Activating and Optimizing MoS_2 Basal Planes for Hydrogen Evolution through the Formation of Strained Sulphur Vacancies

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As a promising non-precious catalyst for the hydrogen evolution reaction (HER)[1-5], molybdenum disulphide (MoS_2) is known to contain active edge-sites and an inert basal plane[1,6-8]. Activating the MoS_2 basal plane could further enhance its HER activity but is not often a strategy for doing so. Herein, we report the first activation and optimization of the basal plane of monolayer 2*H*-MoS_2 for HER by introducing sulphur (S) vacancies and strain. Our theoretical and experimental results show that the S-vacancies are new catalytic sites in the basal plane, where gap states around the Fermi level allow hydrogen to bind directly to exposed Mo atoms. The hydrogen adsorption free energy (ΔG_H) can be further manipulated by straining the surface with S-vacancies, which fine-tunes the catalytic activity. Proper combinations of S-vacancy and strain yield the optimal $\Delta G_H = 0$ eV, which allows us to achieve the highest intrinsic HER activity among molybdenum sulphide-based catalysts.

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Due to its relatively low-cost, earth-abundance, high catalytic activity and good stability[1,3,5], MoS_2 is a promising alternative to platinum (Pt) for catalyzing electrochemical hydrogen (H_2) production from water. MoS_2 has been studied in various forms for HER applications, where the guiding principle has most often been to optimize the active edge-sites over the inert basal plane sites[1,6-8]. One strategy focuses on maximally exposing edge-sites using nanostructured MoS_2 such as nanoparticles[7], vertical nanoflakes[9], nanowires[10], defect-rich films[11] or mesoporous film[12]. Another strategy strives to enhance the intrinsic activity of the edge-sites by atomic-scale modifications such as chemical doping[13,14]. Besides the metastable 1*T*-phase transformation[15,16], few approaches have sought to utilize the basal plane, which constitutes the majority of the bulk material. In order to fully utilize common 2*H*-MoS_2 materials, alternative methods for activating the basal plane are still needed.

Herein, we report the first successful activation and optimization of the basal plane of monolayer 2*H*-MoS_2 by creating and straining S-vacancies (Fig. 1a). Our density functional theory (DFT) calculations indicate that S-vacancies introduce gap states that allow for favourable hydrogen adsorption. Increasing the number of S-vacancy sites strengthens hydrogen adsorption, allowing for the simultaneous manipulation of ΔG_H and the active site density. Straining the S-vacancy sites shifts the gap states even closer to the Fermi level and leads to optimal ΔG_H. Experimentally, optimized monolayers of strained MoS_2 with S-vacancies exhibit unprecedentedly high intrinsic HER activity, with a turnover frequency per S-vacancy site ($TOF_{\text{s-vacancy}}$) of 0.31 H_2 molecules per second at 0 V versus RHE. This *TOF* is higher than those of the best-characterized edge-sites, the 1*T*-basal plane, and to the best of our knowledge, any MoS_2-based HER catalyst reported to date[5].

The process for activating the basal plane is illustrated in Fig. 1a. We first used DFT calculations (see Methods) to evaluate the HER activity of the S-vacancy sites on the basal plane (computational cell shown in Supplementary Fig. S1), where the hydrogen adsorption free energy ΔG_H was determined for different amounts of S-vacancies (Fig. 1b). ΔG_H is known to scale with activation energies[17] and has been successfully used as a descriptor for correlating theoretical predictions with experimental measurements of catalytic activity for various systems[18-20] including MoS_2 edge-sites[1,21]. The optimal value of ΔG_H is 0 eV, where hydrogen is bound neither too strongly nor too weakly[1]. For the basal plane of pristine 2*H*-MoS_2, ΔG_H is ~2 eV uphill (Fig. 1b), indicating that basal plane is inert[22]. When 3.12% S-vacancies are introduced

(% = percentage of sulphur atoms removed), hydrogen is stabilized on the exposed Mo-atoms and ΔG_H decreases to 0.18 eV. ΔG_H continues to decrease with increasing concentrations of S-vacancies. In the range of 9% to 19% S-vacancy, ΔG_H lies between ± 0.08 eV, which is similar to or better than that of edge-sites (0.06 eV)[1,21] .

