Supporting Information

Ni-MOF precursor assisted formation of vanadium doped nickel sulfide nanorods for boosted electrocatalytic oxygen evolution reaction

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1. Chemicals and reagents

Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$, ≥98%), Terephthalic acid (BDC, ≥99%)) and Ammonium fluoride (NH_4F) were purchased from Aladdin (China). Trisodium tetraoxovanadate dodecahydrate (Na_3VO_4 $12H_2O$, ≥99%) and Thioacetamide (TAA, ≥99%) were purchased from Macklin (China). N,N-Dimethylacetamide (DMF) and Ethanol (C_2H_5OH, ≥99.7%)was purchased from Tianjin Rionlon Medicinal Chemical Co., Ltd. (China). Urea (CH_4N_2O, ≥99%), Hydrochloric acid (HCl, AR) and Potassium hydroxide (KOH, ≥85%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). All aqueous solutions used during the synthesis were prepared using deionized water (18.25 Ω).

2. Preparation of catalyst

2.1 Preparation of NiV-MOF/NF

Firstly, NF (1 × 2 cm^2) was ultrasonic treated with ethanol, deionized water and HCl for 20 min, respectively. Secondly, Na_3VO_4 $12H_2O$ (1 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.5 mmol), BDC (0.6 mmol) were dissolved in 21 mL DMF and were added the 1.5 mL ethanol and 1.5 mL deionized water under stirring progress. And the above mixture solution and the pretreated NF were transferred to a 50 mL Teflon-lined stainless steel autoclave. After treatment at 125 °C for 12 h, the NiV-MOF/NF was received. The obtained NiV-MOF/NF was washed separately with deionized water and ethanol, and dried in an oven at 60℃ for 10 h.

2.2 Preparation of V-Ni_3S_2/NF

0.12 g TAA was dissolved into 30 mL deionized water with constantly stirring form solution A. Subsequently, the solution A and the NiV-MOF/NF were transferred into a 50 mL Teflon-lined stainless steel autoclave to heat at 140℃ for 12 h. After cooled to ambient temperature, the V-Ni_3S_2/NF was received. Finally, the V-Ni_3S_2/NF was cleaned with deionized water and ethanol, respectively. And was dried in an oven at 60℃ for 10 h.

2.3 Preparation of Ni-MOF/NF and Ni_3S_2/NF

For comparison, the synthesized method of Ni-MOF/NF and Ni_3S_2/NF by using the same as NiV-MOF/NF and V-Ni_3S_2/NF.

3. Structure characterizations

The crystal information and structural information of the catalyst were characterized with the following instruments**.** The crystalline phases and chemical states of resulting were analyzed with an X-ray powder diffraction (XRD, Rigaku D/Max-2400) using a Cu Kα radiation source. The morphological structure and morphology of the catalyst was characterized by transmission electron microscopy (TEM, FEI TECNAI G^2 F_{20}, America) and field-emission scanning electron microscopy (FE-SEM, Carl Zeiss Ultra Plus, Germany). The elemental mappings and chemical compositions of the samples were characterized by energy-dispersive X-ray spectroscopy (EDX, Oxford, England) equipped with an Aztec-X-80. The X-ray photoelectron (XPS) spectroscopy of the catalyst was characterized by a monochromatic Al Kα radiation source.

4. Electrochemical measurements

All of electrochemical measurements were conducted using a standard three electrode system (CHI760e, Shanghai, China). V-Ni_3S_2/NF, Ni_3S_2/NF, NiV-MOF/NF, Ni-MOF/NF, NF, and RuO_2/NF (1 cm × 2 cm) were used as the working electrodes, HgO (1 M KOH) electrode as the reference electrode and carbon rod as the counter electrode. The reversible hydrogen electrode is calibrated by equation: E(RHE) = E(HgO) + 0.098 + 0.0592 pH. The Tafel slope is calculated by the Tafel equation ($\eta = a + b \log j$, where η is the overpotential, b is the Tafel slope, and j is the current density). Before the OER measurement, the electrolyte was saturated with N_2 by passing in nitrogen gas for 30 min. The OER activity of the catalyst was obtained by linear sweep voltammetry (LSV) at a sweep rate of 5 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was measured at frequencies ranging from 0.01 Hz to 100 kHz. The electrochemical active surface area (ECSA) was determined by cyclic voltammetry (CV) scanning at 20-100 mV s^{-1} sweep rate, and the double layer (C_{dl}) capacitance was calculated. The stability of the catalyst was tested at 10 mA cm^{-2} by the constant current method.

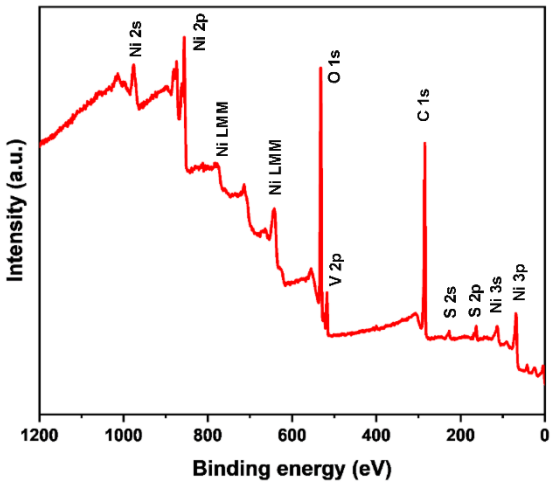

Fig. S1. XPS total spectra of V-Ni_3S_2/NF.

