

## Supporting information

# Hierarchically Nanostructured MoS<sub>2</sub> with Rich In-plane Edges as a High-performance Electrocatalyst for Hydrogen Evolution Reaction

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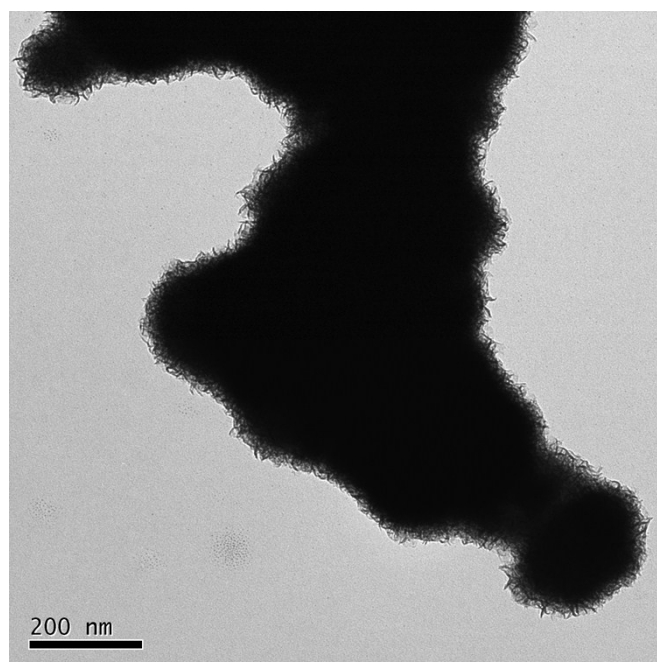
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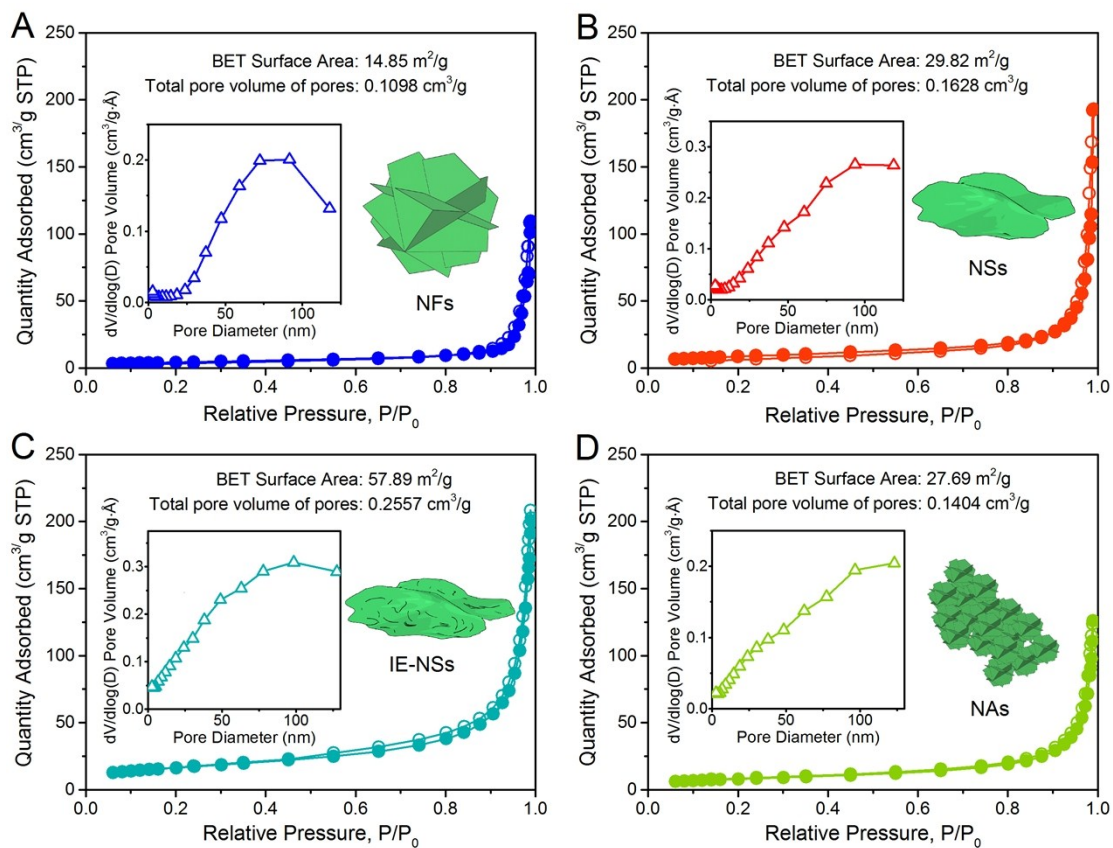