Next, we investigated the effect of uniaxial elastic strain on the ΔG_H of S-vacancy sites (strain configuration discussed in Supplementary Note 1 and Fig. S1b). For any fixed concentration of S-vacancies, larger elastic strains strengthen hydrogen binding similarly to previous studies[23-25], leading to more negative ΔG_H (Fig. 1c). In the absence of S-vacancies, elastic strain (Fig. 1c, "0.0%" curve) is insufficient for activating the basal plane. Smaller S-vacancy concentrations require greater strain to reach the optimal ΔG_H of 0 eV, and the optimal condition can be satisfied under multiple combinations of S-vacancy concentrations and strain magnitudes: *e.g.*, 3.12% S-vacancy with 8% strain and 12.5% S-vacancy with 1% strain. This offers flexibility for simultaneously tuning the activity and density of S-vacancy sites on the basal plane.

To investigate the stability of the strained S-vacancies, the surface energy per unit cell, γ was calculated. Higher concentrations of S-vacancies and/or higher magnitudes of strain lead to larger γ and less stable surfaces (coloured contour plot in Fig. 1d, equivalent linear plots in Supplementary Fig. S2). While maintaining the optimal condition of $\Delta G_H = 0$ eV (black line in Fig. 1d), increasing the S-vacancy concentration beyond 11% leads to larger increases in γ, indicating a decline in surface stability. Therefore, the optimal S-vacancy concentration should be around 11%, which simultaneously maximizes the active site density (top axis of Fig. 1d) while preserving stability.

The nature of the S-vacancies' activity is revealed through its electronic structure. Band structures for 2*H*-MoS_2 with S-vacancy concentrations of 0% and 25% are shown in Figs 2a and 2b, respectively (further details in Supplementary Note 1). When S-vacancies are introduced, new bands appear in the gap near the Fermi level (Fig. 2b, red curves). These new gap states are responsible for hydrogen adsorption on the S-vacancies, and the corresponding Kohn-Sham orbitals for the band directly below the Fermi level indicate that these states are localized around the S-vacancy (Fig. 2c). With increasing S-vacancies, the bands move closer to the Fermi level and increase the number of gap states (Fig. 2d), which explains the gradual strengthening of H

binding seen earlier (Fig. 1b). When tensile strain is applied, the positions of these new bands further shift towards the Fermi level (Fig. 2e), resulting in a narrowing band gap and increasing number of gap states around the Fermi level, which also increases the adsorption strength on the S-vacancy site. The strategy of creating and straining S-vacancies to optimize HER activity is thus grounded in the engineering of the electronic structure of MoS_2.

To confirm the predictions from DFT, we synthesized monolayer 2*H*-MoS_2 (Fig. 3a, Supplementary Fig. S7), applied tensile strain (Fig. 3b), generated S-vacancies (Fig. 3c), and tested the HER activity. The CVD-grown MoS_2 film consists of large continuous MoS_2 monolayer flakes with a very small edge-site density (see Methods and Supplementary Note 2), which allows us to focus on the basal planes. This provides a well-defined system for quantifying the S-vacancies and strain for accurately determining the intrinsic activities (*TOF*s). The MoS_2 film was strained *via* a patterned gold (Au) nanocone support (Fig. 3d, inset) through capillary force (Supplementary Fig. S8)[26]. The resulting average tensile strain on MoS_2 is estimated to be 1.35±0.15% based on the red-shift magnitudes of the Raman E_{2g}^1 and A_{1g} peaks (Fig. 3d and Supplementary Note 2).

