

Fluorine anions enriched nickle hydroxyl oxide as efficient oxygen evolution reaction electrocatalyst

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Experimental

Preparation of F-NHO

All reagents were of analytical grade and used as obtained without further purification. In the hydrothermal synthesis of F⁻ enriched Ni hydroxyl oxide (F-NHO), 3 mmol of Ni(NO₃)₂·6H₂O and 10 mmol of NH₄F were dissolved in 30 mL mixed solvent composing of isopyknic H₂O and CH₃OH. The homogeneous reactants solution was transferred into a 50 mL Teflon-lined stainless steel autoclave for hydrothermal reaction at 120 °C for 12 h. The yielded precipitate was centrifuged, rinsed in turn with deionized water and ethanol and then dried at 80 °C. F⁻ anions free sample (Ni₃(OH)₄(NO₃)₂, abbreviated as NHN) was prepared by the same procedure but replaced NH₄F with 10 mmol of urea.

Heat treatment and sulfuration of F-NHO: 0.5 g of F-NHO or NHN was calcinated at 300 °C for 2 h in air to assess the phase stability against thermo-decomposition toward NiO. In the sulfuration treatment, 0.25g F-NHO or NHN was added in 30 mL aqueous solution containing 0.5 g thiourea (NH₂CSNH₂) and subjected to hydrothermal sulfuration at 120 °C for 6 h.

Characterizations

The morphologies, microstructures, phases and chemical status of F-NHO and NHN were identified respectively by scanning electron microscopy (SEM, Hitachi SU-8000), transmittance electron microscopy (TEM, JEOL JEM-2100), X-ray powder diffraction (XRD, Bruker D8 diffractometer with Cu K α radiation) and X-ray photoelectron spectroscopy (XPS, Kratos Amicus X-ray photoelectron spectrometer with Mg K α radiation under 2 \times 10⁻⁶ Pa). In water contact angle test, a drop of dangled water bead (6 μ L) was slowly touched onto the surface of compressed F-NHO or NHN tablet, the profile of the water bead was recorded in 2 s to evaluate the surface wettability.

Electrochemical tests

The OER efficiencies of both catalysts were tested in a three-electrode cell using 1.0 M KOH as electrolyte. Ag/AgCl (saturated KCl) electrode and Pt foil (1 cm²) were used respectively as reference and auxiliary electrodes. A piece of carbon cloth (CC, 1 \times 1 cm²) was used as inert current collector of working electrode to avoid the possible influence metallic current collector to OER. 2 mg of the prepared catalyst powder was ultrasonically dispersed in a mixed medium comprising 0.45 mL ethanol and 0.05 mL of 5 wt.% nafion solution to form a homogeneous ink, which was dripped onto the CC substrate at a loading amount of 0.5 mg cm⁻². After being dried at room temperature, the catalyst loaded CC was served as working electrode for electrochemical tests. All potentials in this study referred to

the reversible hydrogen electrode (RHE), which were calculated according to: $E(\text{RHE})=E(\text{Ag}/\text{AgCl})+0.059\times\text{pH}+0.197$ [1]. The overpotential (η) was calculated according to following formula: $\eta=E(\text{RHE})-1.23\text{V}$. Polarization curves were recorded by linear sweep voltammetry (LSV) at a scan rate of 5 mV s^{-1} . 100 cycles of cyclic voltammetry tests (CVs) at the same scan rate were performed beforehand to stabilize the current density. The polarization curves were replotted as η versus log current density (j) to afford Tafel plots ($\eta=b \log|j|+a$), which was employed to assess the OER kinetics of catalytic electrodes. Long-term durability of the F-NHO electrode was performed at 1.55 V ($j=20\text{ mA cm}^{-2}$) for 24 h. To estimate the electrochemical active surface area (ECSA), CVs within $1.0\sim 1.1\text{ V}$ (non-faradic range) at different potential scan rates were used to evaluate the electric double layer capacitances (C_{dl}) of the electrodes, the slope of cathodic-to-anodic current density difference (at 1.05 V) against scan rate equals diploid value of C_{dl} [2], which reflects the ECSA.

