Supporting Information

Electronic origin of gas selectivity on Co/Fe-modified WS_2 monolayers for NO_2 sensing

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Details of thermodynamic calculation

These mainly include enthalpy, entropy, Binding Energy, and the Gibbs free energy.

First, enthalpy (H) is calculated by

$$H = H_{trans} + H_{rot} + H_{vib} + RT$$

$$= \frac{R}{2k}\sum_i hv_i + \frac{R}{k}\sum_i \frac{hv_i exp(-hv_i/kT)}{[1 - exp(hv_i/kT)]^2} + 4R \quad (1)$$

where H_{trans}, H_{rot} and H_{vid} are the translation enthalpy, rotation enthalpy, and vibration enthalpy (kcal/mol), respectively. *R* and *T* are the ideal gas constant (8.314 J/mol/K) and the absolute temperature (K), accordingly. *k* is the Boltzmann constant, *h* is Planck's constant, and v_i, is the vibrational frequency.

Second, entropy (S) is given by

$$S = S_{trans} + S_{rot} + S_{vib}$$

$$= \frac{5}{2}RlnT + \frac{5}{2}Rlnw - \frac{5}{2}lnp - 2.3482$$

$$+ \frac{R}{2}ln\left[\frac{\pi}{\sqrt{\sigma}}\frac{8\pi^2 cl_A}{h}\frac{8\pi^2 cl_B}{h}\frac{8\pi^2 cl_C}{h}\left(\frac{kT}{hc}\right)^3\right]$$

$$+ \frac{3}{2}R + R\sum_i \frac{hv_i/kT\ exp(-hv_i/kT)}{1 - exp(-hv_i/kT)}$$

$$- R\sum_i \ln\left[1 - exp(-hv_i/kT)\right] \quad (2)$$

where S_{trans}, S_{rot}, and S_{vid} are the translation, rotation, and vibration entropies (cal/mol/K), accordingly. *w* is the molecular mass, *p* is the pressure, σ is the symmetry number, c is the molar concentration of the molecules, and $I_{A\ (B,\ C)}$ is the moment of inertia.

Finally, the Gibbs free energy (G) (kJ/mol) is defined as

$$G = E(OK) + H - T \cdot S \tag{3}$$

where E (0 K) is the zero-point energy (kcal/mol).

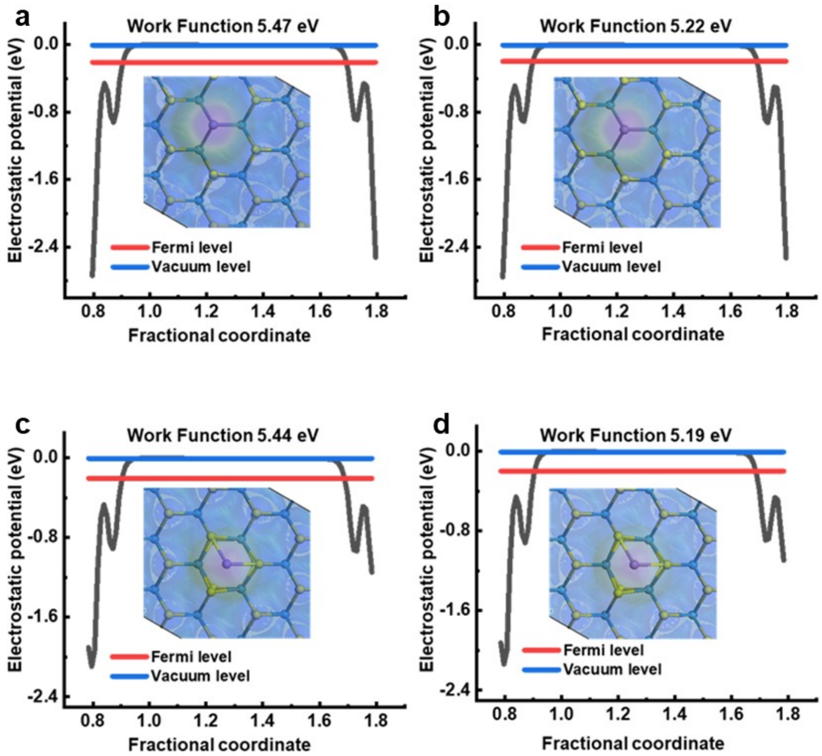

Figure S1. Electrostatic potential and work function of the (a) doped-Fe-WS_2, (b) doped-Co-WS_2, (c) Loaded-Fe-WS_2, and (d) Loaded-Co-WS_2 monolayer.

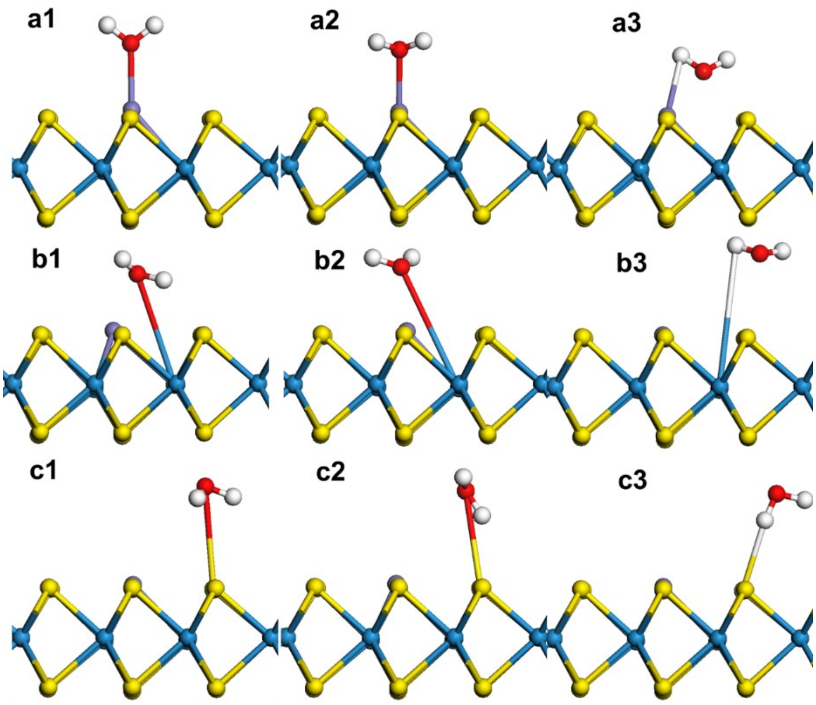

Figure S2. Various adsorption sites of H_2O with different orientations on doped-Fe-WS_2

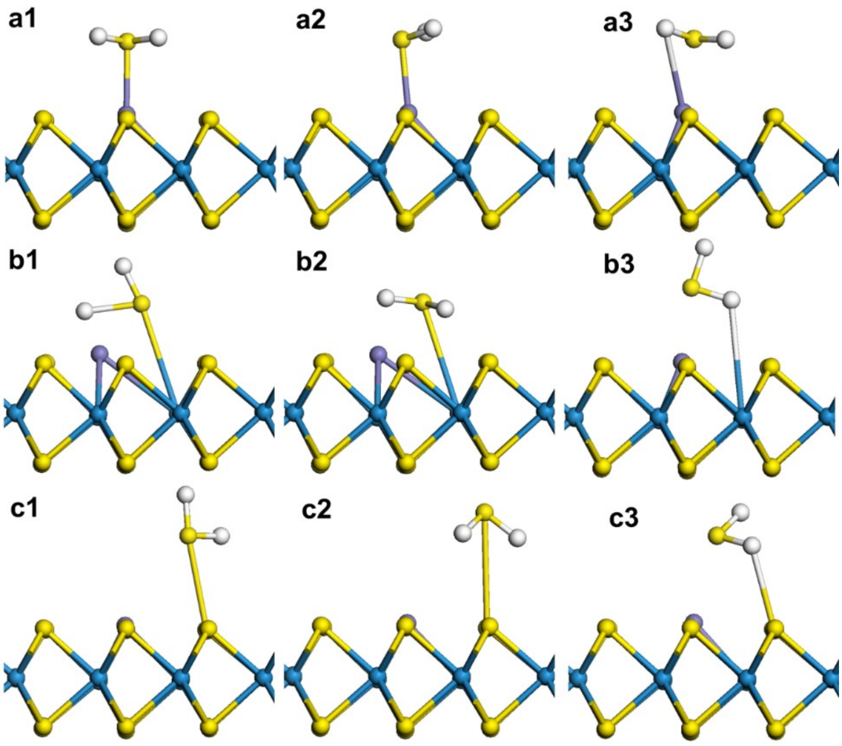

Figure S3. Various adsorption sites of H_2S with different orientations on doped-Fe-WS_2.