S-vacancies were then created in the basal plane by exposing it to mild argon (Ar) plasma [27], where the amount of S-vacancies was controlled by varying the Ar-plasma treatment time (Supplementary Fig. S9). For all MoS_2 samples investigated, the E_{2g}^1 and A_{1g} peaks remain dominant in the Raman spectra, indicating the *2H*-phase is not damaged by either strain or S-vacancy. Our DFT calculations further show that under all combinations of strain and S-vacancy, the 2*H*-phase is the most stable under our experimental conditions (Supplementary Note 1). The aberration-corrected transmission electron microscopy (ACTEM) image (Fig. 3e) shows that an Ar-plasma treated MoS_2 film (30 s) contains spots with the usual two S atoms (2S, brighter and bigger dots), with one S atom (1S, darker and smaller dots) and with no S atom (0S, totally dark), but no Mo-vacancy (Mo removal), confirming the successful formation of S-vacancies[27]. The total number of S-vacancies in Fig. 3e is about 43 (out of 190 Mo atoms, ~11.3% S-vacancies) and the average S-vacancy percentage over ten such areas is 12.5±2.5%, which is consistent with the 13.0±2.0% S-vacancies (Fig. 3f) estimated by X-ray photoemission spectroscopy (XPS) (Supplementary Fig. S10). The local electronic structure of the S-vacancies was directly probed using STM/STS, where a pronounced peak appears in the gap states (Fig. 3g, blue line). Both the

shape and the position of the new peak are in excellent qualitative agreement with the DFT calculated *d*-orbital projected density of states on the Mo-atom of the S-vacancy (using 12.5%, Fig. 3g red line). This comparison supports the earlier prediction (Fig. 2b) that the presence of S-vacancies introduces additional electronic states in the gap, which are responsible for hydrogen adsorption on the S-vacancies.

Next, we examined the separate and combined effects of strain and S-vacancy on the catalytic HER activity of monolayer *2H*-MoS_2. Figure 4a shows representative linear sweep voltammograms (LSV) for the Au substrate, Pt electrode, as-transferred MoS_2 (strain: 0% and S-vacancy: 0%), strained MoS_2 without S-vacancy (S-MoS_2), unstrained MoS_2 with S-vacancy (V-MoS_2), and strained MoS_2 with S-vacancy (SV-MoS_2). First, the Au substrate has negligible HER activity and is also expected not to influence ΔG_H for the S-vacancy (Supplementary Note 1). The Pt electrode shows the highest HER activity. Second, the as-transferred MoS_2 (MoS_2) has very low HER activity, confirming that our as-grown MoS_2 monolayer consists mainly of the inactive basal plane. Third, strain alone (S-MoS_2) only slightly increases the HER activity while S-vacancy alone (V-MoS_2) significantly increases the HER activity, consistent with the predicted ΔG_H. Fourth, the combination of strain and S-vacancy (SV-MoS_2) leads to even higher HER activity.

The corresponding Tafel plots (Fig. 4b) show that strain decreases the Tafel slope from 98 to 90 mV/dec while S-vacancies reduce the Tafel slope from 98 to 82 mV/dec. In contrast, combining strain and S-vacancies decreases the Tafel slope to 60 mV/dec. This Tafel slope has been observed for Mo_3S_{13} clusters[28], which was ascribed to a chemical rearrangement prior to H_2 desorption becoming the rate-limiting step. The larger onset potential of SV-MoS_2 compared to that of Pt could be partially due to competition between OH* and H* adsorption onto the S-vacancies sites at potentials near 0 vs. RHE (Supplementary Note 1).

