Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2024

Ambient temperature constructing nickel iron sulfide on Fe foam for high-current overall water splitting

Shuang Gao, Zhuo Wang, Ping Nie, Juan Jian, Hairui Wang, Fen Yao* and Limin Chang*

Key Laboratory of Preparation and Application of Environmental Friendly Materials (Jilin Normal University), Ministry of Education, Changchun, 130103, China

E-mail address: changlimin2139@163.com

Experimental section

Chemicals and reagents

The chemicals and materials were purchased from commercial sources and have not been further purified and processed. Iron foam (labeled as IF) with a thickness of 1.5 mm was purchased from Kunshan Longsheng Bao electronic Material Co.Ltd. Nickel sulfate($NiSO_4·7H_2O$), sodium thiosulfate ($Na_2S_2O_3·5H_2O$) and potassium hydroxide (KOH) were purchased from Beijing Chemical Corp.

Preparation of FeNiS/IF

Iron foam (10 mm×50 mm) was cleaned with acetone and ethanol before use. 2.62g $NiSO_4·7H_2O$ and 1.245g $Na_2S_2O_3·5H_2O$ were dissolved in 100 mL deionized water. Then, a piece of iron foam was immersed in the above solution at room temperature for 24 h. The iron foam was washed with water and ethanol for several times to obtain FeNiS/IF.

For comparison, a piece of iron foam was directly immersed in 1.245g $Na_2S_2O_3·5H_2O$ solution and kept at room temperature for 24 h. The iron foam was washed with water and ethanol for several times to obtain FeS/IF.

In order to investigate the effect of the reaction time on the synthesis of materials, we maintained the above reaction conditions and reacted at room temperature for 1 h, 6 h, 12 h and 48 h. The resulting samples were named as FNS-x (where x represents the time).

Characterization

To comprehend the composition and structure of the materials, we conducted the powder X-ray diffraction (XRD) patterns on a Rigaku D/Max 2550 PC. The X-ray photoelectron spectroscopy (XPS) was collected on PHI 5000 C ESCA to investigate the chemical valence state of elements. Among them, the binding energy is calibrated at 284.6 eV by graphite carbon. The morphology and composition of the catalysts were observed by Transmission electron microscope (TEM) (JEM-2100F) and Scanning electron microscope (SEM) images (JSM-7800F).

Electrochemical measurements

The electrochemical performance measurements were carried out by electrochemical working station (CHI760E) using a three-electrode system. The reference electrode and the counter electrode are an Hg/HgO electrode and a carbon rod, respectively. The obtained FeNiS/IF with an area of 0.5*0.5 cm^2 was directly used as the working electrode. The linear scan voltammetry curves (LSV) were acquired at a scan rate of 0.5 mV s^{-1}. In addition, the LSV curves required 10 scans to keep the material relatively stable. All LSV data were subjected to 85% iR-compensation without special instructions.

Computational details

All the density functional theory (DFT) calculations were conducted with the Vienna Ab-initio Simulation Package (VASP) with the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) approach [1,2]. 500 eV kinetic energy cutoff and 0.05 eV $Å^{-1}$ Hellmann-force threshold were used for accurate optimization of the structural relaxations, respectively. A 20 Å vacuum slab in a direction perpendicular to the surface was adopted to avoid periodic interactions. The Monkhorst-Pack k-point of 3×3×1 was applied for the optimization of surface stuctures. All the surface structures were calculated with half of the atoms fixed from the bottom and the rest of the atoms relaxed.

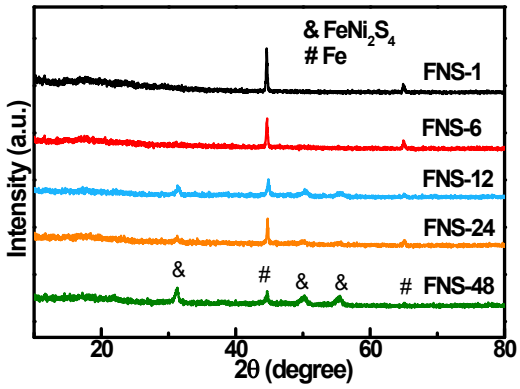

Fig. S1 The XRD patterns of FNS-x (where x represents the time)

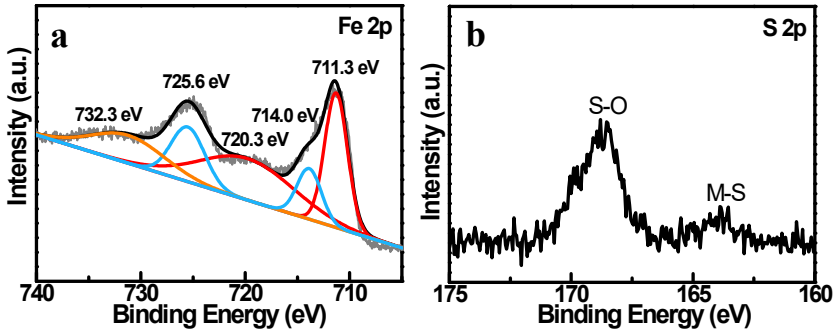

Fig. S2 The XPS spectra of FeS/IF for the a) Fe 2p and b) S 2p regions.