The Faradic efficiency (FE) of OER at F-NHO electrode was estimated by rotating ring-disk electrode test at 1600 rpm, which comprises a concentric glassy-carbon (GC) disk electrode and a Pt ring electrode, the F-NHO catalyst (0.12 mg) was coated onto the GC electrode, the ring-disk electrode was immersed in N_2 purged 1 M KOH electrolyte. The current at Pt ring electrode was determined at 0.4 V vs RHE and constant disk current of 0.3 mA (I_{disk}). At the initial stage, the OER of OH^- at F-NHO catalyst generates O_2 , which diffuses to Pt ring electrode and subjects to oxygen reduction reaction back to form OH^- ; the recorded ring current (I_{ring}) was used to calculate the FE according to: $\text{FE}=I_{\text{ring}}/(I_{\text{disk}}\times C_e)$, C_e herein represents the oxygen collection coefficient 0.2 [3].

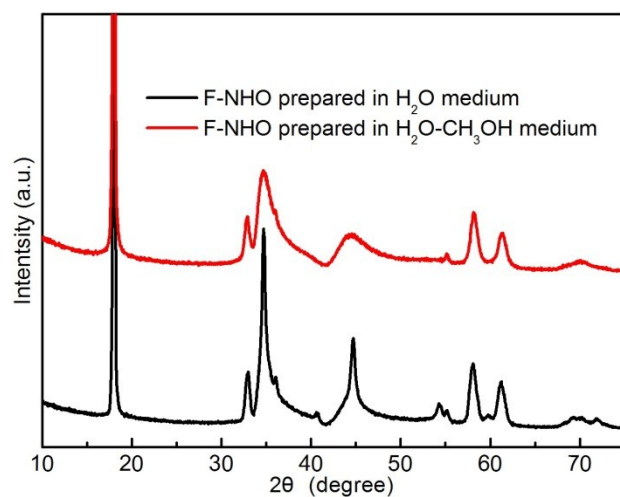


Fig. S1 F-NHO prepared in different media.

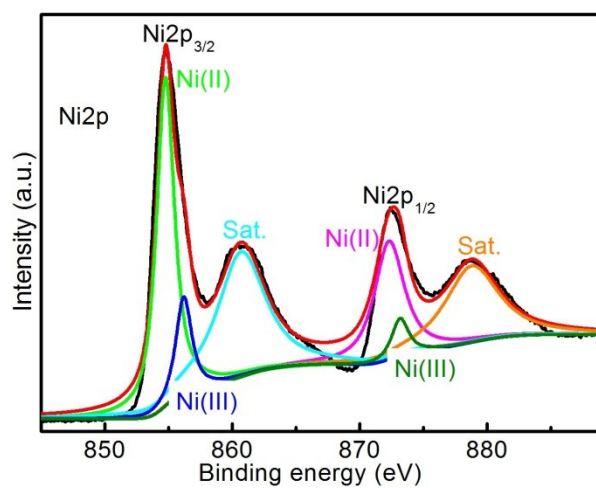


Fig. S2 Ni2p XPS of NHN.

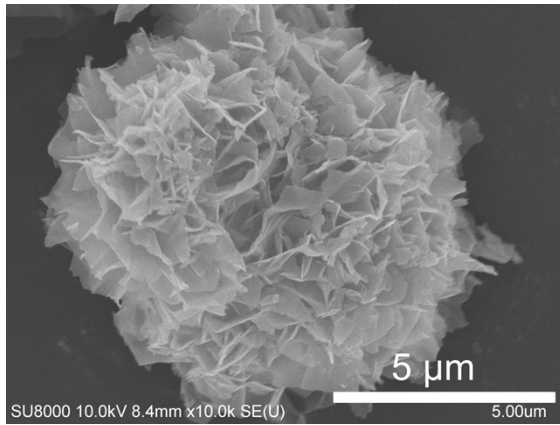


Fig. S3 SEM of NHN.

