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


# *Supporting Information*

## Using ternary steric hindrance synergism of defective $MoS_2$ monolayer to manipulate electrocatalytic mechanism toward nitric oxide reduction: A first-principles and machine learning study

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**Figure S1**. The Gibbs free energy changes of NORR on Fe@$MoS_2$ with the different spins of Fe atom.

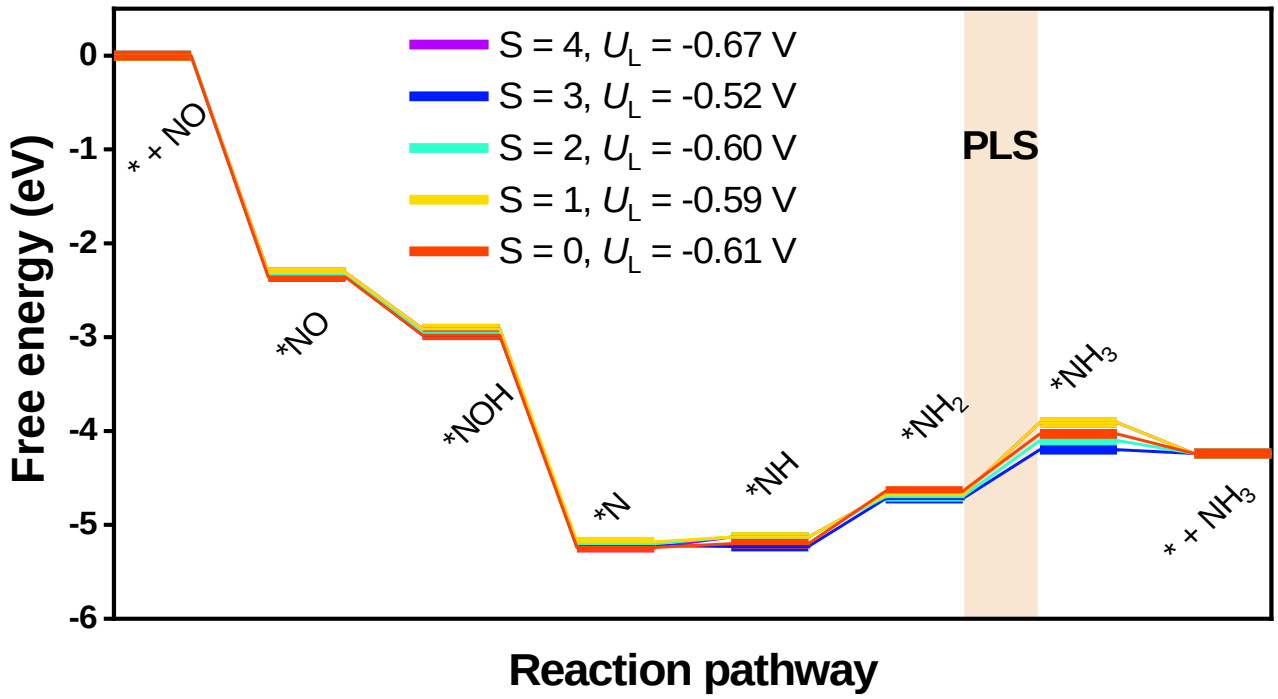

**Figure S2**. The corresponding energies (Ha) of different species adsorbed on Fe@$MoS_2$ after geometry optimization with initial spins set from 0 to 4.