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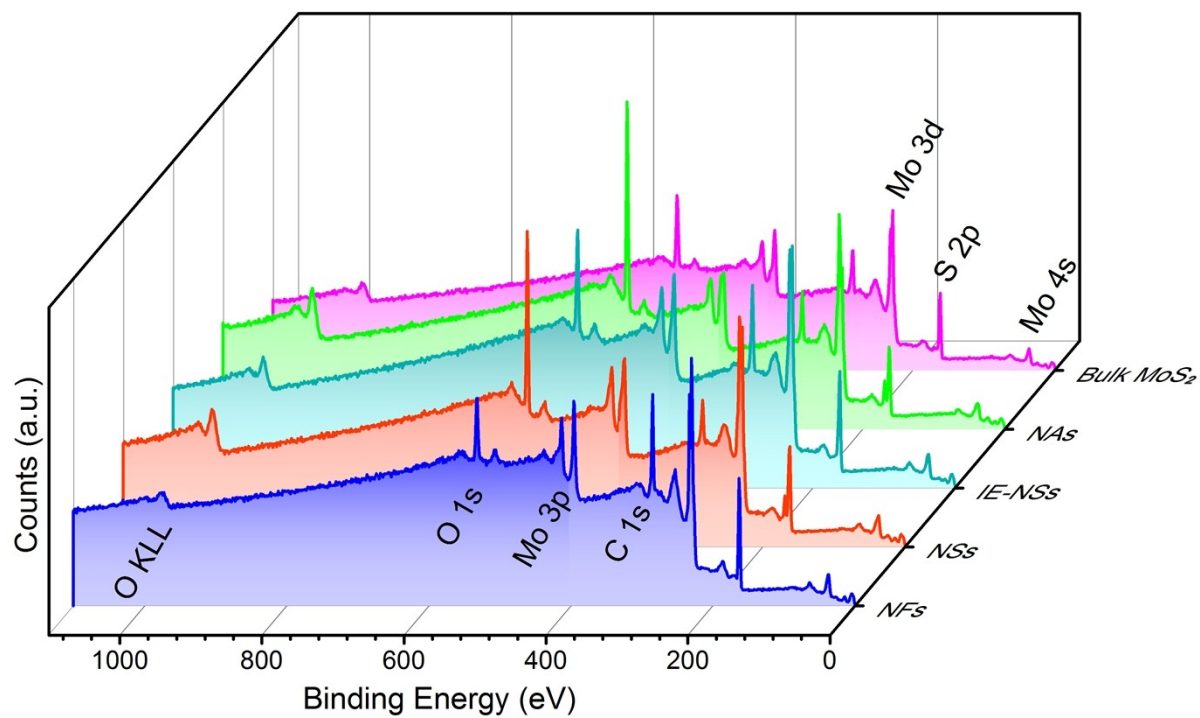
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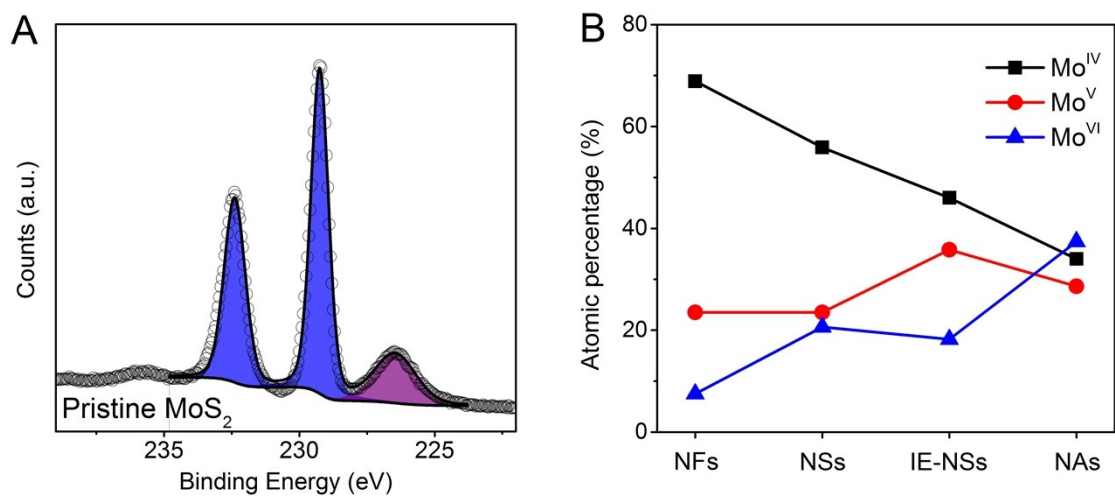
**Figure S1.** TEM image of MoS<sub>2</sub> aggregates synthesized in 100% EG.



