Electronic Supplementary Information

Vapor-phase hydrothermal transformation of nanosheet array structure $Ni(OH)_2$ into ultrathin Ni_3S_2 nanosheets on nickel foam for high-efficiency overall water splitting

Guoqiang Liu[a,b†], Zhongti Sun[c†], Xian Zhang,[a,b] Haojie Wang[a,b], Guozhong Wang[a], Xioajun Wu[c], Haimin Zhang*[a], Huijun Zhao[a,d]

[a] Key Laboratory of Materials Physics, Centre for Environmental and Energy Nanomaterials, Anhui Key Laboratory of Nanomaterials and Nanotechnology, CAS Center for Excellence in Nanoscience, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China.

[b] University of Science and Technology of China, Hefei 230026, China.

[c] CAS Key Laboratory of Materials for Energy Conversion and Department of Material Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

[d] Centre for Clean Environment and Energy, Griffith University, Gold Coast Campus, QLD 4222, Australia.

* Corresponding author: Fax: +86 (0)551 65591434; Tel: +86 (0)551 65591973; zhanghm@issp.ac.cn

Table S1 Comparison of OER property of Ni_3S_2/NF-2 with other nonnoble-metal electrocatalysts in 1.0 M KOH electrolyte.

Catalyst	J (mA cm^{-2})	Overpotential (mV)	Ref.
$Co_3O_4/Co(OH)_2$-8	10	373	1
$Ni(OH)_2/Ni_3S_2$-12	20	300	2
$NiCo_2O_4/Ni_3S_2/NF$	40	360	3
$MnCo_2S_4$	50	325	4
$Fe(TCNQ)_2$	50	353	5
$Ni(OH)_2$-TCNQ	100	354	6
$Ni_{2.3\%}$-CoS_2/CC	100	370	7
Co-P	100	413	8
Co-S/Ti	100	430	9
Ni_3S_2/NF-2	100	425	This work

Table S2 The adsorption energy of N_2H_4 and H_2O molecule（ΔE, in the unit of eV) , the O-H bond length of H_2O (D_{O-H}, in the unit of Å), the N-N and N-H of N_2H_4 (D_{N-N} and D_{N-H}, in the unit of Å), the H-O-H bond angle of H_2O (<H-O-H, in the unit of °), the H-N-N and H-N-H bond angle of N_2H_4 (<H-N-N and <H-N-H, in the unit of °), the charge transfer through bader analysis, negative value indicates electron accumulations.

	ΔE	D_{O-H}	D_{N-N}	D_{N-H}	<H-O-H	<H-N-N	<H-N-H	Charge
H_2O-1	-0.82	0.985	-	-	105.597	-	-	-0.0511

H_2O -2	-0.17	0.977	-	-	104.964	-	-	-0.0166
N_2H_4-1	-1.35	-	1.459	1.031	-	111.943	108.814	-0.1464
N_2H_4-2	-1.41	-	1.450	1.030	-	112.625	107.777	-0.1216
H_2O-mole	-	0.972	-	-	104.533	-	-	-
N_2H_4-mole	-	-	1.488	1.029	-	103.871	102.403	-

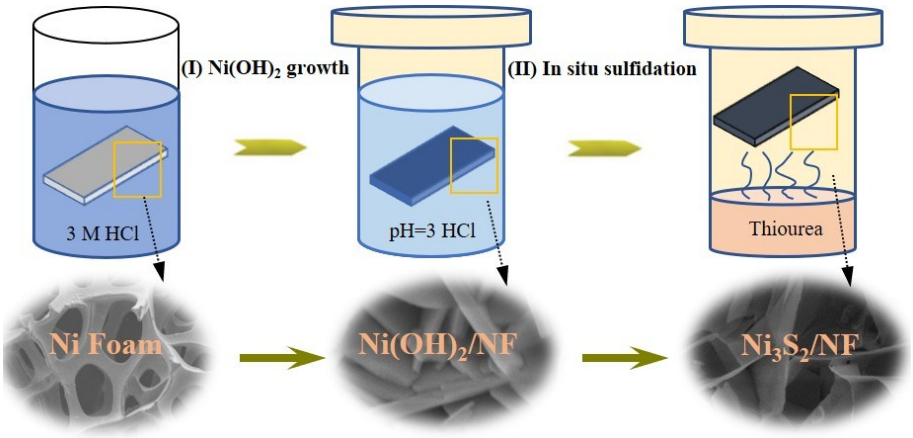

Fig. S1 Schematic illustration of the fabrication processes of Ni_3S_2/NF.

