## **Supporting Information**

# Deep Reconstruction of Nickel-Based Precatalysts for Water Oxidation Catalysis

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#### **Experimental section**

#### 1.1 Synthesis of NiO sheet arrays grown on the nickel foam (NF).

Firstly, the nickel hydroxide sheet arrays grown on the nickel foam (denoted as precursor/NF) were fabricated referred to the previous report<sup>1</sup>, and only the carbon cloth was changed to nickel foam with the same size. Next, a piece of precursor/NF was

calcined at 400 °C in air, and the NiO sheet arrays on the nickel foam (NiO/NF) could be obtained. The NiO/NF was then cut into wafers with a diameter of 1 cm.

#### 1.2 Synthesis of the DR-NiOOH sheet arrays grown on the NF.

A piece of NiO/NF wafer directly served as a working electrode and the 2016-type coin cells were assembled. Among them, a lithium chip was used as a counter electrode and 1 M lithium hexafluorophosphate (LiPF<sub>6</sub>) solution in ethylene carbon (EC)-dimethyl carbonate (DMC) (1:1 v/v) was used as an electrolyte. The galvanostatic discharging tests were operated by using the LAND CT2001A multichannel battery testing system. After fully discharging to 0.01 V to achieve a lithiation process, the cells were disassembled. The nickel foam samples were carefully washed with plenty of alcohol and deionized water to remove the residual electrolyte and Li<sub>2</sub>O. Next, the ultrasmall nanoparticle-assembled NiO sheet arrays (lithiated NiO/NF) were obtained (Herein, the lithiated NiO was derived from Ni due to its ultrasmall size and oxygen sensitivity). The electro-oxidation of lithiated NiO to robust DR-NiOOH was carried out by CV measurements in a standard three-electrode system using unused Hg/HgO as the reference electrode and a graphite rod as the counter electrode. CV measurements were then performed in 0-0.8  $V_{Hg/HgO}$  at a scan rate of 50 mV s<sup>-1</sup> for 30 cycles. Finally, the deeply reconstructed NiOOH sheet arrays grown on the nickel foam served as the stable catalysts for OER. The average mass loading of DR-NiOOH on the NF was ~3.5 mg cm<sup>-2</sup> based on multiple experiments. Herein, the mass change of nickel foam samples during lithiation and electro-oxidation processes for the formation of DR-NiOOH/NF were shown in Table S4.

#### 1.3 Synthesis of the surface reconstructed Ni@NiOOH particles on the NF.

A piece of NiO/NF was calcined at 575 °C in Ar/H<sub>2</sub>, and the Ni particles on the NF (Ni/NF) were obtained. Next, the same electro-oxidation process on the Ni/NF was carried out and the Ni@NiOOH/NF was obtained after 30-cycle CV. The mass loading of Ni@NiOOH on the NF was ~3.3 mg cm<sup>-2</sup>.

#### 1.4 Synthesis of the deeply reconstructed Ni-Mo-O nanowire arrays on the NF.

The nickel molybdate nanowire precursor grown on the nickel foam was obtained referred to the previous reports.<sup>2,3</sup> In detail, 2 mmol Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 2 mmol Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O were dissolved in 60 mL deionized water to form a homogeneous solution. Next, the mixture was transferred to a 100 mL Teflon-lined sealed autoclave and a piece of nickel foam with the size of 3 cm\*4 cm was added. After reaction at 120 °C for 6 h and washing, the nickel molybdate nanowire precursor was obtained. After the calcination in air at 550 °C, the NiMoO<sub>4</sub> nanowire arrays on the nickel foam (NiMoO<sub>4</sub>/NF) were obtained. A piece of NiMoO<sub>4</sub>/NF wafer was then directly used to achieve a lithiation process. After the same steps of washing and electro-oxidation, the deeply reconstructed Ni-MoO (NiOOH-MoO<sub>x</sub>) nanowire arrays were fabricated. The mass loadings of NiOOH-MoO<sub>x</sub> and NiMoO<sub>4</sub>@NiOOH on the nickel foam were similar as ~3 mg cm<sup>-2</sup>.

