Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

MoS_2 stacking matters: 3R polytype significantly outperforms 2H MoS_2 for hydrogen evolution reaction

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KEYWORDS: molybdenum sulfide, polytypes, electrochemistry, exfoliation, electrocatalysis, hydrogen evolution reaction

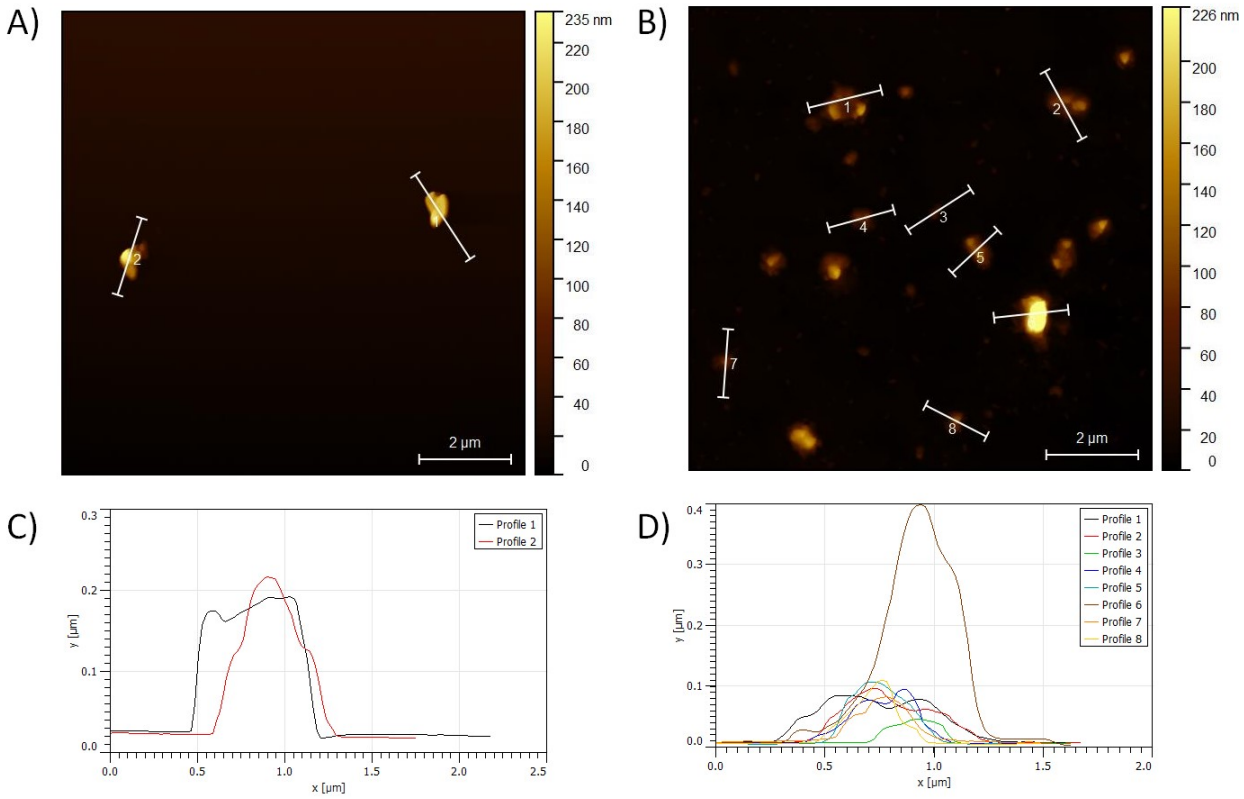

Figure S1. Atomic force microscopy image of A) MoS_2 2H exf. together with C) extracted height profiles. Atomic force microscopy image of B MoS_2 3R exf. together with D) extracted height profiles.