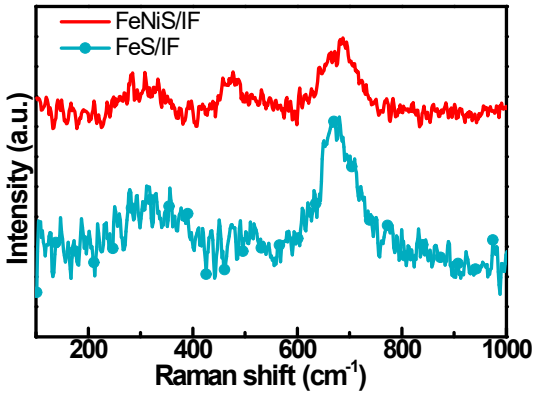

Fig. S3 Raman spectrum of FeNiS/IF and FeS/IF

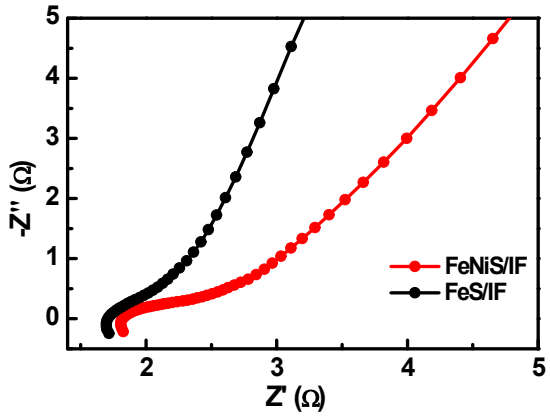

Fig. S4 The electrochemical impedance spectroscopy of FeNiS/IF and FeS/IF.

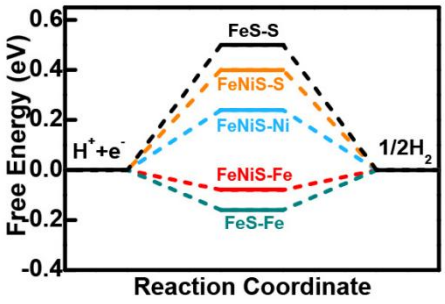

Fig. S5 The calculated free-energy diagram of FeNiS/IF and FeS/IF

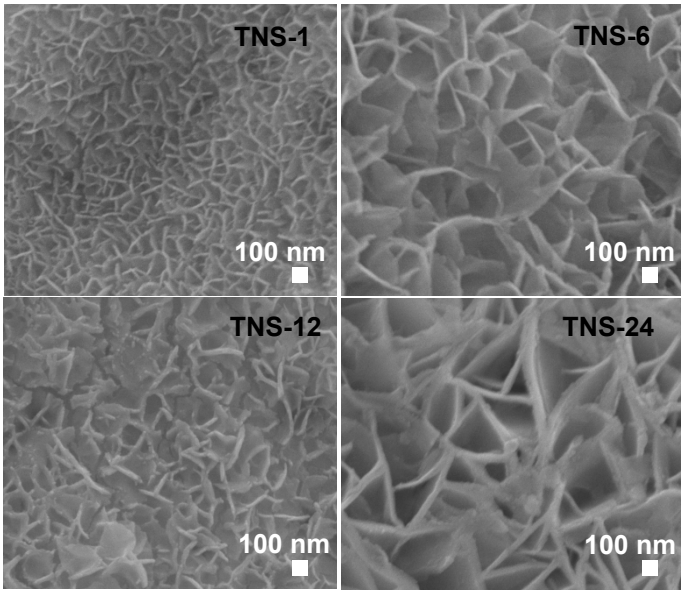

Fig. S6 The SEM images of FNS-x (where x represents the time)

