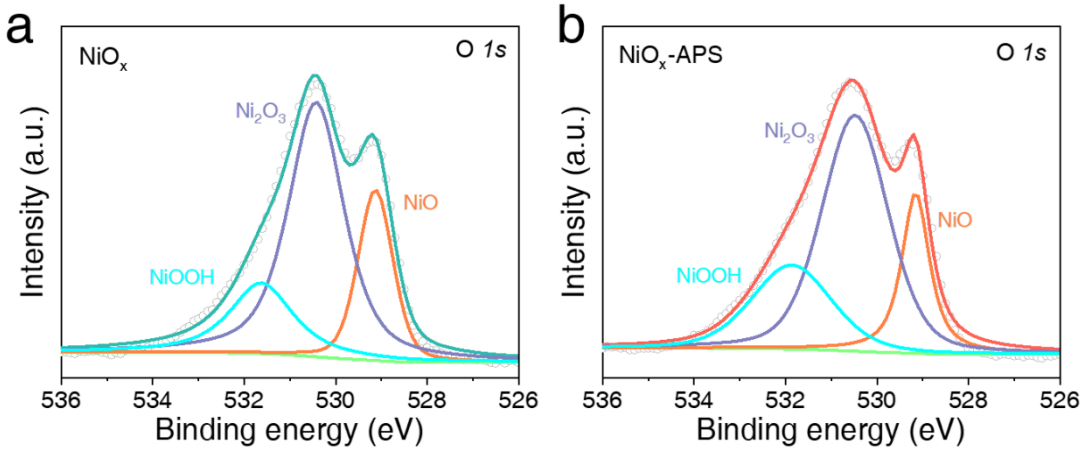

Figure S7. XPS O *1s* spectra of NiO_x and NiO_x-APS films.

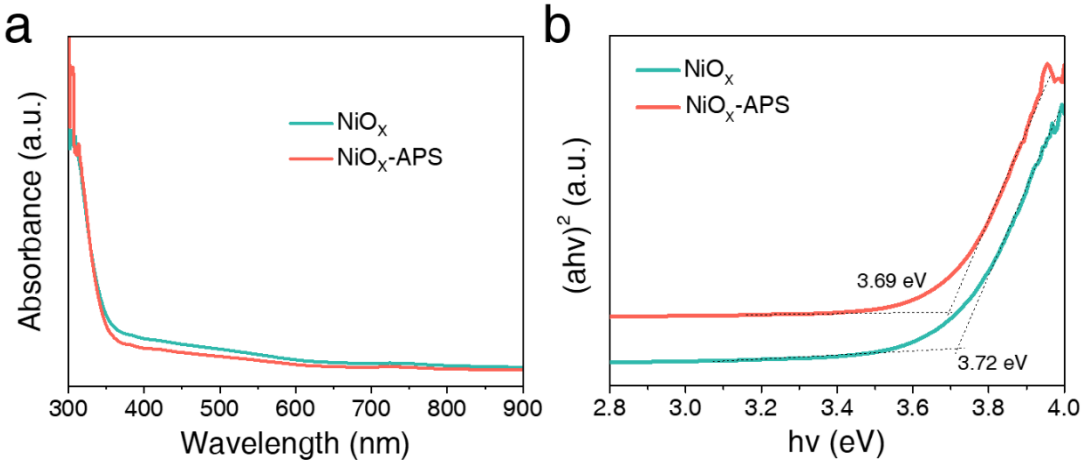

Figure S8. a) UV-vis absorption spectra of NiO_x and NiO_x-APS films. b) Tauc plot showing an optical bandgap of NiO_x and NiO_x-APS films.

