Supplementary Information

Tuning the Threshold Voltage of MoS₂ Field-Effect

Transistors via Surface Treatment

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Figure S1. (a) Typical atomic force microscopy (AFM) topography image of an exfoliated MoS₂ strip. (b) Height profile along the dotted line in (a).



Figure S2. Schematic showing the experimental setup for sulfur treatment of MoS_2 flakes. The sample (exfoliated MoS_2 flakes on a p⁺ Si / SiO_2 substrate) was placed into a test tube and 6 cm away from the sulfur powder (500 milligrams) at the closed end. The test tube was positioned in the tube furnace such that sulfur powder is at the center of heating zone. The furnace temperature was ramped up to the melting point of sulfur (445 °C) at a total pressure of 3 x 10⁻¹ mbar and held for 2 hours. Throughout the annealing process, Argon gas flow (16 sccm) was introduced to control the diffusion rate of sulfur vapor and the sample temperature was ~435 °C.



Figure S3. I_D - V_G characteristics of 3 typical back-gated MoS₂ transistors fabricated on (a) pristine, (b) sulfur-treated, and (c) hydrogen-treated MoS₂ flake, during the day when they were freshly-fabricated and after 2 weeks of storage in ambient conditions (25 °C, 1 atm).



Figure S4. (a) I_D - V_D characteristics of a typical back-gated MoS₂ transistor that was first fabricated on a sulfur-treated MoS₂ flake and followed by a hydrogen-treatment. (b) I_D - V_D characteristics of a typical back-gated MoS₂ transistor that was fabricated on a pristine MoS₂ flake.



Figure S5. Electronic band structure of (a) Ti-covered-perfect-bilayer-MoS₂ unit cell, (b) perfect bilayer MoS₂ unit cell, (c) imperfect bilayer MoS₂ with one sulfur vacancy in $3 \times 3 \times 1$ supercell, and (d) imperfect bilayer MoS₂ with one sulfur vacancy in $5 \times 5 \times 1$ supercell. The characteristic band of MoS₂ is shown in red dots for the Ti-covered-MoS₂ combined system. We assigned the conduction band minimum and valence band maximum of the Ti-covered-perfect-bilayer-MoS₂ shown in (a) according to the band shape of the isolated MoS₂ shown in (b), and neglect the influence of the hybrid state (near Fermi level) induced by the adjacent metal.

Table S1: Energy eigenvalues (in eV) for the Fermi level (E_{fermi}), valence band maximum (E_{VBM}), conduction band minimum (E_{CBM}), bottom edge of defect band (E_{def}) and defect band width (ΔD) for the perfect and defect containing systems. 3×3 -1Vs refers to one sulfur vacancy in the 3×3 bilayer MoS₂ supercell. All the energies are referenced to the vacuum level (which is set to 0 eV). ΔE is the energy shift required to align the E_{def} in MoS₂ channel (bare MoS₂) to the Fermi level in the Ti-covered-MoS₂ electrode (-5.1 eV).

Bilayer MoS ₂ Supercell	2×2 -1Vs	3×3 -1Vs	4×4 -1Vs	5×5 -1Vs	6×6 -1Vs	Perfect
Density of sulfur vacancy (×10 ¹³ cm ⁻²)	29.6	13.1	7.4	4.7	3.2	0
E _{fermi} (eV)	-5.43	-5.34	-5.33	-5.31	-5.31	-5.06
E _{VBM} (eV)	-5.54	-5.60	-5.62	-5.62	-5.63	-5.62
ECBM (eV)	-4.36	-4.39	-4.45	-4.44	-4.45	-4.46
Defect band edge, Edef (eV)	-5.23	-5.00	-4.95	-4.91	-4.90	
Center of defect band (eV)	-4.84	-4.87	-4.91	-4.90	-4.90	
Defect band width, ΔD (eV)	0.78	0.27	0.09	0.03	0.01	
$\Delta \mathbf{E} = \mathbf{E}_{def} - (-5.1 \text{ eV}) (\text{eV})$	-0.13	0.10	0.15	0.19	0.20	

Table S2: Energy values of the Fermi level (E_{fermi}), valence band maximum (E_{VBM}), conduction band minimum (E_{CBM}), bottom edge of defect band (E_{def}) and defect band width (ΔD) for the 3×3 -1Vs and 6×6 -1Vs in different convergence parameters. All the energies are referenced to the vacuum level (which is set to 0 eV). E_{cut} is the cutoff energy used in the calculation. Both set of values are almost the same, indicating the calculation is converged, and the trend of the defect band is robust with more converged parameters.