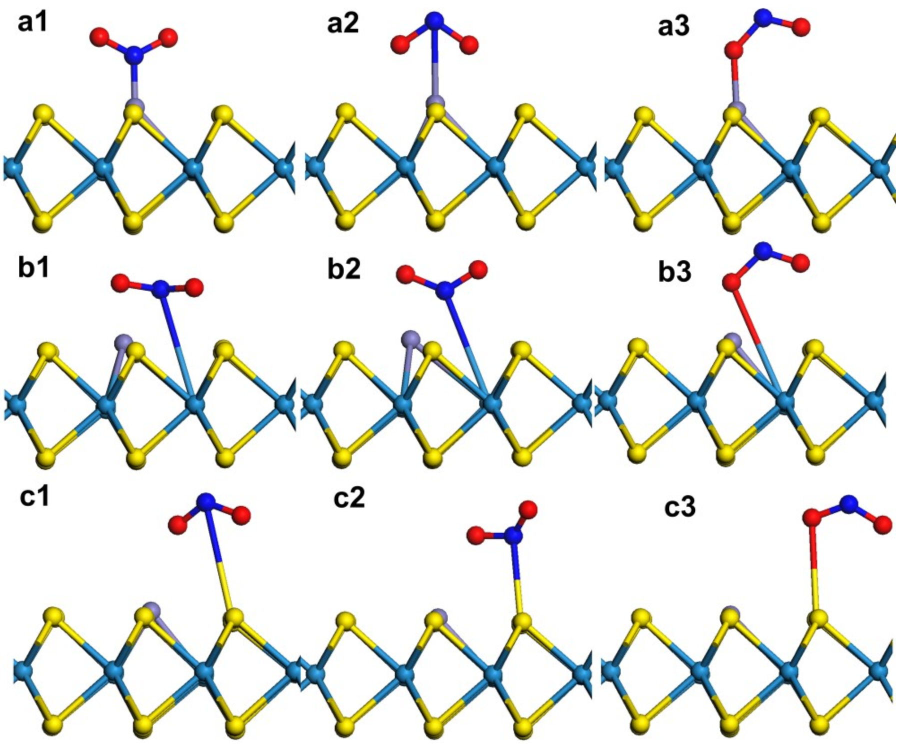

Figure S4. Various adsorption sites of NO_2 with different orientations on doped-Fe-WS_2.

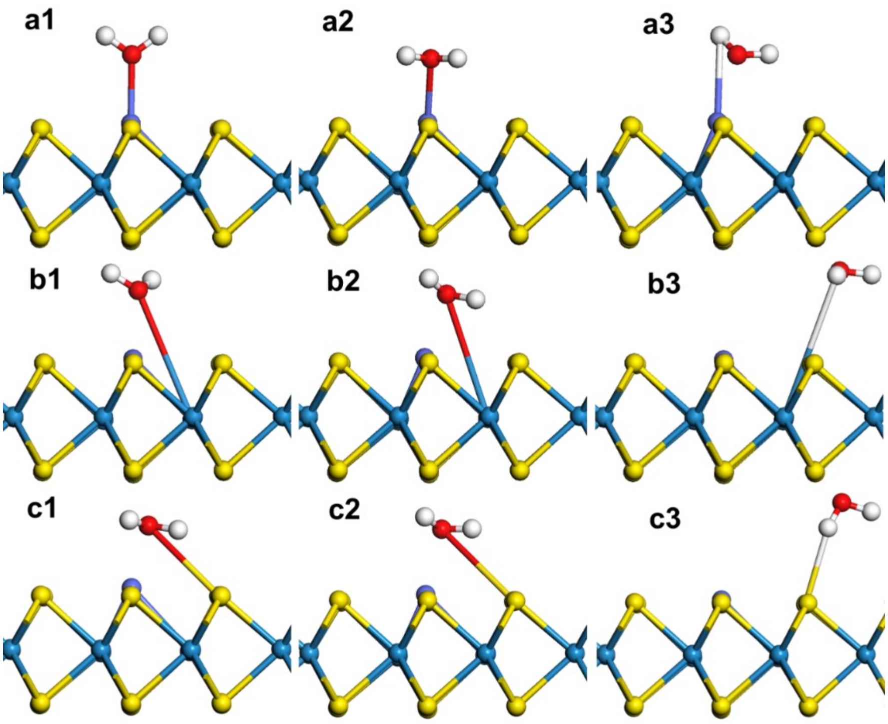

Figure S5. Various adsorption sites of H_2O with different orientations on doped-Co-WS_2.

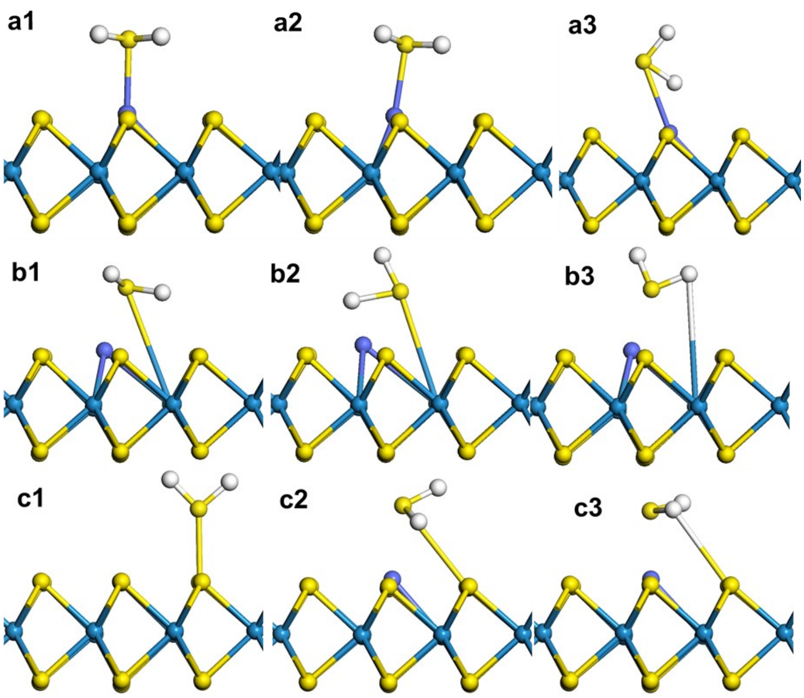

Figure S6. Various adsorption sites of H_2S with different orientations on doped-Co-WS_2.