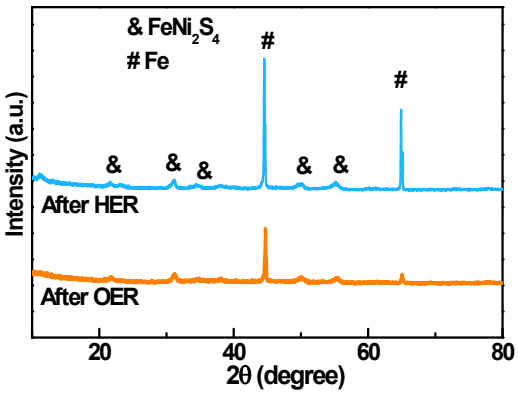

Fig. S7 The XRD pattern of FeNiS/IF after HER and OER treatment

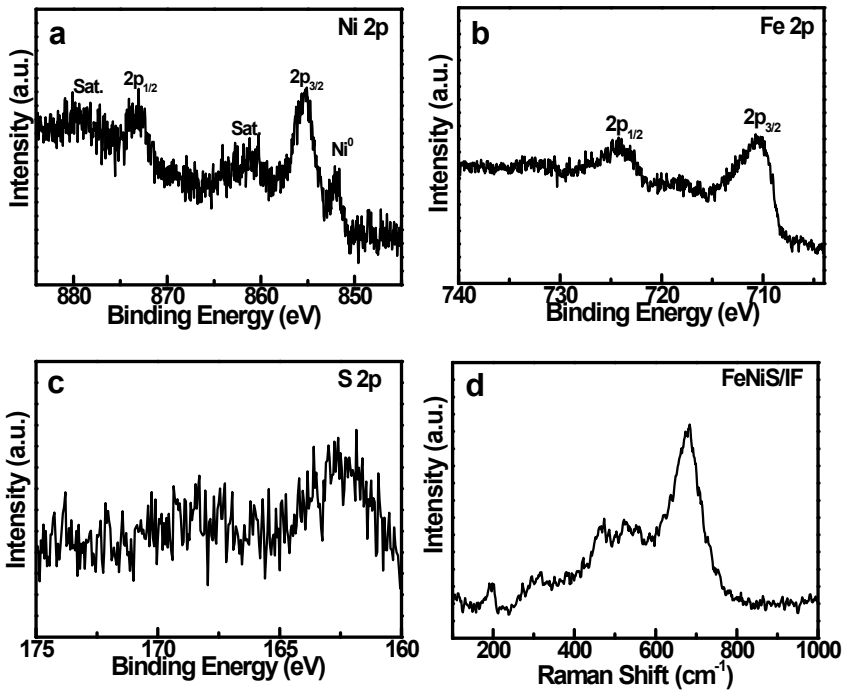

Fig. S8 The XPS spectra of a) Ni 2p, b) Fe 2p, c) S 2p regions image and d) Raman spectrum of FeNiS/IF after OER durability test

Table S1 Performance comparison of recently reported Ni- or/and Fe-based HER electrodes in KOH solution.

Electrode	Electrolyte	Overpotential	Ref.
FeNiS/IF	**1 M KOH**	**68 mV @10mA cm^{-2} 171 mV @100mA cm^{-2}**	**This work**
NiFeS/NF	1 M KOH	196 mV @100 mA cm^{-2}	*J. Mater. Chem. A*, 2023, **11**, 1116.
Ni_3S_2/Fe_9S_{10}@NF	1 M KOH	285 mV @100 mA cm^{-2}	*J. Alloys Comp.*, 2021, **874**, 159874
Fe-H_2cat	1 M KOH	300 mV @100 mA cm^{-2}	*Chem* 2018, **4**, 1139.
Ni-SN@C	1 M KOH	150 mV @10 mA cm^{-2}	*Adv. Mater.,* 2021, **33**, 2007508
Ni_2P-Fe_2P/NF	1 M KOH	225 mV @100 mA cm^{-2}	*Adv. Funct. Mater.,* 2021, **31**, 2006484
NiCoP-120	1 M KOH	128 mV @100 mA cm^{-2}	*Adv. Energy Mater.,* 2023, **13**, 2300499
Ni_3S_2@Ni_3B/NP	1 M KOH	304 mV @100 mA cm^{-2}	*Nanoscale*, 2021, **13**, 17953.
N-NiS/NiS_2	0.1 M KOH	185 mV @10 mA cm^{-2}	*Chem. Eng. J.*, 2020, **397**, 125507
amorphous FeCoNi-S	1 M KOH	80 mV @10 mA cm^{-2}	Chin. Chem. Lett., 2022, 34, 107241.

[1] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple, Phys. Rev. Lett. 77 (1996) 3865-3868.

[2] J. P. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, K. Burke, Restoring the density-gradient expansion for exchange in solids and surfaces, Phys. Rev. Lett. 100 (13) (2008) 136406.