

Supporting Information

Functionalized nickel oxide as hole transport layers for organic solar cells with simultaneous enhancement of efficiency and stability

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Experimental Section

1. Materials

PM6 was purchased from Solarmer Material Inc., Y6 was purchased from Derthon, 2PACz was purchased from TCI, Ethanolamine and Nickel acetate tetrahydrate was purchased from Sigma-Adrich, PEDOT:PSS solution was purchased from Clevios™.

2. Device fabrication and testing

NiO_x Precursor Solution¹: Nickel acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O) was dissolved in ethanol with monoethanolamine (NH₂CH₂CH₂OH) (0.1 mol L⁻¹). The mole ratio of Ni²⁺ : MEA was maintained at 1:1 in solution. Dissolution took place while stirring in a sealed glass vial under air at 70 °C overnight. The solution appeared homogeneous and deep green after approximately 40 min.

SAM solution: 2PACz (molar weight 335.3 g mol⁻¹) was dissolved in anhydrous Ethanol at a concentration of 1 mmol L⁻¹. Dissolution took place while stirring in a sealed glass vial under air at 50 °C overnight.

ITO cleaning: The ITO glass substrates were washed sequentially under sonication with acetone, detergent, deionized water, and isopropyl alcohol, and then dried at 65°C in a baking oven overnight, followed by an oxygen plasma treatment of 4 minutes. All hole transport layer (HTL) films were deposited by spin-casting onto the prepared ITO.

SAM film preparation: SAM solution was dropped onto the ITO substrate and left undisturbed for 15 seconds before spin-coating (30 s at 3000 rpm) and then air-dried at 100°C for 10 minutes.

NiO_x film preparation: The NiO_x precursor solution was spin-coated (30 s at 3000 rpm) on ITO substrates and heated to 275 °C for 45 minutes in air, then processed under UV-ozone (UVO) for 30 minutes.

NiO_x/SAM film preparation: Prepared NiO_x was transferred to a glovebox under nitrogen (N₂) atmosphere, then spin-coated the SAM solution (being undisturbed for 15 s before spin-coating at 3000 rpm) on prepared NiO_x substrates and dried at 100°C for 10 minutes.

PEDOT:PSS preparation: PEDOT:PSS (~40 nm) was spin-coated on ITO substrates and air-dried at 150°C for 15 minutes.

Device Fabrication and Characterization: All prepared HTL substrates were then transferred to a glovebox under nitrogen (N₂) atmosphere for subsequent deposition of active layers. The weight ratio of PM6 to Y6 was maintained at 1:1.2. PM6:Y6 blend solution was prepared in chloroform at the polymer concentration of 7 mg mL⁻¹ with 0.5% CN by volume, and stirred on a hot plate at 50°C overnight to ensure complete dissolution. Then the active layers solution was spin-coated on different HTL substrates at room temperature to obtain the required thickness of about 100 nm. Then, the films were treated with thermal annealing at 110°C for 10 minutes. After fabricating the active layers, a 5-nm PFN-Br cathode interfacial layer was spin-coated with the PFN-Br methanol solution at a concentration of 0.5 mg mL⁻¹ at 2000 rpm for 30 seconds on the active layers, and the samples were transferred to the vacuum chamber. At a vacuum level of 1×10⁻⁷ Torr, 100 nm of Ag was thermally deposited as the top electrode through a shadow mask. The active area of all devices was 0.08 cm². The J-V curves were measured on a computer-controlled Keithley 2400 source meter under 1 sun, the AM 1.5 G spectra came from a class solar simulator (Enlitech, Taiwan), and the light intensity was 100 mW cm⁻² as calibrated by a China General Certification Center (CGC) certified reference monocrystal silicon cell (Enlitech). Before the J-V test, a physical mask with an aperture with precise area of 0.04 cm² was used to define the device area. The EQE spectra measurements were performed on a commercial QE measurement system (QE-R3011, Enlitech).

3. Instruments and Measurement

Kelvin Probe: Kelvin Probe Force Microscopy was used to test work function of different HTL samples that are directly spin-coated on ITO. The KP measurements were calibrated using commercial ITO substrate whose WF is 4.70 eV. All the samples were measured 200 times and the average values were taken to calculate their WF.