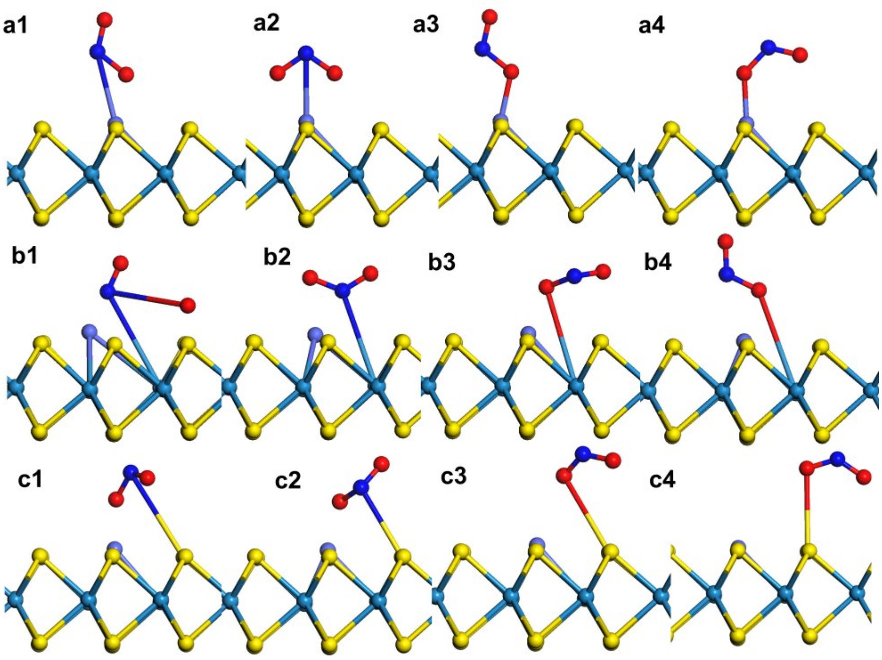

Figure S7. Various adsorption sites of NO_2 with different orientations on doped-Co-WS_2.

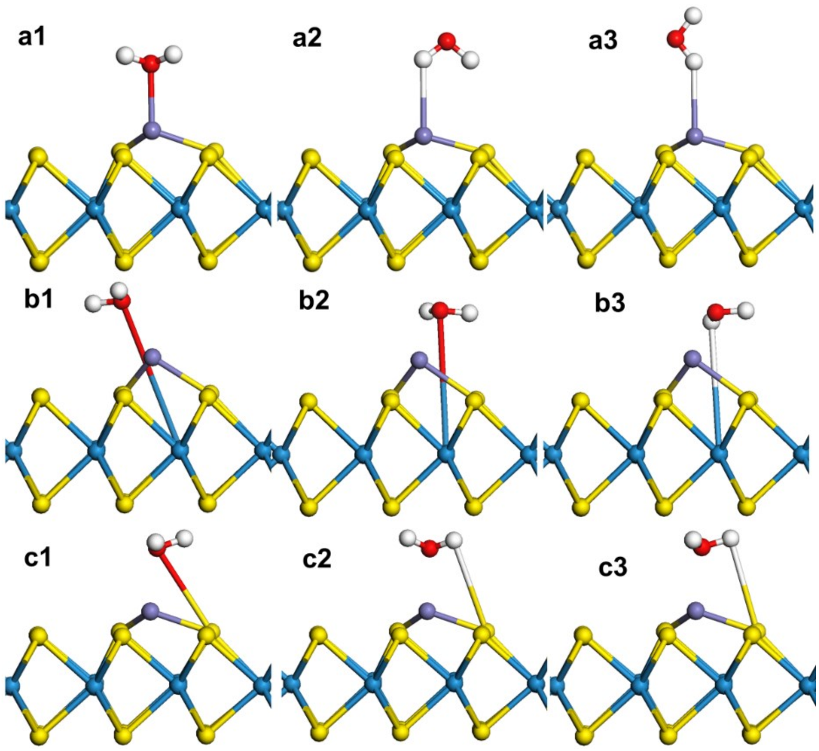

Figure S8. Various adsorption sites of H_2O with different orientations on Loaded-Fe-WS_2

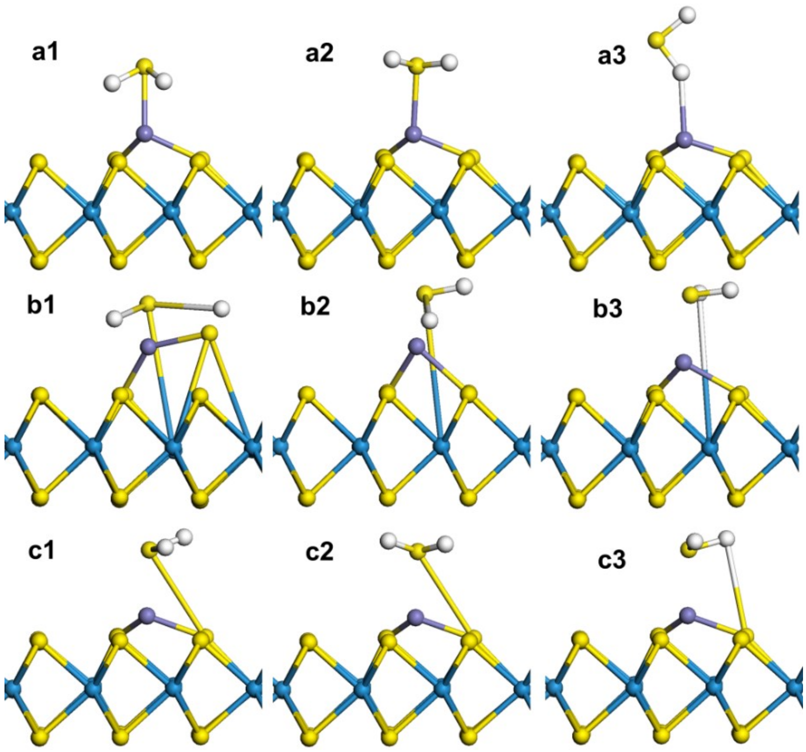

Figure S9. Various adsorption sites of H_2S with different orientations on Loaded-Fe-WS_2.

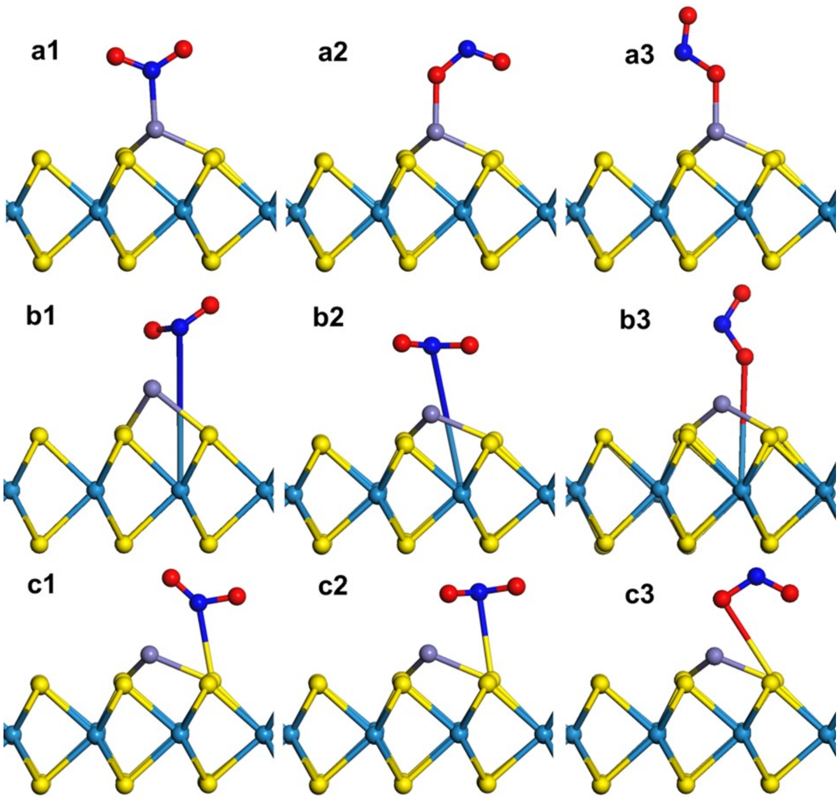

Figure S10. Various adsorption sites of NO_2 with different orientations on Loaded-Fe-WS_2.