We then calculated the turnover frequency per surface Mo atom (TOF_{Mo}) (Supplementary Note 2) to compare the intrinsic activity among various MoS_2 materials (Fig. 4c). S-vacancies (V-MoS_2) are much more effective than strain (S-MoS_2) for increasing TOF_{Mo} since strain alone cannot create highly active sites. The TOF_{Mo} of SV-MoS_2 is even higher than those of the MoS_2 edge-sites[5] and the basal plane of 1*T*-phase MoS_2[16], indicating that the Mo-sites are even more active than the under-coordinated S-sites in those systems. These observations are in agreement

with the theoretical ΔG_H values for the strained S-vacancies (~0 eV), the edge-sites (0.06 eV)[21], and the 1*T*-basal plane sites (0.12 eV)[22]. Nevertheless, additional factors beyond ΔG_H such as the reaction mechanisms could also contribute to the differences in TOF_{Mo}.

Finally, to correlate the intrinsic HER activity of each S-vacancy site between our experiments and theory, we calculated the turnover frequency per S-vacancy site ($TOF_{s\text{-}vacancy}$) (Supplementary Note 2). Figure 5a shows the experimental $TOF_{s\text{-}vacancy}$ (at 0 V versus RHE) as a function of %S-vacancy for both V-MoS_2 and SV-MoS_2. First, the combination of strain and S-vacancy (SV-MoS_2, 0.08~0.31 s^{-1}) leads to higher $TOF_{s\text{-}vacancy}$ than those with only S-vacancy (V-MoS_2, 0.05~0.16 s^{-1}). Although the $TOF_{s\text{-}vacancy}$ of SV-MoS_2 is still below that of Pt (1~1000 s^{-1})[5], it is better than those of the best characterized MoS_2 edge-sites (nanoparticles[6]: 0.02 s^{-1}, vertical MoS_2 flakes[9]: 0.013 s^{-1}) and $[Mo_3S_4]^{4+}$ cluster of amorphous MoS_2 (0.07 s^{-1})[29]. Second, regardless of the strain, the $TOF_{s\text{-}vacancy}$ first increases and then decreases with increasing %S-vacancy, which confirms that there is an optimal amount of S-vacancies at each level of strain for ΔG_H = 0 eV (Figs 1b, c). Third, when the S-vacancy concentration increases beyond the optimal value, the intrinsic activity of each site decreases while the total number of active sites increases, so the exchange current density j_0 decreases only slightly (Fig. 5a, inset). Fourth, the only discrepancy between theory and experiments comes when S-vacancies are larger than 18%. Theory predicts that the strained sample should have smaller *TOFs* than those of unstrained samples due to ΔG_H being too negative (Fig. 1c). This is likely caused by having unevenly distributed S-vacancies when their concentrations are high. Locally low concentrations of S-vacancies will resemble systems with smaller S-vacancy concentrations and exhibit higher *TOF*s under strain. Finally, when the experimental $TOF_{s\text{-}vacancy}$ (at 0 V versus RHE) is plotted as a function of their corresponding ΔG_H, we obtain a clearly defined volcano relation with the peak around ΔG_H = 0 eV (Fig. 5b). Our best-performing catalyst lies around the peak position of the volcano plot, suggesting that we have succeeded in using ΔG_H as a descriptor for optimizing the HER activity of the S-vacancy sites of SV-MoS_2.

In summary, we have theoretically predicted and then experimentally verified that strained S-vacancies in the basal plane of *2H*-phase monolayer MoS_2 act as a new highly active and tunable catalytic site for HER. This is the first account of using S-vacancies in the basal plane to introduce gap states, which can be varied using the S-vacancy concentration and elastic

strain. With optimized combinations of strain and S-vacancies, the strained S-vacancy sites exhibit a $TOF_{\text{s-vacancy}}$ (at 0 V versus RHE) of 0.08~0.31 s^{-1}, exceeding those of the MoS_2 edge-sites (0.013~0.02 s^{-1}) and $[Mo_3S_4]^{4+}$ clusters (0.07 s^{-1}). In order to facilitate robust comparisons between theory and experiments, we have restricted the study to nearly continuous monolayers of MoS_2 with very few edge-sites. However, the generation of S-vacancy sites could be a general post-synthesis treatment for other high surface area electrodes, such as mesoporous nanostructure[12], vertical nanoflakes[9] and MoS_2 nanotube[30]/nanowire[10] arrays, which could lead to even higher total activity. The methodology of combining vacancies (*e.g.*, sulphur, selenide or oxygen vacancies) with elastic strain could also be a general way of generating new active sites in two-dimensional materials (transition metal dichalcogenides and oxides). Our work thus has wide implications for reactions beyond HER and for materials beyond MoS_2.