#### **1.5 Characterization.**

XRD characterizations were performed using a D8 Advance X-ray diffractometer with non-monochromated Cu Ka X-ray source. SEM images were collected using a JSM-7100F microscope. TEM, HRTEM, and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected by a JEM-2100F/Titan G2 60-300 microscope. XPS (Mg and Al sources) and Ar<sup>+</sup> sputtering measurements were performed on an ESCALAB 250Xi system. The Raman measurements were recorded using a HORIBA HR EVO Raman system (633 nm laser) and an electrochemical workstation (CHI 760E). The potential-dependent *in-situ* Raman spectra were recorded with interval potential of 25 mV and meanwhile the LSV measurements were carried out in 0.924-1.724 V<sub>RHE</sub> at 0.25 mV s<sup>-1</sup> in 1 M KOH.

#### **1.6 Electrochemical measurements.**

All the OER measurements, including CV, LSV, electrochemical impedance spectroscopy (EIS) and chronopotentiometry, were conducted with a CHI 760E electrochemical workstation (Chenhua, China) using a standard three-electrode system. The catalysts grown on the nickel foam directly served as a working electrode, and an unused Hg/HgO electrode and a graphite rod were applied as a reference electrode and a counter electrode, respectively. The calculation of current density was based on the geometric area of an electrode or mass loading, and the LSV data were corrected by iR compensation. Nyquist plots were carried out in a frequency range from 100000 Hz to 0.01 Hz at a potential of 1.524 V<sub>RHE</sub>.

Using a standard three-electrode system, the UOR tests were evaluated in 1 M KOH with 0.5 M urea. All the LSV curves were carried out at 1 mV s<sup>-1</sup>. The chronopotentiometry measurements were measured at a constant current density of 10 mA cm<sup>-2</sup>.

The commercial IrO<sub>2</sub>/C was also tested as a control sample. The IrO<sub>2</sub>/C-based ink was prepared via dispersing 10 mg of IrO<sub>2</sub>/C and 2 mg of Vulcan XC-72R in the mixed solution of 700  $\mu$ L deionized water, 250  $\mu$ L ethanol and 50  $\mu$ L Nafion solution (5 wt.%), and then ultrasound to form homogeneous ink. Next, the ink was dropped onto a carbon cloth within 1 cm<sup>2</sup> for the subsequent electrocatalytic measurements. The mass loading of IrO<sub>2</sub>/C was ~1.4 mg cm<sup>-2</sup>.

#### 1.7 No Fe impurities.

Fe impurities can greatly improve the OER performance of catalysts. Herein, the XPS spectra of DR-NiOOH were provided (Figure S24). As reported, using Al source results in the overlap of Ni LMM Auger with Fe 2p peaks<sup>4</sup>, thus the XPS measurements of DR-NiOOH were conducted using Al and Mg sources for comparison. As can be seen, no obvious Fe 2p peak was observed while using Mg source, which indicates the inexistence of Fe species.

Besides, to avoid the Fe impurity incorporation from electrolyte, the KOH purity needs to be very high.<sup>4</sup> The KOH reagent with Fe content of below 0.001% was used in this work. In addition, the ICP measurements of 1 M KOH solution and DR-NiOOH show that the negligible Fe content (Table S5).

