

Supporting Information

Entropy-assisted nitrogen-doped carbon-anchored high-entropy alloy composites for efficient and stable universal photovoltaic electrode

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Experimental section

Materials

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, Aladdin, 99%), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aladdin, 99%), methyl alcohol (MeOH, Macklin, 99.5%), ethyl alcohol (EtOH, Macklin, 99.5%), isopropyl alcohol (IPA, Macklin, 99.5%), ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aladdin, 99%), nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aladdin, 99%), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Aladdin, 99%), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aladdin, 99%), and 2-methylimidazole (2-MeIM, Aladdin, 99%) were used directly without further purification. Lead iodide (PbI_2 , 99.999%), methylammonium iodide (MAI, 99.5%), and tin dioxide solution (SnO_2 (IV), 12 wt% in H_2O colloidal dispersion) were obtained from Xi'an Yuri Solar Co., Ltd. N,N-Dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), 4-tert-butylpyridine (tBP), acetonitrile (ACN, 99.8%), lithium trifluoromethylsulfonimide (Li-TFSI, 99.95%), ethyl acetate (EA, 99.8%), and chlorobenzene (CB, 99.99%) were produced by Sigma-Aldrich. Acetone ($\text{C}_3\text{H}_6\text{O}$, 99.7%) was purchased from Sinopharm Chemical Reagent co., Ltd. Lithium iodide (LiI, Alfa, 99.95%), iodine (I_2 , Alfa, 99.5%), guanidine thiocyanate (TCI, 99.0%), lithium perchlorate (LiClO_4 , Alfa, 99%), acetonitrile (Aladdin, 99.99%), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, Aladdin, $\text{Pt} \geq 37.5\%$) and N719 dye (Solaronix SA) were commercially available without further purification. ITO conductive glass substrates ($9 \Omega \text{ sq}^{-1}$) were purchased from Advanced Election Technology Co., Ltd. FTO glass substrates were sourced from Asahi Glass (Japan). The TiO_2 photoanodes were obtained from Jiangsu YanchangSunlaite Group (China).

Materials characterization

The morphology of the samples can be observed by scanning electron microscopy (SEM, ZEISS G500, Germany) and transmission electron microscopy (TEM, ThermoFisher Talos F200X, USA). The crystal structures of the samples were obtained by X-ray diffractometer (XRD, MDI D/Max 2200, Japan) analyzed with $\text{Cu K}\alpha$ radiation at 30 kV. The chemical state of prepared materials was checked by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI, USA). The work function

of the material was measured by ultraviolet photoelectron spectroscopy (UPS, PHI5000 Versa Probe III, Japan).

Electrochemical and photovoltaic measurements

Photocurrent-voltage performance and on-off tests of SSCs and HTL-free C-PSCs were measured by a standard sunlight simulator (AM 1.5G, Xe Arc Lamp, EASISOLAR-50-3A, CROWNTECH, INC., USA) and a Keithley 2400 digital light source meter under 100 mW cm⁻² light conditions. The effective area was 0.16 cm² for SSCs and 0.09 cm² for HTL-free C-PSCs, defined by the actual area of TiO₂ photoanode and carbon electrode, respectively. The electrode thickness of SSCs was approximately 26 μm and HTL-free C-PSCs was approximately 30 μm, both measured by cross-sectional SEM (Fig. S6). The electrocatalytic performance of SSCs was evaluated in a three-electrode system using cyclic voltammetry (CV) and Tafel polarization. Measurements were carried out in an acetonitrile solution containing 10 mM LiI, 0.1 M LiClO₄, and 1 mM I₂, with a potential window from -0.4 to 1.1 V. The system comprised the prepared electrode as the working electrode, a Pt as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The electrochemical impedance spectra (EIS) of SSCs and HTL-free C-PSCs were tested by a CHI 660E (Chenhua, Shanghai, China) electrochemical workstation, and Nyquist curves were measured at a bias potential of -0.75 V with an alternating current amplitude of 10 mV within the frequency range of 0.1 to 10⁵ Hz. The external quantum efficiency (EQE) of the HTL-free C-PSCs was measured by means of a solar cell quantum efficiency test system (QTEST HIFINITY 5).

