Supporting Information (SI):

In-situ construction of superhydrophilic crystalline Ni_3S_2@amorphous VO_x heterostructure nanorod arrays for hydrogen evolution reaction with industry-compatible current density

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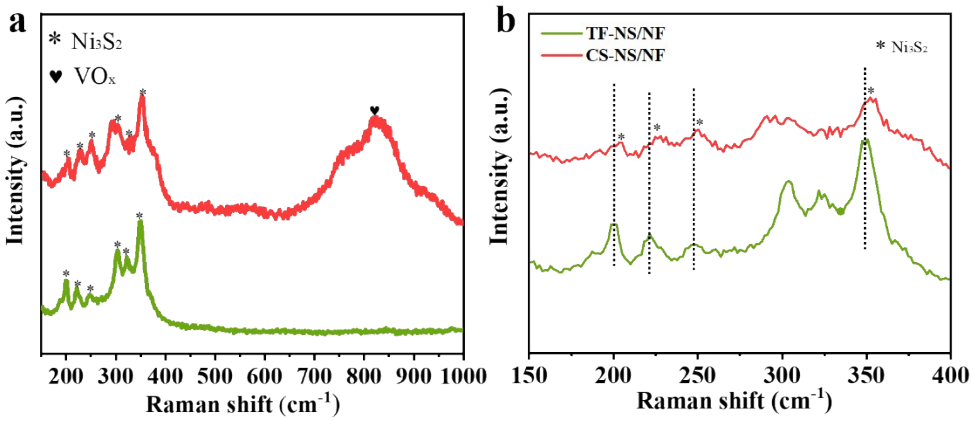

Fig. S1 (a) Raman spectra and (b) local magnification of CS-NC/NF and TF-NS/NF.

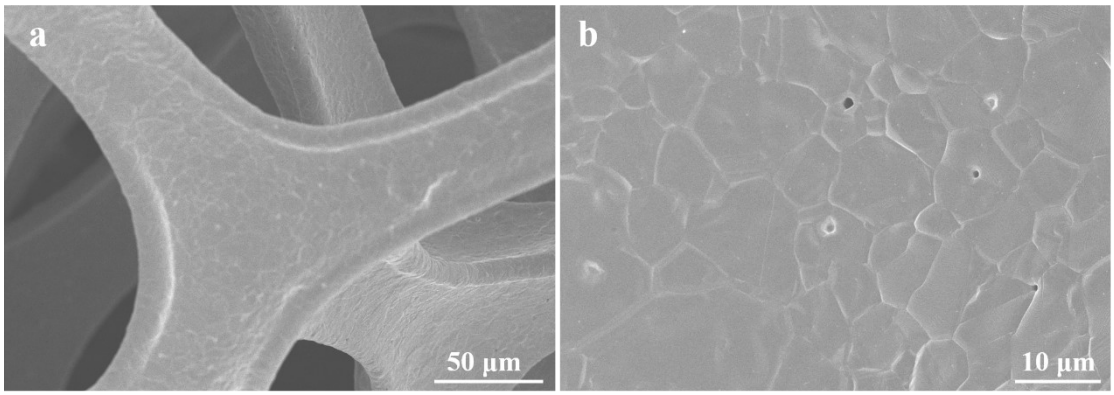

Fig. S2 SEM images of bare Ni foam (NF).

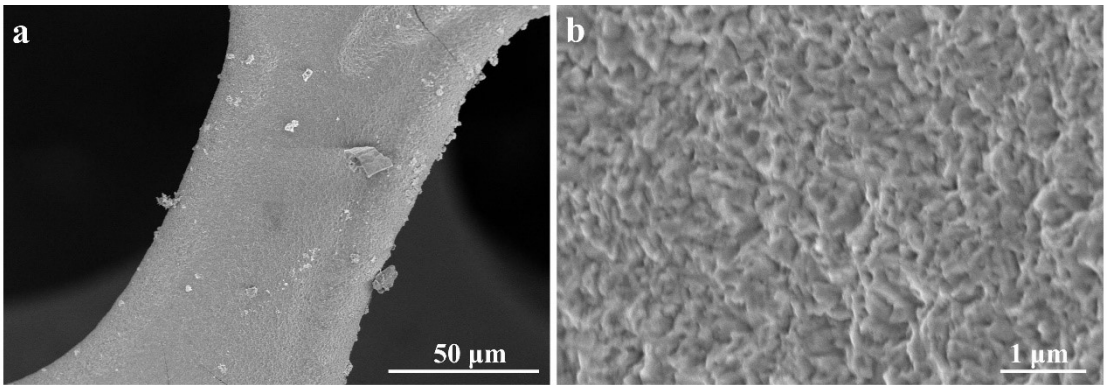

Fig. S3 (a, b) SEM images of TF-NS/NF.