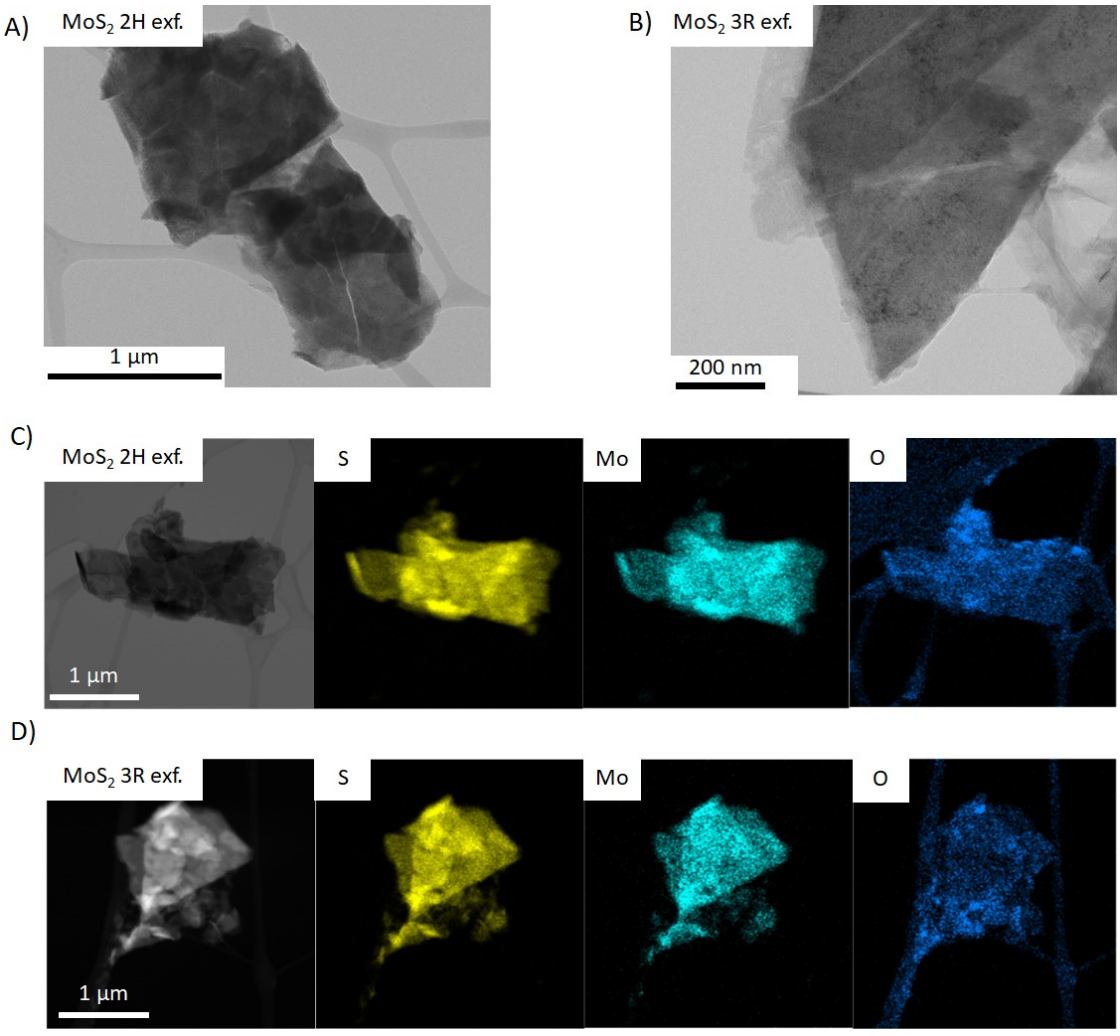

Figure S2. TEM images of A) MoS_2 2H exf.; B) MoS_2 3R exf.. Elemental composition maps for C) MoS_2 2H exf.; D) MoS_2 3R exf..