Density functional theory (DFT) calculation

All atomic models were constructed using the Materials Studio software package. A vacuum layer with a thickness of 15 Å was introduced to completely eliminate the interlayer coupling effect between periodic mirror-image supercells. Considering the

weak van der Waals (vdW) interactions, the Grimme DFT-D3 dispersion correction method was employed to accurately correct such interactions, thus improving the reliability of the calculated results.¹

For the ionic relaxation process, strict convergence criteria were set to ensure the validity of structural optimization: the convergence threshold for atomic forces was $0.01 \text{ eV}\cdot\text{\AA}^{-1}$ and that for the total energy was $1\times 10^{-5} \text{ eV}$.² The cutoff energy of the plane-wave basis set was fixed at 500 eV, which was verified to be sufficient to ensure the completeness of the basis set and avoid calculation errors caused by an excessively low cutoff energy. In addition, the Gamma-centered k-point mesh with a spacing of 0.04 \AA^{-1} was generated using the VASP software and adopted for static self-consistent calculations, balancing the computational accuracy and efficiency.³

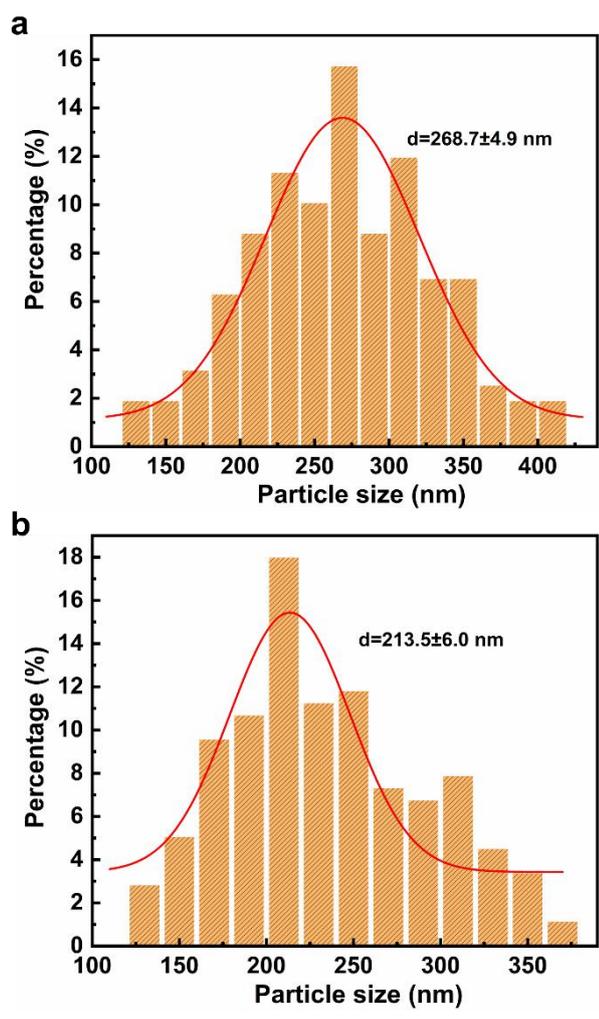


Fig. S1 Statistical plots of the particle size distribution of (a) NC and (b) HEA NPs@NC.