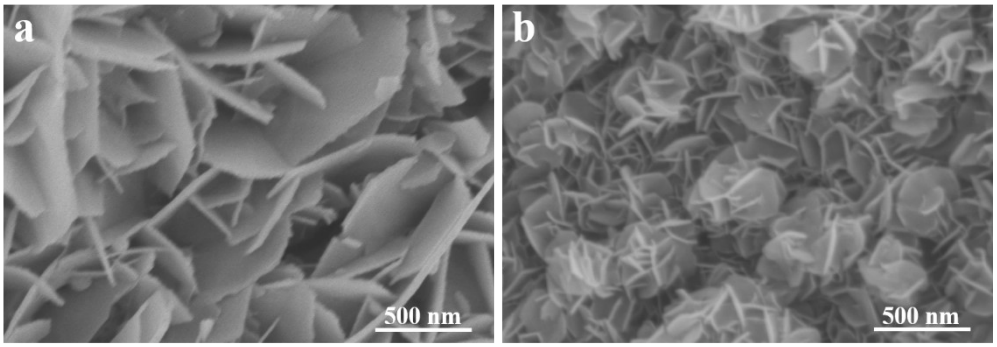

Fig. S4 SEM images of the precursor of (a)CS-NS/NF and (b)TF-NS/NF.

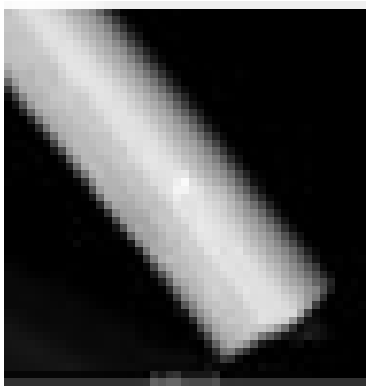

Fig. S5 The STEM image of the CS-NS/NF.

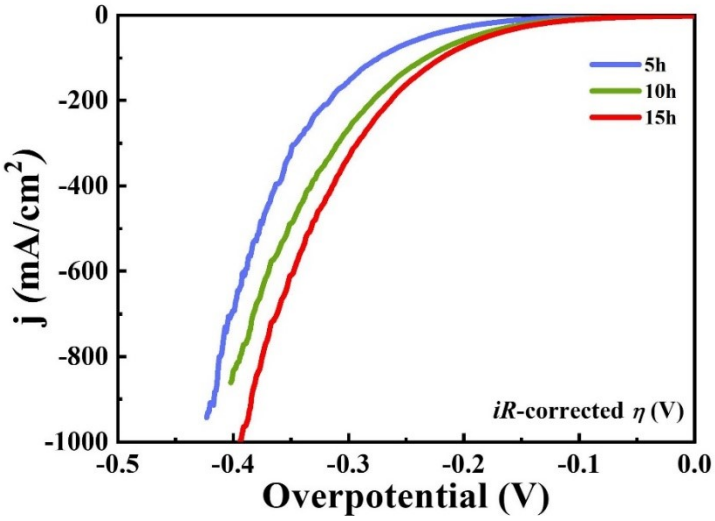

Fig. S6 HER LSV curves obtained from control experiments under the different reaction time.