Methods

Theoretical calculations. All calculations in this work were performed using plane-wave DFT employing periodic boundary conditions as implemented in the Quantum ESPRESSO code. The Bayesian error estimation exchange-correlation functional with van der Waals interactions (BEEF-vdW) was used[31]. This functional has been optimized for chemisorption energies as well as van der Waals interactions, and previous results using both the RPBE and BEEF-vdW functional have been found to be in close agreement[1,21]. A plane-wave cutoff of 500 eV and a density cutoff of 5000 eV were used, and a Monkhorst-Pack 2×2×1 *k*-point grid was used to sample the Brillouin zone. Periodic boundary conditions were used in all directions and 11 Å of vacuum was used in the *z*-direction to separate the slabs, which are 4 Mo atoms × 4 Mo atoms in size. The hydrogen adsorption free energies were determined in the same way as in previous studies[22]. For the structural relaxations, a convergence criteria of 0.05 eV/Å was used for the maximum force. As a first approximation, we have neglected the solvation effects, as they are expected to be small in this case[32]. For the comparison between the calculated density of states and the STM measurements, the GLLB-sc functional[33], which can more accurately describe the band gap, was used. The band structures (Fig. 2) were calculated using BEEF-vdW to be consistent with all other calculations in this work, but we find good agreement with the GLLB-sc results (Supplementary Note 1).

Growth of monolayer 2*H*-MoS_2 flakes. Monolayer 2*H*-MoS_2 were grown in a tube furnace by chemical vapour deposition (CVD) with molybdenum trioxide (MoO_3) and sulphur (S) powder as sources with Ar as the carrier gas[34]. A Si/SiO_2 wafer was suspended on an alumina boat containing MoO_3 source and used as the growth substrate. Oxygen was carefully removed through a repeated purging (with Ar) and pumping process before each growth. The growth was conducted at 750 ^{o}C with 6-sccm Ar flow at atmosphere pressure. Connected large flakes of 2*H*-phase monolayer MoS_2 was grown on the SiO_2 wafer after 15 minutes. The growth of MoS_2 is symmetric *w.r.t.* the centerline of the wafer/MoO_3 source boat (see Supplementary Fig. S7 for more details) so that we can use similar MoS_2 films to fabricate V-MoS_2 and SV-MoS_2 devices to have a fair comparison.

Transfer and strain monolayer 2*H*-MoS_2. As-grown CVD MoS_2 monolayer were transferred onto a gold nanocone substrate using the PMMA-assisted wet transfer process (see

Supplementary Note 2 for more details). The transferred sample was then baked at 100 °C for 10 minutes. Afterward, PMMA was removed by sequential soaking in acetone (10 minutes) and chloroform (1 hour) at 60 °C. Then, the gold nanocone substrate with transferred MoS_2 was immersed in ethylene glycol in vacuum for 1 hour to ensure that both sides of MoS_2 sheet were wetted by ethylene glycol. Finally, the sample was dried in ambient air to completely evaporate ethylene glycol. The capillary force generated during ethylene glycol evaporation strains MoS_2 to follow the topography of the gold nanocones (see Supplementary Fig. S8 for more details).

The formation of S-vacancies on MoS_2. The transferred MoS_2 samples were exposed to mild argon plasma for various durations. The mild Ar plasma was generated by dispersing a 4-W RF power in a 6-inch diameter vacuum chamber at 1 bar that results in short mean-free-paths for the radicals in the plasma. The small RF power and the short mean-free-path ensure a cold and mild Ar plasma on the MoS_2 surface, resulting in a controllable desulphurization process.