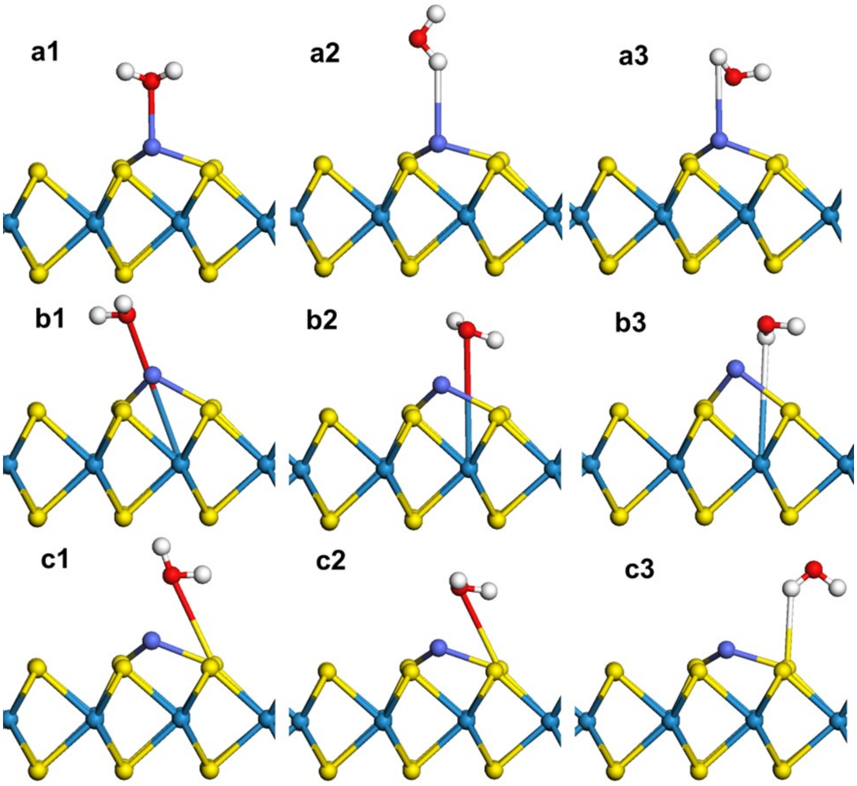

Figure S11. Various adsorption sites of H_2O with different orientations on Loaded-Co-WS_2

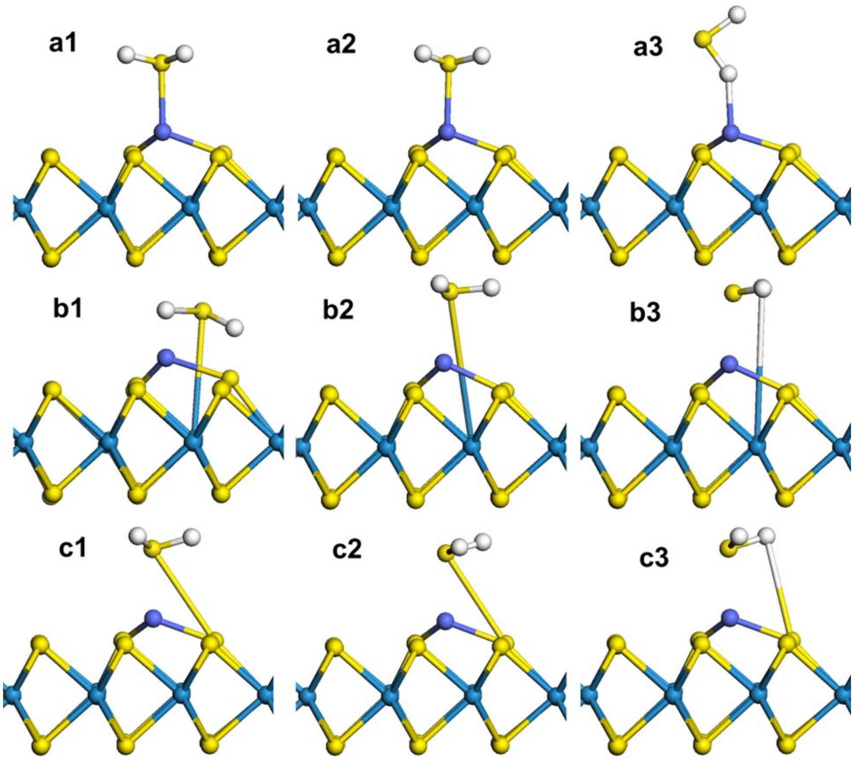

Figure S12. Various adsorption sites of H_2S with different orientations on Loaded-Co-WS_2.

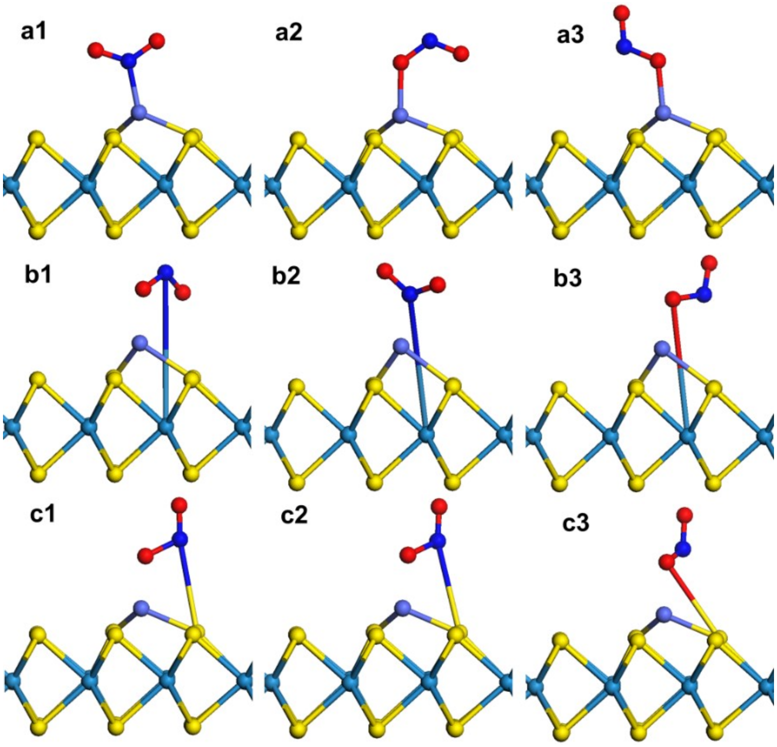

Figure S13. Various adsorption sites of NO_2 with different orientations on Loaded-Co-WS_2.

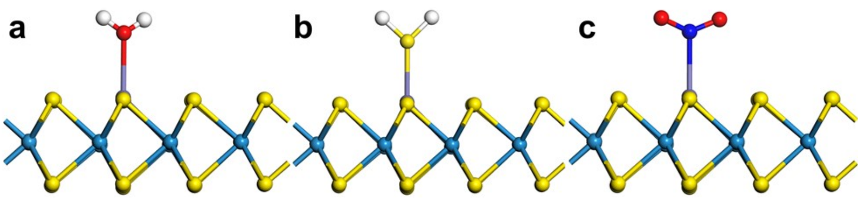

Figure S14. The initial adsorption configuration of gases H_2O, H_2S, and NO_2 on the Doped-Fe-WS_2.

