Supporting Information

Engineering Substrate Interaction to Improve Hydrogen Evolution Catalysis of Monolayer MoS_2 Films Beyond Pt

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S1. Calculation of turnover frequency.

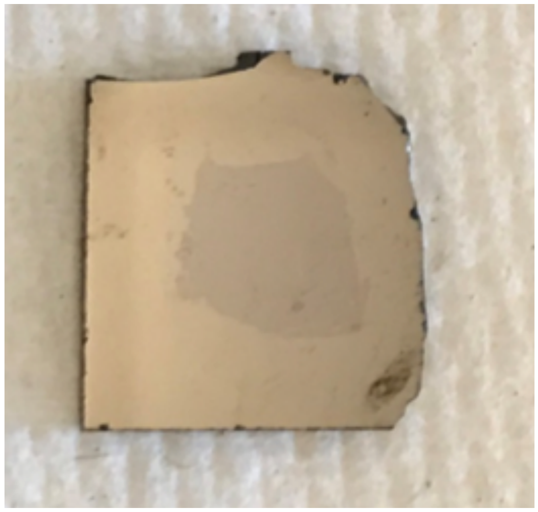

Fig. S1. Optical image of a typical transferred monolayer MoS_2 film. The substrate is glassy carbon and the size of the monolayer film is around 1 cm x 1 cm. There is no visible crack, void, and winkles in the transferred film.

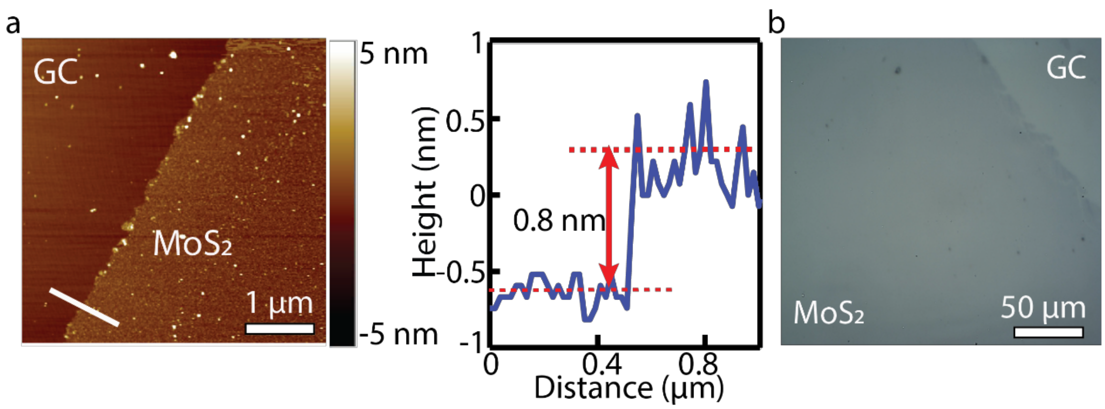

Fig. S2. Morphological features of transferred MoS_2 films. (a) AFM image and height profile of transferred monolayer MoS_2 films on glassy carbon substrates. (b) optical images of transferred monolayer MoS_2 films on glassy carbon substrates.