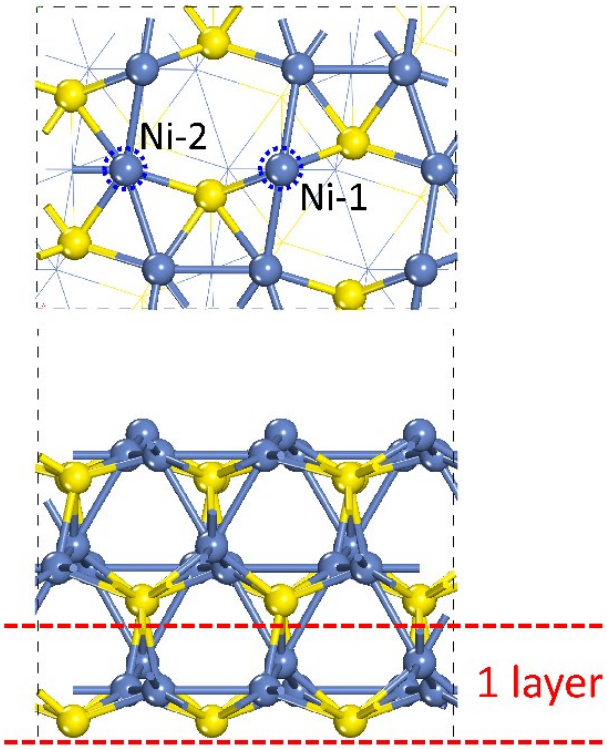

Fig. S2 The top (up) and side (down) $Ni_3S_2(110)$ surface model with three atomic layer, one atomic layer with two red dashed line was composed of three Ni_3S_2 unit, Ni and S atom in light blue and yellow, respectively. The dashed blue circle indicates low and high coordinate Ni atoms, named as Ni-1 and Ni-2, respectively.

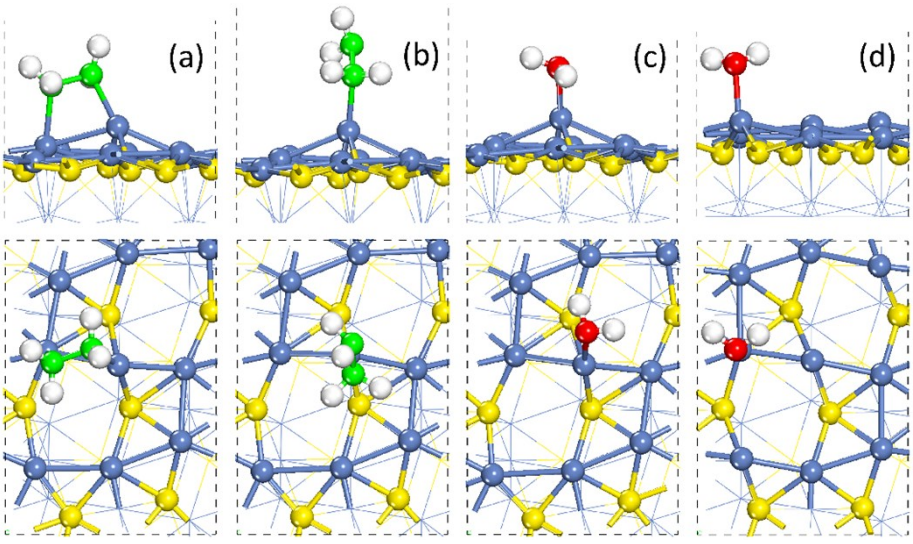

Fig. S3 The possible adsorption configurations of N_2H_4 and H_2O molecule with side (up) and top (down) view, named as (a) N_2H_4-1, (b) N_2H_4-2, (c) H_2O-1, (d) H_2O-2. Ni, S, O, N, and H in light blue, yellow, red, green and white, respectively.

