Supporting Information

for

Activated Basal Plane of WS$_2$ by Intrinsic Defects as a Catalyst for

Electrocatalytic Nitrogen Reduction Reaction

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Computational details of formation energies

Our calculations give that $E_{\text{S(single)}} = -397.990901$ Ha, $E_{\text{W(single)}} = -137.310857$ Ha, and $E_{\text{m-WS}_2} = -933.7120494$ Ha. According to the relationship that $E_{\text{Bond}} = (E_{\text{m-WS}_2} - E_{\text{W(single)}} - 2E_{\text{S(single)}})/3$, it gives $E_{\text{Bond}} = -0.1397968$ Ha, and then $E_{\text{S0}} = -398.1306978$ Ha and $E_{\text{W0}} = -137.4506538$ Ha. Moreover, the $E_{\text{defect}}$ values have been calculated to be -14678.5807089 Ha for W$_S$, -14280.4258873 Ha for W$_{S2}$, -14541.2188587 Ha for V$_S$, and -14143.0592056 Ha for V$_{S2}$. Based on the equation that $E_f = E_{\text{defect}} - N_{\text{S}} \times E_{\text{S0}} - N_{\text{W}} \times E_{\text{W0}}$, it has $E_f = 0.1320375$, 0.1561613, 0.0432339 and 0.0721892 Ha for W$_S$, W$_{S2}$, V$_S$ and V$_{S2}$, respectively. Namely, $E_f = 3.59$ eV for W$_S$, 4.25 eV for W$_{S2}$, 1.18 eV for V$_S$, and 1.96 eV for V$_{S2}$. 
Fig. S1 The optimized structures of N\textsubscript{2} adsorbed on (a) V\textsubscript{S} and (b) V\textsubscript{S2}, including the nearest distances between any N atom and any exposed W atom.
Fig. S2 Schematic illustration of the distal, alternating, and enzymatic mechanisms for the reduction of $\text{N}_2$ to $\text{NH}_3$. 

\[
\text{N}_2 \xrightarrow{\text{end-on}} \text{NH} \xrightarrow{\text{distal}} \text{NH}_2 \xrightarrow{\text{NH}} \text{NH}_3 \\
\text{N}_2 \xrightarrow{\text{side-on}} \text{NH} \xrightarrow{\text{alternating}} \text{NH}_2 \xrightarrow{\text{NH}} \text{NH}_3 \\
\text{N}_2 \xrightarrow{\text{enzymatic}} \text{NH} \xrightarrow{\text{NH}_2} \text{NH}_3
\]
Fig. S3 Free energy profile and the corresponding geometric structures of intermediate states of NRR on $W_{S2}$ at an applied potential of 0 V for the distal mechanism.
**Fig. S4** Free energy profile and the corresponding geometric structures of intermediate states of NRR on $W_{S2}$ at an applied potential of 0 V for the alternating mechanism.
**Fig. S5** Free energy profile and the corresponding geometric structures of intermediate states of NRR on W$_{S2}$ at an applied potential of 0 V for the enzymatic mechanism. $^a$

$^a$ The adsorption of side-on adsorbed N$_2$ on W$_{S2}$ ($E_{\text{ad}} = -0.39$ eV) is weaker than that of H atom ($E_{\text{ad}} = -0.50$ eV), suggesting that the enzymatic mechanism is significantly difficult to be present for NRR on W$_{S2}$. 
Fig. S6 The top (the upper) and side views (the lower) of (a) W₄S₆ cluster and (b) W₄S₄ cluster. *

* To model the coordination environment of active W₀ atom in W₅, a tetrahedron containing as least four W atoms is required. According to the literatures,¹,² W₄S₆ is the most stable one among W₄Sₓ clusters with x = 1-12. Considering that active W atom only form bonds with W atoms while other W atoms should be bonded to as many S atoms as possible, S₁, S₂, and S₃ atoms in W₄S₆ are removed and S₇ atom is added to fabricate W₄S₄ cluster. In addition, the active W atom (Wₐ) of W₄S₄ is positive with the charge of 0.28, similar to the active W₀ atom (0.29) of W₅.
References