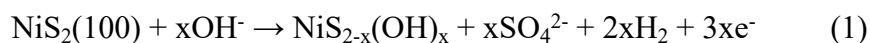# Supporting Information

Supplemental Methods

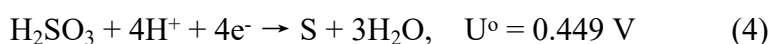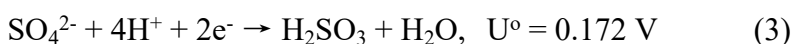## S1. Thermodynamic modeling of electrochemical stability

The process of gradual replacement of the sulfur atoms by hydroxyl molecules on $NiS_2(100)$ under an applied voltage was simulated. The reaction equation for the process is shown as
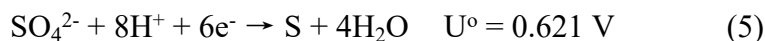
$$NiS_2(100) + xOH^- \rightarrow NiS_{2-x}(OH)_x + xSO_4^{2-} + 2xH_2 + 3xe^- \quad (1)$$

where x represents the number of anions substituted by OH^- in the reconstitution process, and the relationship between the reaction free energy $\triangle G$ and the applied voltage U can be written as

$$\triangle G = G_{NiS2-x(OH)x} + xG_{SO4}^{2-} + 2xG_{H2} + 3xeU - G_{NiS2(100)} - 5xG_{OH^-} \quad (2)$$

G_{SO4}^{2-} is calculated from the following equation:

$$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O, \quad U^o = 0.172 \text{ V} \quad (3)$$

$$H_2SO_3 + 4H^+ + 4e^- \rightarrow S + 3H_2O, \quad U^o = 0.449 \text{ V} \quad (4)$$

Adding the above equations gives:

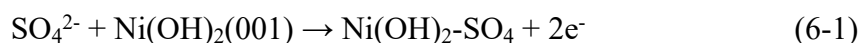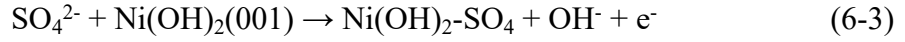$$SO_4^{2-} + 8H^+ + 6e^- \rightarrow S + 4H_2O \quad U^o = 0.621 \text{ V} \quad (5)$$

When at the standard electrode potential, G_{SO4}^{2-} can be calculated from the following equation：

$$G_{SO4}^{2-} = G_S + 4G_{H2O} - 8G_H^+ - 6eU + \triangle G_{pH}$$

$\triangle G_{pH}$ is the pH correction term ($\triangle G_{pH} = pH \times k_B T\ln 10$).

The reaction equations for the adsorption of soluble SO_4^{2-} on $Ni(OH)_2$ are shown below,

$$SO_4^{2-} + Ni(OH)_2(001) \rightarrow Ni(OH)_2\text{-}SO_4 + 2e^- \quad (6\text{-}1)$$

$$SO_4^{2-} + Ni(OH)_2(001) \rightarrow Ni(OH)_2\text{-}SO_4 + Ni(OH)_2(bulk) + 2e^- \qquad (6\text{-}2)$$

$$SO_4^{2-} + Ni(OH)_2(001) \rightarrow Ni(OH)_2\text{-}SO_4 + OH^- + e^- \qquad (6\text{-}3)$$

where equation (6-1) represents surface physisorption and interlayer adsorption, equation (6-2) represents defect, and equation (6-3) represents surface chemisorption.

Similarly, the reaction equations for the in-situ construction of SO_4 from NiS_2 and combination with $Ni(OH)_2$ are shown below:

$$1/2NiS_2(bulk) + Ni(OH)_2 + 9OH^- \rightarrow Ni(OH)_2\text{-}SO_4 + 1/2Ni(OH)_2(bulk) + 4H_2O + 9e^-(7\text{-}1)$$

$$1/2NiS_2(bulk) + Ni(OH)_2 + 9OH^- \rightarrow Ni(OH)_2\text{-}SO_4 + 3/2Ni(OH)_2(bulk) + 4H_2O + 9e^-(7\text{-}2)$$

$$1/2NiS_2(bulk) + Ni(OH)_2 + 8OH^- \rightarrow Ni(OH)_2\text{-}SO_4 + 1/2Ni(OH)_2(bulk) + 4H_2O + 8e^-(7\text{-}3)$$
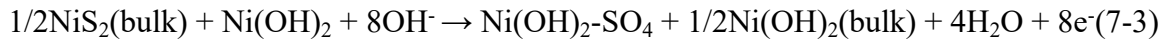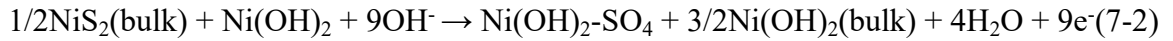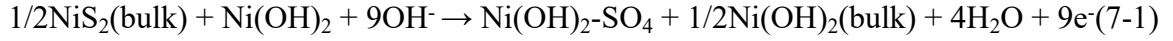
where equation (4-1) represents surface physisorption and interlayer adsorption, equation (4-2) represents defect, and equation (4-3) represents surface chemisorption.
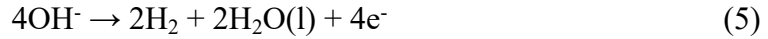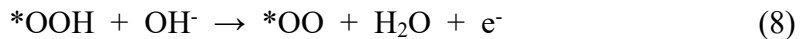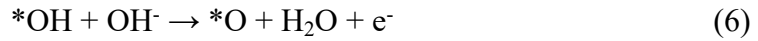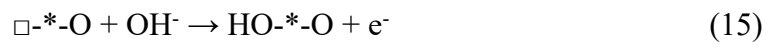

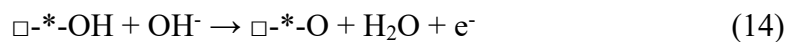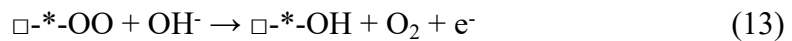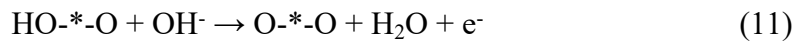## S2. Gibbs free energy profile of OER