#### **1.8 Calculation method.**

All density functional theory (DFT) simulations were performed by using Vienna ab initio simulation package (VASP) software.<sup>5</sup> The exchange-correlation interactions were described by generalized gradient approximation (GGA)<sup>6</sup> within the Perdew-Burke-Ernzerhof (PBE) function<sup>7</sup>. A plane wave basis set was adopted with cutoff of 500 eV. Gaussian type smearing with energy window of 0.05 eV was used for optimization and frequency calculation, and tetrahedron method with Blöchl corrections with energy window of 0.05 eV was used for DOS calculation. The energy convergence tolerance was 0.01 meV for optimization and frequency calculation, and 0.001 meV for DOS calculation. The force tolerance for optimization task was 0.05 eV/Å. All calculations were performed with spin unrestricted and initial magnetic moments of 2µB for Ni and 0µB for O and H were set. The linear mixing parameter was set to 0.06 and cutoff wave vector for Kerker mixing scheme was set to 0.0001 to make electron state converge more stable than default settings. To describe long-range interaction, DFT-D3 method was adopted. K points were sampled as gamma only for optimization and 2\*2\*1 for differential charge density calculation for the supercell of the interlayer contacting model. Gamma centered K points were sampled as 3\*4\*1 for optimizations of NiOOH models for Gibbs free energy diagram calculation and as 4\*5\*3 for single energy calculations and frequency analysis. GGA+U method was adopted for Ni species for Gibbs free energy diagram calculation with U-J value of 6.6 eV, same as previous report.<sup>8</sup> To obtain the Gibbs free energy diagram of OER reaction in alkali condition, we set off from the four-step reaction of OER referred to the previous reports.<sup>9</sup> In alkaline solution, the equilibrium potential is calculated by following formula:

$$U_{equ-alk} = 1.23 \text{ V} - 0.059 \times \text{pH}$$

Where  $U_{equ-alk}$  is the equilibrium potential in alkaline solution. When considering alkaline condition, pH equals 14, thus,  $U_{equ-alk}$  equals 0.404 V. Therefore, the overpotential equals applied potential minus 0.404 V.<sup>10</sup>



Figure S1. Schematic illustration of multilevel structure catalyst interconnected by OER-active NCUs.



**Figure S2.** (a,b) SEM images and (c) Raman spectrum of NiO/NF. (d) TEM and (e) HRTEM images of NiO nanosheet. (f) XRD pattern of NiO/NF.



**Figure S3.** Two schematic routes to fabricate (a) the lithiation-induced collapse of entire structure and the formation of sub-10 nm nanoparticle-assembled Ni nanosheet and (b) the reduction of NiO to form bulk Ni particles with the sizes of 100-400 nm. (c) SEM image of lithiated NiO sheet arrays. (d) HAADF STEM image of DR-NiOOH

and the corresponding energy-dispersive X-ray spectroscopy (EDX) elemental mappings of Ni, O, and mixed elements. (e) SEM image of Ni particles on the nickel foam. (f) Size distribution of Ni particles on the nickel foam.



**Figure S4.** (a) SEM image of Ni@NiOOH. (b) TEM image and (inset) SAED pattern of core-shell Ni@NiOOH. (c) The related HAADF STEM and the corresponding EDX elemental mappings of Ni, O, and mixed elements. (d) Ni 2p XPS spectra of DR-NiOOH and Ni@NiOOH. Low-magnified SEM images of (e) DR-NiOOH/NF and (f) Ni@NiOOH/NF.

The core-shell structure is shown intuitively from the elemental mappings on a single Ni@NiOOH particle (Figure S4c), which further confirms the surface reconstruction on the bulk Ni particle.



**Figure S5.** (a) HRTEM image of NiO after lithiation and oxidation in air, showing the ultrasmall nanoparticle structure. (b) HAADF STEM image and (c) EDX spectrum of NiO after lithiation and oxidation in air.

In detail, the NiO sheet is polycrystalline with the grains of ~5 nm. The lattice fringes of 0.208 and 0.241 nm are assigned to the (200) and (111) planes of NiO, respectively. Besides, the ultrasmall nanoparticles are visible from HAADF STEM image. The calculated O/Ni atomic ratio is close to 1 from the corresponding EDX spectrum, further demonstrating the formation of NiO.



**Figure S6.** The relationship between the current densities of redox peaks and CV cycles which origins from the data in Figure 3a.



**Figure S7.** (a) OER polarization curves of DR-NiOOH, Ni@NiOOH, nickel foam and the commercial IrO<sub>2</sub>/C. (b) CV curves of DR-NiOOH with and without iR compensation. (c) The initial 30-cycle CV curves of Ni@NF.