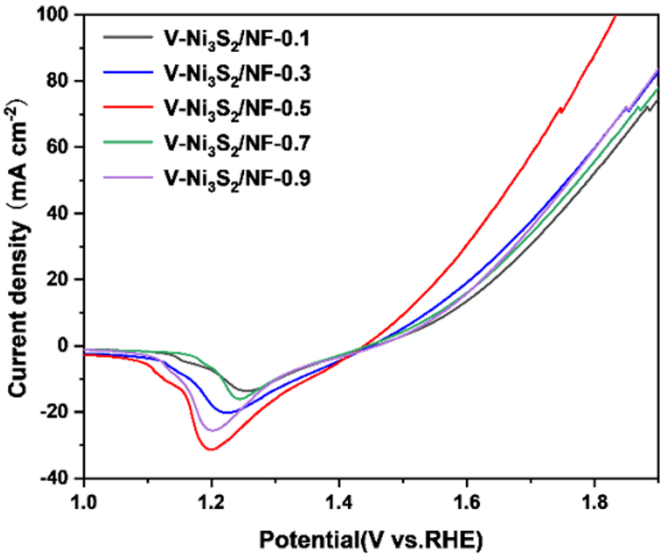

Fig. S2. LSV comparison of different V doping amounts in 1 M KOH solution.

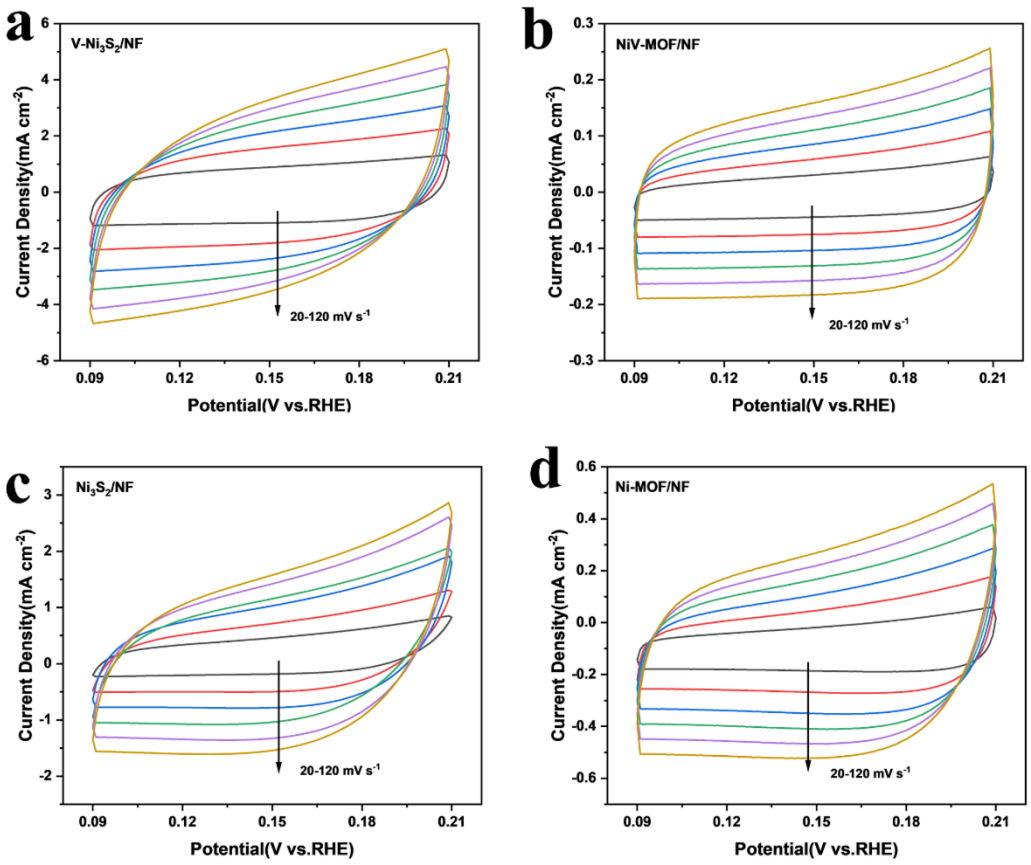

Fig. S3. CV curves of V-Ni_3S_2/NF, Ni_3S_2/NF, NiV-MOF /NF and Ni-MOF/NF at different sweep speeds of 20, 40, 60, 80, 100, 120 mV s^{-1}.

Table S1 Comparison of HER activity of V-Ni_3S_2/NF (red words) and recently reported other electrocatalysts for OER.

HER catalysts	**η_{10} (mV)**	**Tafel slope ($mV\ dec^{-1}$)**	**Reference**
V-Ni_3S_2/NF	273	56.67	This work
$Fe_{0.5}Co_{0.5}Se_2$/CFC	290	64	[S1]
Fe-NiS/MoS_2	297	54.7	[S2]
NiSe-$Ni_{0.85}Se$/CP	300	98	[S3]
FeS_2/CoS_2NSs	302	42.0	[S4]
MoS_2/NiS_2/CC	303	58.0	[S5]
3D-GNs@Ni_3S_2	305	50.0	[S6]
Ni_3S_2 NWs/Ni	317	84.8	[S7]
NiS	320	59.0	[S8]
$F_{0.2}$-V-Co_3O_4	320	75.9	[S9]
NiSe-Ni_3Se_2/MWCNT	325	70.2	[S10]

Table S2 OER parameters of various catalysts prepared in 1 M KOH

Catalyst	η10 (mV)	Tafel slope ($mVdec^{-1}$)	C_{dl} ($mFcm^{-2}$)	Rct(Ω)
V-Ni_3S_2/NF	273	56.67	22.08	0.52
Ni_3S_2/NF	321	99.84	12.49	1.14
NiV-MOF/NF	318	93.56	1.33	2.01
Ni-MOF/NF	310	106.14	3.11	18.99

Reference

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