Since the OER reaction explored in this paper was carried out in a alkaline solution (pH=14), the overall reaction equation for the $4e^-$ reaction is:

$$4OH^- \rightarrow 2H_2 + 2H_2O(l) + 4e^- \qquad (5)$$

The reaction equation for each elementary step via AEM is,

$$*OH + OH^- \rightarrow *O + H_2O + e^- \qquad (6)$$

$$*O + OH^- \rightarrow *OOH + e^- \qquad (7)$$

$$*OOH + OH^- \rightarrow *OO + H_2O + e^- \qquad (8)$$

$$*OO \rightarrow * + O_2 \qquad (9)$$

$$* + OH^- \rightarrow *OH + e^- \qquad (10)$$

In addition to this, OER may occur via LOM, with the following reaction equation,

$$HO\text{-}*\text{-}O + OH^- \rightarrow O\text{-}*\text{-}O + H_2O + e^- \qquad (11)$$

$$O\text{-}*\text{-}O \rightarrow \square\text{-}*\text{-}OO \qquad (12)$$

$$\square\text{-}*\text{-}OO + OH^- \rightarrow \square\text{-}*\text{-}OH + O_2 + e^- \qquad (13)$$

$$\square\text{-}*\text{-}OH + OH^- \rightarrow \square\text{-}*\text{-}O + H_2O + e^- \qquad (14)$$

$$\square\text{-}*\text{-}O + OH^- \rightarrow HO\text{-}*\text{-}O + e^- \qquad (15)$$

The change in Gibbs free energy (ΔG) for each step of the primitive reaction can be

calculated by the following equation:

$$\triangle G = \triangle E - T\triangle S + \triangle ZPE + \triangle G_U + \triangle G_{pH} \qquad (16)$$

where $\triangle E$ is the difference of the total energy obtained from the DFT calculation. $\triangle S$ and $\triangle ZPE$ represent the entropy and zero-point energy, respectively, both obtained from the VASPKIT correction. T represents the temperature and takes the value of 298.15 K (room temperature). $\triangle G_U = -eU$, e is the number of charge transfers per electron transfer step and U is the applied voltage. $\triangle G_{pH}$ represents the value of Gibbs free energy change caused by pH change and can be calculated by $\triangle Gp_H = k_B T \times \ln 10 \times pH$, k_B is Boltzmann constant, pH = 14 in alkaline environment. The Gibbs free energy of intermediates, reaction free energy of elementary step and overpotential of OER were listed in Table S1-S4.
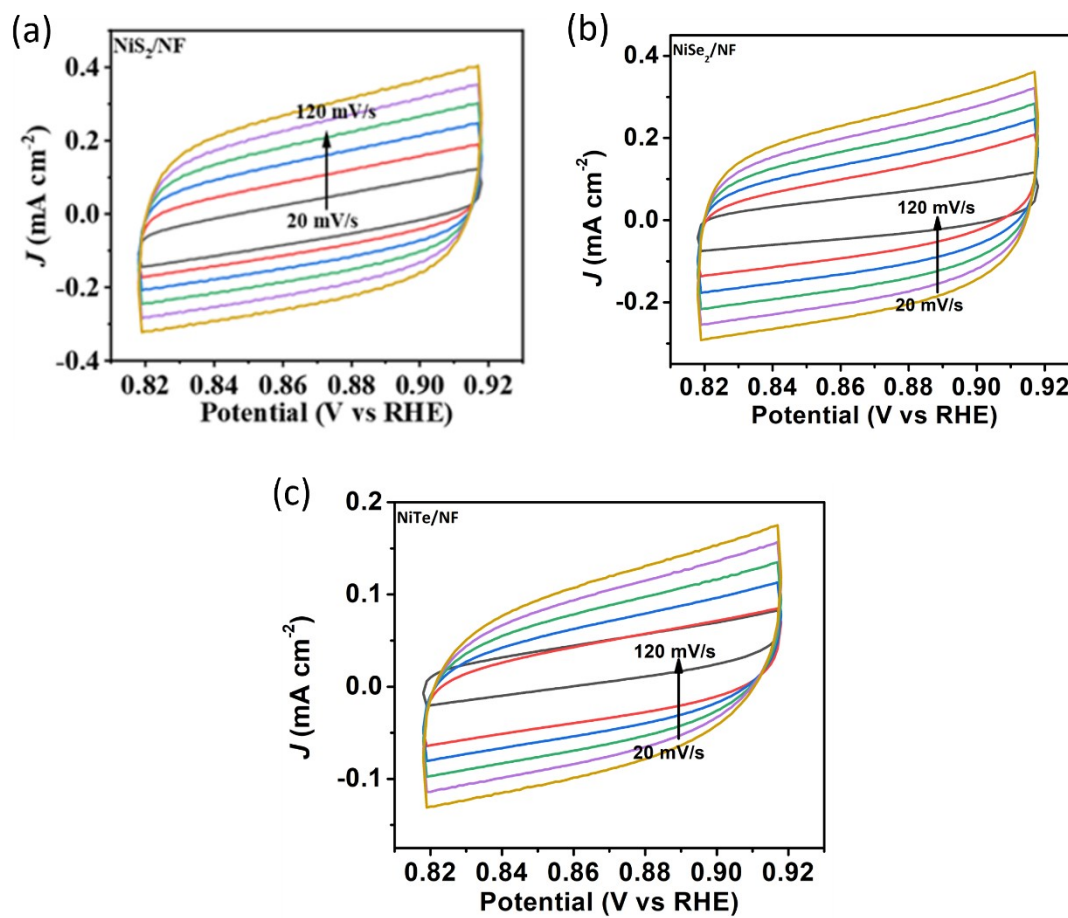
Supplemental Figures