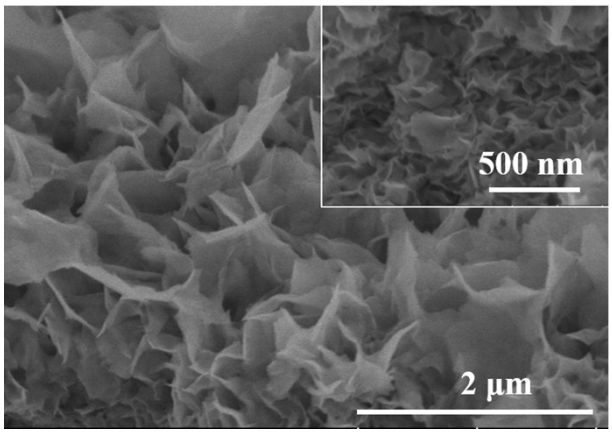

Fig. S4 SEM images of Ni_3S_2/NF-3.

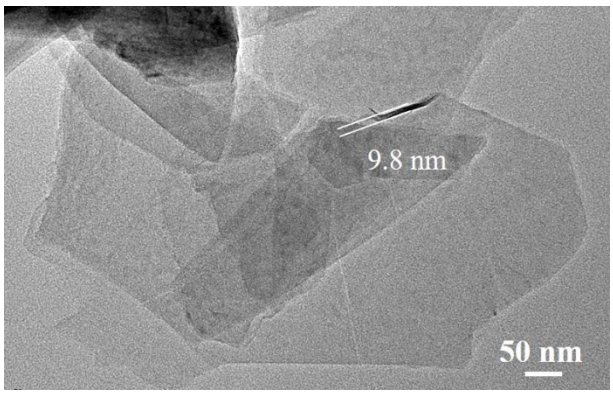

Fig. S5 TEM image of Ni_3S_2/NF-2 with overlapped nanosheet.

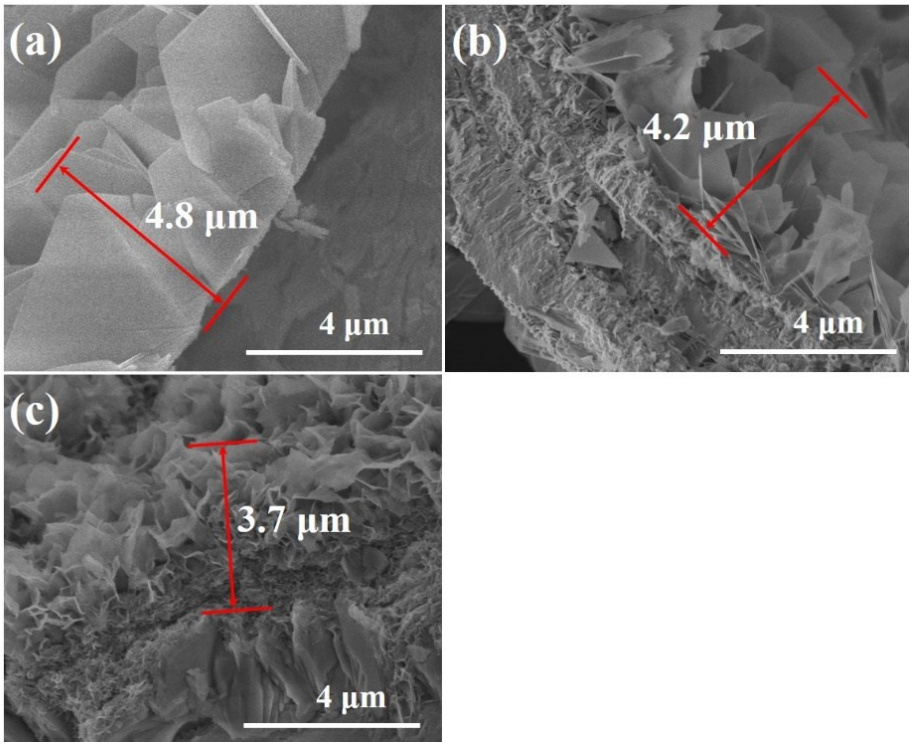

Fig. S6 Cross-sectional SEM images of (a) Ni_3S_2/NF-1, (b) Ni_3S_2/NF-2 and (c) Ni_3S_2/NF-3.