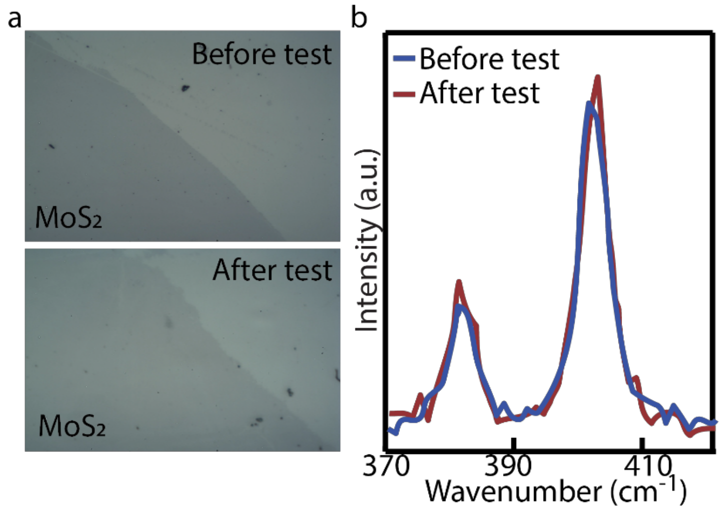

Fig. S3. Negligible change in the morphology and composition of the film before and after the catalytic reaction. (a) Optical images of MoS_2 before (top) and after (bottom) the reaction, which show no obvious change in the morphology. (b) Raman spectrum of MoS_2 before (blue) and after (red) the reaction, which show no change in the composition and structure.

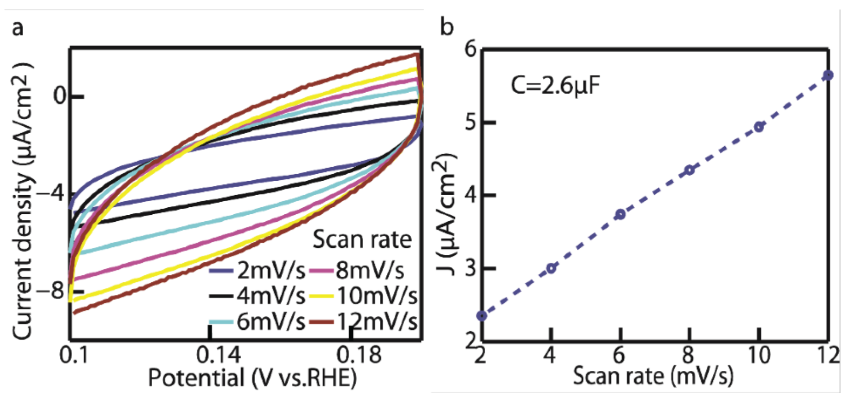

Fig.S4. (a) Cyclic voltammetry recorded at monolayer MoS_2 film on glassy carbon substrates with various scan rates. (b) the current density at CV as function of scanning rate. The double layer capacitance extracted from the measurement is given as shown.

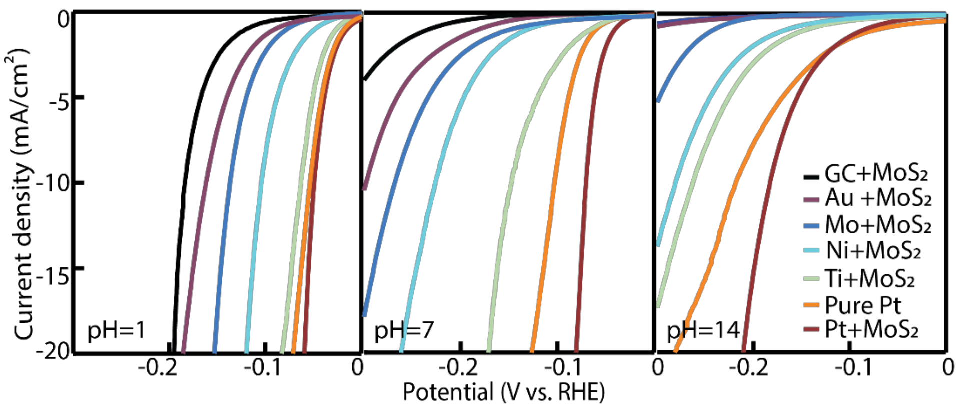

Fig. S5. Polarization curves of MoS_2 on different substrates in electrolytes with different pH values. From left to the right, the electrolytes are acid (pH = 1), neutral (pH = 7) and alkaline electrolyte (pH = 14).

