Electronic Supplementary Information

## Amorphous nickel sulfide nanosheets with embedded vanadium

# oxide nanocrystals on nickel foam for efficient electrochemical

### water oxidation

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Fig. S1 Photographs of pristine NF,  $VO_x/Ni(OH)_2$ @NF and  $VO_x/Ni_3S_2$ @NF (from left to right).



Fig. S2 High resolution XPS spectrum of Ni 2p in VO<sub>x</sub>/Ni(OH)<sub>2</sub>@NF.



Fig. S3 SEM image of  $Ni(OH)_2$ @NF synthesized by hydrothermally treating NF in urea solution at 120 °C for 12 h.



Fig. S4 SEM image of free-standing  $VO_x$  power.



Fig. S5 EDS (a) and element V (b), O (c) and S (d) mapping images of  $VO_x/Ni_3S_2@NF$ 



Fig. S6 TEM images of  $VO_x/Ni_3S_2$ .



Fig. S7 SEM images of  $Ni_3S_2@NF$  synthesized by hydrothermally treating NF in urea solution at 120 °C for 12 h and subsequent in 0.1 M Na<sub>2</sub>S solution at 80 °C for 8 h.



**Fig. S8** TEM image (a), Ni, O, V, S (b-e) elemental distribution images and combined image (f) of VO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>.



Fig. S9 XPS survey and S 2p spectra of free-standing VO<sub>x</sub> power after being processed in 0.1 M Na<sub>2</sub>S solution at 80  $^{\circ}$ C for 8 h.



Fig. S10 LSV curves of  $VO_x/Ni_3S_2$ @NF before and after 95% iR correction. The R is measured to be 1.06  $\Omega$  according to EIS in Fig 7a.



Fig. S11 Tafel plots of four catalysts.



Fig. S12 Chronoamperometric curve of NF at 1.475 V, showing a much lower current density compared to  $VO_x/Ni_3S_2@NF$  at the same potential (Fig. 6c).



Fig. S13 CV curves of  $VO_x/Ni_3S_2@NF$  (a) and  $VO_x/Ni(OH)_2@NF$  (b) in 1.0 M KOH solution at different scanning rates.



Fig. S14 ECSA-normalized LSV curves of  $VO_x/Ni_3S_2@NF$  and  $VO_x/Ni(OH)_2@NF$ .



Fig. S15 Chronoamperometric curve of Ni3S2@NF at 1.65 V.



Fig. S16 XPS of VO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>@NF-0.5 showing negligible signal from V 2p.



Fig. S17 SEM images of  $VO_x/Ni_3S_2@NF-0.5$  (a, b) and  $VO_x/Ni_3S_2@NF-1.5$  (c, d)



Fig. S18 SEM images of VO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>@NF-100 °C.



**Fig. S19** XPS spectra of  $VO_x/Ni_3S_2@NF$  after electrolysis (1.6 V for 1 h). a. Ni 2p; b. S 2p. c. V 2p and O 1s. The S 2p signal considerably decreases while the O 2p increases compared to the fresh catalyst (namely in Fig. 4), suggesting the formation of metal oxyhydroxide after electrolysis. At the same time, the binding energy of Ni 2p and V 2p increase, suggesting their higher oxidation state.

Catalysts	η (mV)	j	ESCA	iR	Morphology	Substrate	Ref.
		(mA		correction			
		cm <sup>-2</sup> )					
VO <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> @NF	358	100	15.98	w/o	nanosheet	NF <sup>a</sup>	This work
VO <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> @NF	330	100		with	nanosheet	NF	This work
Ni <sub>3</sub> S <sub>2</sub> /NF	430	100	121.3	with	porous film	NF	1
MoS <sub>2</sub> -Ni <sub>3</sub> S <sub>2</sub>	341	100	121.3	with	nanorod	NF	2

Table S1. OER activity of Ni-base catalysts in alkaline media reported in recent literature.

Ni/NiS	340	30	with	nanoparticle	NF	3
NiS/NF	335	50	with	microsphere	NF	4
				film		
NiCo <sub>2</sub> S <sub>4</sub> NA/CC	340	100	with	nanowire	CC <sup>b</sup>	5
NixCo <sub>3-x</sub> S <sub>4</sub> /Ni <sub>3</sub> S <sub>2</sub> /NF	320	100	w/o	nanosheet	NF	6
MoO <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> /NF	310	100	w/o	microspherical	NF	7
NiS/NF	370	20	with	nanosheet	NF	8
N-Ni <sub>3</sub> S <sub>2</sub> /NF	330	100	with	porous structure	NF	9
Zn-Ni <sub>3</sub> S <sub>2</sub> /NF	330	100	with	nanosheet	NF	10
$Ni_{0.7}Fe_{0.3}S_2$	287	100	with	microflower	NF	11
NiS/NiS <sub>2</sub>	416	100	with	nanoparticle	GCE °	12
Ni <sub>2.3%</sub> -CoS <sub>2</sub> /CC	370	100	with	nanowire	CC	13