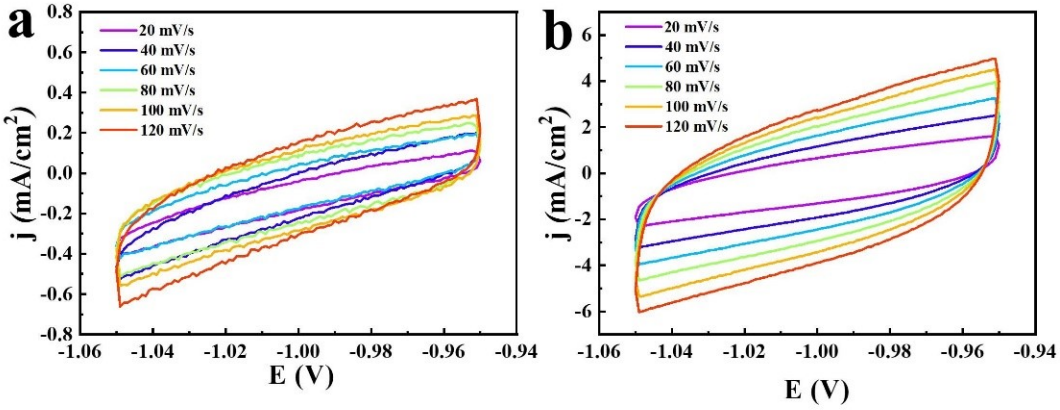

Fig. S7 CV curves of (a) TF-NS/NF and (b) CS-NS/NF at different scan rates.

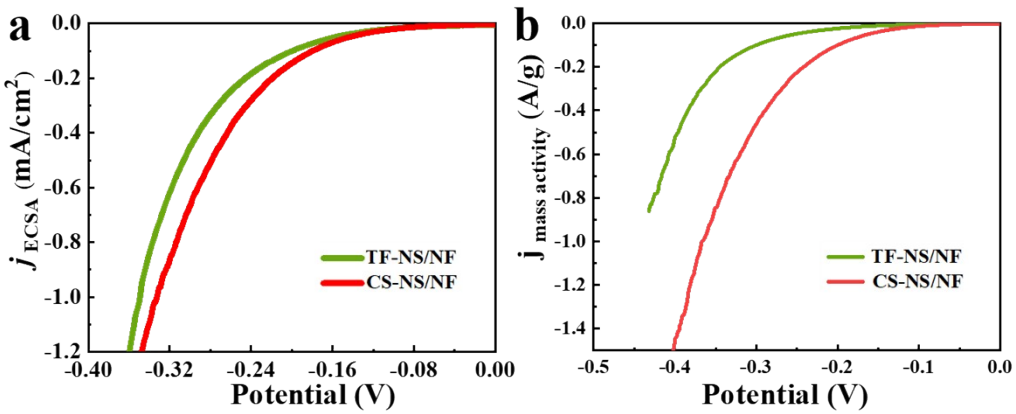

Fig. S8 (a)HER ECSA-normalized LSV curves of CS-NS/NF and TF-NS/NF. (b) The mass normalized current density of two catalysts.

The current densities measured have been normalized by the electrochemically active surface area (ECSA) value ($j_{ECSA} = \frac{j}{ECSA}$). As shown in Fig.S7, the CS-NS/NF still exhibits the better catalytic activity, implying the improved intrinsic HER activity [1].

The ECSA of a catalyst sample is calculated from the double-layer capacitance according to the following equation:

$$ECSA = \frac{C_{dl}}{C_s}$$

Cs presents the specific capacitance, the value of which is 0.040 mF cm^{-2} in 1 M KOH based on the previous reported literature [2].

[1] Y. Niu, W. Li, X. Wu, et al., J.Mater. Chem. A 7 (2019) 10534-10542.

[2] C. L. McCrory, S. Jung, J. Peters, et al., J. Am. Chem. Soc. 135 (2013) 16977-16987.