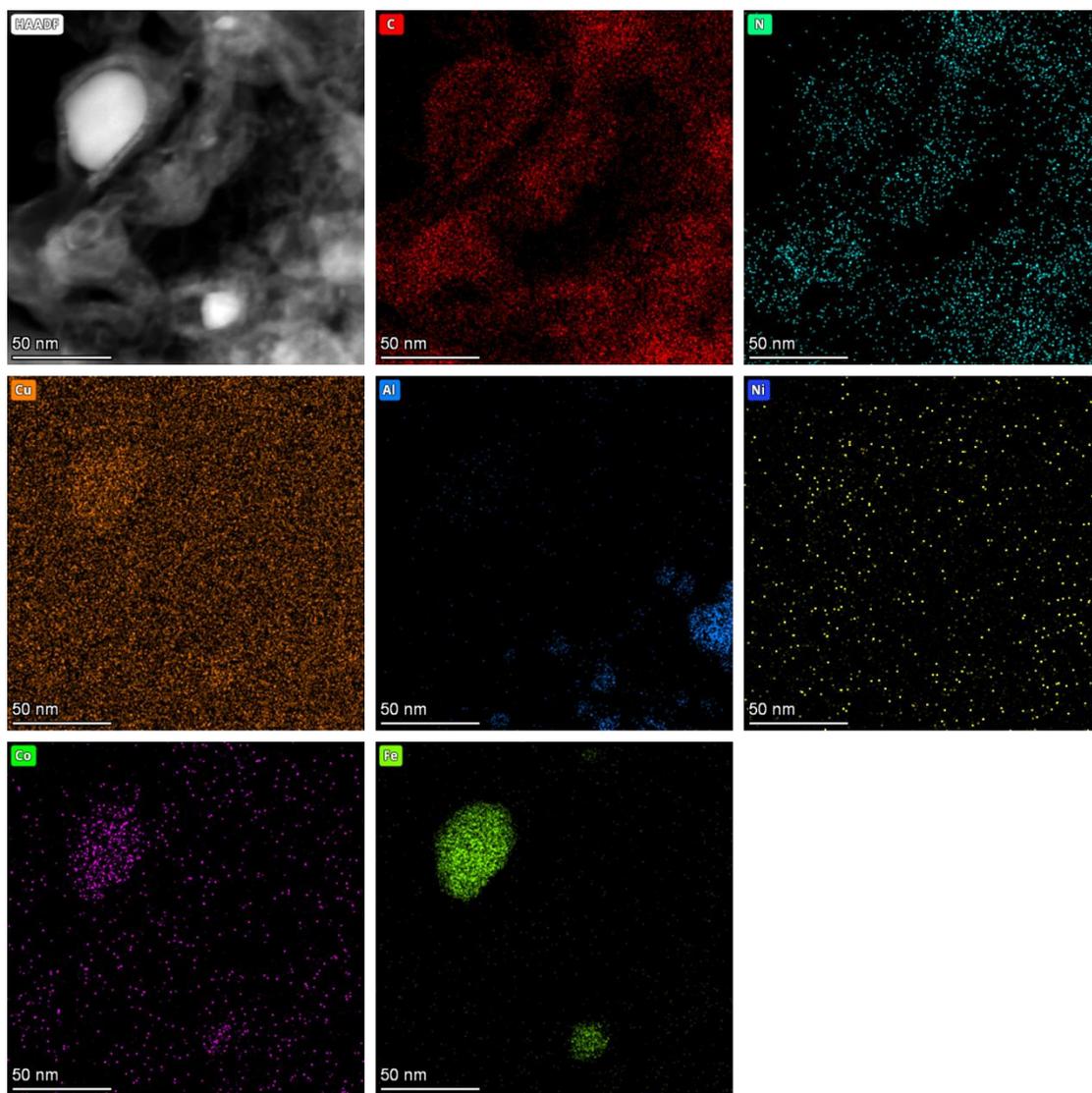


Fig. S2 HADF-STEM EDS diagram of HEA NPs@NC.

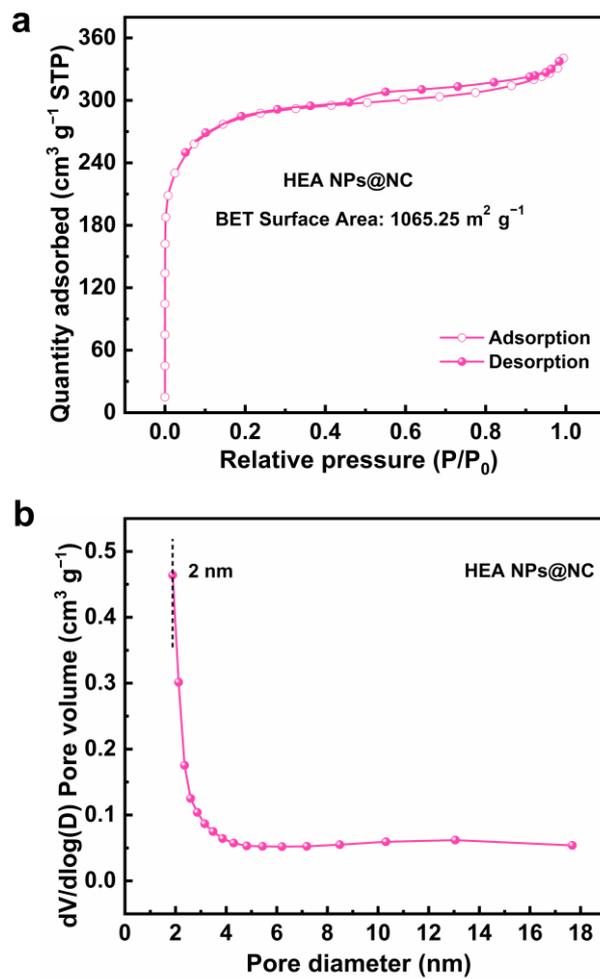


Fig. S3 (a) N_2 adsorption-desorption isotherm and (b) the corresponding pore-size distribution plot of HEA NPs@NC.