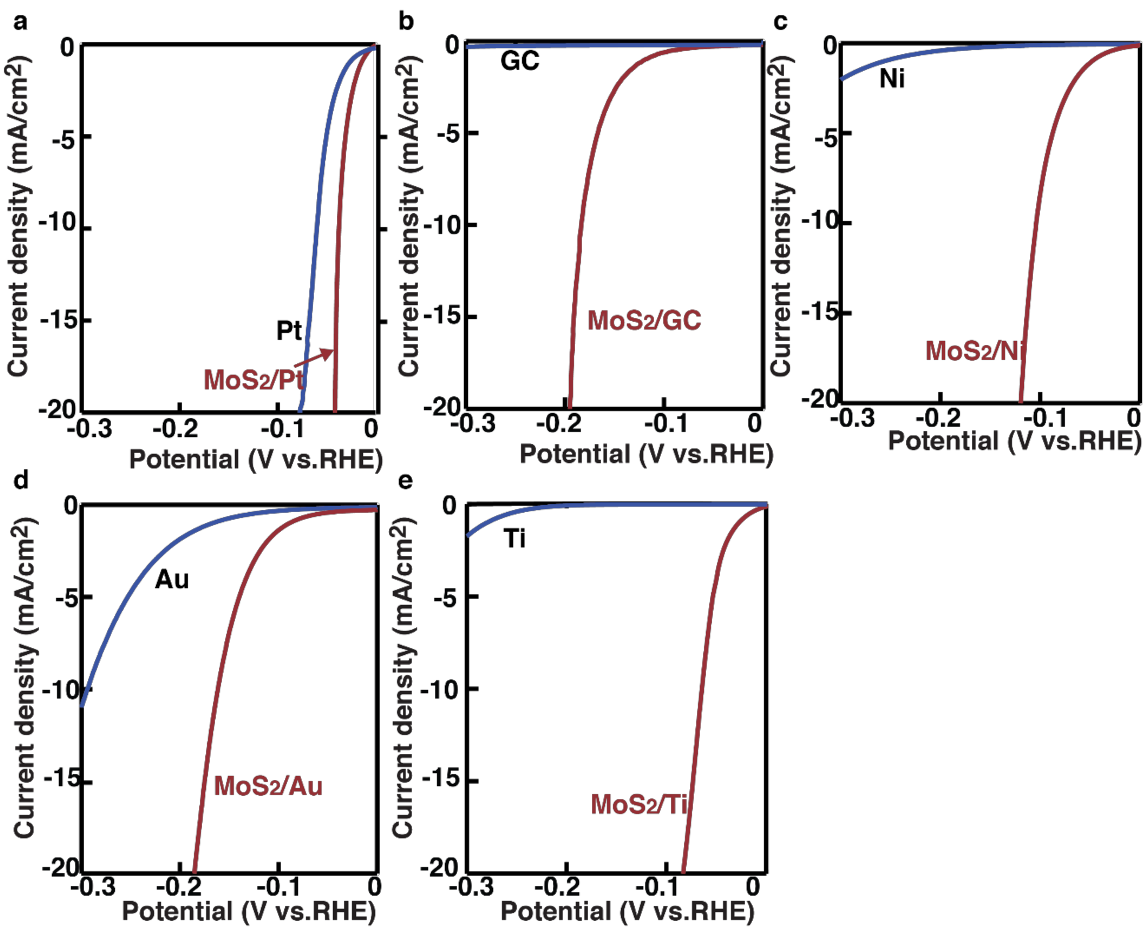

Fig. S6. Polarization curves collected from bare substrates and the substrates covered by a monolayer MoS_2 film.