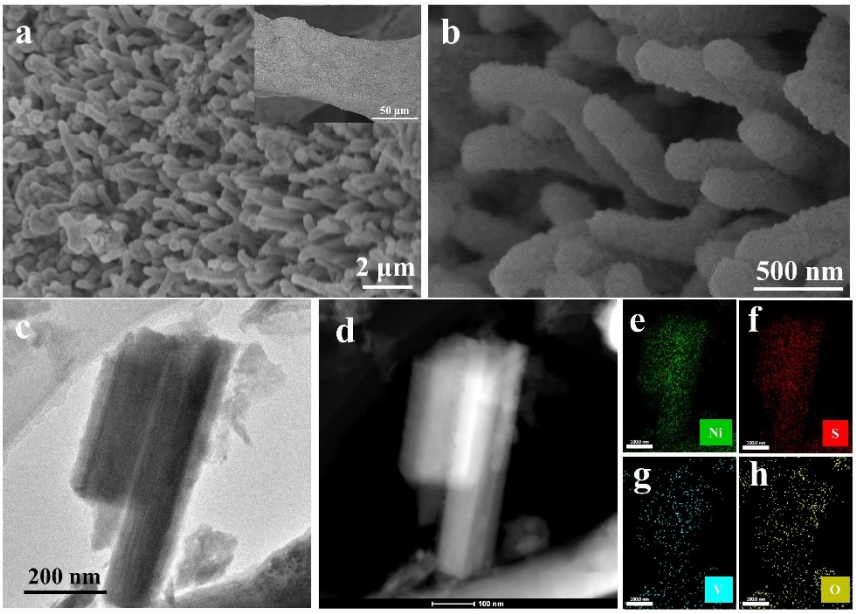

Fig. S9 (a, b) SEM images; (c) TEM image; (d) The STEM image and (e-h) EDS elemental mapping images Ni, V, O and S of the CS-NS/NF electrode after the HER stability test**.**

Table S1. Comparison of the HER performance at large current density of CS-NS/NF with some Ni_3S_2-based electrocatalysts reported recently.

Catalyst	Electrolyte	Overpotential (mV)	Stability test (h)	Reference
CS-NS/NF	**1 M KOH**	**99@10 mA/cm^2**	**68**	**This work**

		221@100 mA/cm^2 **335@500 mA/cm^2** **394@1000 mA/cm^2**		
Fe-Mo-S/Ni_3S_2@NF	1 M KOH	141@10 mA/cm^2 266@100 mA/cm^2 384@500 mA/cm^2	24	Chem. Eng. J. 2021, 404, 126483
Ni_3S_2@NGCLs/NF	1 M KOH	134@10 mA/cm^2 225@100 mA/cm^2	40	Chem. Eng. J. 2020, 401, 126045
$NiWO_4/Ni_3S_2$	1 M KOH	136@10 mA/cm^2 274@100 mA/cm^2	75	Appl. Catal. B Environ. 2020, 274, 119120
$CoNi_2S_4/Ni_3S_2$@NF	1 M KOH	171@10 mA/cm^2 350@100 mA/cm^2 500@200 mA/cm^2	20	J. Alloys Compd. 2020, 844,156252
CoS_x-Ni_3S_2/NF	1 M KOH	90@10 mA/cm^2 275@100 mA/cm^2 318@300 mA/cm^2	18	Appl. Catal., B 2020, 269, 118780.
Co_9S_8-Ni_3S_2/NF	1 M KOH	210@10 mA/cm^2 450@100 mA/cm^2	24	Chem. Eur. J. 2020, 26, 7900-7911
NS-horn/NF	1 M KOH	177@10 mA/cm^2 350@100 mA cm^{-2}	20	Appl. Catal. B Environ. 2019, 257, 117911
Fe-Ni_3S_2/NF	1 M KOH	47@10 mA/cm^2 232@100 mA cm^{-2}	20	ACS Catal. 2018, 8, 6, 5431–5441
Co-Ni_3S_2@CNTs/GNF	1 M KOH	155@10 mA/cm^2 350@100 mA/cm^2	20	J. Mater. Chem. A, 2018, 6, 10490-10496
Sn-Ni_3S_2/NF	1 M KOH	137@10 mA/cm^2 320@100 mA/cm^2	20	Chemelectrochem 2017, 4, 594-600

Turnover frequency (TOF) calculations

Because it is hard to identify the number of electrochemical active sites for metal substrate supported electrocatalysts, in our calculations, all metal atoms are assumed to be catalytically active. However, because a fraction of metal sites might not contribute

to the catalytic reaction, the calculated TOF represents a lower limit. It means that the true TOF is higher.

The values of turnover frequency (TOF) were calculated according to the following equation:

$$\mathrm{TOF} = |j| \times S / 2F \times n \quad (1)$$

where, j (mA/cm^2) is the measured current density at the potentials; S represents the surface area of the working electrode (CS-NS on NF, cm^2); the number 2 stands for a fourelectron transfer per mole of H_2; F is Faraday's constant (96 485.3 C/mol), and n represents the moles of the metal atom on the electrode which can be calculated by using the mass and the molecular weight of the coated catalysts. The corresponding descriptions have been added into the revised manuscript and are expected to meet your requirements.

Table S2. TOF calculation results of electrocatalysts.

Samples	**amount of loading (mg/cm^2)**	**surface area of the working electrode (cm^2)**	***j*@*η*=200 mV (mA/cm^2)**	**TOF (h^{-1})**
CS-NS/NF	0.71	0.25	80	**36.942**
TF-NS/NF	0.60	0.25	25	**7.773**