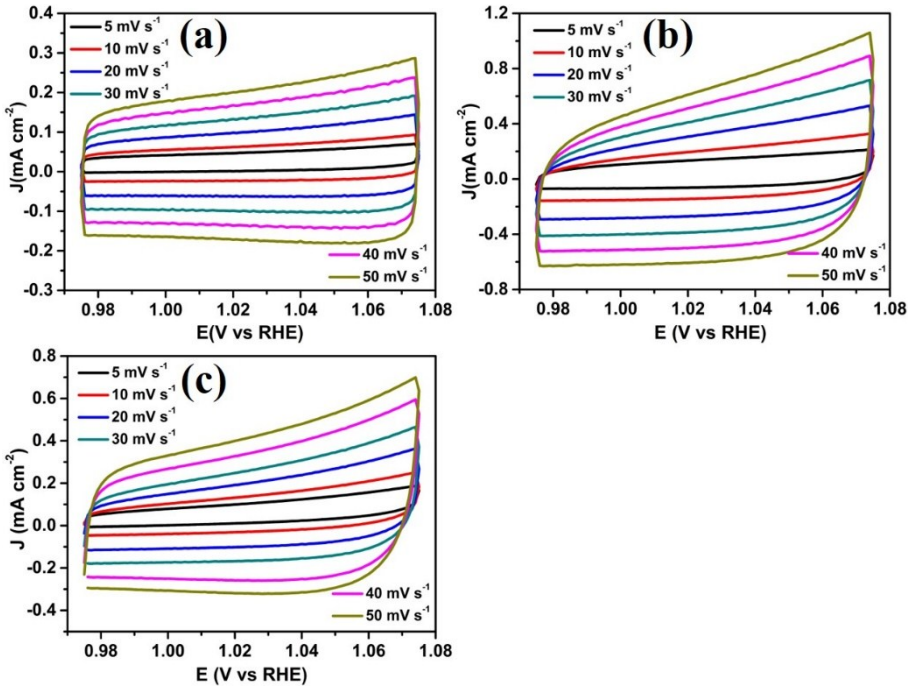

Fig. S7 Cyclic voltammogram measurements of (a) Ni_3S_2/NF-1, (b) Ni_3S_2/NF-2 and (c) Ni_3S_2/NF-3 with different scanning rates in 1.0 M KOH.

To appraise the electrochemical capacitance surface area (ECSA) of the as-prepared samples, we record the electrochemical double-layer capacitances (C_{dl}) by

CV curves in the sweeping region without faradaic process happens.[10] CV measurements are swept from 0.975 to 1.075 V *vs.* RHE electrode with different scan rates of 5, 10, 20, 30, 40 and 50 mV s^{-1}. The electrochemical double-layer capacitive current densities are measured at 1.025 V *vs.* RHE and plotted as a function with scan rate to obtain electrochemical double-layer capacitance (C_{dl}, the slope of the current density *vs.* scan rate plots). The ECSA is proportional to their C_{dl}.[11]

The obtained potentials in all experiment were converted into the potentials *vs.* RHE (reversible hydrogen electrode), according to the equation of E (*vs.* RHE) = E^0 (*vs.* Hg/HgO) + 0.098 V + 0.059pH, (0.098 V is the standard electrode potential for Hg/HgO at 25℃).[12]