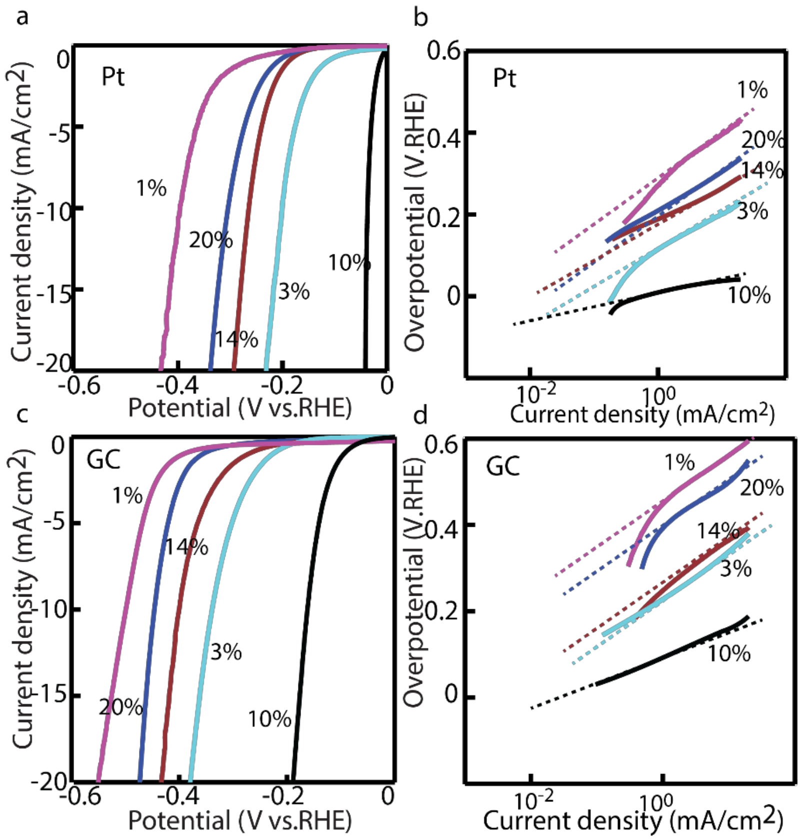

Fig. S7. Polarization curves and Tafel plots of MoS_2 films with different sulfur vacancy densities on glassy carbon and Pt substrates. (a) Polarization curves and (b) Tafel plots of MoS_2 films Pt substrate. The density of sulfur vacancies in each of the film is given in the figure as shown. (a) Polarization curves and (b) Tafel plots of MoS_2 films glassy carbon substrate. The density of sulfur vacancies in each of the film is given in the figure as shown. The detailed values of Tafel slopes and exchange current density are listed in Supporting Table S3.