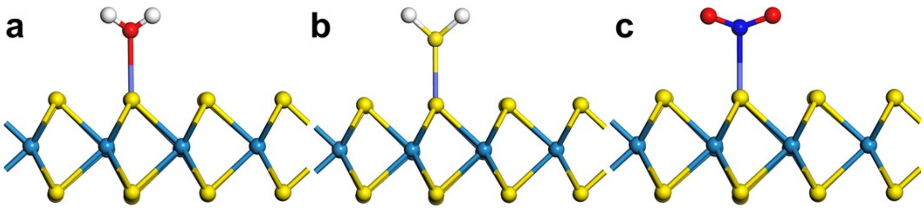

Figure S15. The initial adsorption configuration of gases H_2O, H_2S, and NO_2 on the Doped-Co-WS_2.

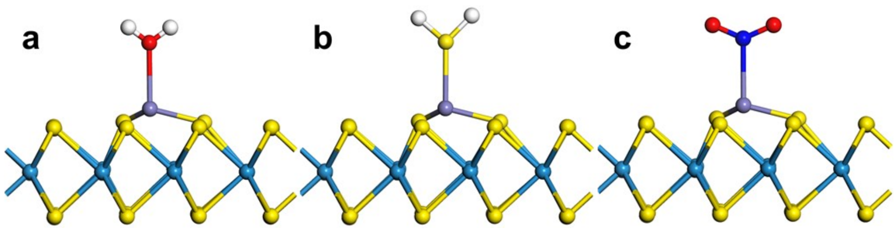

Figure S16. The initial adsorption configuration of gases H_2O, H_2S, and NO_2 on the Loaded-Fe-WS_2.

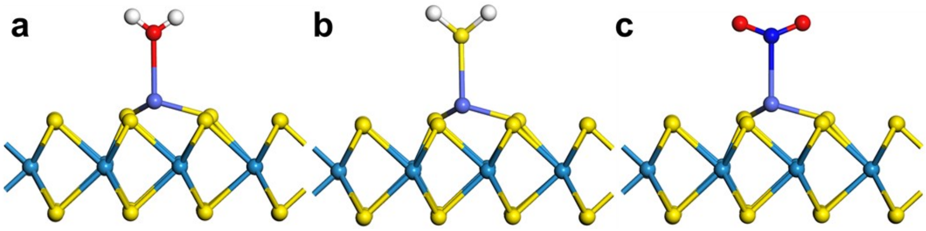

Figure S17. The initial adsorption configuration of gases H_2O, H_2S, and NO_2 on the Loaded-Co-WS_2.

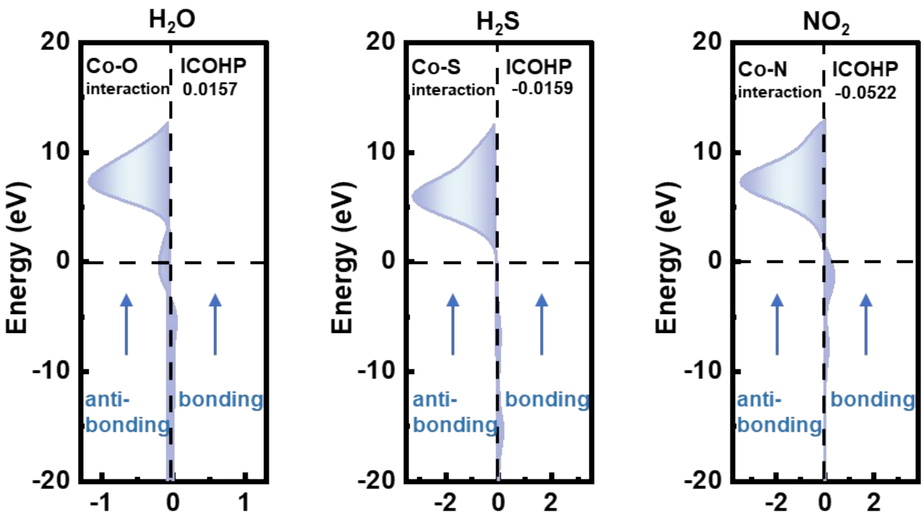

Figure S18. The COHP between gases (H_2O, H_2S, and NO_2) and the Doped-Co-WS_2.

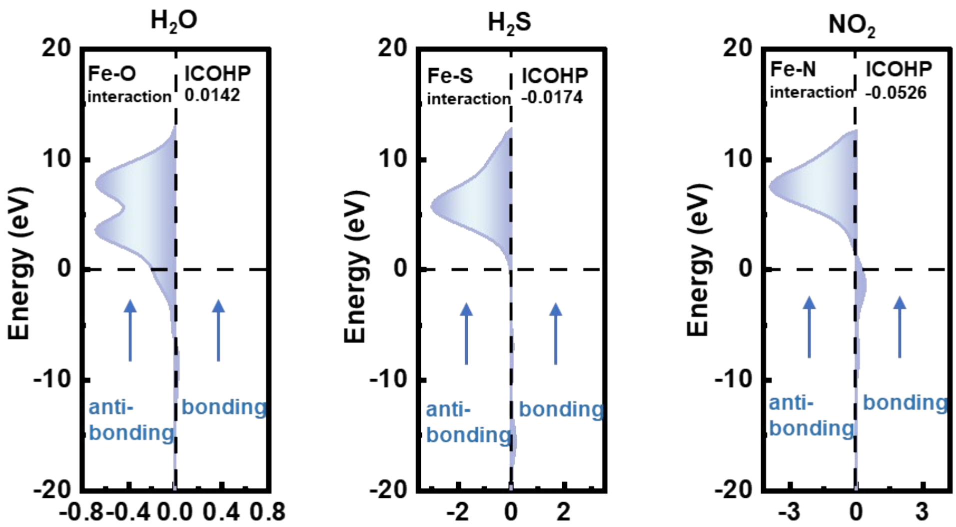

Figure S19. The COHP between gases (H_2O, H_2S, and NO_2) and the Doped-Fe-WS_2.

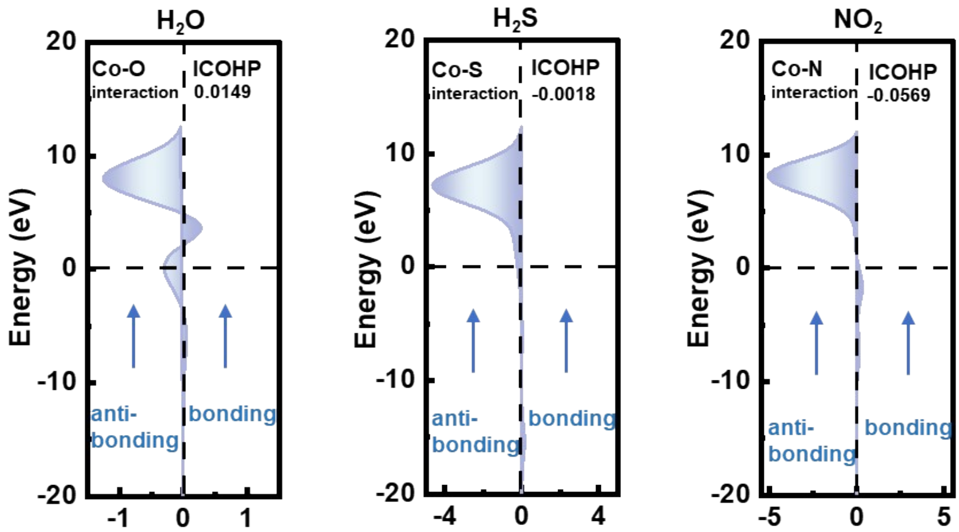

Figure S20. The COHP between gases (H_2O, H_2S, and NO_2) and the Loaded-Co-WS_2.