Material characterizations. The TEM characterization was carried out with a FEI spherical aberration (image)-corrected 80-300 Titan environmental (scanning) (FEI Titan E-(S)TEM) operated at 80 kV. The Raman and photoluminescence (PL) measurements were performed using a WITEC alpha500 Confocal Raman system in ambient air environment with an excitation laser line of 532 nm. The power of the excitation laser line was kept well below 1 mW to avoid damage of MoS_2. The Raman scattering was collected by an Olympus 100 × objective (N.A. = 0.9) and dispersed by 1800 and 600 lines/mm gratings for Raman and PL measurements, respectively. The monolayer nature of MoS_2 is confirmed by the frequency difference between E^1_{2g} and A_{1g} peaks (~18.3 cm^{-1} in Fig. 3d). The XPS measurement was performed with excitation by Al (ka) radiation at 5×10^{-10} Torr. The S:Mo atom ratios were obtained from the XPS peak area ratio of S 2p to Mo 3d states. The S:Mo atom ratio for as-grown MoS_2 was set as 2.0 to normalize other samples. Scanning tunneling microscopy and spectroscopy (STM/STS) measurements were performed at 77 K in ultrahigh vacuum.

Electrochemical characterizations. A three-electrode electrochemical compression cell was used for electrochemical measurements with a Gamry 600 potentiostat. The monolayer 2*H*-MoS_2 acted as the working electrode with a Pt wire as the counter electrode, and a Ag|$AgCl_2$ reference electrode that has a redox potential of + 0.196 V versus NHE in a 3M sodium chloride. All measurements were conducted using a sulphuric acid electrolyte with pH value of 0.2.

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Author Contributions

H.L. and X.L.Z. conceived the idea and designed the experiments. H.L. performed material growth, electrode fabrication and electrochemical measurements. C.T., J.K.N. and F.A.-P. carried out the theoretical calculations. A.L.K. conducted the TEM characterization, L.L.C. performed the XPS measurement. A.W.C., A.H.F. and H.C.M. conducted the STM/STS measurements. J.Z. and H.S.H. assisted with the electrochemical measurements. H.L., C.T. and X.L.Z. wrote the manuscript, and all authors discussed the results and commented on the manuscript.

Competing Financial Interests

The authors declare no competing financial interests.

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Figure 1| Theoretical calculations for the effects of S-vacancy and strain on the HER activity of MoS_2. **a**, Schematic of the top (upper panel) and side (lower panel) views of MoS_2 with strained S-vacancies on the basal plane where S-vacancies serve as the active sites for hydrogen evolution and applied strain further tunes the HER activity. **b**, Free energy versus the reaction coordinate of HER for a range of 0 to 25% S-vacancy. **c**, ΔG_H versus %x-strain under various %S-vacancy, ranging from 0.0% (pristine) to 18.75%. **d**, Coloured contour plot of surface energy per unit cell γ (*w.r.t.* bulk MoS_2) as a function of S-vacancy and uniaxial strain. Inset: colour bar for γ. The black lines in (**c**) and (**d**) indicate combinations of S-vacancy and strain that yield $\Delta G_H = 0$ eV, the optimal thermodynamic requirement for HER activity.

Figure 2| Effects of S-vacancy and strain on the electronic structure of MoS_2. Band structure of monolayer 2*H*-MoS_2 with **a.** 0% and with **b.** 25% vacancies (calculated using a reduced 2×2 unit cell for clarity). S-vacancies introduce new bands (red curves) in the gap, near the Fermi level. **c.** The Kohn-Sham orbitals (red) corresponding to the new band just below the Fermi level. **d.** Tuning of the band structure due to increasing S-vacancy concentrations (calculated using the full 4×4 unit cell). The bands nearest to the Fermi level are highlighted in black and the extra bands are due to the larger unit cell size needed to reflect the smaller S-vacancy concentrations. **e.** Fine-tuning of the band structure for 25% S-vacancy under applied strain. With increasing strain, the bands approach the Fermi level and narrow the gap.