Fig.S1 Cyclic voltammograms of (a) NiS$_2$/NF, (b) NiSe$_2$/NF and (c) NiTe/NF from 0.82 to 0.92 V vs RHE at different scan rates in 1 M KOH.
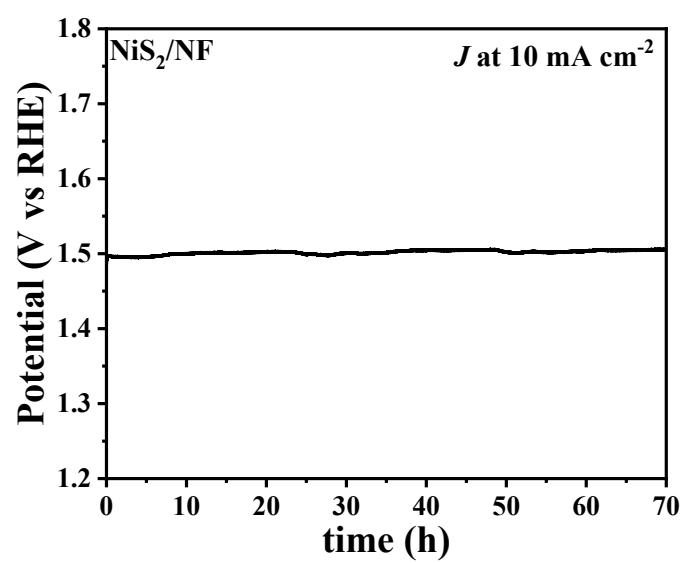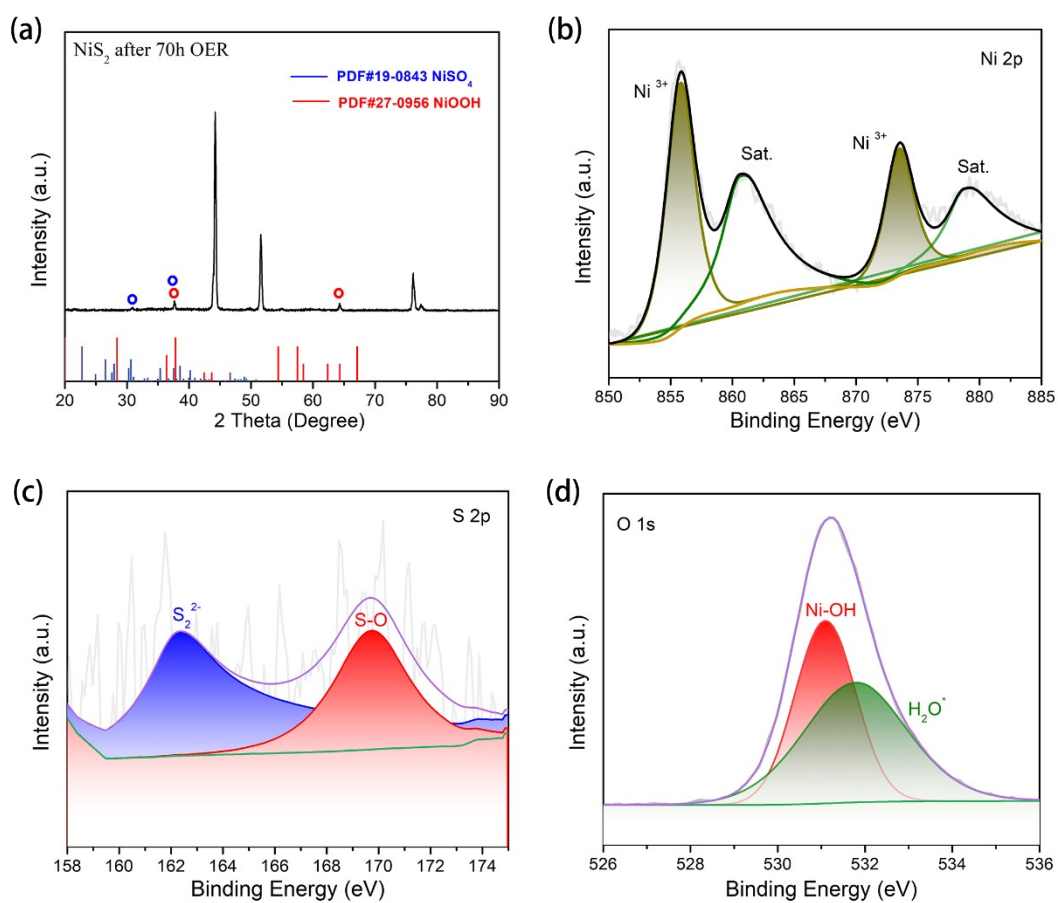
Fig.S2 Long durability of NiS_2/NF at 10 mA cm^{-2} in 1 M KOH.

Fig S3. (a) XRD patterns, (b) Ni 2p spectrum, (c) S 2p specrum and (d) O 1s spectrum of NiS$_2$/NF after 70h of OER at 10 mA cm^{-2} in 1 M KOH.
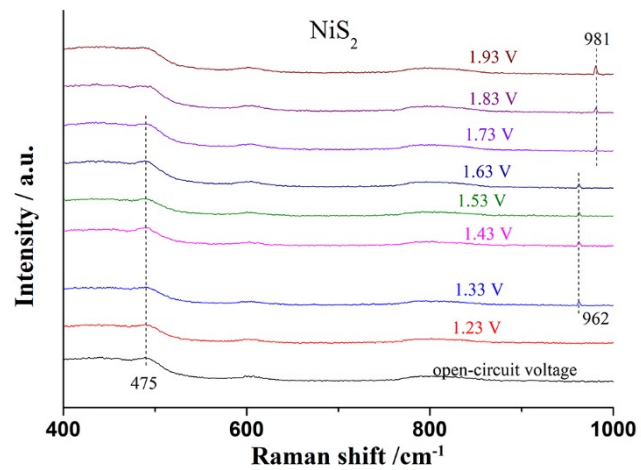
Fig S4. Potential-dependent (vs RHE) in-situ Raman spectra of NiS$_2$ under OER conditions in 1 M KOH.
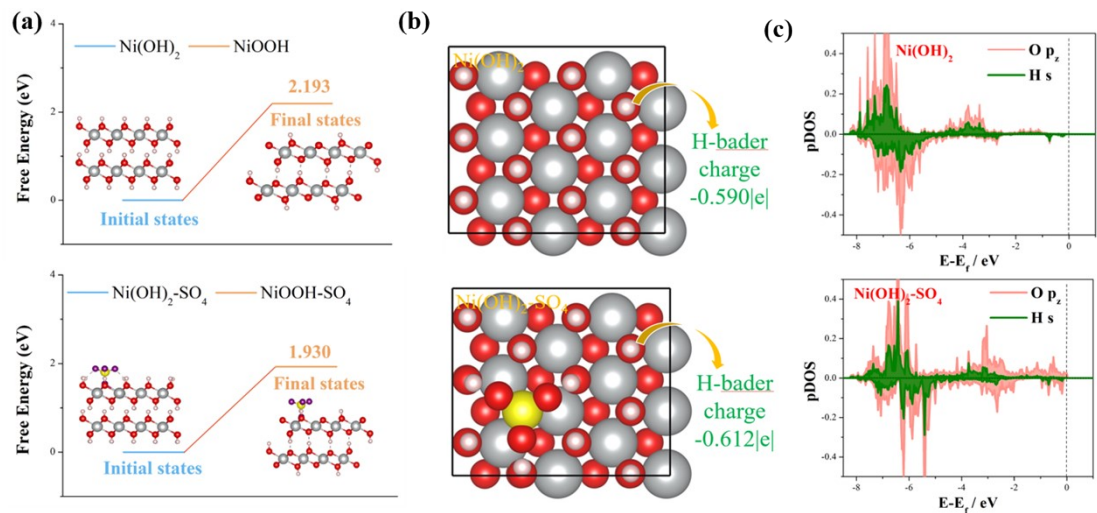
Fig. S5 (a) Profiles of the free energy for dehydrogenation of Ni(OH)$_2$ with and without sulfate chemisorption, (b) Comparison of Bader charge of H atoms in Ni(OH)$_2$ with and without sulfate chemisorption, (c) PDOS of p$_z$ orbital of O atom and s orbital of H atom in Ni(OH)$_2$ with and without sulfate chemisorption.
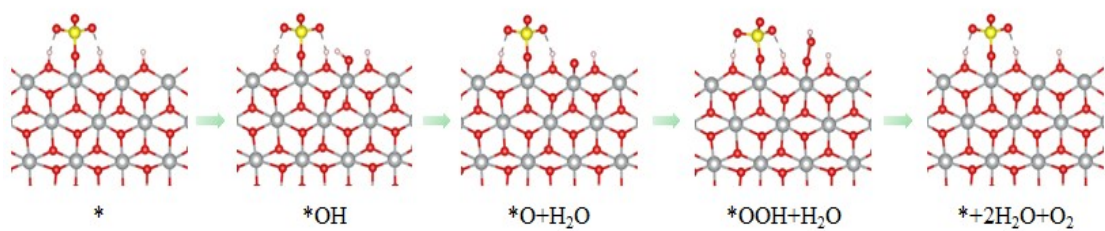