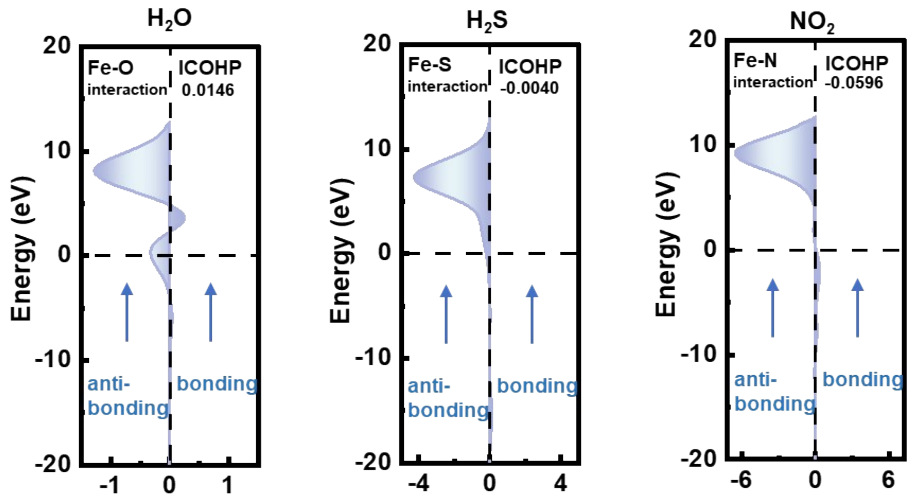

Figure S21. The COHP between gases (H_2O, H_2S, and NO_2) and the Loaded-Fe-WS_2.

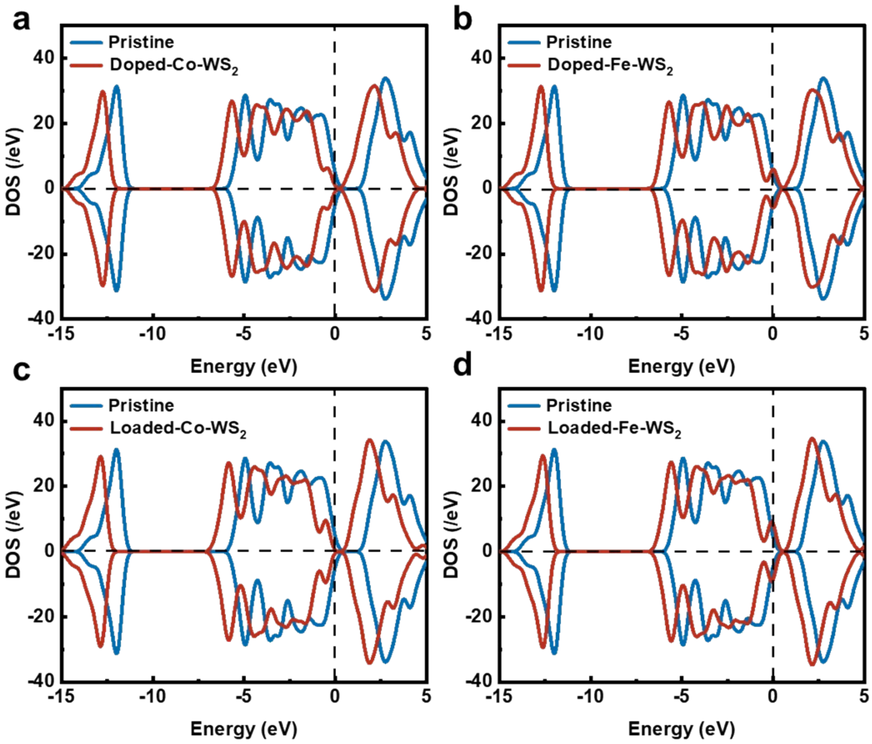

Figure S22. DOS of the (a) Doped-Co-WS_2, (b) Doped-Fe-WS_2, (c) Loaded-Co-WS_2, and (d) Loaded-Fe-WS_2 monolayer.

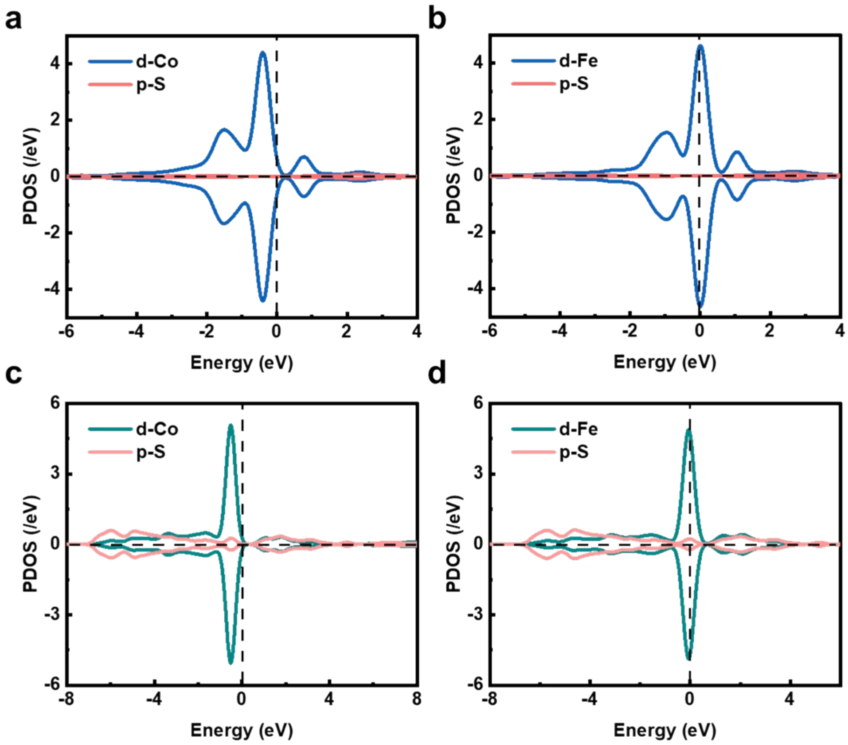

Figure S23. PDOS of the (a) Doped-Co-WS_2, (b) Doped-Fe-WS_2, (c) Loaded-Co-WS_2, and (d) Loaded-Fe-WS_2 monolayer.