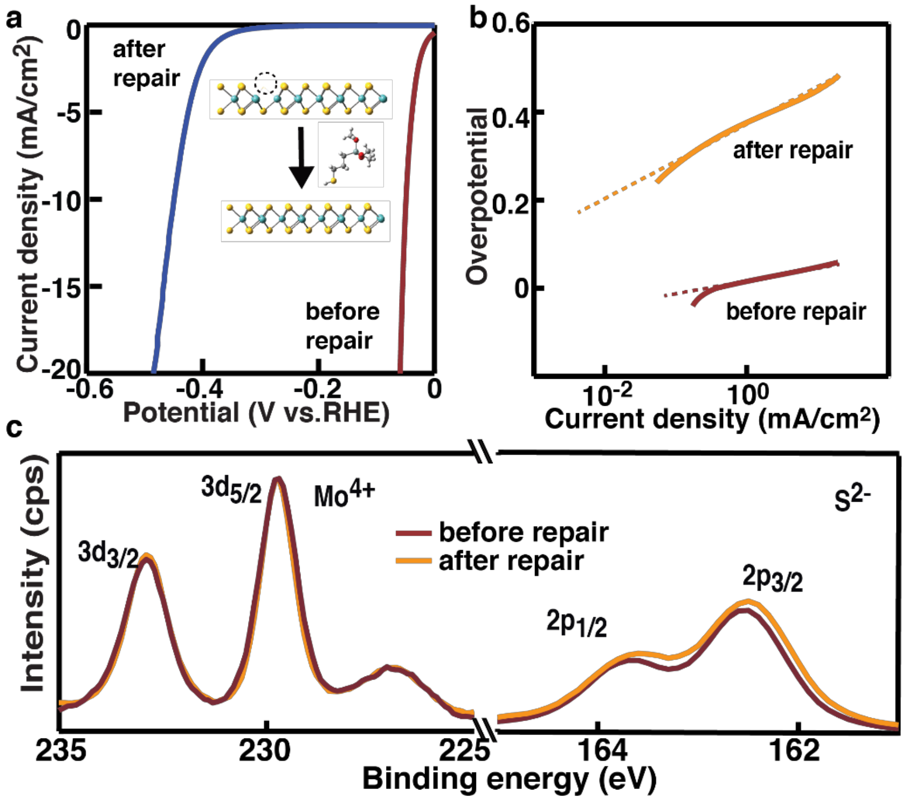

Fig. S8. Catalytic performance of the monolayer MoS_2 on Pt substrates before and after treated by the sulfur vacancy repair process. (a)Polarization curves collected from a monolayer MoS_2 film on Pt substrates before and after the repair treatment (pH =1). The inset is a schematic illustration for the repair of sulfur vacancies by organic molecules. The detail of the repairing process can be found in Ref. 29. (b) Tafel plots of the monolayer MoS_2 on Pt substrates before and after the repair process. (c) XPS measurement for the monolayer before (red curve) and after (orange curve) the sulfur vacancy repair process.

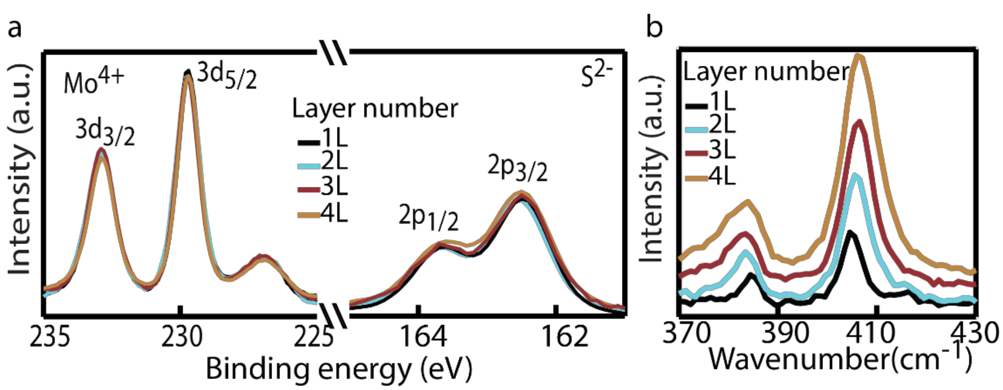

Fig. S9. Characterization for the MoS_2 films with different layer number. (a) XPS spectra collected from the films, showing comparable density of sulfur vacancies in all the films. (b) Raman spectra of the MoS_2 films with different layer numbers.