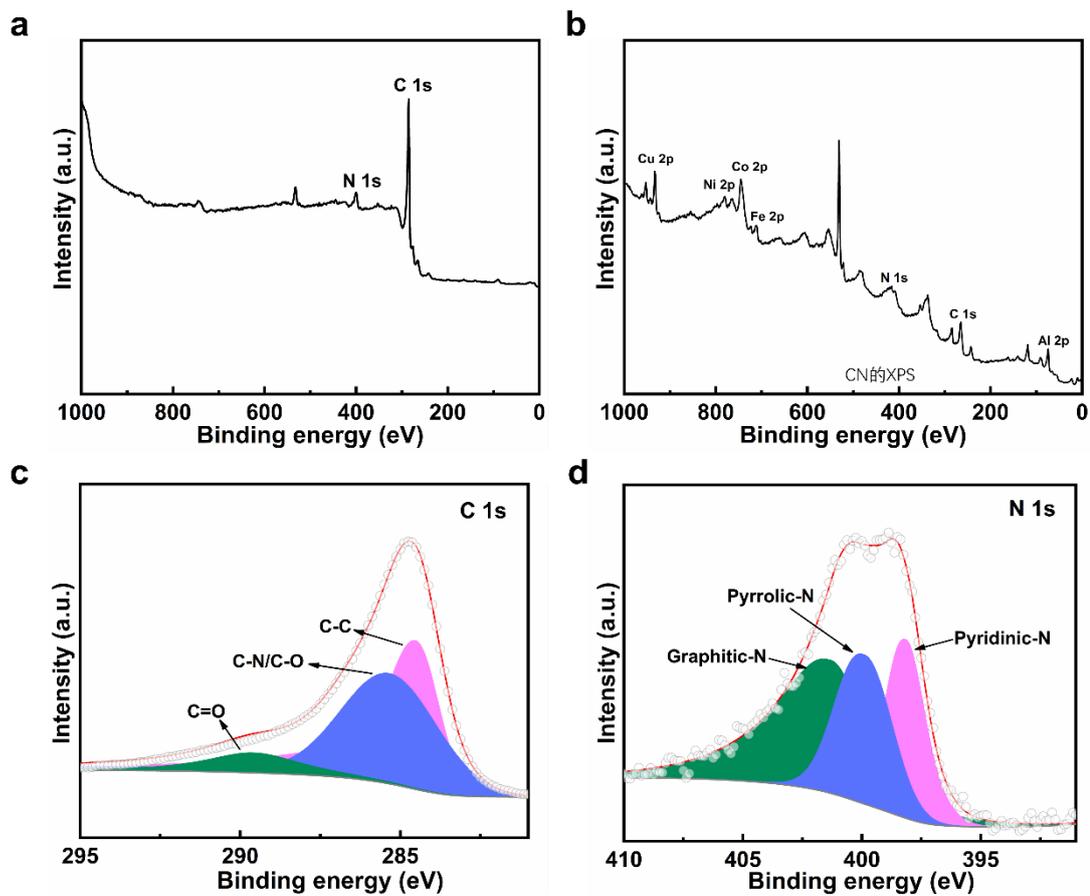


Fig. S4 XPS survey spectra of (a) NC and (b) HEA NPs@NC. High-resolution XPS spectra of (c) C 1s and (d) N 1s of NC.