The DR-NiOOH outperforms the commercial IrO<sub>2</sub>/C ( $\eta_{10}$  of 326 mV), demonstrating it as a potential IrO<sub>2</sub>-substituted OER catalyst.



Figure S8. SEM images of (a) NF and (b) NF after 1 day chronopotentiometry measurement.





60, 80, and 100 mV s<sup>-1</sup> of (a) Ni@NiOOH and (b) DR-NiOOH, respectively.



**Figure S10.** (a) SEM and (b) HRTEM images of DR-NiOOH after 1 day chronopotentiometry measurement.



**Figure S11.** (a) Chronopotentiometry measurement of DR-NiOOH using new Hg/HgO after operation in Figure 3d. (b) Chronopotentiometry measurement of DR-NiOOH after operation in Figure 3e.

The new Hg/HgO electrode was also used to show the accuracy of Hg/HgO used in the measurements in Figure 3d and 3e. In Figure S11a, the potential remains ~1.52 V. In Figure S11b, the chronopotentiometry curves almost overlap.



Figure S12. Different contact conditions between Ni (200) and NiOOH (101). The initial structure before optimization with (a) Ni layer, (b) OH layer, (c) O<sub>1</sub> atom layer, and (d) O<sub>2</sub> atom layer of 2-layer NiOOH contact with the Ni surface (denoted as modelx, x = 1, 2, 3, 4). (e-h) The corresponding structure and energy after optimization. The blue, red, and white balls refer to Ni, O, and H atoms, respectively.

As can be seen, the reconstruction of model-1 and model-3 after structural optimization is obvious with the NiOOH structure destroyed seriously. For the model-2 and model-4, the reconstruction only exists in the Ni-NiOOH interface. Besides, the system energy for the model-4 is lowest. Therefore, for the following calculation of differential charge densities, the contact mode of model-4 was adopted.



The blue, red, and white balls refer to Ni, O, and H atoms, respectively. (e-g) Calculated differential charge densities of Ni-*x* L NiOOH models (x = 3, 4, and 5).



Figure S14. EIS results of DR-NiOOH, Ni@NiOOH, and nickel foam measured at

 $1.524 \ V_{\text{RHE}}.$ 



**Figure S15.** NiOOH models with different OH coverages ( $\theta_{OH*}$ ) of (a) 0, (b) 0.5, (c)

0.875, and (d) 1 ML on the Ni-terminated (101) planes.



**Figure S16.** Free energy diagrams for the four elementary steps during the OER processes on NiOOH (101) with different OH coverages of (a) 0, (b) 0.5, (c) 0.875, and (d) 1 ML.



**Figure S17.** (a-d) Side views of four elementary steps for NiOOH with the optimal structure of 0.5 ML. The blue, red, white, green, and yellow balls refer to Ni, O, H, O (ads.), and H (ads.), respectively.



Figure S18. OER mechanism on NiOOH with the optimal structure (top view and side

view) of 0 ML at each stage.



Figure S19. OER mechanism on NiOOH with the optimal structure (top view and side

view) of 0.875 ML at each stage.



Figure S20. OER mechanism on NiOOH with the optimal structure (top view and side



view) of 1 ML at each stage.

Figure S21. (a,b) SEM images of NiMoO<sub>4</sub>/NF.



**Figure S22.** (a) TEM, (b) HRTEM, (c) HAADF STEM images, and the corresponding EDX elemental mappings of NiOOH-MoO<sub>x</sub>. (d) Raman spectra of NiMoO<sub>4</sub>, lithiated NiMoO<sub>4</sub>, and the derived products after reconstruction (i.e. NiMoO<sub>4</sub>@NiOOH and NiOOH-MoO<sub>x</sub>). (e) TEM and (f) HRTEM images of core-shell NiMoO<sub>4</sub>@NiOOH nanowire which was derived from NiMoO<sub>4</sub> after construction.