**Figure S2.**  $N_2$  adsorption-desorption isotherms and corresponding absorption pore size distributions using BJH model (inset) of as-prepared samples ( $\text{MoS}_2$  NFs,  $\text{MoS}_2$  NSs, IE- $\text{MoS}_2$  NSs and  $\text{MoS}_2$  NAs).



**Figure S3.** XPS survey spectra of bulk MoS<sub>2</sub> crystal, and as-prepared samples (MoS<sub>2</sub> NFs, MoS<sub>2</sub> NSs, IE-MoS<sub>2</sub> NSs and MoS<sub>2</sub> NAs). Only Mo, S, O and C can be detected in these five samples, and the atomic ratios between Mo and S approach to the stoichiometric number of MoS<sub>2</sub>, varying from 1.8 to 2.1 (1.9 in bulk MoS<sub>2</sub> crystal, 2.1 in MoS<sub>2</sub> NFs, 1.9 in MoS<sub>2</sub> NSs, 2.1 in IE-MoS<sub>2</sub> NSs and 1.8 in MoS<sub>2</sub> NAs).



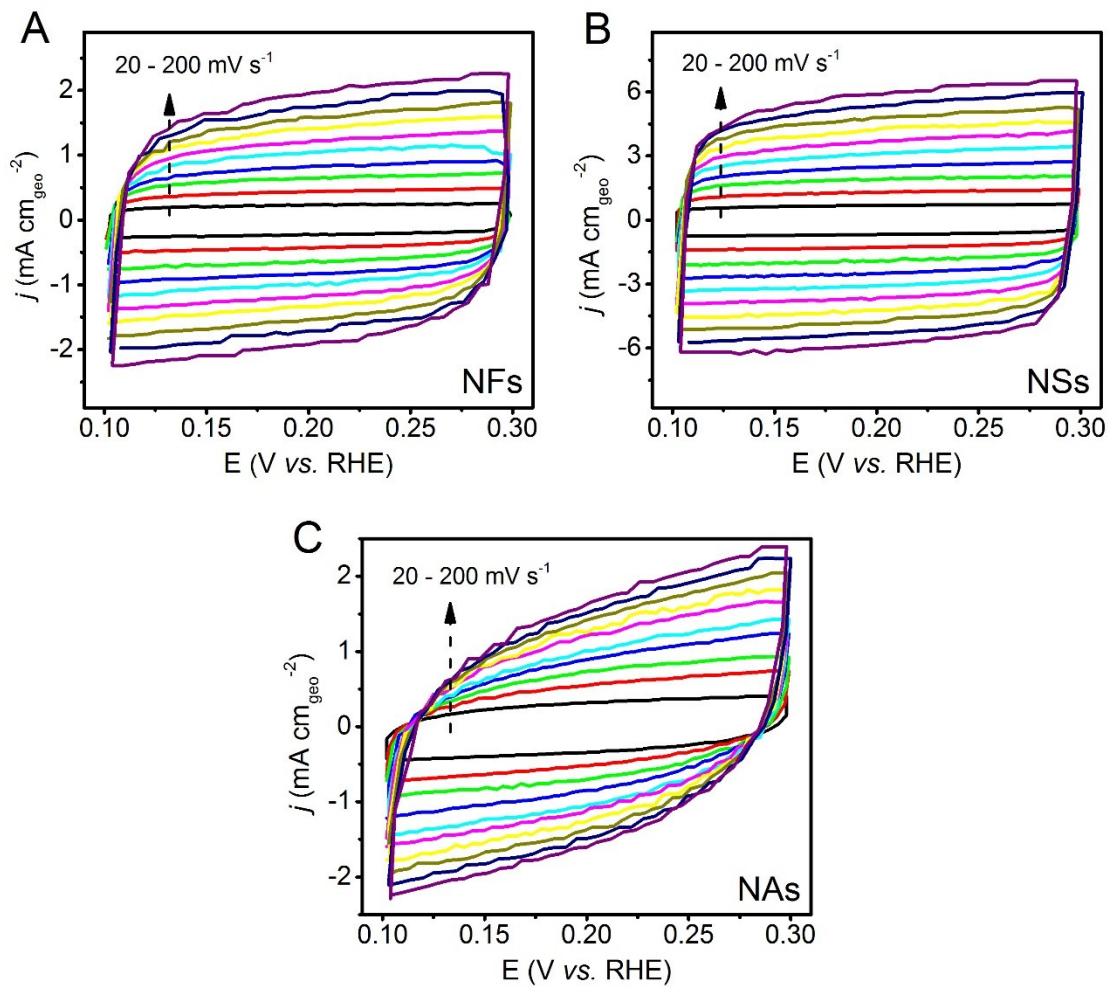
**Figure S4.** (A) High-resolution XPS survey spectra of pristine MoS<sub>2</sub> crystal within of Mo 3d and S 2s regions. (B) Chemical environments of Mo in as-prepared MoS<sub>2</sub> electrocatalyst.

**Table S1.** Electrochemical parameters of the as-prepared nanostructured MoS<sub>2</sub>.

	Onset $\eta$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	EDLC (mF cm <sup>-2</sup> )	ECSA factor	Intrinsic activity @ $\eta=0.25$ V ( $\mu\text{A cm}_{\text{ECSA}}^{-2}$ )	R <sub>ct</sub> ( $\Omega$ )
MoS <sub>2</sub> NFs	162	48.9	9.30	155	-51.1	114
MoS <sub>2</sub> NSs	122	47.5	28.8	480	-85.0	35.0
IE-MoS <sub>2</sub> NSs	87.2	41.0	40.4	673	-222	11.2
MoS <sub>2</sub> NAs	128	56.1	6.95	116	-127	97.1