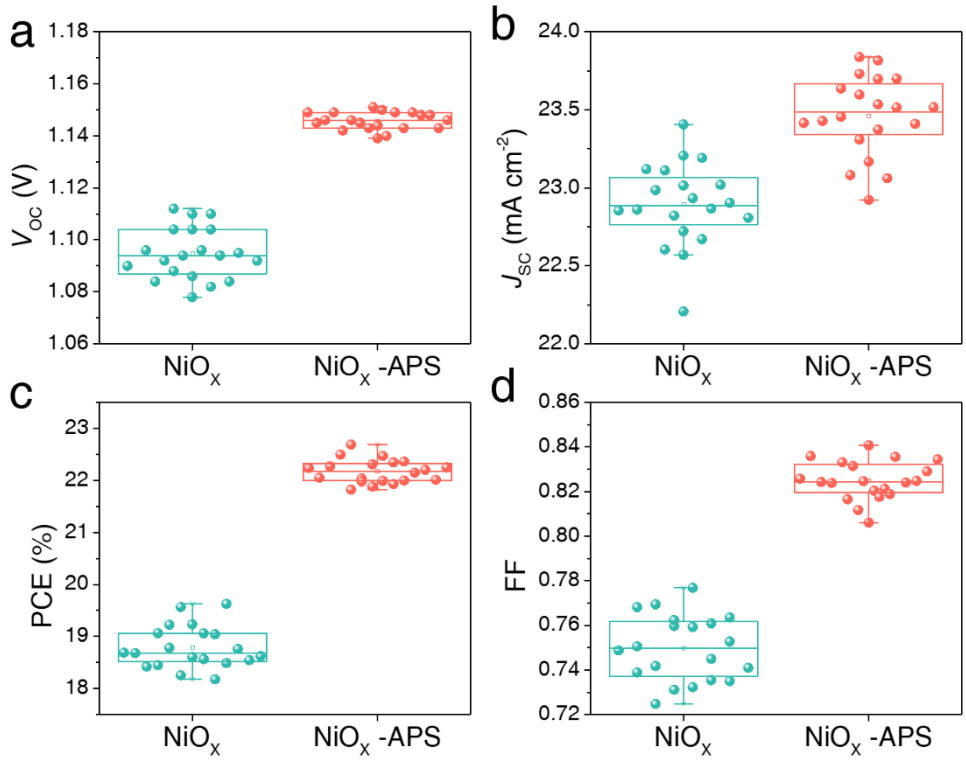

Figure S9. Photovoltaic parameters statistics distribution of V_{OC}, J_{SC}, PCE, and FF for the F-PSCs based on NiO_x and NiO_x-APS HTLs.

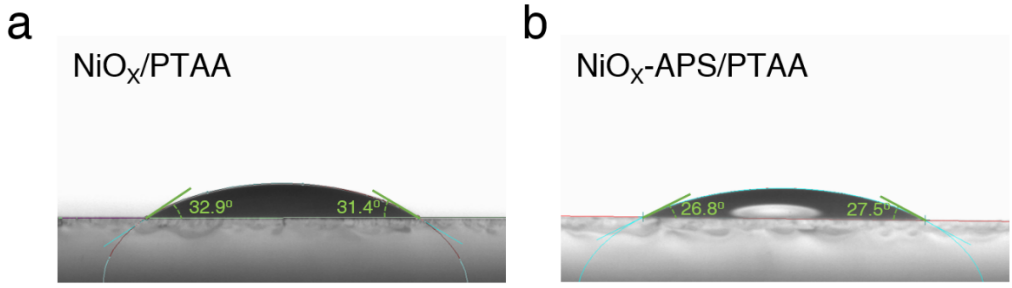

Figure S10. The contact angle of perovskite precursor solution on the surface of NiO_x and NiO_x-APS films.