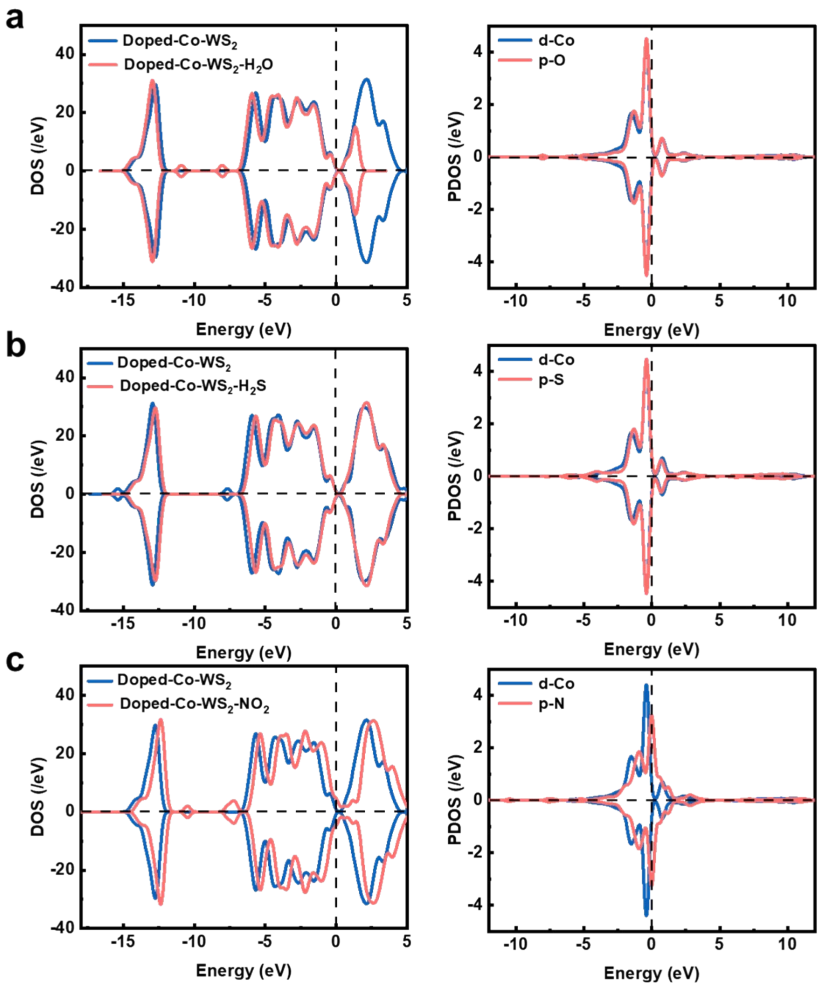

Figure S24. DOS and PDOS of (a) H_2O, (b) H_2S, and (c) NO_2 on the Doped-WS_2-Co monolayer.

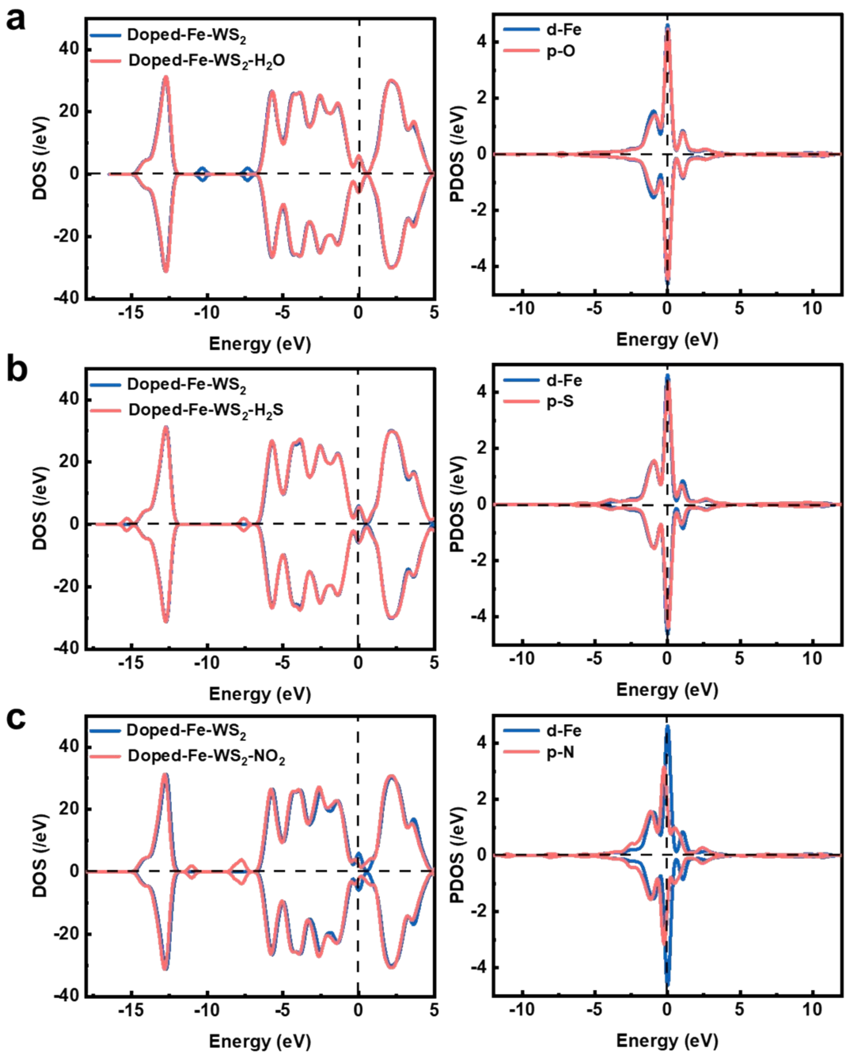

Figure S25. DOS and PDOS of (a) H_2O, (b) H_2S, and (c) NO_2 on the Doped-WS_2-Fe monolayer.

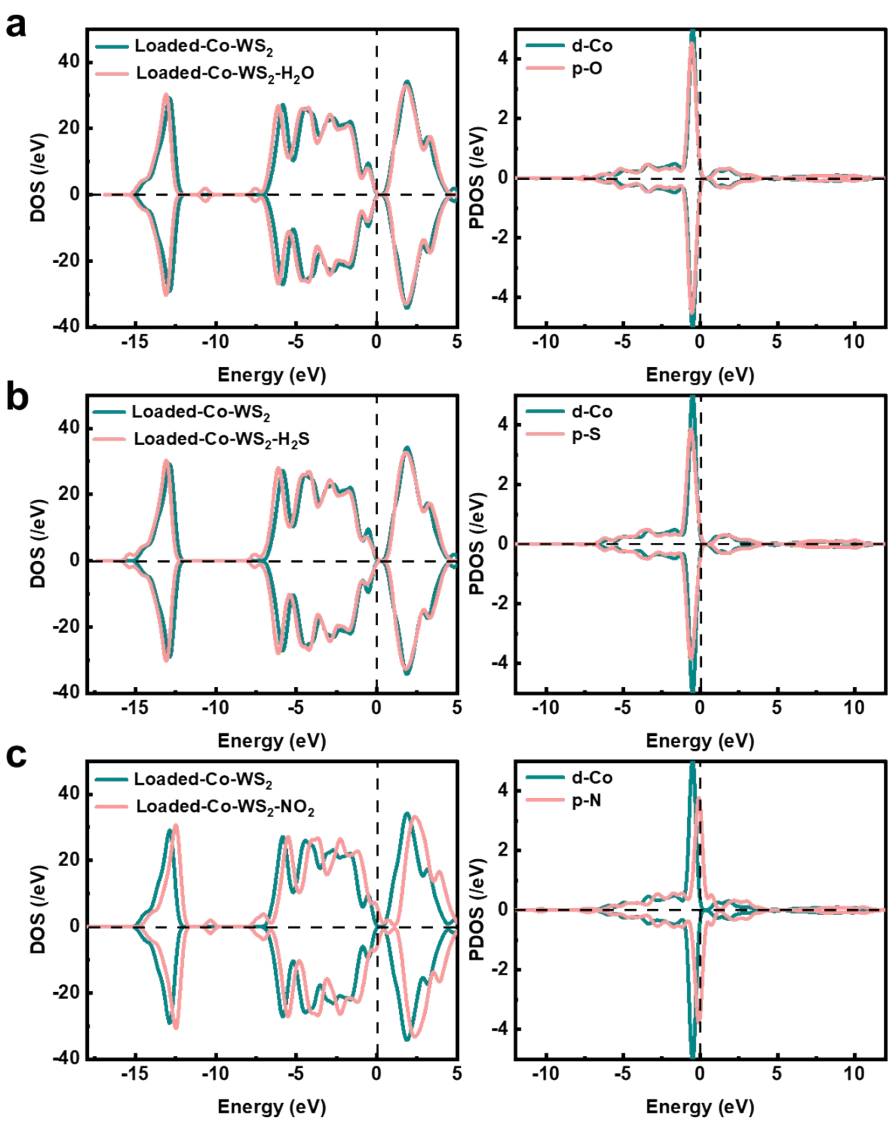

Figure S26. DOS and PDOS of (a) H_2O, (b) H_2S, and (c) NO_2 on the Loaded-WS_2-Co monolayer.