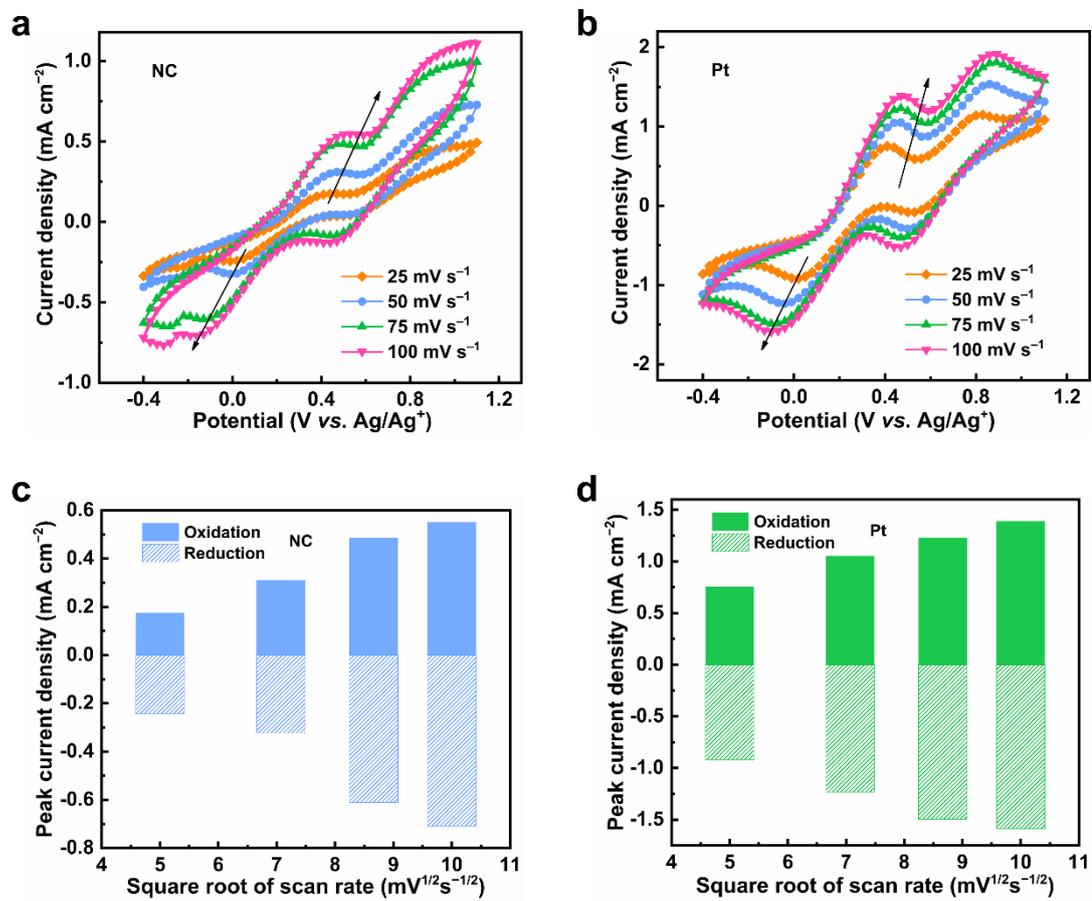


Fig. S5 CV curves of (a) NC and (b) Pt recorded at different scan rates. Linear relationships curves between I_p and the square root of scan rate of (c) NC and (d) Pt.