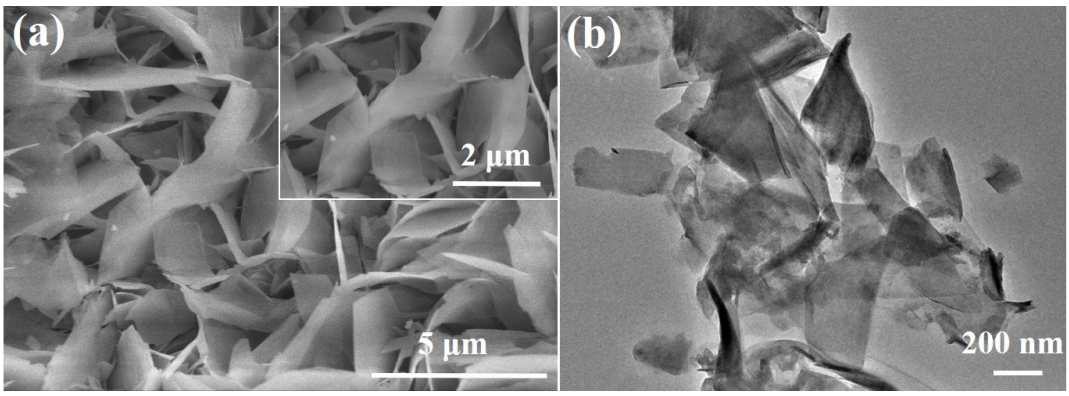

Fig. S8 (a) SEM and (b) TEM images of Ni_3S_2/NF-2 after long-term stability test of OER process.

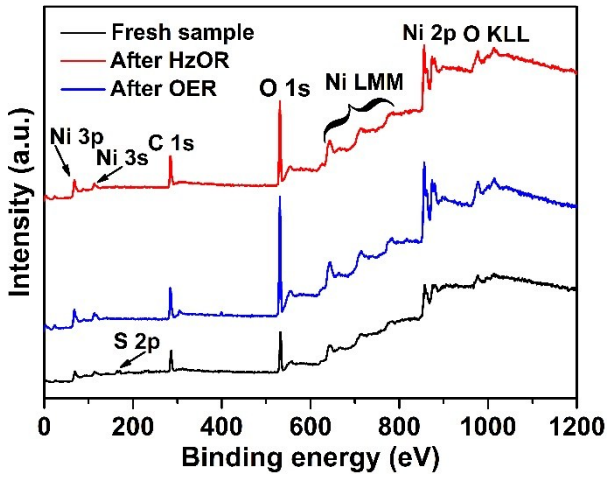

Fig. S9 Survey XPS spectra of Ni_3S_2/NF-2 before (fresh sample) and after electrocatalytic HzOR and OER process.

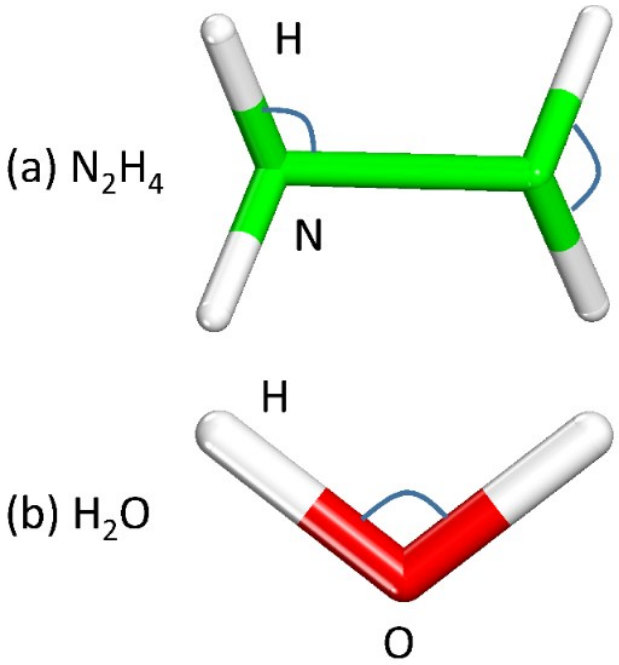

Fig. S10 The molecule model of (a) N_2H_4 and (b) H_2O, among O, N and H in red, green, white, respectively.