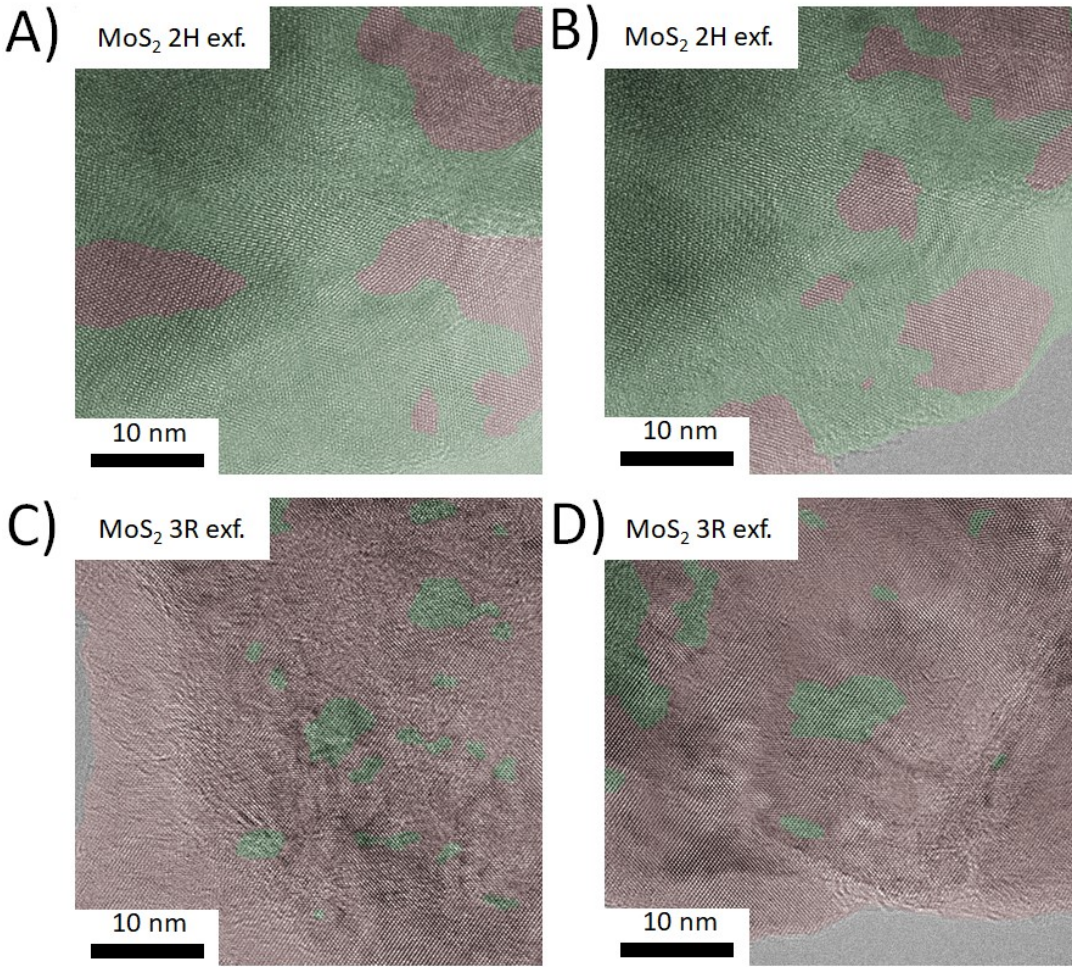

Figure S3. HR-TEM images showing the representation of trigonal prismatic (green) and octahedral (red) coordination of central atom in A) and B) MoS_2 2H exf. And C) and D) MoS_2 3R exf..