Fig.S6 Schematic diagram of intermediates of OER on NiOOH-SO$_4$ (100) via adsorbate evolution mechanisms (AEM)
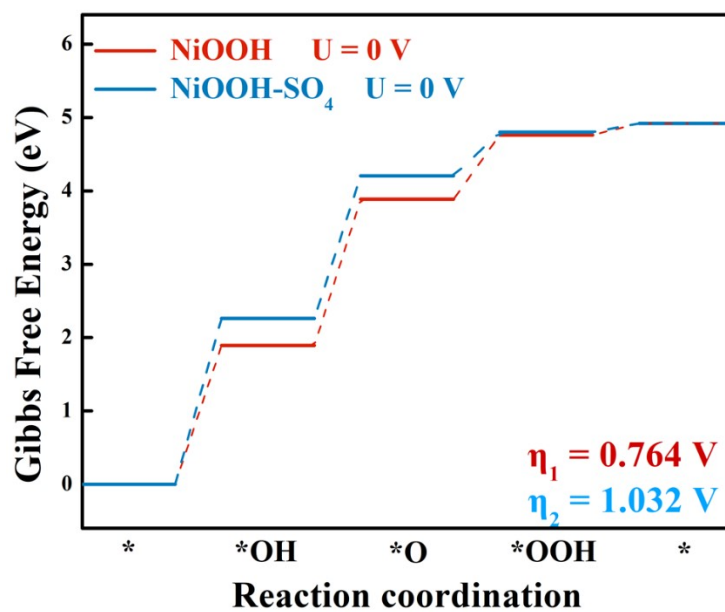
Fig.S7 Reaction free energy step diagram of NiOOH(1 0 0) and NiOOH-SO$_4$(1 0 0) via AEM
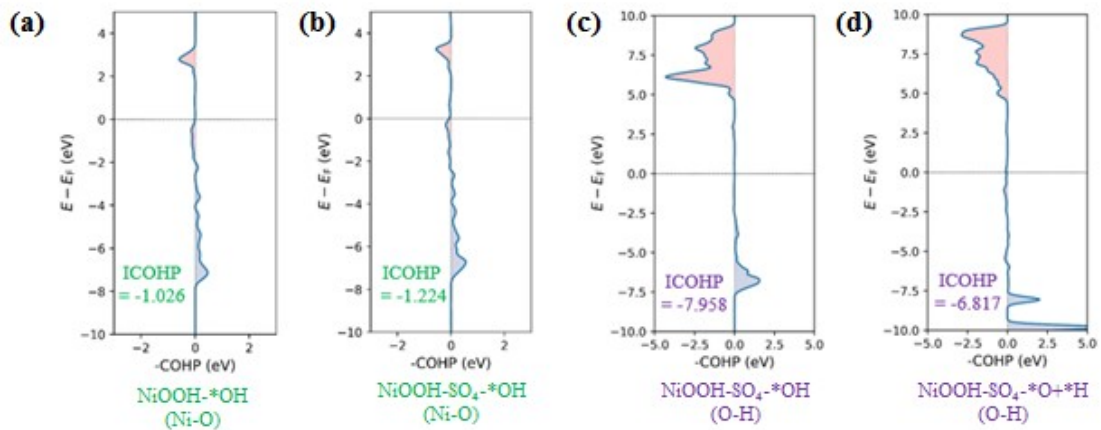
Fig.S8 Ni-O COHP diagram of the *OH intermediate of (a)NiOOH and (b)NiOOH-SO₄, and O-H COHP diagram of the *OH intermediate of (c)NiOOH and (d)NiOOH-SO₄-H.
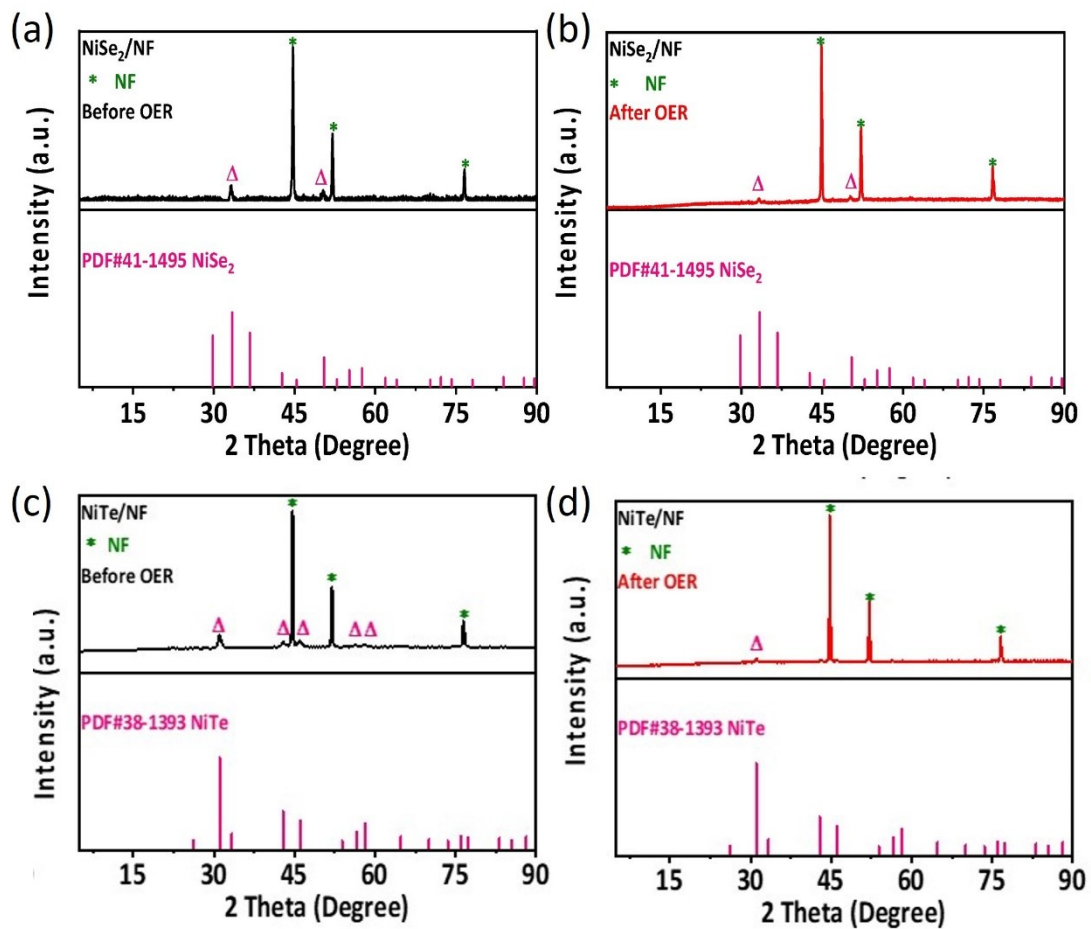
Fig.S9 (a)(c) XRD patterns of NiSe₂/NF and NiTe/NF before OER. (b)(d) XRD patterns of NiSe₂/NF and NiTe/NF after OER