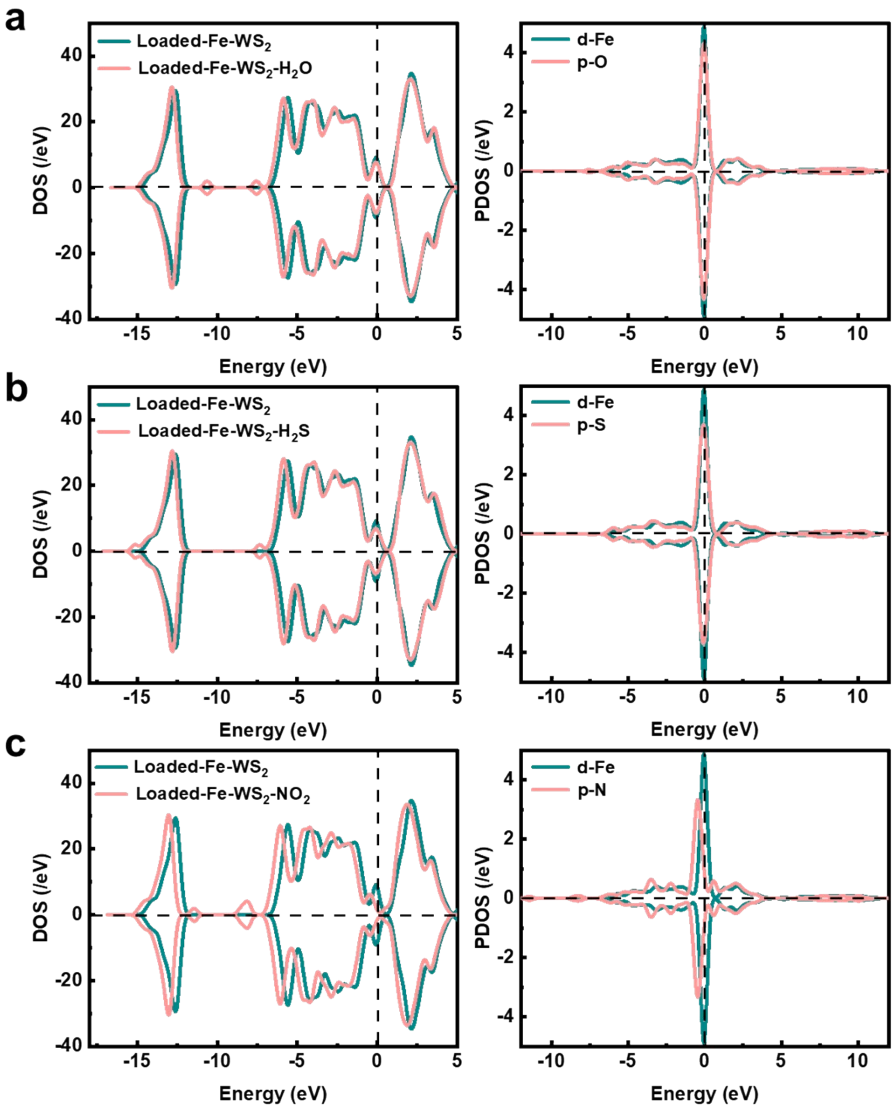

Figure S27. DOS and PDOS of (a) H_2O, (b) H_2S, and (c) NO_2 on the Loaded-WS_2-Fe monolayer.

Table S1. The amount of charge transferred by the gas adsorbed.

Gas	H_2O	NO_2	H_2S
Doped-Co-WS_2	0.11	-0.24	0.2
Doped-Fe-WS_2	0.13	-0.25	0.19
Loaded-Co-WS_2	0.14	-0.27	0.18
Loaded-Fe-WS_2	0.14	-0.30	0.15

Table S2. The recovery time (s) of the gas on the Doped-Co-WS_2.

T (K)	H_2O	H_2S	NO_2
273	1.6×10^{45}	3.24×10^{51}	7.2×10^{59}
300	1.7×10^{42}	9.0×10^{47}	3.5×10^{55}
400	4.6×10^{34}	9.2×10^{38}	4.6×10^{44}
500	1.4×10^{30}	3.7×10^{33}	1.4×10^{38}
600	1.3×10^{27}	9.5×10^{29}	6.0×10^{33}
700	9.0×10^{24}	2.6×10^{27}	4.6×10^{30}
800	2.2×10^{23}	3.0×10^{25}	2.1×10^{28}
900	1.2×10^{22}	9.7×10^{23}	3.3×10^{26}
1000	1.2×10^{21}	6.1×10^{22}	1.2×10^{25}

Table S3. The recovery time (s) of the gas on the Doped-Fe-WS_2.

T (K)	H_2O	H_2S	NO_2
273	9.4×10^{34}	3.3×10^{38}	3.9×10^{50}
300	8.1×10^{32}	1.4×10^{36}	1.3×10^{47}
400	4.8×10^{27}	1.3×10^{30}	2.2×10^{38}
500	3.5×10^{24}	3.0×10^{26}	1.2×10^{33}
600	2.8×10^{22}	1.2×10^{24}	3.6×10^{29}
700	9.1×10^{20}	2.2×10^{22}	1.1×10^{27}
800	6.9×10^{19}	1.1×10^{21}	1.5×10^{25}
900	9.3×10^{18}	1.1×10^{20}	5.1×10^{23}
1000	1.9×10^{18}	1.7×10^{19}	3.4×10^{22}

Table S4. The recovery time (s) of the gas on the Loaded-Co-WS_2.

T (K)	H_2O	H_2S	NO_2
273	1.5×10^{43}	1.9×10^{51}	1.8×10^{61}
300	2.3×10^{40}	5.5×10^{47}	6.5×10^{56}
400	1.9×10^{33}	6.4×10^{38}	4.1×10^{45}
500	1.1×10^{29}	2.8×10^{33}	7.7×10^{38}
600	1.5×10^{26}	7.4×10^{29}	2.6×10^{34}
700	1.4×10^{24}	2.0×10^{27}	1.6×10^{31}
800	4.4×10^{22}	2.5×10^{25}	6.4×10^{28}
900	2.9×10^{21}	8.2×10^{23}	8.7×10^{26}
1000	3.2×10^{20}	5.3×10^{22}	2.8×10^{25}

Table S5. The recovery time (s) of the gas on the Loaded-Fe-WS_2.

T(K)	H_2O	H_2S	NO_2
273	2.9×10^{45}	2.4×10^{53}	4.7×10^{67}
300	2.8×10^{42}	4.5×10^{49}	4.6×10^{62}
400	6.9×10^{34}	1.7×10^{40}	9.9×10^{49}
500	1.9×10^{30}	3.9×10^{34}	2.5×10^{42}
600	1.7×10^{27}	6.7×10^{30}	2.1×10^{37}
700	1.1×10^{25}	1.4×10^{28}	5.2×10^{33}
800	2.6×10^{23}	1.3×10^{26}	9.9×10^{30}
900	1.4×10^{22}	3.6×10^{24}	7.7×10^{28}
1000	1.4×10^{21}	2.0×10^{23}	1.6×10^{27}