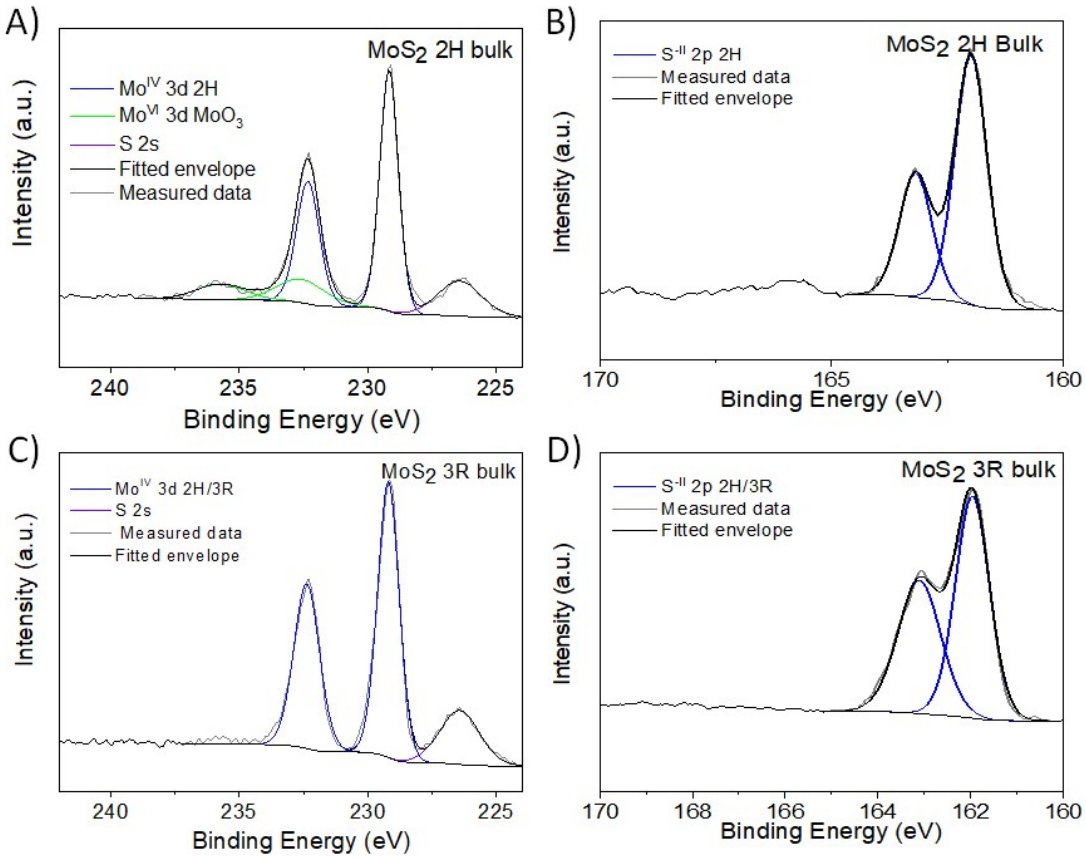

Figure S4. Core-level spectra of Mo 3d regions for A) MoS_2 2H Bulk and C) MoS_2 3R Bulk and core-level spectra of S 2p regions for B) MoS_2 2H Bulk and D) MoS_2 3R Bulk.

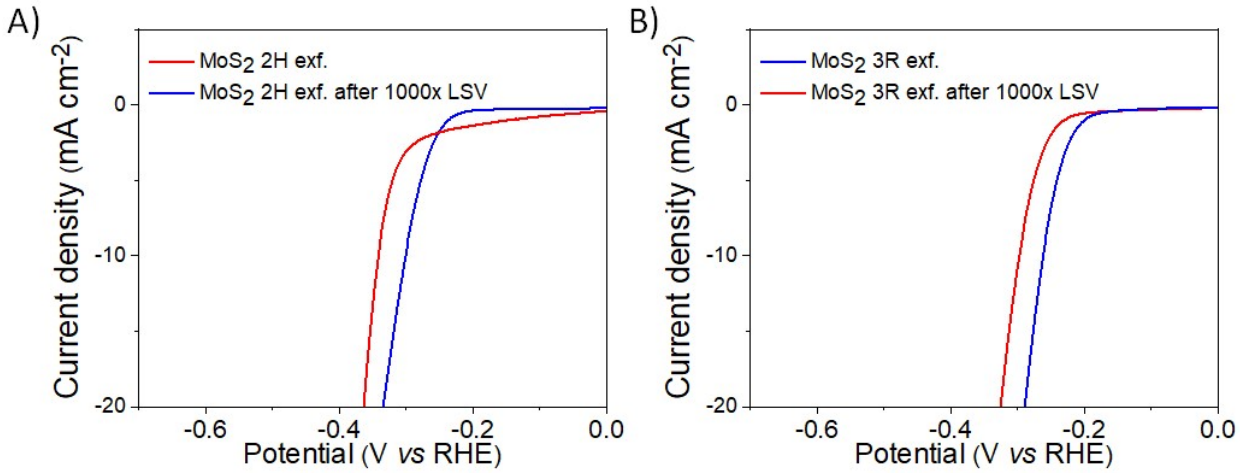

Figure S5. HER stability test after 1000 LSV cycles for A) MoS_2 2H exf. and B) MoS_2 3R exf.