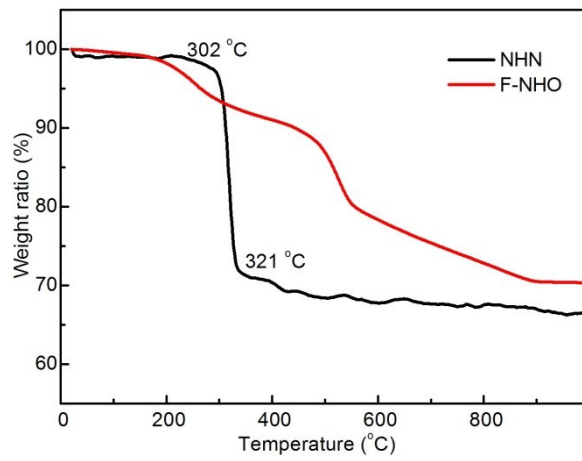


Fig. S4 TG curves of F-NHO and NHN in air.

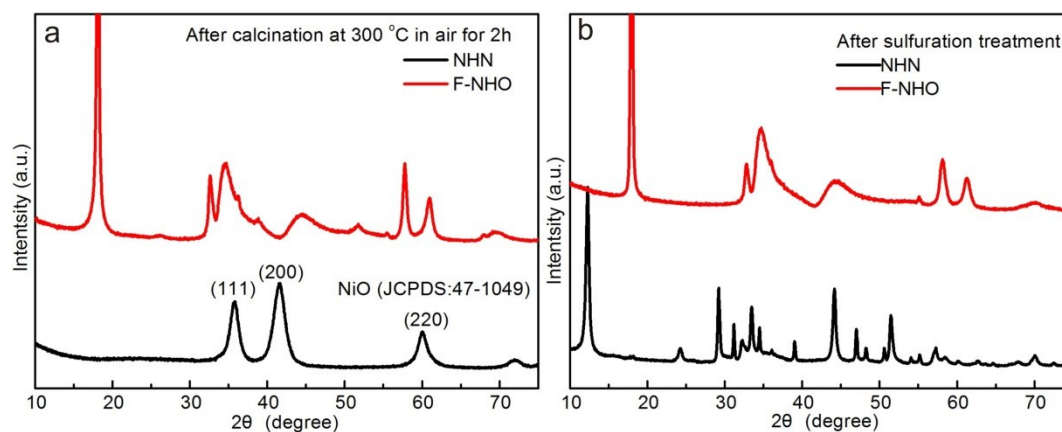


Fig. S5 XRD patterns of NHN and F-NHO after (a) calcination and (b) sulfuration treatment.

From Fig. S5a, the XRD pattern of F-NHO maintains unvaried after calcination treatment at 300 °C for 2 h, the unvaried phase indicates the high thermal stability. Undergoes the same calcination treatment, the NHN turns to NiO phase, showing the low thermal stability.

Fig. S5b displays the XRD patterns of NHN and F-NHO undergoes hydrothermal sulfuration at 120 °C for 12 h, the phase of F-NHO maintains unvaried, showing the good chemical stability of the F⁻ anions enriched F-NHO under harsh chemical condition. In contrast, the NHN turns to sulfide with complex diffraction peaks. These comparisons clearly demonstrate the high thermal and chemical stability of the former sample.

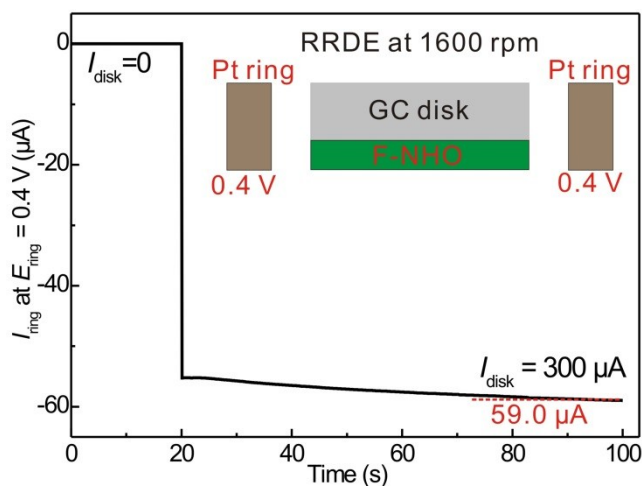


Fig. S6 Ring current of F-NHO on RRDE at a ring potential of 0.4 V, constant disk current of 300 μA in N_2 -saturated 1 M KOH solution. Inset is the profile schematic diagram of RRDE.