Fig.S10 (a) SEM, (b) HRTEM, (c) STEM and corresponding EDS mapping images of NiSe$_2$/NF. (d) SEM, (e) HRTEM, (f) corresponding EDS mapping images of NiTe/NF

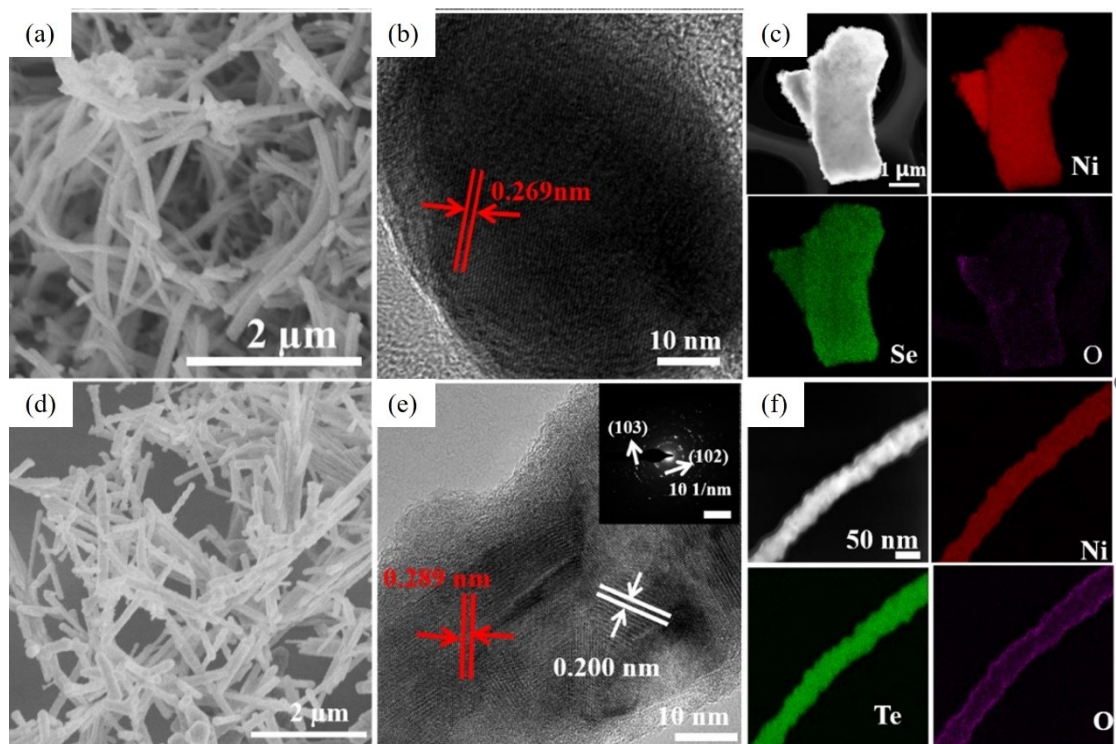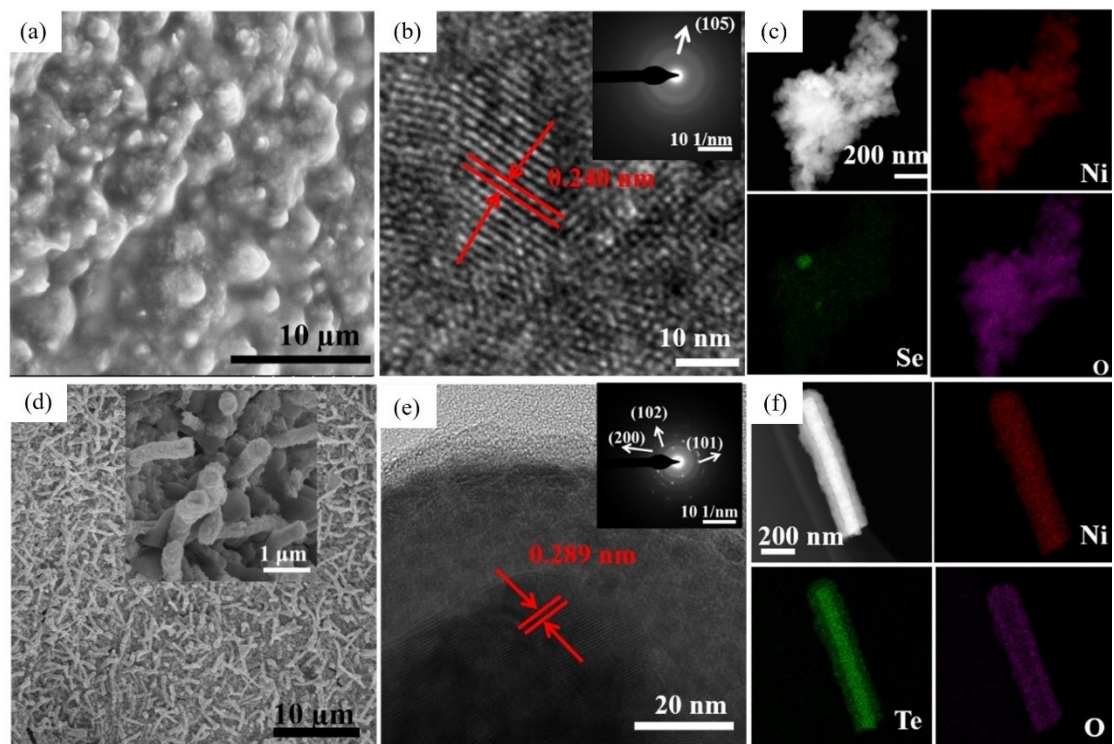**Fig.S11** (a) SEM, (b) HRTEM, (c) STEM and corresponding EDS mapping images of NiSe$_2$/NF after OER. (d) SEM, (e) HRTEM, (f) corresponding EDS mapping images of NiTe/NF after OER.
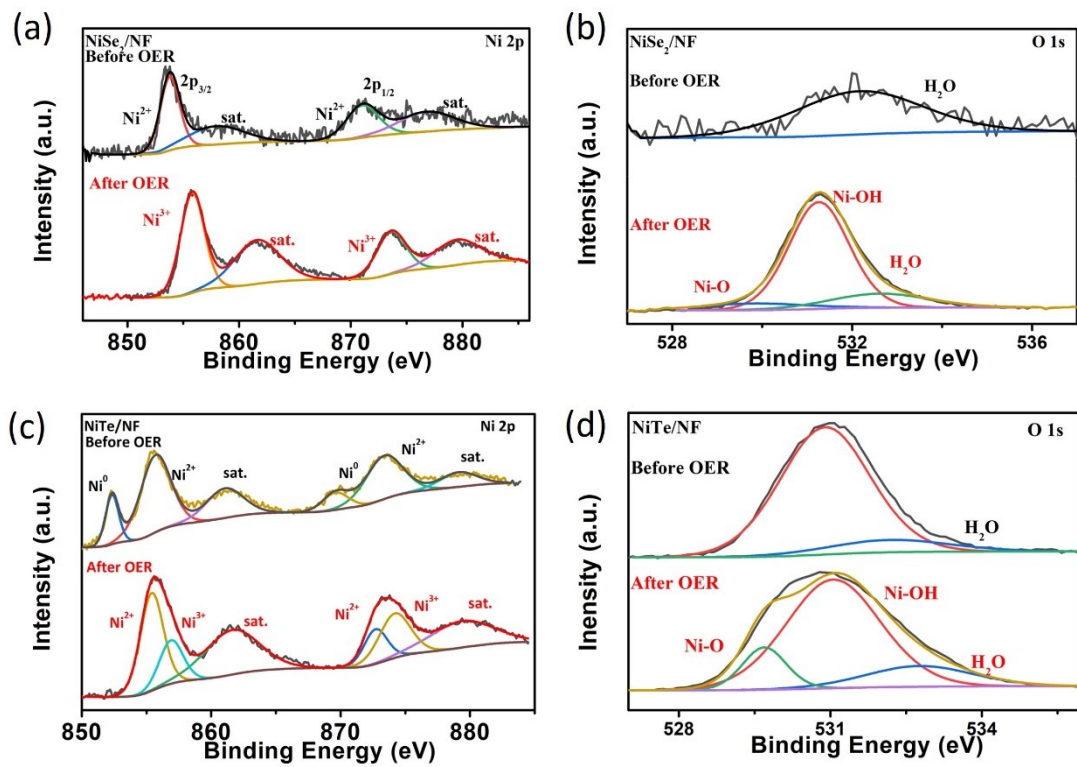
Fig.S12 (a) Ni 2p spectrum of NiSe$_2$/NF before and after OER. (b) O 1s spectrum of NiSe$_2$/NF