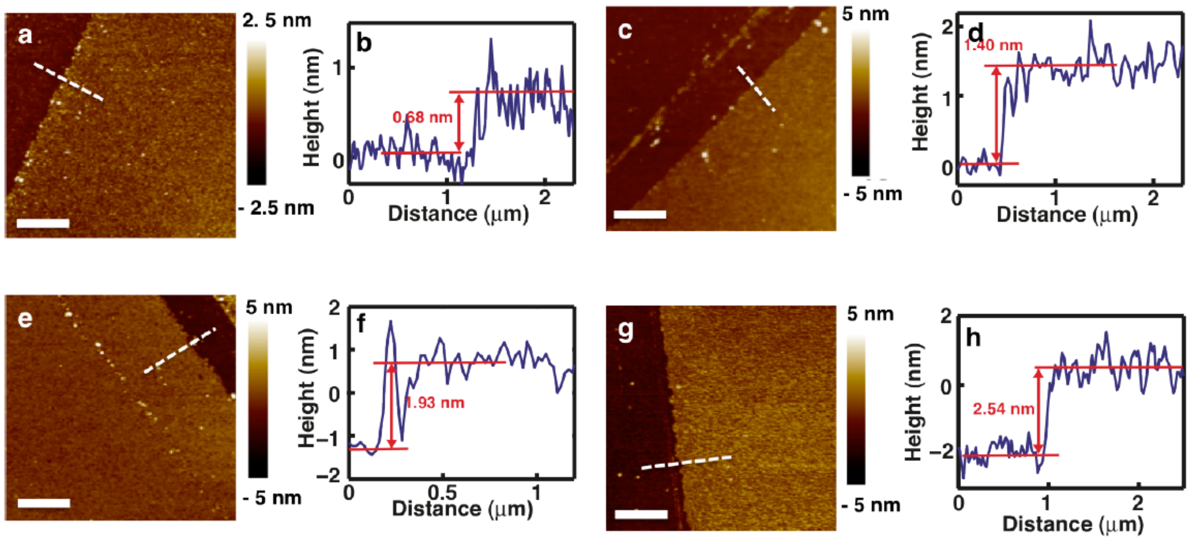

Fig. S10. AFM images and corresponding height profiles for MoS2 filmS with different layer numbers (1-4L).

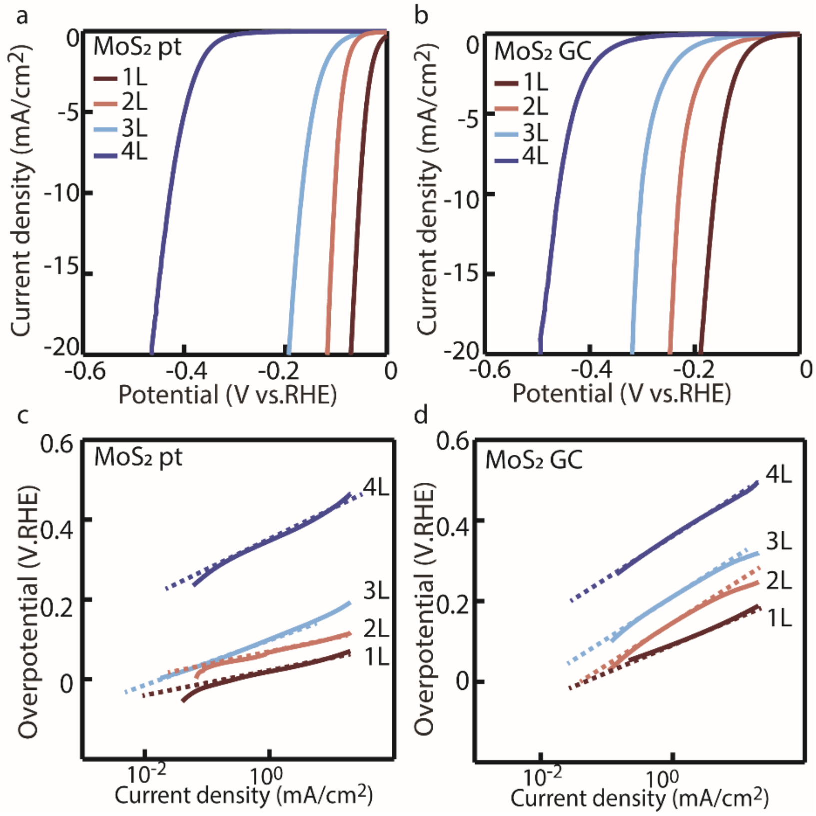

Fig. S11. Polarization curves and Tafel plots of MoS_2 films with different layer numbers on glassy carbon and Pt substrates. (a) Polarization curves and (b) Tafel plots of MoS_2 films Pt substrate. The layer number in each film is given in the figure as shown. (a) Polarization curves and (b) Tafel plots of MoS_2 films glassy carbon substrate. The layer number of each film is given in the figure as shown. The detailed values of Tafel slopes and exchange current density are listed in Supporting Table S3.

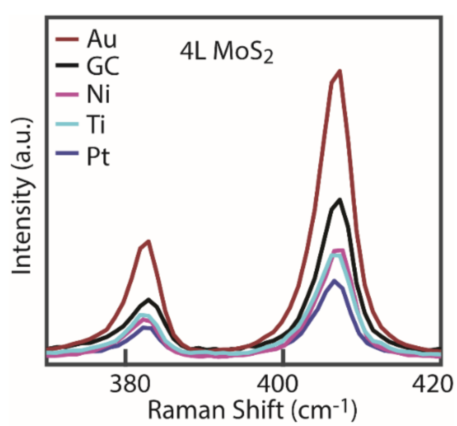

Fig. S12.Raman spectra of 4L MoS_2 on different substrates. The Raman peaks of the films on different substrates show negligible difference in frequency.

