Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Materials

Monolayer MoS_2 with S Vacancy from Interlayer Spacing Expanded Counterparts for Highly Efficient Electrochemical Hydrogen Production

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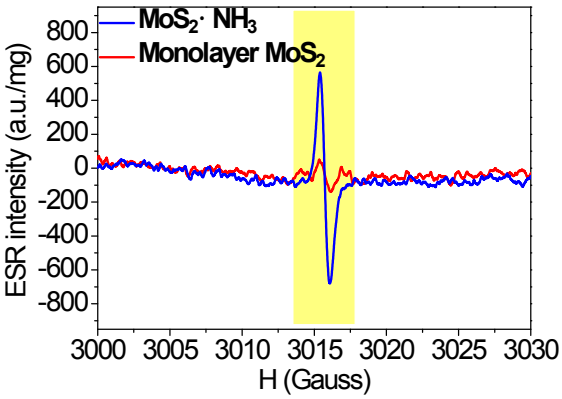

Figure S1 Electron spin resonance spectra for various MoS_2 samples.

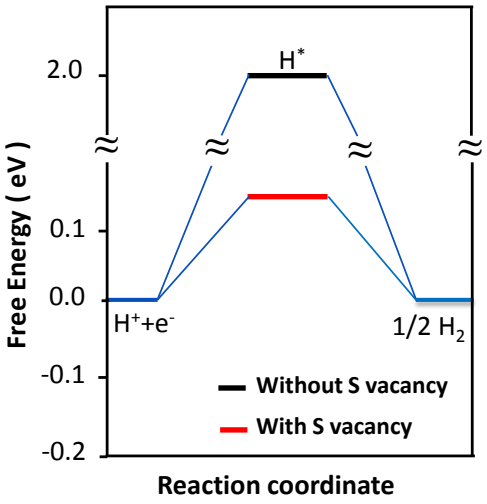

Figure S2 Free energy versus the reaction coordinate of HER for the S vacancy

The hydrogen adsorption free energies, ΔG_H, were determined in the same way as in previous studies [1, 2]. The adsorption energy is defined as

$$\Delta E_H = E(MoS_2+H) - E(MoS_2) - \tfrac{1}{2} E(H_2) \quad (1)$$

where (MoS_2+H) refers to hydrogen adsorbed on the MoS_2 surface, (MoS_2) refers to a clean MoS_2 surface, and H_2 refers to gas phase hydrogen molecule. The hydrogen adsorption free energy was calculated at zero potential and pH = 0 as

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T\Delta S \quad (2)$$

where ΔE_H is the hydrogen adsorption energy, ΔE_{ZPE} is the difference in zero point energy, T is the temperature (300 K) and ΔS is the difference in entropy between H that is adsorbed and in the gas phase at 101325 Pa. A normal mode analysis was used to determine the vibrational frequencies of the adsorbed species, which were used to determine the zero point energy correction and the entropy. The adsorption is too strong if ΔG_H is very negative or too weak if ΔG_H is very positive.

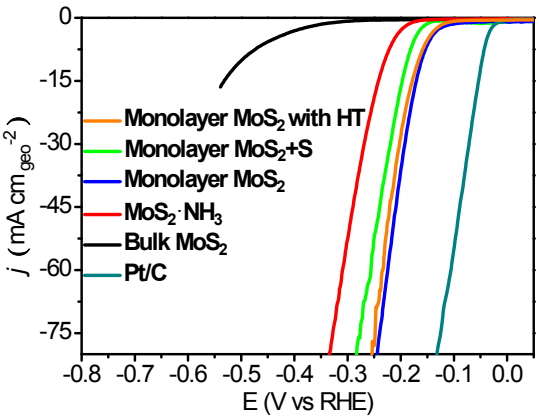

Figure S3 The correlation between the enhanced HER activities and internal S vacancies in the present monolayer MoS_2.

The preparation of the monolayer MoS_2 with sulfur compensation (monolayer MoS_2+S) are as follow: an alumina boat loaded with 8 mg of monolayer MoS_2 was placed at the downstream end of the tube furnace. Then, 1g of sulfur powder in another alumina boat was positioned at the upstream end of the quartz tube. The distance between the two boats was ~30 cm. The tube furnace was then evacuated, and high-purity argon was flowed at ~50 sccm for 20 min while the temperature was ramped to 550°C. The temperature was held for 2 h at 550°C with 80 sccm argon carrier gas flow. Finally, the furnace was then naturally cooled to room temperature. The HER activities of as-prepared monolayer MoS_2 with sulfur compensation (monolayer MoS_2+S) was tested with all other factors being equal to other MoS_2 samples. In order to exclude some other changes which could affect the HER activities, the monolayer MoS_2 also underwent the same heat treatment without sulfur powder (monolayer MoS_2 with HT) in the tube furnace as the control.