before and after OER. (c) Ni 2p spectrum of NiTe/NF before and after OER. (d) O 1s spectrum of NiTe/NF before and after OER.
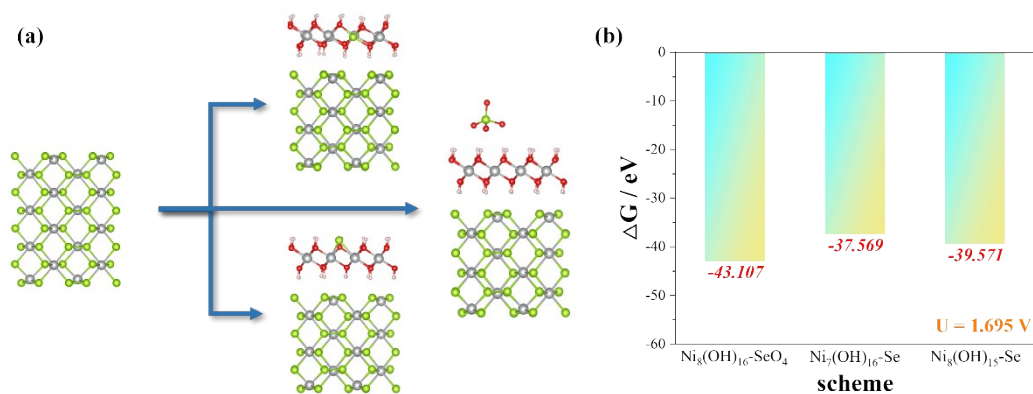
Fig. S13 (a) Different existence forms of Se anions after electrochemical oxidation and (b) the corresponding formation energy under OER working potential (U=1.695 V vs RHE) of $NiSe_2$.
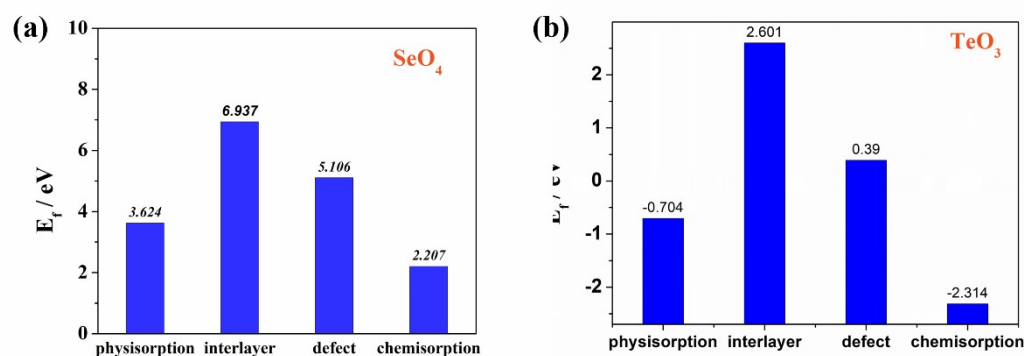
Fig. S14 (a) Selenates and (b) tellurite formation energy from Se and Te anion of $NiSe_2$ and NiTe, respectively, for diverse interaction with the layered $Ni(OH)_2$.