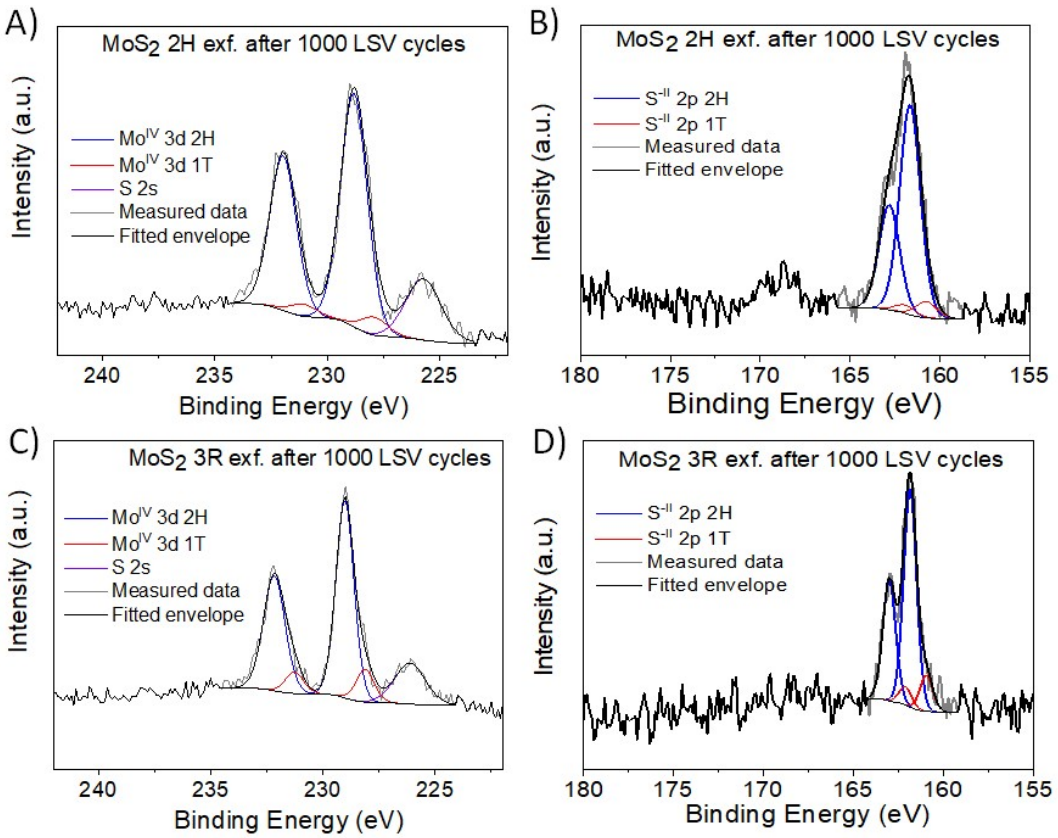

Figure S6. Core-level XP spectra after stability test of Mo 3d region for A) MoS_2 2H exf. and C) MoS_2 3R exf. and core-level XP spectra of S 2p region for B) MoS_2 2H exf. and D) MoS_2 3R exf.