Hole-only Devices: Devices were fabricated to measure hole mobility using the space charge limited current (SCLC) method. The hole-only device structure was ITO/(PEDOT:PSS or NiO_x/SAM)/PM6:Y6/MoO₃/Ag. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation: $J = (9/8)\epsilon_0\epsilon_r\mu(V^2/d^3)$, where J is the current, μ is the zero-field mobility, ϵ_0 is the permittivity of free space, ϵ_r is the relative permittivity of the material, d is the thickness of the active layers, and V is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the series resistance of the whole device except for the active layers from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The hole mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

Contact angle measurement: The contact angle tests were performed on a DataPhysics OCA40 Micro surface contact angle analyzer. The surface energy of the polymers was characterized and calculated by the contact angles of the two probe liquids using the Owens and Wendt equation: $(1 + \cos\theta)\gamma_{pl} = 2(\gamma_s^d\gamma_{pl}^d)^{1/2} + 2(\gamma_s^p\gamma_{pl}^p)^{1/2}$, where γ_s and γ_{pl} are the surface energy of the sample and the probe liquid, respectively. The superscripts d and p refer to the dispersion and polar components of the surface energy, respectively.

Grazing Incidence Wide-angle X-ray Scattering (GIWAXS): The GIWAXS measurements were collected using a Xeuss 2.0 spectrometer (Xenocs company) with MetalJet-D2 (Excillum) as the X-ray source and Pilatus 3R 1M (Dectris) as the detector and were performed on an Si/PEDOT:PSS/PM6:Y6 and Si/NiO_x/SAM/PM6:Y6 structure.

Trap density of states: Capacitance-Frequency (C-F) and Mott-Schottky measurement were performed using an electrochemical workstation (PARSTAT MC) in the dark.

Light-soaking degradation: The J-V characteristics of the studied devices were probed continuously under illumination by a light emitting diode (LED) light source irradiating at a wide wavelength range of 380–1000 nm

Other Characterizations: UV-visible transmittance spectra were measured using a Maya 2000pro spectrometer. The transient photovoltage of the devices were measured using the Paios 4.0 measurement system.

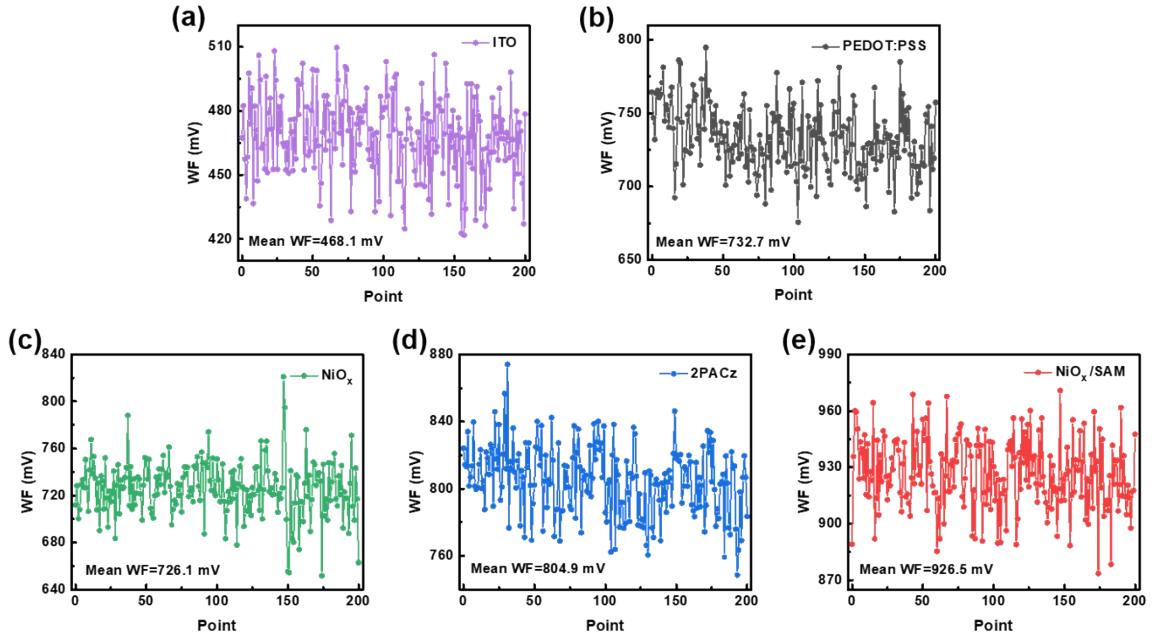


Figure S1. Work function of different HTL samples. (a) ITO; (b) PEDOT:PSS; (c) NiO_x; (d) SAM (2PACz); (e) NiO_x/SAM.

