Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

AA Low-cost 2D WO_3/Ni_3S_2 heterojunctions for high stably hydrogen evolution

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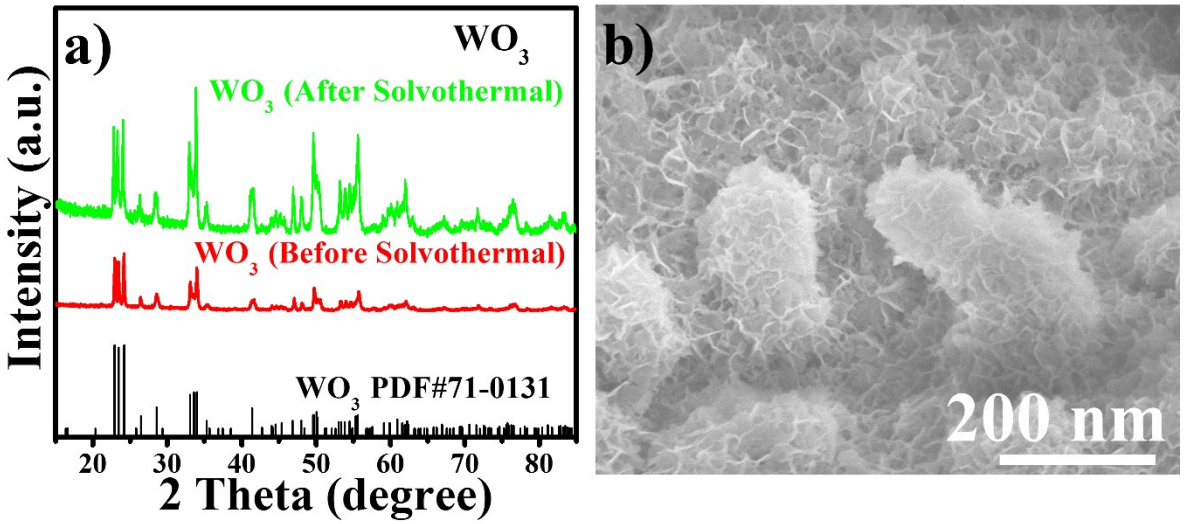

Figure S1 (a) PXRD patterns of WO_3 nanosheets before and after solvothermal process. (b) SEM image of 2D WO_3/Ni_3S_2 heterojunction nanosheets.

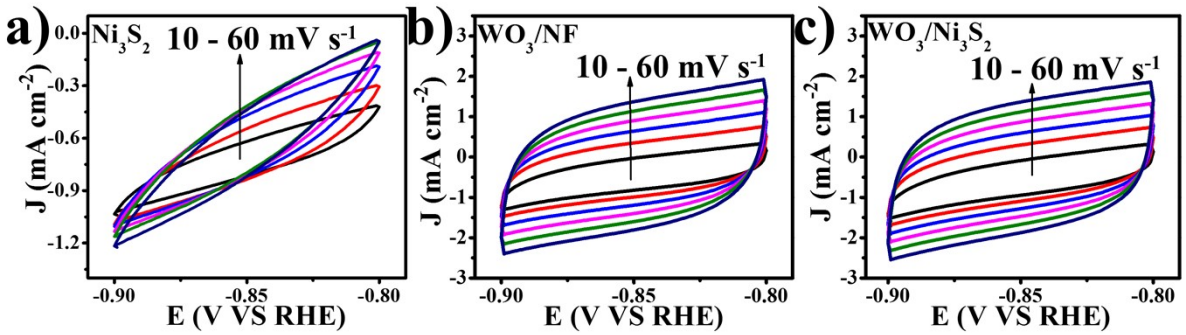

Figure S2 Cyclic voltammograms of electrodes of (a) Ni_3S_2, (b) WO_3/NF, and (c) WO_3/Ni_3S_2 electrodes from -0.8 V to -0.9 V under 10 - 60 mV s^{-1}.

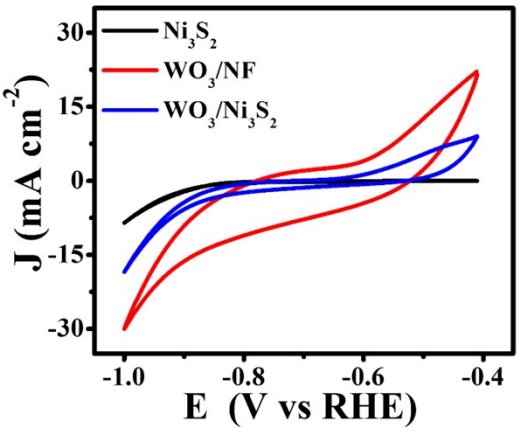

Figure S3 CV curves of three electrodes in 1M PBS at a scan rate of 50 mV s^{-1} for HER from -0.4 V to -1.0 V.