During the RRDE test, the applied disk current caused the catalytic OER to generate O_2 , which diffuses to Pt ring electrode and subjects to reduction at 0.4 V, which leads to a reductive ring current of 59.0 μA , thus results in a FE of 98.3 % and indicates the OER current at F-NHO electrode is indeed originated from water oxidation reaction toward O_2 .

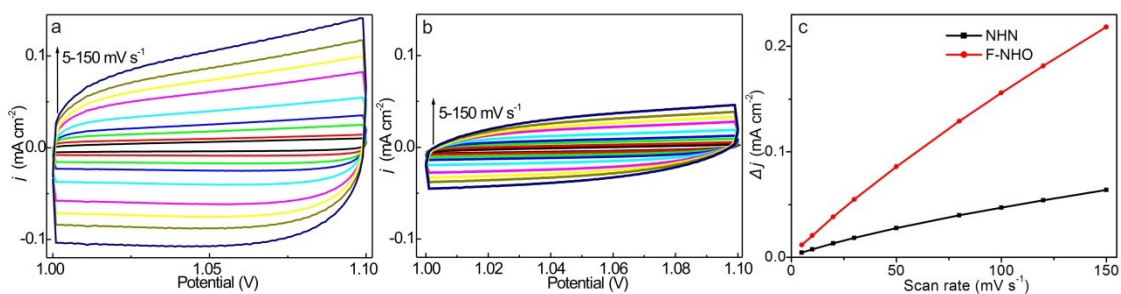


Fig. S7 CVs of (a) F-NHO, (b) NHN electrodes at 5, 10, 20, 30, 50, 80, 100, 120, 150 mV s^{-1} , (c) difference between cathodic and anodic current densities as a function of potential scan rate for F-NHO and NHN.

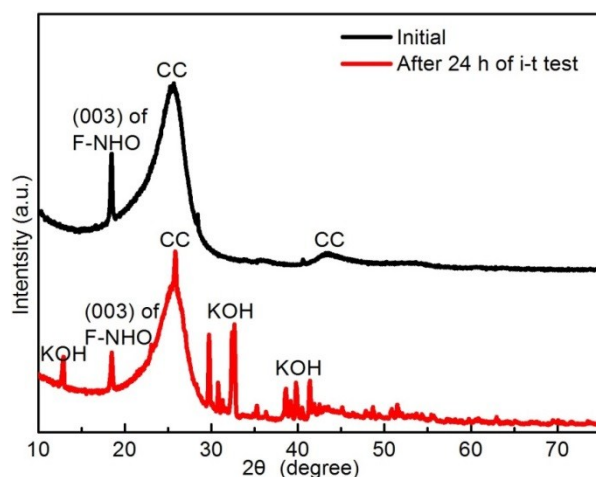


Fig. S8 XRD patterns of F-NHO electrode before (black) and after (red) 24 h of i-t test.

Fig. S8 compares the XRD patterns of F-NHO electrode (including the carbon cloth substrate), both patterns demonstrate strong and wide peaks at 26 and 43 ° belonging to graphitic carbon, which is derived from carbon cloth. F-NHO only show (003) peak at 18 ° in both patterns, the other diffractions with weak peak intensities were easily covered by the carbon peaks. After i-t test, a lot of diffractions associated with the inevitably remained KOH appear, which disturb the judgement of diffractions of F-NHO. Despite this, the (003) planes diffraction maintains unvaried, we can only tentatively inferred that the phase of F-NHO is stable undergoes i-t test.

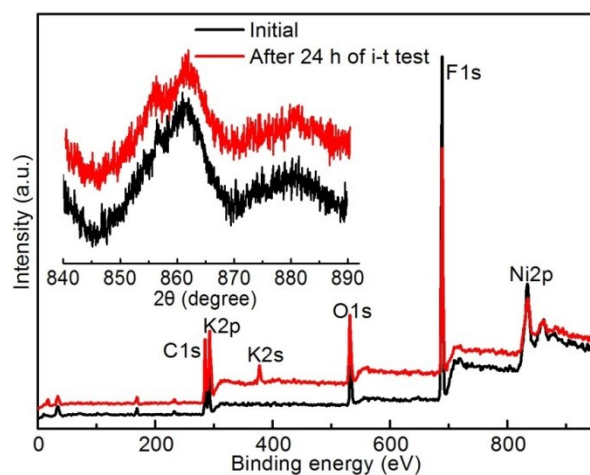


Fig. S9 XPS survey spectra and Ni2p spectra (inset) of F-NHO electrode before (black) and after (red) 24 h of i-t test.