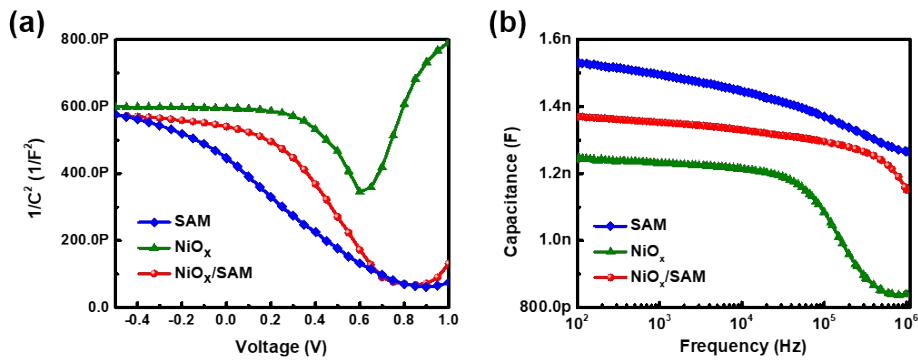


Figure S2. (a) Mott-Schottky analysis of OSCs based on NiO_x, SAM and NiO_x/SAM measured at 3 kHz; (b) C-F curves of OSCs based on NiO_x, SAM and NiO_x/SAM.

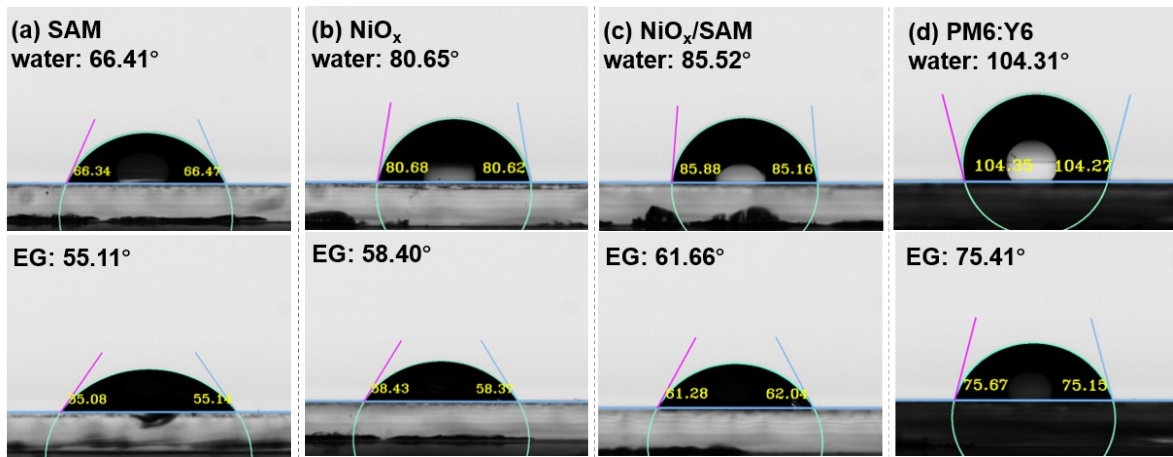


Figure S3. Different HTL films of contact angle measurements. (a) SAM; (b) NiO_x; (c) NiO_x/SAM; (d) PM6:Y6. The measurements are carried out by using deionized water (upper row) and ethylene glycol (under row) as the wetting liquid.

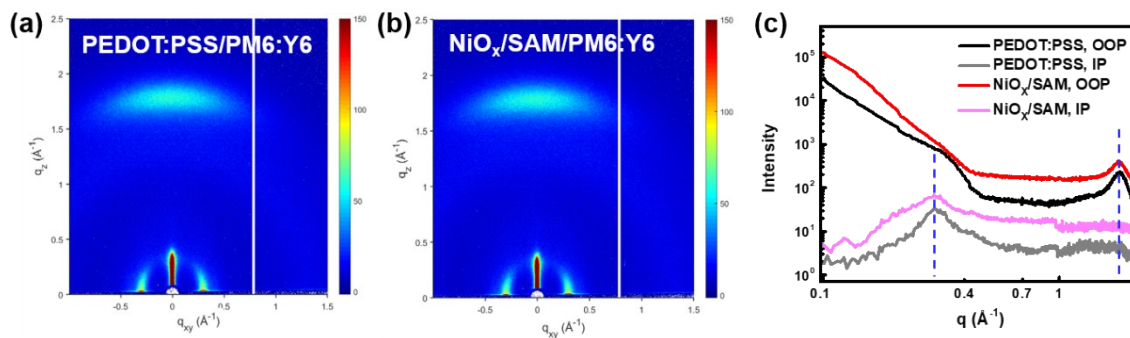


Figure S4. GIWAXS image of PM6:Y6 blend films based on (a) PEDOT:PSS or (b) NiO_x/SAM, and (c) corresponding line-cut profiles in in-plane and out-of-plane directions, respectively.