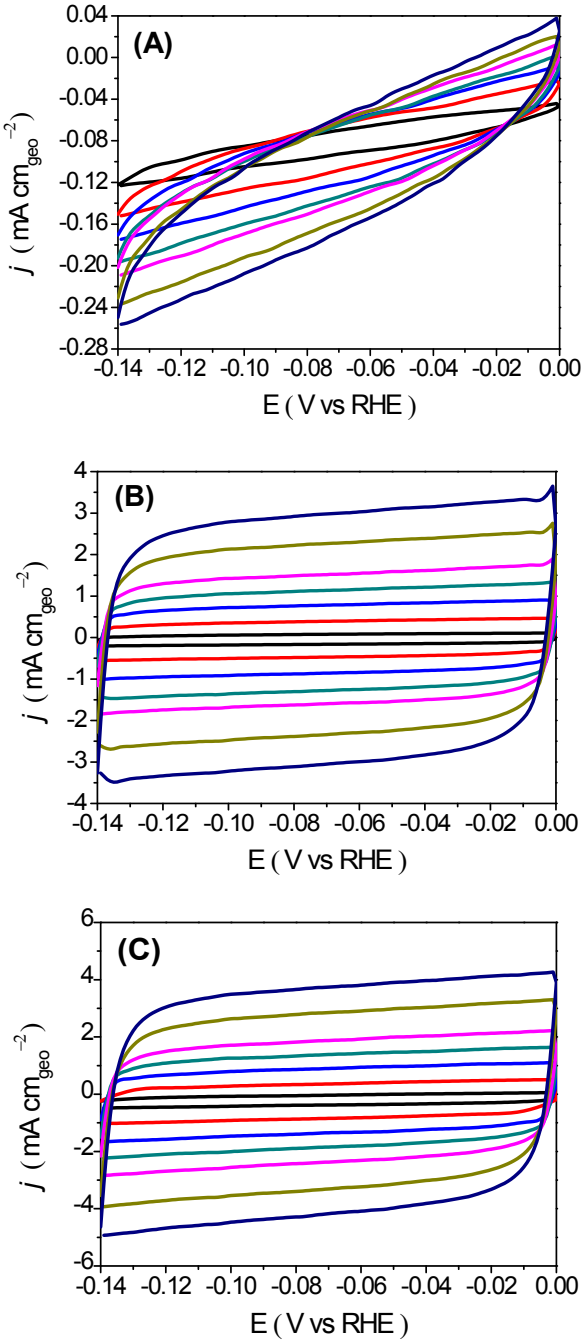

Figure S4 CV curves in the region of 0.0-0.14 V (V *vs* RHE) for bulk MoS_2 (A), MoS_2·NH_3 (B), and monolayer MoS_2 with S vacancy (C).

Due to its unclear capacitive behavior, it's difficult to measure the electrochemical active surface area for MoS_2 accurately. In this sense, double layer capacitance (C_{dl}) which is linearly proportional to effective active surface area paves an alternative way to calculate the active surface area for different MoS_2 samples. The C_{dl} value was estimated by plotting the ΔJ (J_a-J_c) at -0.07V (V *vs* RHE) against the scan rate, where the slope of the line is double C_{dl} (Fig. 6D in main text).

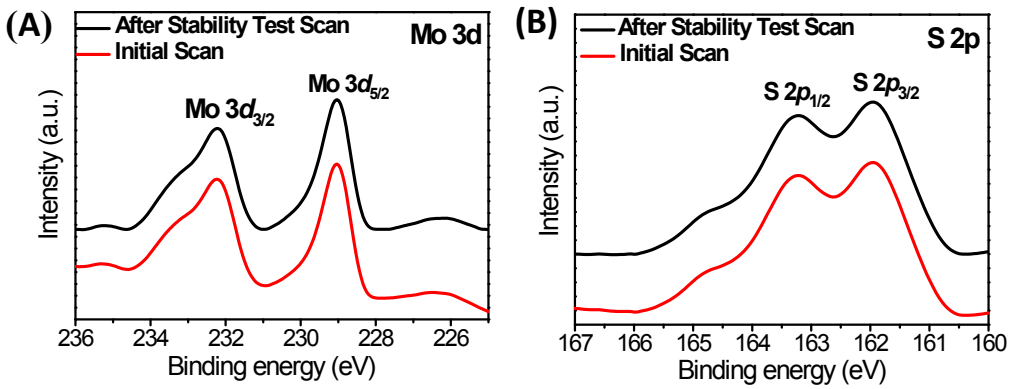

Figure S5 High-resolution XPS spectra of Mo 3d (A) and S 2p (B) in MoS_2 before and after stability test.

Supplementary Note 1 Calculation of corresponding spacing (*d*) between two adjacent S-Mo-S layers

The corresponding spacing (*d*) between two adjacent S-Mo-S layers can be calculated using Bragg's law:

$$n\lambda = 2d\sin\theta$$

Where n is the order of reflection, λ is the wavelength of incident x-ray (Cu Kα, 0.154 nm), *d* is the interlayer spacing, and θ is the angle between the incident x-ray and the scattering planes.

1. C.Tsai, K.Chan, F. Abild-Pedersen, J. K.Nørskov, *Phys.Chem. Chem. Phys*. 2014, **16,** 13156-13164.
2. C.Tsai, K.Chan, J. K.Nørskov, F. Abild-Pedersen, *Surf. Sci.* 2015, **640**, 133-140.