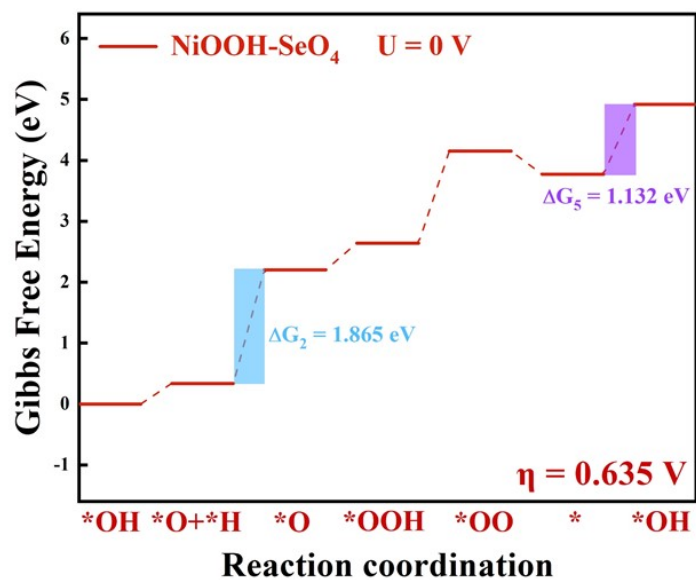
Fig. S15 Reaction path diagram and reaction free energy step diagram of NiOOH-SeO₄(SeO₄ involved in the reaction) via AEM
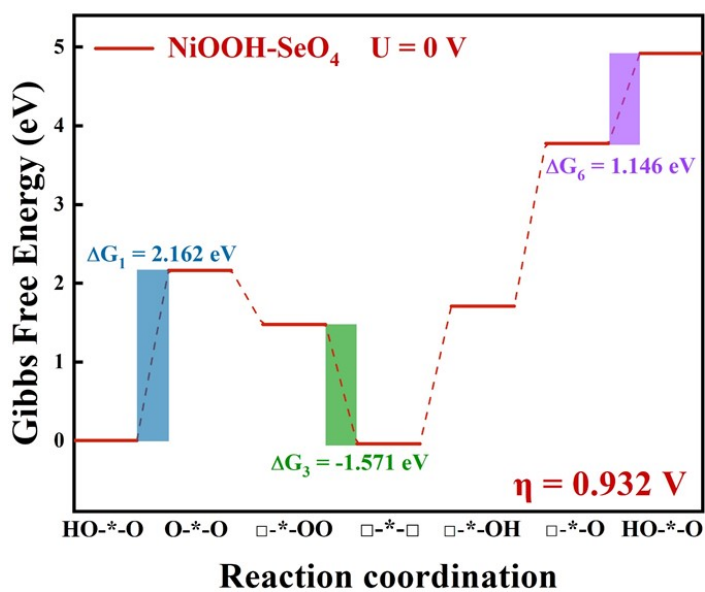
Fig.S16 Reaction free energy step diagram of NiOOH-SeO₄ via LOM
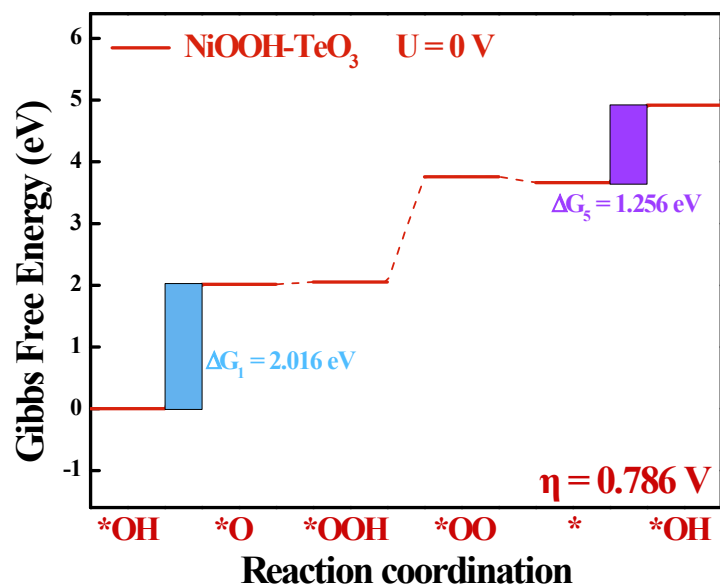
Fig. S17 Reaction path diagram and reaction free energy step diagram of NiOOH-TeO$_3$ (TeO$_3$ can't be involved in the reaction) via AEM
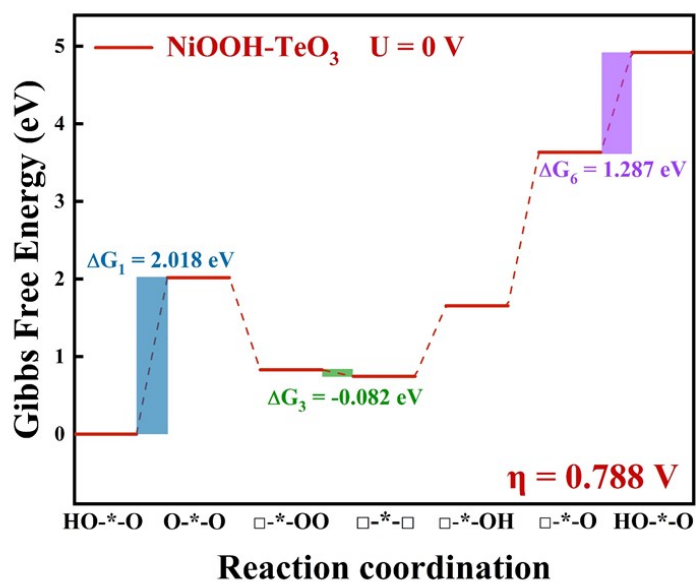
Fig.S18 Reaction free energy step diagram of NiOOH-TeO$_4$ via LOM