From the inset, the chemical shift in binding energy of Ni2P XPS maintains unvaried after long term i-t operation, showing the compositional stability of F-NHO catalyst. Because of the Nafion contains F and O elements, F1s and O1s spectra can not be used to analyses the compositional changes.

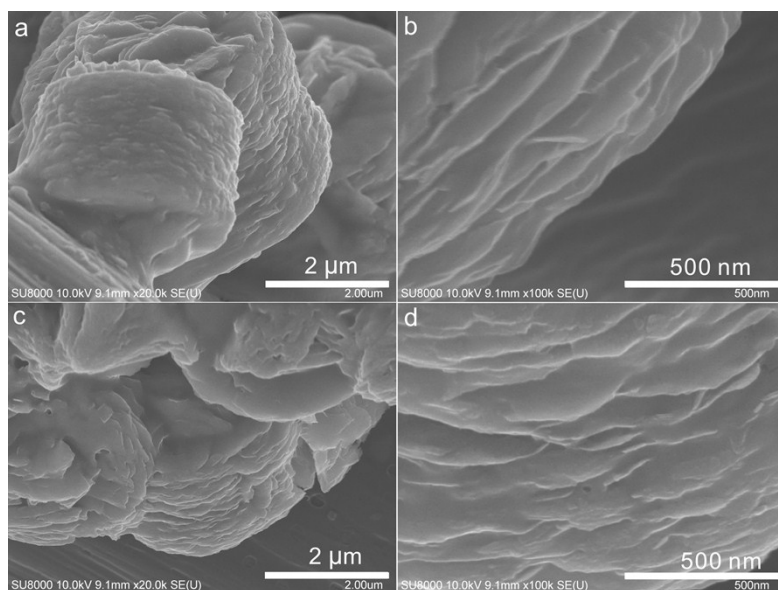


Fig. S10 SEM of F-NHO electrode before (a, b) and after (c, d) 24 h of i-t test.

From the SEM images at lower magnification (panel a and c), the less-defined primary nanosheets are mainly due to the presence of Nafion binder onto the outer surface of the microspheres in electrode fabrication. Albeit this, the profile of nanosheets can still be observable. From the SEM images at higher magnification (panel b and d), thin nanosheets with high density can be more clearly observed. The total morphologies basically coincide with the F-NHO solid in Fig. 3 in main text. To be specific, the densely attached thin nanosheets morphology after i-t test (panel c and d) almost not changed relative to the initial morphology (panel a and b), showing the initial morphology is well maintained after i-t test.

References

- [1] W. Gao, Z.M. Xia, F.X. Cao, J.C. Ho, Z. Jiang, Y.Q. Qu, Comprehensive understanding of the spatial configurations of CeO₂ in NiO for the electrocatalytic oxygen evolution reaction: Embedded or surface-loaded, *Adv. Funct. Mater.* 2018, 1706056.
- [2] W. Zhou, X.F. Lu, J.J. Chen, T. Zhou, P.Q. Liao, M.M. Wu, G.R. Li, Hierarchical porous prism arrays composed of hybrid Ni-NiO-carbon as highly efficient electrocatalysts for overall water splitting, *ACS Appl. Mater. Interfaces* 2018, 10, 38906–38914.
- [3] S.L. Zhao, Y. Wang, J.C. Dong, C.T. He, H.J. Yin, P.F. An, K. Zhao, X.F. Zhang, C. Gao, L.J. Zhang, J.W. Lv, J.X. Wang, J.Q. Zhang, A.M. Khattak, N.A. Khan, Z.X. Wei, J. Zhang, S.A. Liu, H.J. Zhao, Z.Y. Tang, Ultrathin metalorganic framework nanosheets for electrocatalytic oxygen evolution. *Nat. Energy* 2016, 1, 16184.