<sup>a</sup>NF stands for nickel foam, <sup>b</sup>CC stands for carbon cloth, <sup>c</sup>GCE stands for glassy carbon electrode

<u> </u>		j	iR		<u> </u>	Ref.
Catalysts	η (mV)	(mA cm <sup>-2</sup> )	correction	Morphology	Substrate	
VO <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> @NF	358	100	w/o	nanosheet	NF <sup>a</sup>	This work
VO <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> @NF	330	100	with	nanosheet	NF	This work
NiV-LDHs.	350	27	w/o	nanosheet	GCE <sup>b</sup>	14
CoV <sub>2</sub> O <sub>6</sub> -	220	10	w/o	porous flake	GCE	15
V <sub>2</sub> O <sub>5</sub> /RGO-1	239					
V/NF	292	10	with	nanobelt	NF	16
$Fe_{0.5}V_{0.5}$	380	10	with	hollow sphere	GCE	17
VOOH	270	10	with	hollow nanosphere	GCE	18
eFe/NiVS/NF	340	100	w/o	nanowire	NF	19
Co/VN	385	100	with	nanosheet	GCE	20
$\mathrm{Co_2V_2O_7}$	452	100	with	nanosheet	GCE	20
a-CoVOx	347	10	with	nanoneedle	GCE	21
a-CoVOx	254	10	with	nanoneedle	NF	21
V- pNiS <sub>2</sub>	290	10	with	nanosheet	GCE	22

Table S2. OER activity of V-base catalysts in alkaline media reported in recent literature.

<sup>a</sup> NF stands for nickel foam, <sup>b</sup> GCE stands for glassy carbon electrode.

### 1.1 Turnover frequency (TOF) calculation

TOF was calculated using the method that widely used in the literature, e.g. Nano Energy 2018, 51, 26. The quantity of active sites (N) on electrode was first calculated

Firstly, CV curve of each electrode was collected at the scan rate of 0.05 V S<sup>-1</sup> from -0.2 to

0.6 V vs. RHE in PBS solution. N is calculated according to the following equation:

 $N = Q/2F = i \cdot t/2F = i \cdot V/u$ 

where Q is obtained as the cyclic voltammetric capacity via integrating CV cures, V is the voltage (v), i is the current density (A m<sup>-2</sup>), and F is the Faradaic constant (96485 C mol<sup>-1</sup>).

TOF calculation:

The values of TOF are obtained according to the equation:  $\text{TOF} = \overline{mfN}$ , where A stands for the area of the electrode used for CV (0.5 cm<sup>-2</sup>). |j| is the current density at the overpotential of 330 mV when LSV is measured in 1.0 M solution, and *F* is the Faradaic constant. m refers to the electrons consumed in the process of forming one O<sub>2</sub> molecule from water (4 electrons for oxygen evolution reaction). *N* is the quantity of active sites.

|j|A

The TOF of  $VO_x/Ni_3S_2$ @NF at 330 mV overpotential is calculated to be 7.717 s<sup>-1</sup>.

#### 1.2 Charge calculation

According to Table S1, the quantity (*N*) of surface site (Ni<sup>2+</sup>, V<sup>4+</sup> and V<sup>2+</sup>) on VO<sub>x</sub>/Ni<sub>3</sub>S<sub>2</sub>@NF is the  $3.82 \times 10^{-8}$  mol cm<sup>-2</sup>. Electrochemically converting the Ni<sup>2+</sup>, and V<sup>2+</sup> to higher valence (Ni<sup>3+</sup>, and V<sup>3+</sup>) requires a charge of Q1, Q1=  $3.82 \times 10^{-8}$  mol cm<sup>-2</sup> × 96485 C mol<sup>-1</sup> (Faradaic constant) ×1 (1 electron transferred)= $3.7 \times 10^{-3}$  C cm<sup>-2</sup>.

Using the same calculation method, the oxidation of NF itself requires a charge of  $Q2=1.95 \times 10^{-3}$  C cm<sup>-2</sup>. This calculated charge is close to that experimentally observed on NF at 1.475V for 500 s, as shown in Fig. S12.

In Figure 6c, the passed charge at 1.475V for 500 s equals to Q3=30 mA cm<sup>-2</sup>×500s=15C cm<sup>-2</sup>, which is much larger than Q1 and Q2. Therefore it is confirmed that the anodic currents in Figure 6c come from OER process but not the surface metal oxidation.

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