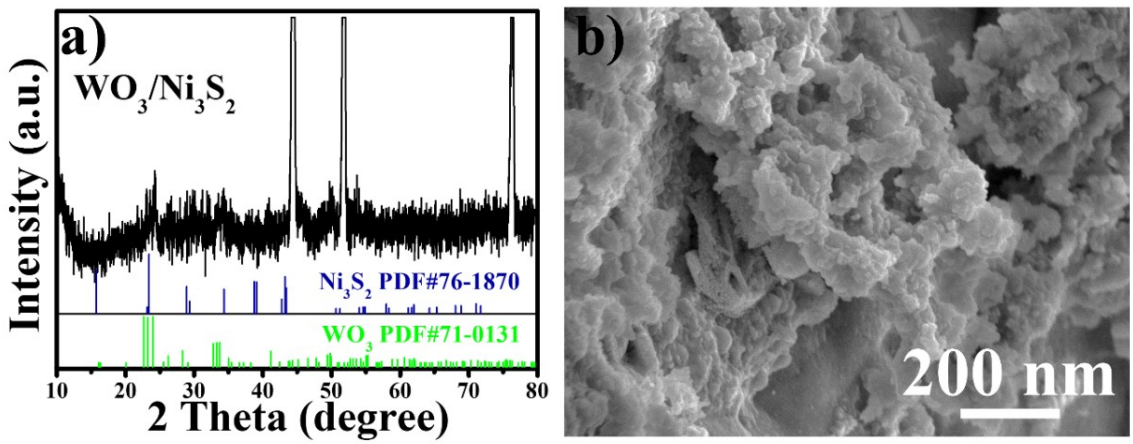

Figure S4 (a) PXRD patterns of WO_3/Ni_3S_2 sample after long time test. (b) SEM pattern of WO_3/Ni_3S_2 sample after long time test.

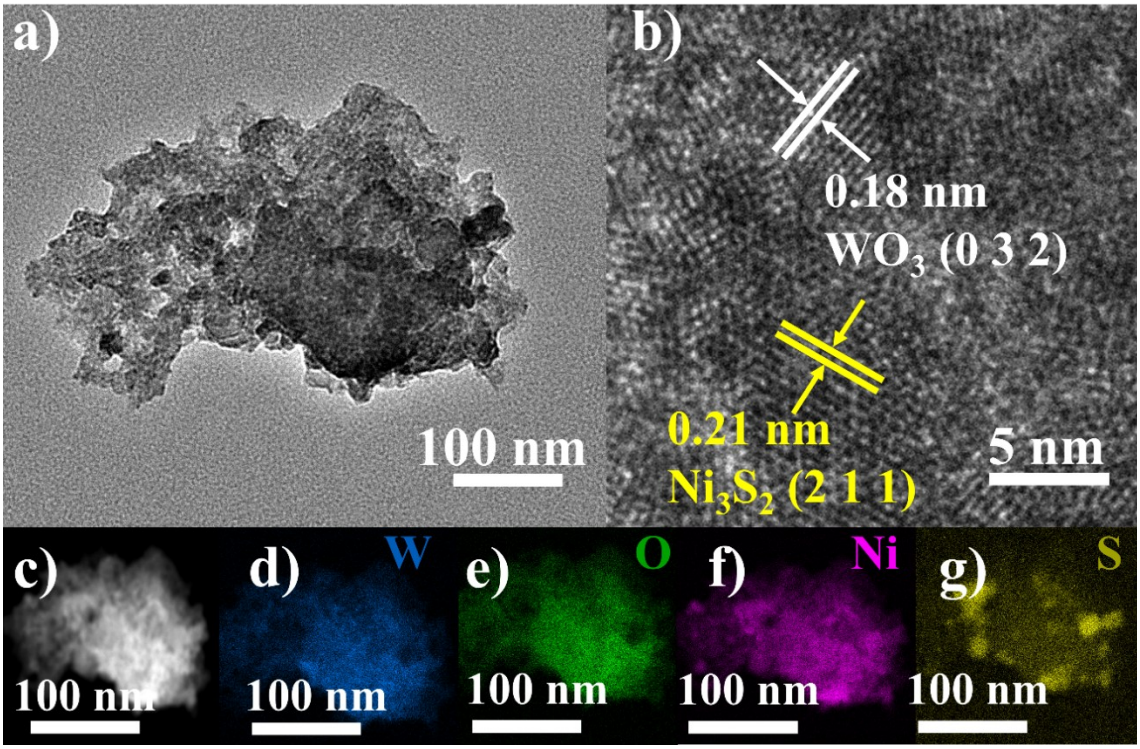

Figure S5 (a) TEM patterns of WO_3/Ni_3S_2 sample after long time test. (b) HRTEM image of WO_3/Ni_3S_2 heterojunction after long time test. (c-g) HAADF-STEM image and corresponding elemental mapping images of WO_3/Ni_3S_2 heterojunction after long time test.