Bilayer MoS ₂ Supercell	3×3 -1Vs		6×6 -1Vs		
Convergence parameters	Ecut: 400eV,	Ecut: 500eV,	Ecut: 400eV,	Ecut: 500eV,	
	k-point: 5×5×1	k-point: 8×8×1	k-point: 2×2×1	k-point: 4×4×1	
E _{fermi} (eV)	-5.341	-5.342	-5.310	-5.309	
Evbm (eV)	-5.600	-5.601	-5.629	-5.629	
ECBM (eV)	-4.386	-4.388	-4.454	-4.454	
Edef (eV)	-5.004	-5.006	-4.906	-4.905	
ΔD (eV)	0.272	0.272	0.011	0.011	



Figure S6. Electronic band structure of imperfect bilayer MoS_2 with one sulfur vacancy in $3 \times 3 \times 1$ supercell, the red line and black line represent the convergent parameters used in this paper and a higher convergent parameters (500 eV energy cutoff for plane wave basic set and $7 \times 7 \times 1$ Monkhorst-Pack *k*-point sampling), respectively. Both lines are almost overlapping, indicating the calculation is converged, and the trend of the defect band is robust with more converged parameters.



Figure S7. (a) Raman spectra of pristine MoS_2 flakes taken at different positions as indicated. Inset: Optical image of the MoS_2 flakes exfoliated on a p⁺ Si / SiO₂ substrate. In particular, positions 2&3 represent few-layer MoS_2 while position 1 represents a monolayer MoS_2 . We note that the Raman spectra of these MoS_2 flakes are the same in terms of both relative intensity and peaks' position when they were was pristine (P), sulfur-treated (S), and followed by the hydrogen treatment (S + H). (b-d) PL spectra of the MoS_2 flakes taken at different positions and stages (P, S, S+H) as indicated.



Figure S8. (a) Optical image of a MoS_2 flake exfoliated on a p⁺ Si / SiO₂ substrate. (b) PL spectra of the MoS_2 flake taken at different positions as indicated in c & d. (c) The PL intensity map of the MoS_2 flake when it was as-exfoliated. (d) The PL intensity maps of the MoS_2 flake after it underwent the hydrogen treatment. All PL maps share the same color intensity bar.

<u>S7. Material composition study on the surface-treated MoS₂ sample</u>

As mentioned in the main text, the proposed sulfur and hydrogen treatments are expected to repair and create sulfur vacancies in the basal plane of MoS₂, respectively. Here, we attest the hypothesis by investigating stoichiometry changes of the MoS₂ prior to and following the proposed treatments through an X-ray photoelectron spectroscopy (XPS) study. A piece of bulk MoS₂ flake was first cleaved from molybdenite crystal (SPI supplies[®]) and its XPS spectrum is shown in Figure S9 (labelled as P). It should be noted that all XPS spectra in this study were obtained by exciting the MoS_2 sample with an Mg K α source (XR 50, SPECS GmbH), and detected with a PHOIBOS 150 Hemispherical Energy Analyzer equipped with a Delay Line Detector (SPECS GmbH) at a pass energy of 30 eV. Subsequently, the MoS₂ sample was subjected to the sulfur treatment and its XPS spectrum is plotted in Figure S9 too (labelled as S). The same MoS₂ sample was then exposed to the hydrogen treatment and its XPS spectrum is also included in Figure S9 (labelled as S+H) for comparison purposes. As can be seen in Figure S9, the Mo 3d and S 2p XPS spectra of the MoS₂ sample show slight changes after the sulfur treatment followed by the hydrogen treatment. Table S3 summarizes the stoichiometry (atomic ratio of Mo:S) of the same MoS₂ sample when it was pristine (P), sulfur-treated (S), and following the hydrogen treatment (S + H), which were identified through components' peak fitting (an example is shown in Figure S10). As expected, for the same MoS₂ sample, the stoichiometry changes from 1.89 to 1.96 after the sulfur treatment, which indicates a reduction of sulfur vacancies in the MoS₂ surface, and more importantly, stoichiometry of the same MoS₂ sample changes to 1.90 after the hydrogen treatment, which signifies an increase in sulfur vacancies in the MoS₂ surface. Overall, the results agree well with our hypothesis that the proposed sulfur / hydrogen treatment reduces / increases the amount of sulfur vacancies in the basal plane of MoS₂.



Figure S9. XPS spectra of the same MoS_2 sample when it was pristine (P), sulfur-treated (S), and followed by the hydrogen treatment (S + H). (a) Mo 3*d* and (b) S 2*p* XPS spectra of the MoS₂ sample.

Table S3. Atomic ratio of Mo:S of the same MoS_2 sample when it was pristine (P), sulfur-treated (S), and following the hydrogen treatment (S + H).

Sample	Atomic ratio of Mo:S
Р	1 : 1.89
S	1 : 1.96
S + H	1 : 1.90



Figure S10. (a) Mo 3*d* and (b) S 2*p* XPS spectra of the "S + H" MoS₂ sample with curve fits to spectral components attributed to molybdenum (Mo $3d_{3/2}$, Mo $3d_{5/2}$) and sulfur (S 2*s*, S 2*p*_{1/2} and S 2*p*_{3/2}) after Shirley background subtraction.