Supplemental Tables

Table S1 DFT energy, thermodynamic correction energy and Gibbs free energy of each intermediate via AEM

| Sample		E / eV	G_T / eV	G / eV
NiOOH (001)	*OH	-467.512	0.359	-467.153
	*O	-461.741	0.046	-461.695
	*OOH	-471.752	0.417	-471.334
	*OO	-467.039	0.100	-466.939
	*	-459.055	-	-459.055
NiOOH (001)-SO$_4$	*OH	-493.957	0.358	-493.599
	*O+*H	-493.553	0.316	-493.237
	*O	-488.175	0.057	-488.118
	*OOH	-498.450	0.390	-498.060
	*OO	-493.067	0.068	-492.999
	*	-483.872	-	-483.872
NiOOH (001)-SeO$_4$	*OH	-484.333	0.348	-483.985
	*O+*H	-483.960	0.313	-483.647
	*O	-478.369	0.040	-478.329
	*OOH	-489.115	0.347	-488.768
	*OO	-483.861	0.051	-483.810
	*	-474.254	-	-474.254
NiOOH (001)-TeO$_3$	*OH	-479.098	0.349	-478.749
	*O	-473.322	0.040	-473.282
	*OOH	-484.454	0.332	-484.122
	*OO			
	*	-469.128	-	-469.128

Table S2 Gibbs reaction energy change each step of and OER overpotential via AEM

Sample		ΔG / eV	η / V
NiOOH (001)	step 1	1.972	
	step 2	1.889	
	step 3	1.184	0.739
	step 4	-1.896	
	step 5	1.781	
NiOOH (001)-SO$_4$	step 1	0.363	
	step 2	1.666	
	step 3	0.935	
	step 4	1.609	0.436
	step 5	-0.803	
	step 6	1.150	
NiOOH (001)-SeO$_4$	step 1	0.338	
	step 2	1.865	
	step 3	0.438	
	step 4	1.506	0.635
	step 5	-0.374	
	step 6	1.147	
NiOOH (001)-TeO$_3$	step 1	2.016	
	step 2	0.037	
	step 3		0.786
	step 4		
	step 5	1.256	

Table S3 DFT energy, thermodynamic correction energy and Gibbs free energy of each intermediate via LOM

Sample		E / eV	G_T / eV	G / eV
NiOOH (001)	HO-*-O	-467.510	0.418	-467.092
	O-*-O	-461.421	0.112	-461.309
	□-*-OO	-463.644	0.081	-463.563
	□-*-□	-454.198	-	-454.198
	□-*-OH	-462.641	0.349	-462.292
	□-*-O	-459.035	0.053	-458.982
NiOOH (001)-SO$_4$	HO-*-O	-488.179	0.704	-487.475
	O-*-O	-482.228	0.090	-482.138
	□-*-OO	-482.922	0.077	-482.845
	□-*-□	-474.156	-	-474.156
	□-*-OH	-483.804	0.343	-483.461
	□-*-O	-478.233	0.058	-478.175
NiOOH (001)-SeO$_4$	HO-*-O	-484.333	0.411	-483.922
	O-*-O	-478.421	0.112	-478.309
	□-*-OO	-479.075	0.080	-478.995
	□-*-□	-470.582	-	-470.582
	□-*-OH	-480.061	0.350	-479.711
	□-*-O	-474.257	0.065	-474.192
NiOOH (001)-TeO$_3$	HO-*-O	-479.100	0.404	-478.696
	O-*-O	-473.322	0.096	-473.226
	□-*-OO	-474.526	0.111	-474.415
	□-*-□	-464.567	-	-464.567
	□-*-OH	-474.870	0.335	-474.535
	□-*-O	-469.173	0.068	-469.105

Table S4 Gibbs reaction energy change each step and OER overpotential via LOM

Sample		ΔG / eV	η / V
NiOOH (001)	step 1	2.330	1.538
	step 2	-2.254	
	step 3	-0.565	
	step 4	2.783	
	step 5	-0.142	
	step 6	2.768	
NiOOH (001)-SO$_4$	step 1	1.885	0.655
	step 2	-0.707	
	step 3	-1.241	
	step 4	1.572	
	step 5	1.834	
	step 6	1.577	
NiOOH (001)-SeO$_4$	step 1	2.162	0.932
	step 2	-0.686	
	step 3	-1.517	
	step 4	1.748	
	step 5	2.067	
	step 6	1.146	
NiOOH (001)-TeO$_3$	step 1	2.018	0.788
	step 2	-1.189	
	step 3	-0.082	
	step 4	0.908	
	step 5	1.978	
	step 6	1.287	