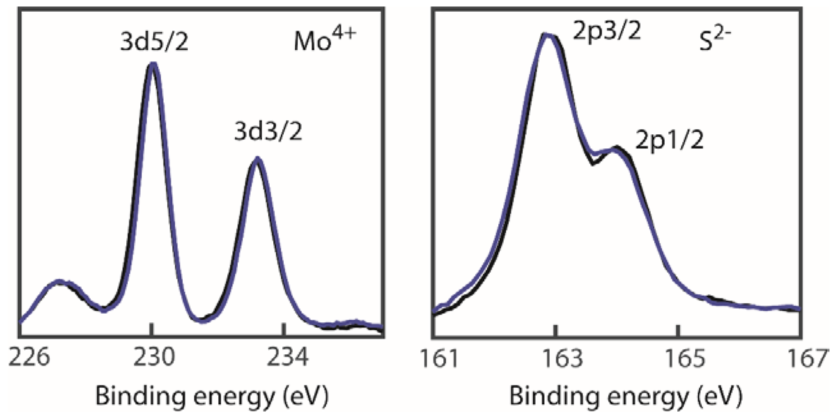

Fig.S13. XPS measured at monolayer MoS_2 before (blue) and after (black) the stability test.

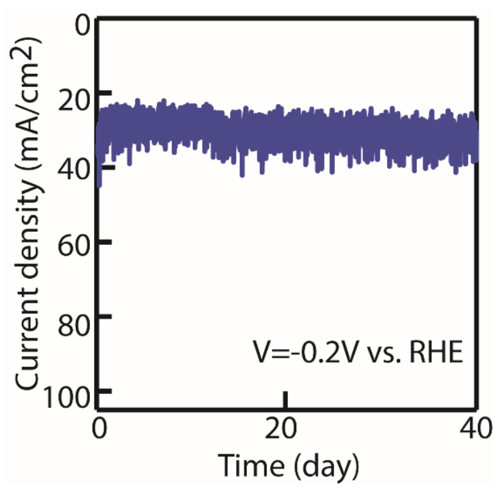

Fig S14. Stability test of MoS_2 on Ti in neutral solution. Stable catalytic performance of monolayer MoS_2 films on Ti-coated polymer substrates with continuous reaction under a current density of > 20 mA/cm^2 for more than two months. The potential is maintained at - 0.2 V (vs. RHE) during the reaction.

Table S1. Comparison of the catalytic activity of MoS_2 for HER

	Samples	Potential @ 20mA/cm2 (V vs. RHE)	Tafel slope (mV/dec)	Exchange current density (A/cm²)	Capacitance ($\mu F/cm^2$)	Reference
Amorphous MoS_2	Electrodeposition amorphous	-0.22	40	Around 3.1E-7		15
	Wet chemistry amorphous	-0.22	53-65	Around 1.0E-6	60	16
	MoS_2 particle on graphene	-0.17	41	Around 1.0E-5		13
MoS_2 Edge Sites Engineering	MoS_2 flake edges	-0.25	83	3.1E-4		17
	Double-gyroid MoS_2	-0.40	50	6.9e-4		18
	Step edges	-0.16	59	2.0e-4		19
MoS_2 Vacancy and Defect Engineering	Heated MoS_2	-0.70	147	6.3E-5		22
	Disordered MoS_2	-0.22	50	8.91e-6		20
	Defect-rich Mos_2 nanosheet	-0.21	55	1.26e-5	37.7	21
Strained MoS_2	Mechanical strained MoS_2 sheets	-0.45	135	1.02e-5		24
	Strained sulfur vacancy MoS_2	-0.21	60	4.0e-5		11
	Strained 1T MoS_2	-0.27	60	9.0e-6		25
Doped MoS_2	Hydrazine treated MoS_2	-0.37	108	1.7e-5		26
	Pt doped MoS_2	-0.35	96	Around 6.0E-4		27
	Zn doped MoS_2	-0.15	51	Around 1.5E-4		28
1T Phase MoS_2	Conductive 1T MoS2 nanosheet	-0.21	40	Around 1.0E-5		29
	Chemical exfoliated MoS2 nanosheet	-0.19	43	Around 1.0E-5		12
	Porous 1T MoS_2	-0.17	43	1.58E-5		30
This work	**Substrate and strain engineering sulfur vacancy MoS2**	**-0.05**	**32**	**6.87E-4**	**2.5**	**This work**