For NiMoO<sub>4</sub>, after fully discharging to 0.01 V, the lithium insertion reaction happens as follows: NiMoO<sub>4</sub>+8Li<sup>+</sup>+8e<sup>-</sup> $\rightarrow$ Ni<sup>0</sup>+Mo<sup>0</sup>+4Li<sub>2</sub>O.<sup>11</sup> After CV measurements in 0.924-1.724 V<sub>RHE</sub> for 30 cycles, the ultrasmall Ni and Mo nanoparticles in the lithiated NiMoO<sub>4</sub> are reconstructed to NiOOH and MoO<sub>x</sub> within the nanowire (denoted as NiOOH-MoO<sub>x</sub>, Figure S22a-c). The obvious NiOOH Raman signals could be observed for NiOOH-MoO<sub>x</sub> (Figure S22d). However, the Raman spectra have almost not changed before and after reconstruction for NiMoO<sub>4</sub>. The undetected NiOOH signals are attributed to its thin layer on the surface of NiMoO<sub>4</sub> after reconstruction (denoted as NiMoO<sub>4</sub>@NiOOH, Figure S22e,f).



**Figure S23.** (a) OER polarization curves of NiOOH-MoO<sub>x</sub> and NiMoO<sub>4</sub>@NiOOH normalized by geometric area; scan rate: 1 mV s<sup>-1</sup>. (b) Charging current density differences ( $\Delta j = j_a - j_c$ ) as a function of the scan rate. Cyclic voltammograms in the double layer region at scan rates of 20, 40, 60, 80, and 100 mV s<sup>-1</sup> for (c) NiOOH-MoO<sub>x</sub> and (d) NiMoO<sub>4</sub>@NiOOH.

The  $C_{dl}$  of NiOOH-MoO<sub>x</sub> is 2.09 times that of NiMoO<sub>4</sub>@NiOOH (1.49 mF cm<sup>-2</sup>), indicating the former possesses more exposure of active sites.



**Figure S24.** (a) XPS measurements of DR-NiOOH using Al and Mg sources. (b) Fe 2p spectrum of DR-NiOOH using Al source.

**Table S1.** A comparison of our work and current main synthetic methods for pureNiOOH.

Typical Methods	Morphologies/characteristic s	Main advantages	Main disadvantages	References
Lithiation- induced deep reconstruction	Multilevel structure containing sub-5 nm nanoparticle- interconnected nanosheets and nanosheet-assembled sheet arrays; Low-crystalline and polycrystalline characteristic	General synthesis in deeply reconstructed nano-catalysts; Fabrication of nano-catalysts with unique structure and richly exposed catalytic sites	Easier to realize the lithiation operation for the supporting catalyst	Our work
Chemical oxidation <sup>[12]</sup>	Spherical structure with diameter of 6-10 µm	High yield	Bulk structure	Electrochem. Commun. <b>2005</b> , 7, 857-862
Sonochemical intercalation <sup>[13]</sup>	Nanoparticles	Particle size at the nanometer level	Agglomeration; Grain coarsening likely occurs after drying	Electrochim. Acta <b>2008</b> , 54, 434-441
Heat treatment <sup>[14]</sup>	Sheet arrays	Facile preparation	Limited to specific materials; Bulk structure	ACS Sustainable Chem. Eng. <b>2017</b> , 5, 3808- 3818