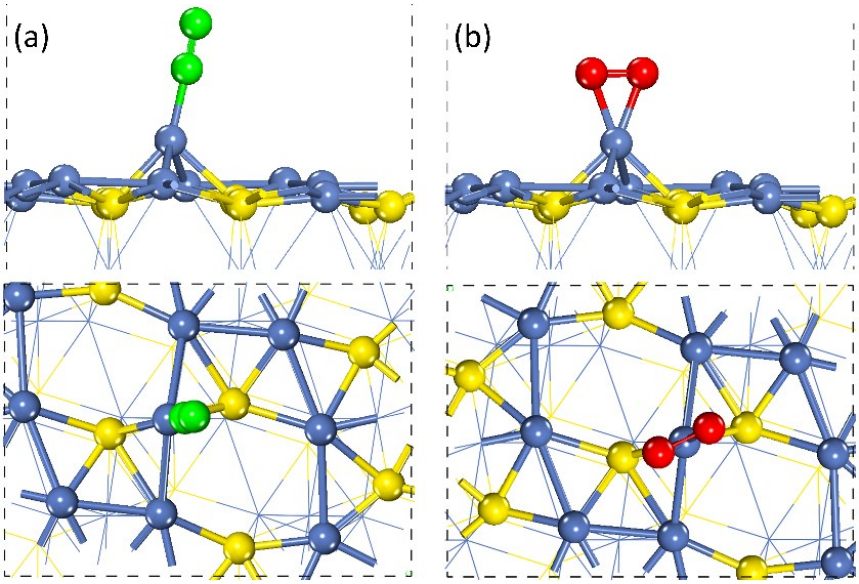

Fig. S11 The side (up) and top (down) view of adsorption configurations of (a) N_2 and

(b) O_2 molecules on the Ni_3S_2 (110) surface. Ni, S, O and N in light blue, yellow, red and green, respectively.

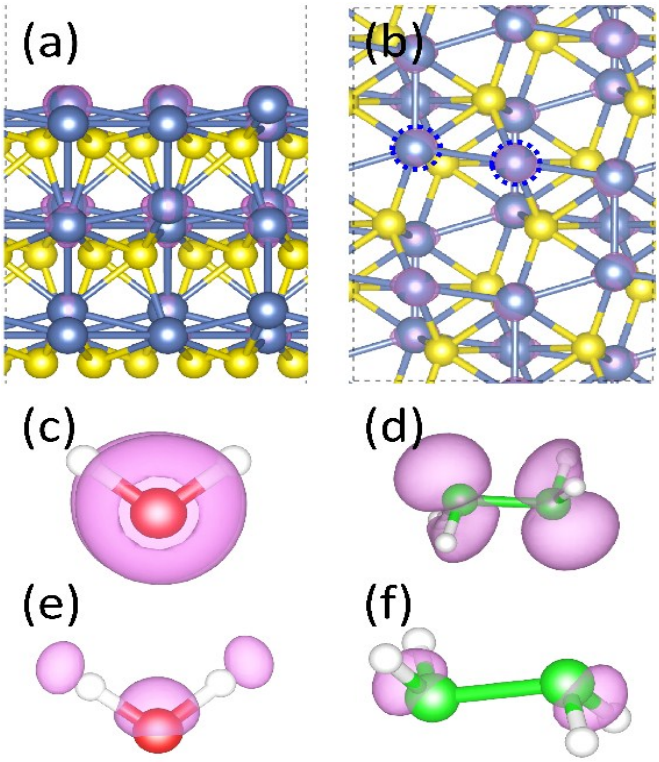

Fig. S12 The partial charge density of Ni_3S_2(110) surface around fermi level of 0.1 eV with side (a) and top (b) view, H_2O and N_2H_4 molecule with HOMO (c, d) and LUMO (e, f). The iso-surface value with pink contour is 0.01 e/bohr^3. Ni, S, O, N, and H in light blue, yellow, red, green and white, respectively. The dashed blue circle indicates high and low coordinate Ni atoms.