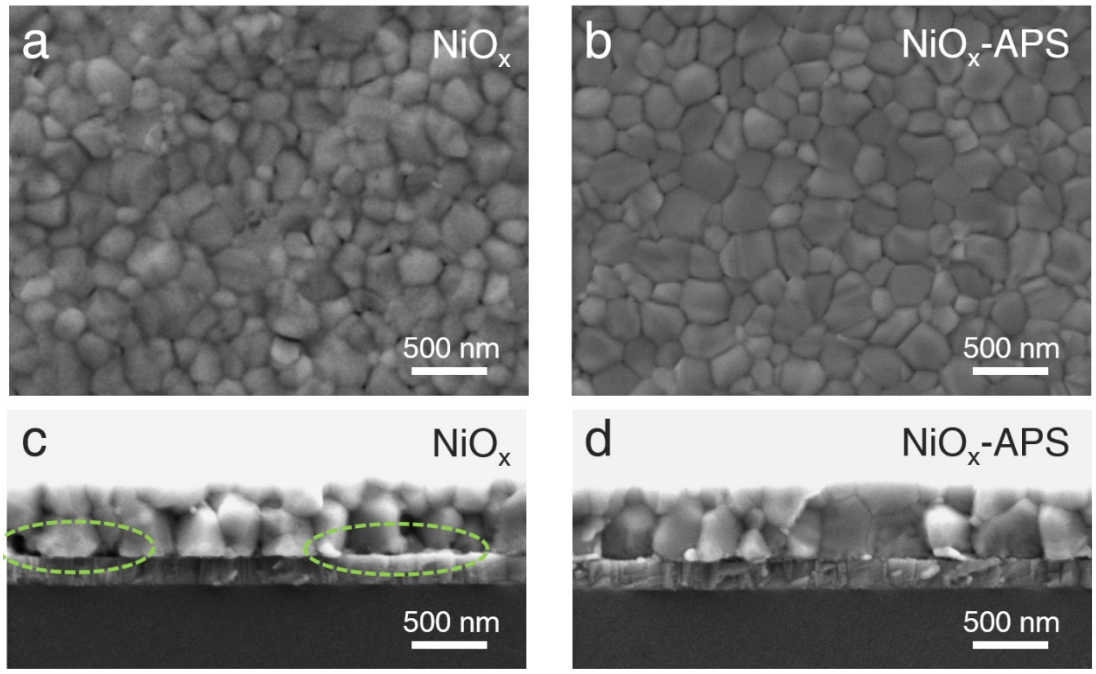

Figure S11. Top-view and cross-section SEM images of the perovskite films deposited on NiO_x and NiO_x-APS films. (Due to the difficulty in preparing cross-sectional samples for flexible films, the cross-sectional sample was prepared on an ITO/glass substrate.)

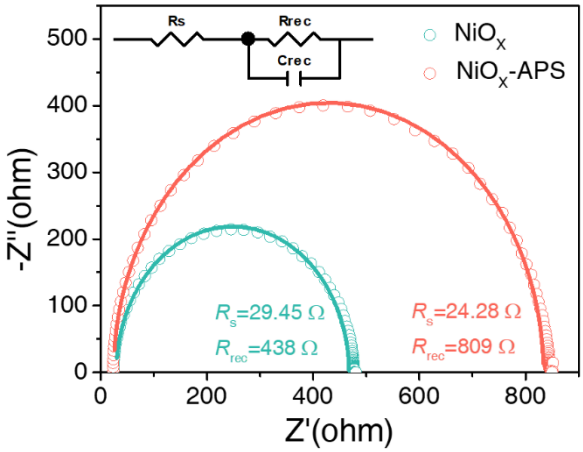

Figure S12. Nyquist plots of the F-PSCs based on NiO_x and NiO_x-APS HTLs, measured with a bias voltage of 1 V in dark condition. Inset: equivalent circuit model.

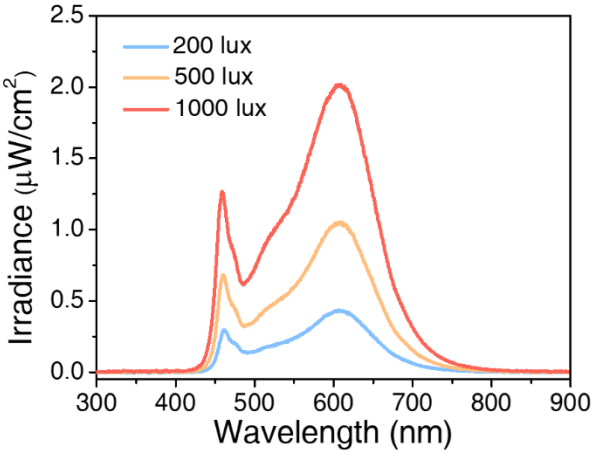

Figure S13. The spectra of 3000 K LED light at 1000 lux, 500 lux, and 200 lux illuminances.