Table S2: Capacitance values for monolayer MoS_2 on different substrates

Samples	Capacitance/μF
MoS2+GC	2.6
MoS2+Ni	2.3
MoS2+Ti	2.5
MoS2+Pt	2.2
MoS2+Au	2.3

Table S3. Tafel slope and exchange current densities of MoS_2 on different supporting substrates in acid electrolyte (pH=1)

Samples	Tafel slopes mV/dec	Exchange current density mA/cm^2
1L on GC	65±4	0.032±0.01
2L on GC	113±4	0.009±0.0009
3L on GC	107±9	0.002 ±0.001
4L on GC	115 ±6	0.0005± 0.00009
1L on Au	72±2	0.039±0.005
2L on Au	107±3	0.102±0.006
3L on Au	104.5±1.5	0.0027±0.0004
4L on Au	114±7	0.00071±0.00008
1L on Ni	47.5±2.5	0.651±0.030
2L on Ni	84±2	0.15±0.01
3L on Ni	111.5±1.5	0.036±0.007
4L on Ni	121±8	0.00841±0.004
1L on Ti	55±3	1.21±0.12
2L on Ti	70±2	0.331±0.020
3L on Ti	108±9	(8.39±0.01)e-2
4L on Ti	119±5	0.0211±0.003
1L on Pt	34±2	0.401±0.01
2L on Pt	41±4	0.103±0.011
3L on Pt	86±8	0.0254±0.004
4L on Pt	113±3	0.0065±0.0005

Table S4. Tafel slope and exchange current densities of MoS_2 in different sulfur vacancy densities

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Density of sulfur vacancy	Substrate	Tafel slope mV/dec	Exchange current density mA/cm^2
1.0%	Glassy carbon	105±5	0.00087±0.0005
	Pt	104±4	0.0084±0.003
3.0%	Glassy carbon	88±4	0.0021±0.0009
	Pt	81±5	0.037±0.007
10%	Glassy carbon	65±4	0.032±0.005
	Pt	34±2	0.50±0.09
14%	Glassy Carbon	94±1	0.0016±0.0004
	Pt	89±2	0.17±0.002
20%	Glassy Carbon	90±2	0.00045±0.00004
	Pt	91±2	0.0065±0.0005

S1. Calculation of turnover frequency.

The turnover frequency (TOF) may be evaluated by normalizing the exchange change current density (J_0) to the planar atomic density of these materials as

$TOF = 0.5 \times J_0 \times 6.24 \times 10^{18} \times A_0$

where A_0 is the area occupied by single unit cell (MoS_2) or single atom (Pt). The constant of 0.5 is because the generation of each H_2 molecules request the involvement of two electrons. For bare Pt, the exchange current density is 0.31 mA/cm^2. Additionally, we assume the crystalline surface of the Pt substrate is (111) planes. The area occupied by single Pt atom is $(0.3912 \times \sqrt{2}/2)^2 \times \sin(\frac{\pi}{3})$ nm^2. For monolayer MoS2 on Pt, the exchange current density is 0.687 mA/cm^2, and the area occupied by single MoS2 unit cell is $0.315^2 \times \sin(\frac{\pi}{3})$ nm^2. The calculation indicates that the TOF is 0.64 s^{-1} at the bare Pt substrate and 1.84 s^{-1} at the monolayer MoS_2 film on Ti substrates.