Figure 3| Experimental creation and quantification of S-vacancy and elastic tensile strain in MoS_2. Schematic of the top (top panel) and side (lower panel) views of **a**, pristine monolayer 2*H*-MoS_2, **b**, strained MoS_2 and **c,** strained MoS_2 with S-vacancies. Arrows illustrate the key experimental processes involved. **d**, Representative Raman spectra for the unstrained and strained MoS_2. Dotted lines indicate the positions of the E_{2g}^1 and A_{1g} peaks for unstrained MoS_2. Inset: tilted SEM image of strained MoS_2. Scale bar is 500 nm. **e**, ACTEM image of a 4×4 nm^2 MoS_2 monolayer with about 43 S-vacancies (~11.3% S-vacancy). The biggest and brightest dots (rhombus) are Mo atoms. Small bright dots (star), small dim dots (circle), and dark spots (triangle) correspond to a pair of S atoms (2S, one S atom above and the other below the Mo plane), a single S atom (1S, only one S atom below the Mo plane) and zero S atoms (0S, both top and bottom S atoms removed), respectively. The scale bar is 5Å. **f**, The S:Mo atom ratio decreases with increasing duration of Ar plasma treatment, as obtained from XPS measurements.

g, STM/STS measured d*I*/d*V* (left y-axis) and DFT calculated projected *d*-orbital density of states on the Mo-atom of the S-vacancy (right y-axis) versus sample bias for the S-vacancy sites (under 12.5% S-vacancy). The STS spectrum is an average over 8 individual spectra. The STM results are in close agreement with DFT results calculated using the GLLB-sc functional.

Figure 4| Individual and combined effects of elastic tensile strain and S-vacancy on the HER activity of monolayer MoS_2. **a**, LSV curves for the Au substrate, Pt electrode, as-transferred MoS_2 (strain: 0% and S-vacancy: 0%), strained MoS_2 without S-vacancies (S-MoS_2, strain: 1.35±0.15% and S-vacancy: 0%), unstrained MoS_2 with S-vacancies (V-MoS_2, strain: 0% and S-vacancy: 12.5±2.5%), and strained MoS_2 with S-vacancies (SV-MoS_2, strain: 1.35±0.15% and S-vacancy: 12.5±2.5%). The potentials corresponding to 10 mA/cm^2 (dotted line) for V-MoS_2 (-250 mV), SV-MoS_2 (-170 mV) and Pt (-59 mV) are labelled. **b**, the corresponding Tafel plots of the LSV curves in (**a**). **c**, Turnover frequency per surface Mo atom (TOF_{Mo}) of various MoS_2 samples shown in (**a**), along with TOF_{Mo} of "edge-site only" from Fig. 11 of ref. 5 and that of "1-*T* phase" from ref. 16.

Figure 5| Correlation of the intrinsic HER activity of S-vacancy sites between experiments and calculations. **a**, Turnover frequency per S-vacancy ($TOF_{S\text{-}vacancy}$) at 0 V versus RHE as a function of %S-vacancy for V-MoS_2 and SV-MoS_2. The strained samples have 1.35±0.15% strain. Inset: exchange current density j_0 as a function of %S-vacancy for V-MoS_2 and SV-MoS_2. **b**, Experimental $TOF_{S\text{-}vacancy}$ versus their corresponding calculated ΔG_H for V-MoS_2 and SV-MoS_2. They follow a volcano relation (dashed lines) with the peak at $\Delta G_H = 0$ eV. The ΔG_H values were calculated at 21.88%, 18.75%, 12.50%, 8.00% and 6.25% S-vacancies (left to right on the plot) and with either 0% or 1.35% applied strain. The error bars in the $TOF_{S\text{-}vacancy}$ represent variations in the experimental samples (Supplementary Fig. S11) and the error bars in ΔG_H are based on the experimental distribution of S-vacancies.