Table S1 Summary of device performance for F-PSCs based on different concentrations of APS assisted synthesized NiO_x-APS.

Device	V_{OC}(V)	J_{SC}(mA/cm^2)	PCE(%)	FF(%)
NiO_x	1.110	23.02	19.63	76.82
NiO_x-APS-1%	1.119	23.35	20.86	79.83
NiO_x-APS-3%	1.149	23.70	22.68	83.28
NiO_x-APS-5%	1.136	23.59	21.76	81.19

Table S2 Photovoltaic parameters for champion F-PSCs based on NiO_x and NiO_x-APS HTLs.

Device	V_{OC}(V)	J_{SC}(mA/cm^2)	PCE(%)	FF(%)
NiO_x_RS	1.110	23.02	19.63	76.82
NiO_x_FS	1.090	23.02	18.54	73.89
NiO_x-APS_RS	1.149	23.70	22.68	83.28
NiO_x-APS_FS	1.149	23.70	22.54	82.77

Table S3 Summary of F-PSCs with NiO_x HTMs in recent years.

Device architecture	V_{OC} [V]	J_{SC} [mA cm^{-2}]	PCE [%]	FF [%]	Ref.
PEN/ITO/NiO_x/$Cs_{0.05}(MA_{0.15}FA_{0.85})_{0.95}Pb(Br_{0.15}I_{0.85})_3$/$PC_{61}BM$/BCP/Ag	1.11	23.50	21.08	80.76	[1]
PET/ITO/NiO_x/$Cs_{0.05}MA_{0.05}$ $FA_{0.9}PbI_{0.95}Br_{0.05}$ /$PC_{61}BM$/BCP/Ag	1.12	21.79	19.17	79	[2]
PET/ITO/NiO_x/Poly(LA)/ $Cs_{0.05}(FA_{0.92}MA_{0.08})_{0.95}Pb(I_{0.92}Br_{0.08})_3$/$PC_{61}BM$/BCP/Ag	1.06	23.78	19.03	76	[3]
PET/ITO/NiO_x/$Cs_{0.05}(FA_{0.77}MA_{0.23})_{0.95}Pb(I_{0.77}Br_{0.23})_3$/$PC_{61}BM$/BCP/Ag	1.230	20.90	21.02	81.76	[4]
PET/ITO/NiO_x/PTAA/$Cs_{0.05}(FA_{0.95}MA_{0.05})_{0.95}Pb(I_{0.95}Br_{0.05})_3$/$PC_{61}BM$/BCP/Ag	1.172	23.89	23.72	84.64	[5]
CPI/ITO/Sp-NiO_x/MeO-2PACz/$Cs_{0.04}(FA_{0.83}MA_{0.17})_{0.96}Pb(I_{0.83}Br_{0.17})_3$/$C_{60}$/Cr/Cu	1.07	19.60	15.52	71.96	[6]
PEN/ITO/NiO_x/2PACz&MeO-2PACz /$(CsPbI_3)_{0.13}(FAPbI_3)_{0.85}(MAPbBr_3)_{0.02}$/$C_{60}$/BCP/Au	1.153	23.27	21.96	81.83	[7]
PET/ITO/NiO_x/$Cs_{0.05}(FA_{0.92}MA_{0.08})_{0.95}Pb(I_{0.92}Br_{0.08})_3$/$PC_{61}BM$/BCP/Ag	1.097	22.62	20.42	82.33	[8]
PET/ITO/NiO_x/PTAA/$Cs_{0.05}(FA_{0.95}MA_{0.05})_{0.95}Pb(I_{0.95}Br_{0.05})_3$/$PC_{61}BM$/BCP/Ag	1.149	23.70	22.68	83.28	This work

Table S4 Statistics of performance parameters of champion devices based on NiO_x-APS HTLs at different light intensities.

Device	Light source	Pin (μW/cm^2)	V_{OC}(V)	J_{SC}(mA/cm^2)	PCE(%)	FF(%)
Target	1000 lux	312	0.926	0.1472	35.59	81.46
	500 lux	158	0.858	0.0755	32.92	80.18
	200 lux	62	0.812	0.0284	28.28	76.02

Supplementary References

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