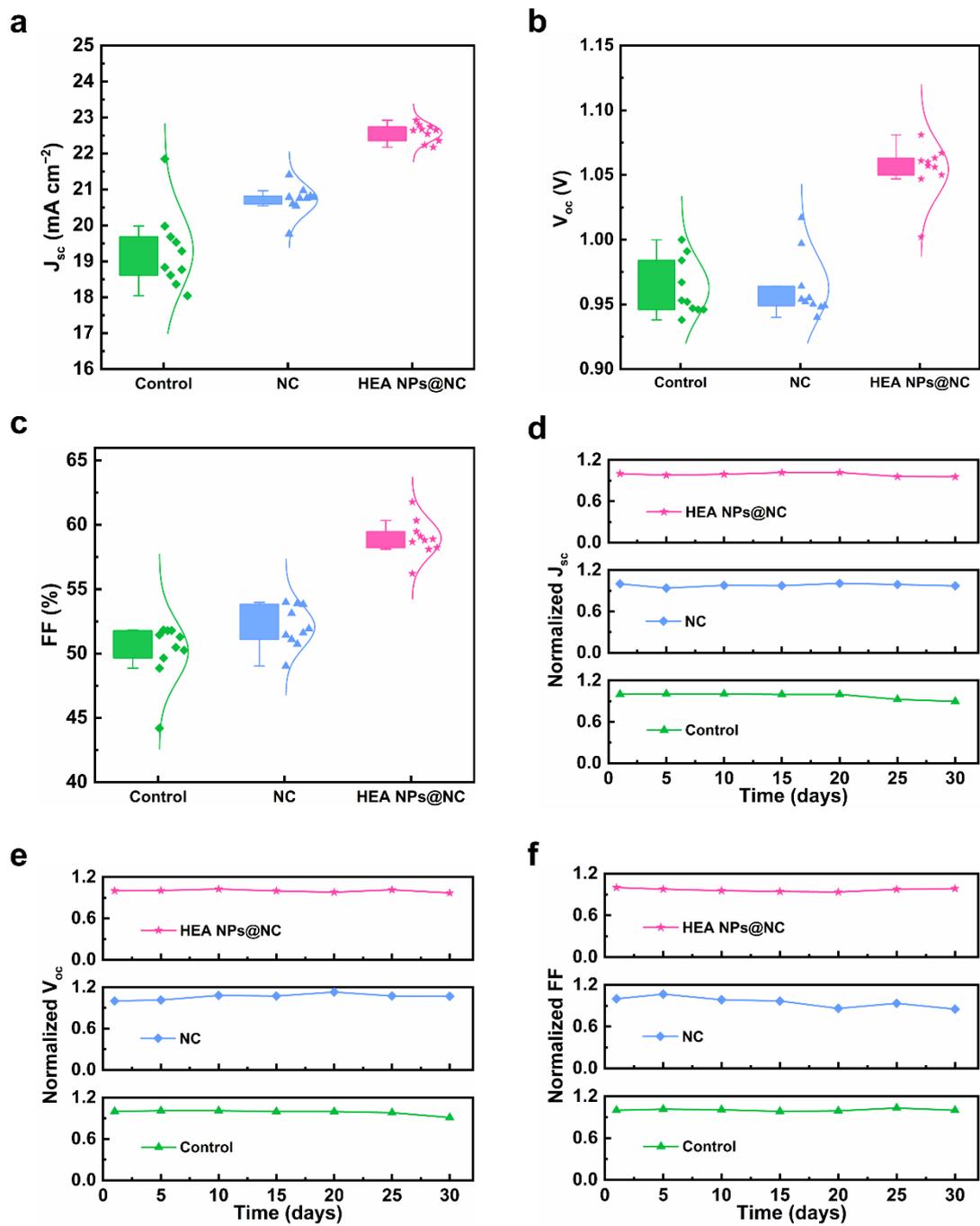


Fig. S6 (a–c) Statistical performance comparison plots and (d–f) 30-day operational stability curves of HTL-free C-PSCs employing control carbon paste, NC, and HEA NPs@NC electrodes.

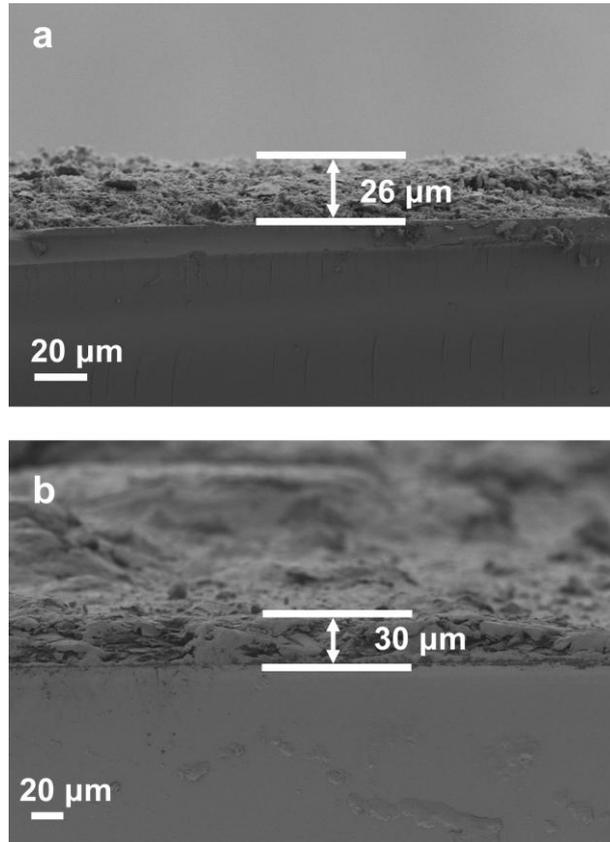


Fig. S7 Cross-sectional SEM patterns of (a) SSCs and (b) HTL-free C-PSCs devices.