Table S2. Activity comparison of DR-NiOOH/NF with recently reported Ni-based

Electrocatalysts	Electrolyte	Current density (mA cm <sup>-2</sup> )	Corresponding overpotential (mV)	references
DR-NiOOH/NF (1st)	1 M KOH	10	281	
DR-NiOOH/NF (2 <sup>nd</sup> )	1 M KOH	10	291	This work
DR-NiOOH/NF (3rd)	1 M KOH	10	296	
Ni-based materials (including Ni <sub>2</sub> Si, NiTe, Ni, NiAs, NiP, NiB) <sup>[15]</sup>	1 M KOH	10	350-410	Adv. Energy Mater. 2019, 9, 1900796
NiFe/laser-induced graphere (LIG) <sup>[16]</sup>	1 M KOH	10	240-279	ACS Energy Lett. 2018, 3, 677- 683
Ni <sub>2</sub> P <sub>4</sub> O <sub>12</sub> /carbon cloth (CC) <sup>[17]</sup>	1 M KOH	10	280	<i>Adv. Mater.</i> <b>2018</b> , <i>30</i> , 1705045
W-doped Ni(OH) <sub>2</sub> /glassy carbon (GC)	1 M KOH	10	237	Nat. commun. <b>2019</b> , 10, 2149
Ni <sub>2</sub> P-VP <sub>2</sub> /NF <sup>[19]</sup>	1 M KOH	50	306	<i>Adv. Mater.</i> <b>2019</b> , <i>31</i> , 1901174
$Ni_3S_4/NF^{[20]}$	1 M KOH	10	257	Adv. Funct. Mater. <b>2019</b> , 29, 1900315
Ni/Mo <sub>2</sub> C <sup>[21]</sup>	1 M KOH	10	288	Adv. Funct. Mater. <b>2019</b> , 9, 1803185
Ni-Cu-P <sup>[22]</sup>	1 M KOH	10	307	Appl. Catal. B Environ. <b>2018</b> , 237, 409-415
MoFe:Ni(OH) <sub>2</sub> /NiO OH <sup>[23]</sup>	1 M KOH	10	240	ACS Catal. 2018, 8, 2359-2363
Ni <sub>3</sub> Fe <sub>0.5</sub> V <sub>0.5</sub> /CC <sup>[24]</sup>	1 M KOH	10	200	Nat. commun. 2018, 9, 2885
La <sub>0.5</sub> Sr <sub>1.5</sub> Ni <sub>0.7</sub> Fe <sub>0.3</sub> O	1 М КОН	10	360	Nat. commun. <b>2018</b> , 9, 3150

OER electrocatalysts in 1 M KOH.

**Table S3.** Parameters of the optimized bulk structure on orthorhombic NiOOH for DFT calculations.

The cif	of the optimized b	ulk structures for	orthorhombic NiOO	Н
_cell_length_a	4.8986			
_cell_length_b			4.2452	
_cell_length_c	2.8780			
_cell_angle_alpha	90.0000			
_cell_angle_beta	90.0000			
_cell_angle_gamma		9	90.0000	
_atom_site_label	_atom_site_type_ symbol	_atom_site_fract _x	_atom_site_fract_y	_atom_site_fract_z
H1	н	0.484380	0.788656	0
H2	н	0.984380	0.211344	0.5
Ni1	Ni	0.998884	0.741833	0
Ni2	Ni	0.498884	0.258167	0.5
O1	0	0.640938	0.508326	0
O2	0	0.140938	0.491674	0.5
O3	0	0.357798	0.993543	0
O4	0	0.857798	0.006457	0.5

Table S4. Mass change of nickel foam samples during lithiation and electro-oxidation

processes for the formation of DR-NiOOH/NF.

Number	Mass per unit area of NF (mg cm <sup>-2</sup> )	Mass per unit area of Ni- precursor/NF (mg cm <sup>-2</sup> )	Mass per unit area of NiO/NF (mg cm <sup>-2</sup> )	Mass per unit area of u-NiO/NF (mg cm <sup>-2</sup> )	Mass per unit area of NiOOH/NF (mg cm <sup>-2</sup> )	Mass loadings of NiOOH (mg cm <sup>-2</sup> )
1	25.34	29.41	28.78	28.78	29.03	3.69
2	24.45	28.39	27.25	27.37	27.76	3.31
3	24.83	28.65	27.63	28.01	28.39	3.57
Average value	24.87	28.82	27.89	28.05	28.39	3.52

Table S5. ICP results of 1 M KOH solution and DR-NiOOH.

Samples	Element co	ontent (mg L <sup>-1</sup> )
	Fe	<0.5
1 M KOH solution	Ni	<0.5
	К	32816.0
	Fe	<0.5
DR-NIOOH	Ni	4.6
	K	32503.4

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