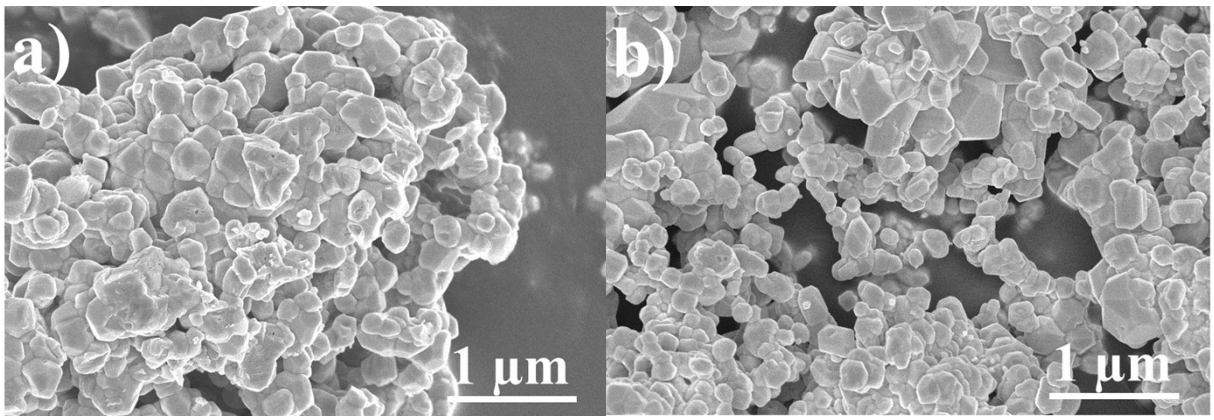

Figure S6 (a) SEM pattern of WO_3 sample before solvothermal. (b) SEM of pattern of WO_3 sample after solvothermal.

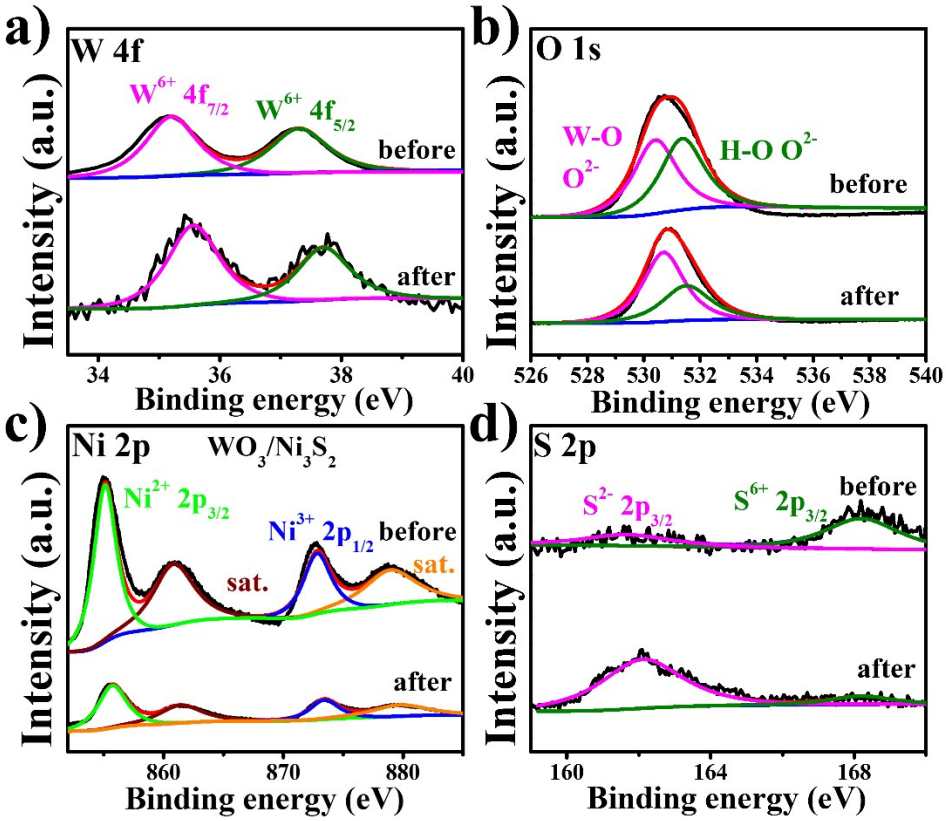

Figure S7 (a-d) High-resolution XPS spectra of W 4f, O 1s, Ni 2p, and S 2p in WO_3/Ni_3S_2 heterojunction before and after long-time testing, respectively.

Table S1 Comparison of catalytic performance with the most recently reported HER catalysts.

HER catalyst	Overpotential (mV) J=10 mA cm^{-2}	Overpotential (mV) J=100 mA cm^{-2}	Reference
WO_3/Ni_3S_2	**100**	**~148**	**This work**
$NiWO_4/Ni_3S_2$	136	~173	1
$W(OH)_x$	110	~290	2
WO_3/C @ CoO/NF	90	~178	3
Ni_2P-WO_3	105	~98	4

Table S2 Comparison of electrochemical C_{dl} and surface area (ECSA) catalysts.

HER catalyst	C_{dl} (mF cm^{-2})	ECSA (cm^2)	Reference
WO_3/Ni_3S_2	**4.91**	**122.75**	**This work**
$NiWO_4/Ni_3S_2$-16	2.88	72	1
Ni_3S_2/CC	5	125	5
Fe-WS_2@CC	1.6	40	6
Mo-NiP_x/NiS_y	2.9	72.5	7

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