Table S1. Elemental contents (wt.%) of HEA NPs@NC.

Al	Fe	Co	Ni	Cu
14.42	26.10	21.21	20.91	17.36

Table S2. Error analysis of photovoltaic parameters of SSCs based on six independent devices.

Counter electrodes	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
NC	13.72±0.85	0.76±0.01	63.57±3.45	6.55±0.25
Pt	13.64±1.17	0.74±0.03	69.91±2.49	7.10±0.14
HEA NPs@NC	14.83±0.28	0.77±0.01	71.62±0.50	8.14±0.14

Table S3. Comparison of photovoltaic parameters of different CEs in SSCs.

CEs	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	Ref.
NiPt	14.67	0.72	66.05	6.93	4
NiPt nanosheets	16.73	0.71	62.32	7.41	5
Ta/Co-N-C	18.11	0.65	68.44	7.96	6
Pt _{0.9} Ni _{0.1} /CB	14.19	0.72	69.67	7.03	7
ONC@FeCo	16.58	0.77	65.53	8.26	8
Fe/Ni-NDPC	16.04	0.78	65.38	8.14	9
Co@CN	15.01	0.78	67.47	7.89	10
FeCoNiMoNb/C	15.12	0.79	71.29	8.50	11
PtFeNi FAs	15.52	0.70	66.36	7.36	12
Fe-NPCD	15.54	0.78	63.21	7.63	13
WS ₂ @CuFe	18.81	0.78	37.00	5.40	14
Ni NPs@Ni-N-C	14.56	0.79	62.35	7.06	15
N-C-in-Co/N-C	15.79	0.74	66.40	7.80	16
HEA NPs@NC	15.26	0.77	71.02	8.34	This work

Table S4. Error analysis of photovoltaic parameters of HTL-free C-PSCs based on eight independent devices.

Device	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
NC	20.71±0.41	0.95±0.04	52.06±1.63	10.38±0.45
Control	19.29±1.09	0.95±0.02	50.12±2.32	9.44±0.23
HEA NPs@NC	22.57±0.25	1.01±0.01	58.96±1.45	14.03±0.44

Table S5. Comparison with reported photovoltaic parameters of HTL-free C-PSCs.

Device structure	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)	Ref.
FTO/SnO ₂ /MAPbI ₃ /Co ₃ O ₄ @NC/C	23.88	0.97	61.53	14.63	17
FTO/TiO ₂ /MAPbI ₃ /(SrCl ₂) _{0.1} /C	20.15	1.05	75.21	15.90	18
FTO/c-TiO ₂ /m-TiO ₂ /MAPbI ₃ /CuPc/C	20.80	1.05	74.56	16.10	19
FTO/SnO ₂ /MAPbI ₃ /F-N-GQDs/C	23.88	0.98	69.35	16.37	20
FTO/c-TiO ₂ /m-TiO ₂ /ZrO ₂ /Cs _{0.1} FA _{0.9} PbI ₃ /C	16.00	0.87	57.34	15.00	21
FTO/TiO ₂ /ZrO ₂ /(5-AVA) _x MA _{1-x} PbI ₃ /C	22.80	0.86	66.31	12.70	22
FTO/c-TiO ₂ /m-TiO ₂ /MAPbI ₃ /SWNT	14.20	0.87	54.70	6.70	23
FTO/TiO ₂ /MAPbI ₃ /IPA-CYHEX/C	21.27	1.04	65.14	14.40	24
FTO/c-TiO ₂ /MAPbI ₃ /CNT	18.50	0.70	60.37	10.70	25
FTO/c-SnO ₂ /MA _{0.8} FA _{0.2} PbI _{2.9} Br _{0.1} /Ni-NG	18.33	0.93	52.30	8.78	26
FTO/SnO ₂ /MAPbI ₃ /NH ₂ -UiO-66-PST+Carbon	22.38	1.04	75.00	17.50	27
FTO/SnO ₂ /MAPbI ₃ /BiOOH/Carbon	22.88	0.97	65.91	14.67	28
FTO/SnO ₂ /FAPbI ₃ /CS	22.08	0.96	71.77	15.16	29
ITO/SnO ₂ /MAPbI ₃ /CS/FS@NDCC	23.34	1.02	59.00	14.11	30
ITO/SnO₂/MAPbI₃/HEA NPs@NC	22.65	1.06	61.78	14.78	This work

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