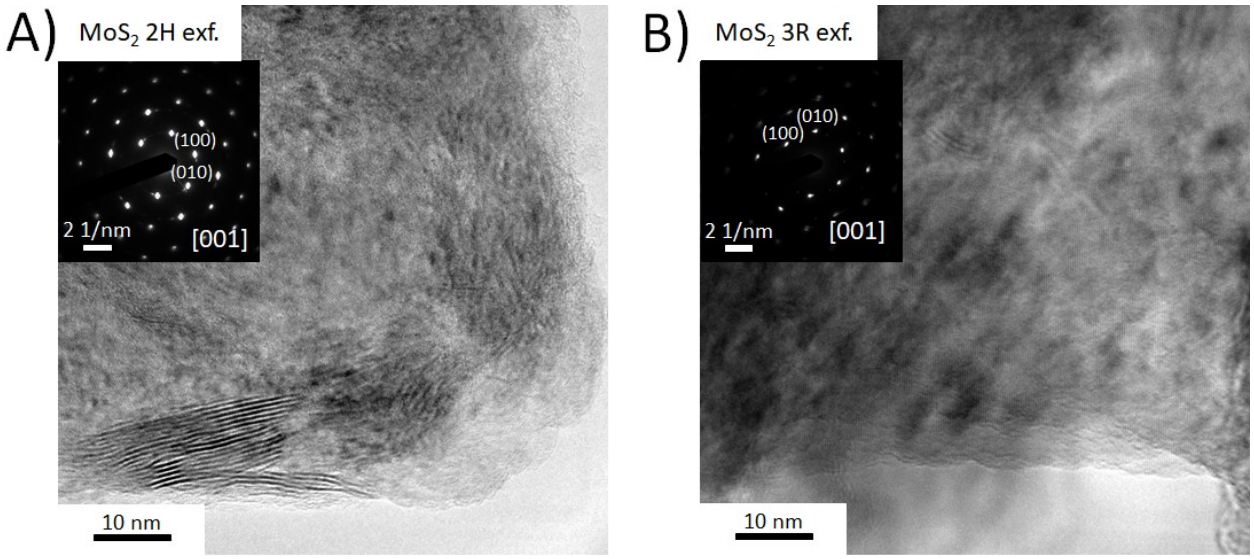

Figure S7. HR-TEM images after 1000 LSV cycles for A) MoS_2 2H exf. and B) MoS_2 3R exf.. The insets show selected area electron diffraction patters.

Table S1. Concentration of individual chemical states in bulk and exfoliated MoS_2 materials obtained by XPS.

Sample	2H/3R (at. %)	1T (at. %)	MoO_2 (at. %)	MoO_3 (at. %)
MoS_2 2H bulk	85.3	-	-	14.7
MoS_2 3R bulk			-	-
MoS_2 2H exf.	64.1	20.8	-	15.1
MoS_2 3R exf.	27.0	55.9	17.1	-
MoS_2 2H exf. after 1000 LSV cycles	92.8	7.2	-	-
MoS_2 3R exf. after 1000 LSV cycles	86.2	13.8	-	-

Table S2. Comparison of various MoS_2 catalysts for HER based on the polytype.

Catalyst	Electrolyte	Overpotential (at - 10 mA cm^{-2})	Tafel slope ($mV\ dec^{-1}$)	Ref.
Exfoliated 3R MoS_2	0.5M H_2SO_4	250 mV	58	This paper
Strained 2H MoS_2	0.5M H_2SO_4	170 mV	60	[1]
Basal plane activated MoS_2	0.5M H_2SO_4	300 mV	49	[2]
Mesoporous 2H MoS_2	0.5M H_2SO_4	218 mV	62	[3]
Mesoporous 1T MoS_2	0.5M H_2SO_4	153 mV	43	[3]
Modified 1T MoS_2	0.5M H_2SO_4	271 mV	61	[4]
Co-doped 1T MoS_2	1M KOH	240 mV	68	[5]
Ni and O_2 doped 1T MoS_2	1M KOH	46 mV	52	[6]
Graphene/1T MoS_2 composite	0.5M H_2SO_4	103 mV	46	[7]
Sulfur intercalated 1T' MoS_2	0.5M H_2SO_4	205 mV	50	[8]
1T' monolayers	0.5M H_2SO_4	191 mV	142	[9]

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