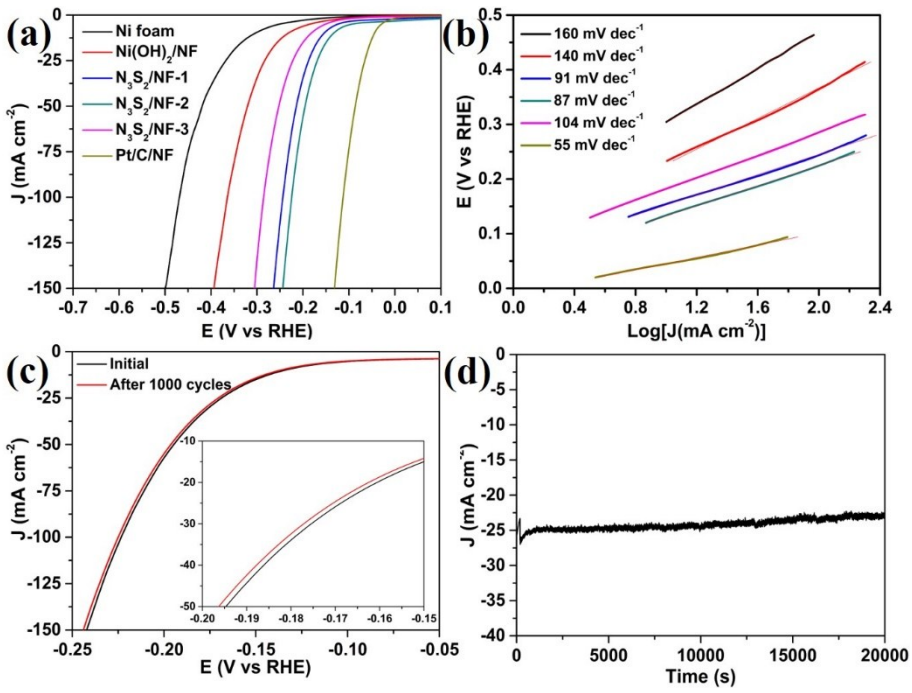

Fig. S13 (a) LSV curves with *i*R drop compensation and (b) the corresponding Tafel plots of NF, $Ni(OH)_2$/NF, Ni_3S_2/NF-1, Ni_3S_2/NF-2, Ni_3S_2/NF-3 and commercial Pt/C at a scanning rate of 5.0 mV s^{-1}. (c) and (d) HER durability tests for the Ni_3S_2/NF-2 electrocatalyst in 1.0 M KOH.

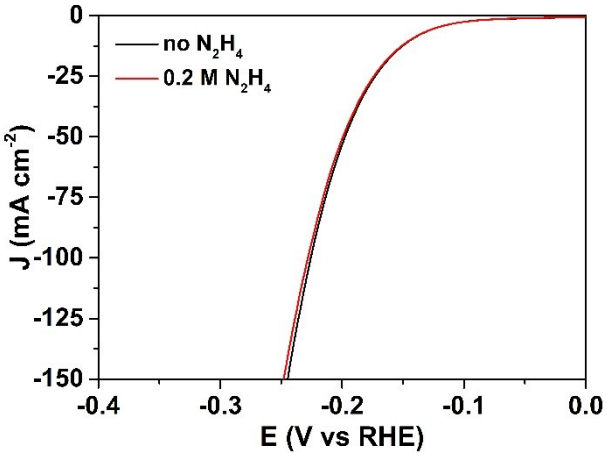

Fig. S14 LSV curves with *i*R drop compensation of Ni_3S_2/NF-2 at a scanning rate of 5.0 mV s^{-1} with (red line) and without (black line) 0.2 M hydrazine.

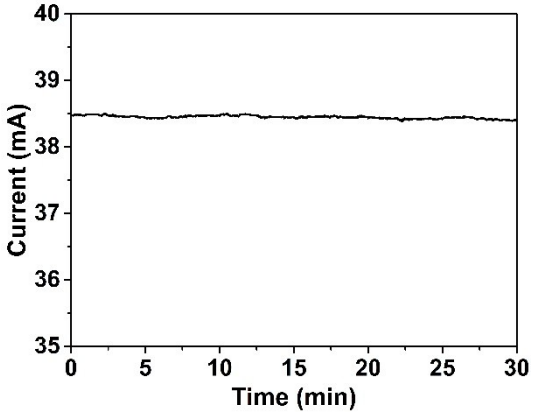

Fig. S15 The current density of Ni_3S_2/NF-2 catalyzed HzOR for H_2 generation with a potential of 0.75 V in two-electrode system (Ni_3S_2/NF-2 as both anode and cathode).