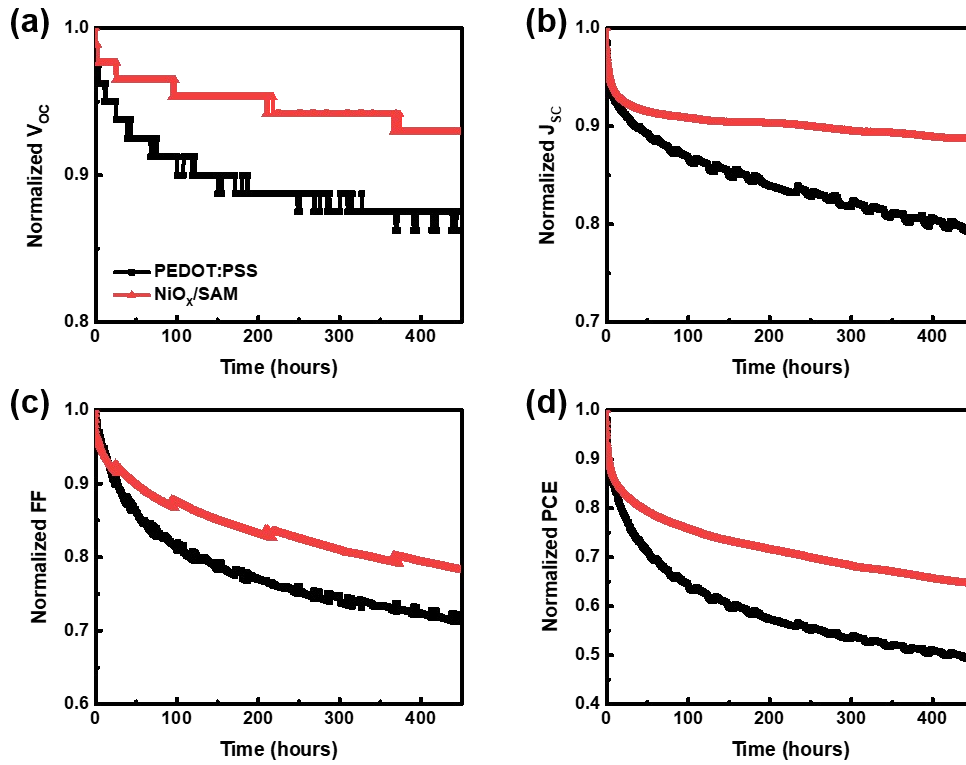


Figure S5. Normalized (a) V_{oc} , (b) J_{sc} , (c) FF, and (d) PCE of encapsulated PM6:Y6 devices based on different HTLs over the course of 450 h of photoaging test.

Table S1. Photovoltaic parameters of PM6:Y6 devices with different HTLs under AM 1.5G irradiation (100 mW cm^{-2}).

HTLs	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE ^{a)} [%]
ITO	0.56	24.6	63.2	8.8
SAM	0.83	27.8	75.2	17.3
SAM-soaked ^{b)}	0.82	26.4	67.7	14.8
NiO _x	0.83	24.8	73.7	15.3
NiO _x /SAM	0.84	26.9	73.8	16.7
NiO _x /SAM-soaked ^{b)}	0.83	26.3	72.1	15.7

a) the best performance of device.

b) HTL films are soaked by ethanol for 30 seconds before spinning coating active layers.

Table S2. The contact angles and surface energy parameters of different HTL films.

films	$\theta_{water} [^\circ]$	$\theta_{oil} [^\circ]_a$	Surface Energy [mJ m ⁻²]
SAM	66.41	55.11	36.18
NiO _x	80.65	58.40	28.11
NiO _x /SAM	85.52	61.66	27.05
PM6:Y6	104.31	75.41	27.92

a) θ_{oil} represents the contact angle of ethylene glycol

Reference

1. Manders, J. R.; Tsang, S. W.; Hartel, M. J.; Lai, T. H.; Chen, S.; Amb, C. M.; Reynolds, J. R.; So, F., Solution-Processed Nickel Oxide Hole Transport Layers in High Efficiency Polymer Photovoltaic Cells. *Adv. Funct. Mater.* **2013**, 23 (23), 2993-3001.