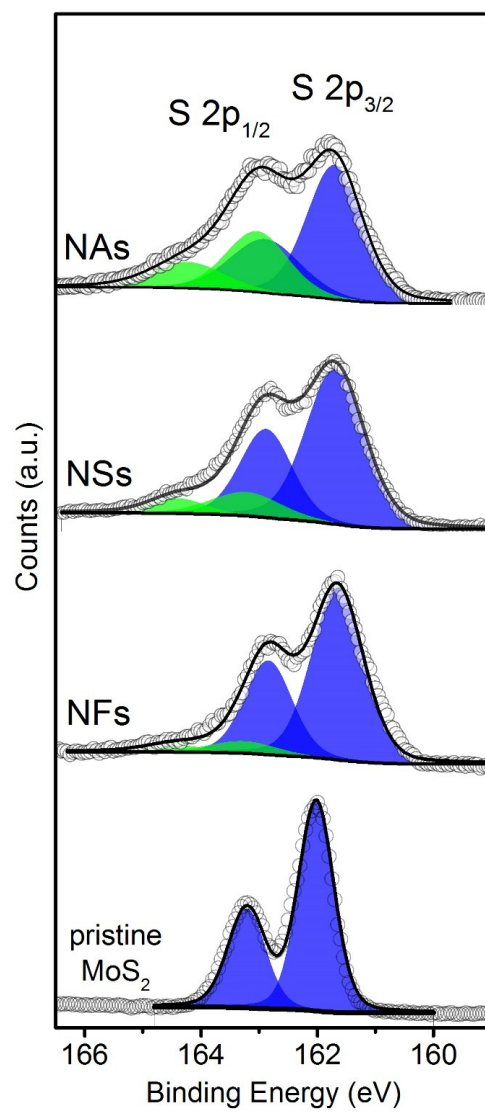
**Table S2.** Comparison of HER performance of in-plane edge rich MoS<sub>2</sub> nanosheets with other MoS<sub>2</sub>-based electrocatalysts.

Catalyst	Onset $\eta$ ( $\eta_0$ , mV)	Tafel slope (mV dec <sup>-1</sup> )	Current density ( $j$ , mA cm <sup>-2</sup> )	Corresponding $\eta$ ( $\eta_j$ , mV)	Electrochemical double layered capacitance ( $C_{dl}$ , mF cm <sup>-2</sup> )	References
Interlayer-expanded MoS <sub>2</sub>	103	49	-10	149	15.3	1
Double-gyroid MoS <sub>2</sub> film	150~200	50	N.A.	N.A.	1.1~4.8	2
Amorphous MoS <sub>2</sub>	150	60	-10	200	5.4	3
Metallic MoS <sub>2</sub> nanosheets	N.A.	43	-10	187	22	4
MoS <sub>2</sub> nanosheet	N.A.	68	-4.56	150	N.A.	5
Few layer MoS <sub>2</sub> nanodots	90	61	-10	248	2.15	6
MoS <sub>2</sub> @OMC	120~132	60~65	-10	178~192	N.A.	7
MoS <sub>2</sub> /rGO hydrogel	125	41	-12	200	29.6	8
Hollow structured micro/nano MoS <sub>2</sub> spheres	112	74	-10	214	15.1	9
Oxygen-incorporated MoS <sub>2</sub> nanosheets	120	55	-126.5	300	37.7	10
active-site-rich MoS <sub>2</sub>	180	53.5	-68	300	25.7	11
MoS <sub>2</sub> /NCNFs	N.A.	48	-65.6	200	22.7	12
MoS <sub>2</sub> nanoparticles/RGO	~ 100	41	N.A.	N.A.	N.A.	13
MoS <sub>2</sub> nanoparticles on mesoporous graphene foams	100	42	-100	200	N.A.	14
Monolayer MoS <sub>2</sub> on nanoporous gold	118	46	-10	226	N.A.	15
MoS <sub>2</sub> nanosheets/RGO	~ 140	41	-23	200	N.A.	16
MoS <sub>2</sub> $\perp$ RGO	N.A.	43	-10	172	6.045	17
MoS <sub>x</sub> on crumpled graphene balls	130	51.9	-220	300	N.A.	18
MoS <sub>x</sub> /N-doped CNT	~75	40	-10	~110	N.A.	19
Defect-rich MoS <sub>2</sub> ultrathin nanosheets	120	50	-13	200	N.A.	20
IE-MoS <sub>2</sub> NSs	87	41	-324 -10	300 167	40.4	This work



**Figure S5.** Cyclic voltammogram curves of MoS<sub>2</sub> NFs, MoS<sub>2</sub> NSs and MoS<sub>2</sub> NAs in the region of 0.1-0.3 V vs. RHE with scan rate from 20 mV s<sup>-1</sup> to 200 mV s<sup>-1</sup>.





**Figure S6.** High-resolution XPS spectra of S 2p region of pristine MoS<sub>2</sub>, MoS<sub>2</sub> NFs, MoS<sub>2</sub> NSs, and MoS<sub>2</sub> NAs.

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