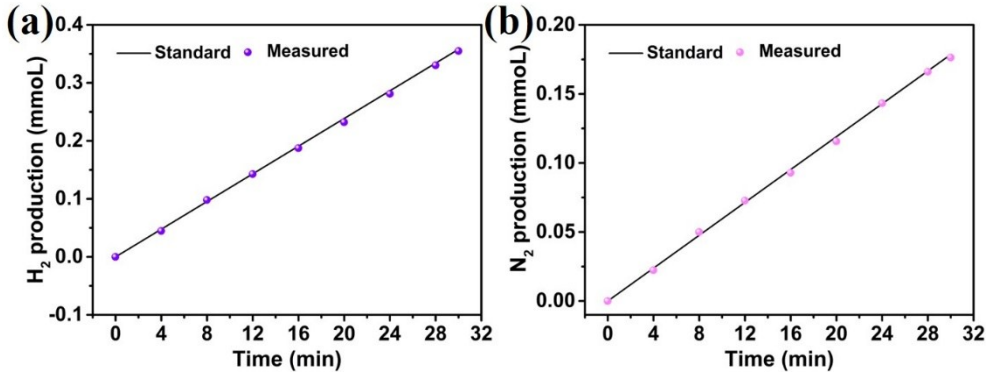

Fig. S16 The collected amount of (a) H_2 and (b) N_2 theoretically calculated and experimentally measured *vs.* time.

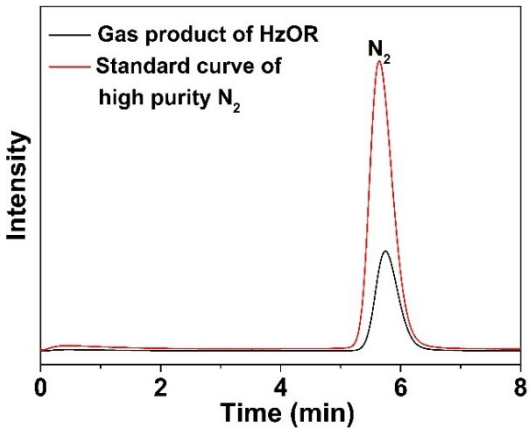

Fig. S17 Chromatograms for the HzOR production catalyzed by Ni_3S_2/NF-2 in two-electrode system with 0.2 M hydrazine in 1.0 M KOH.

The oxidation product of hydrazine was first analyzed by gas chromatography (GC, Beijing aulight Technology Co., Ltd, GC-7920).

References

[1] X. Q. Du, H. L. Pan, Z. Yang, New J. Chem., 2018, 42, 4215-4222.

[2] X. Q. Du, Z. Yang, Y. Li, Y. Q. Gong, M. Zhao, J. Mater. Chem. A, 2018, 6, 6938-6946.

[3] X. Q. Du, Q. B. Wang, Y. Li, X. S. Zhang, Dalton T., 2018, 47, 10273-10280.

[4] X. X. Guo, S. Y. Zhu, R. M. Kong, X. P. Zhang, F. L. Qu, ACS Sustain. Chem. Eng., 2018, 6, 1545-1549.

[5] X. P. Zhang, C. D. Si, X. X. Guo, R. M. Kong, F. L. Qu, J. Mater. Chem. A, 2017, 5, 17211-17215.

[6] X. X. Guo, R. M. Kong, X. P. Zhang, H. T. Du, F. L. Qu, ACS Catal., 2017, 8, 651-655.

[7] W. Z. Fang, D. N. Liu, Q. Lu, X. P. Sun, A. M. Asiri, Electrochem. Commun., 2016, 63, 60-64.

[8] N. Jiang, B. You, M. L. Sheng, Y. J. Sun, Angew. Chem., Int. Ed., 2015, 127, 6349-6352.

[9] T. T. Liu, Y. H. Liang, Q. Liu, X. P. Sun, Y. Q. He, A. M. Asiri, Electrochem. Commun., 2015, 60, 92-96.

[10] C. C. L. McCrory, S. Jung, J. C. Peters, T. F. Jaramillo, J. Am. Chem. Soc., 2013, 135,16977.

[11] X. Y. Yu, Y. Feng, Y. Y. Jeon, B. Y. Guan, X.W. Lou, U. Paik, Adv. Mater., 2016, 28, 9006.

[12] J. X. Feng, S. H. Ye, H. Xu, Y. X. Tong, G. R. Li, Adv. Mater., 2016, 28, 4698.