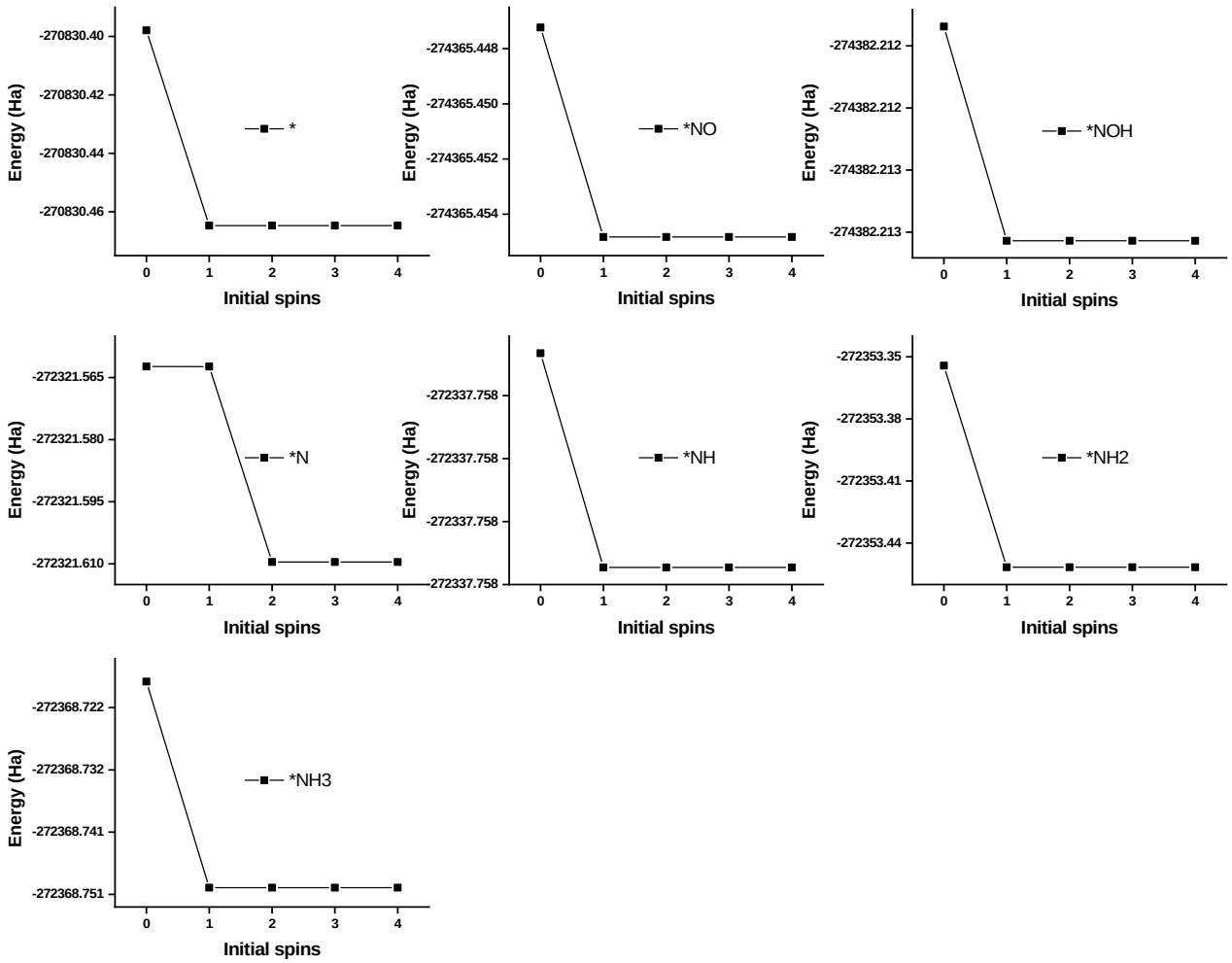

**Table S1.** The calculated $E_f$ and $U_{diss}$ of TM@$MoS_2$. (eV)

| TM | $E_f$ | $U_{diss}$ |
|---|---|---|
| Sc | -5.13 | -0.37 |
| Ti | -5.38 | 1.06 |
| V | -4.44 | 1.04 |
| Cr | -3.41 | 0.79 |
| Mn | -2.92 | 0.27 |
| Fe | -3.23 | 1.17 |
| Co | -3.37 | 1.40 |
| Ni | -2.91 | 1.20 |
| Cu | -1.48 | 1.08 |
| Zn | -1.83 | 0.16 |
| Y | -4.76 | -0.78 |
| Zr | -5.55 | -0.06 |
| Nb | -4.99 | 0.56 |
| Mo | -4.13 | 1.18 |
| Ru | -3.38 | 2.15 |
| Rh | -3.43 | 2.31 |
| Pd | -2.56 | 2.23 |
| Ag | -0.94 | 1.74 |
| Cd | -1.58 | 0.39 |
| Hf | -5.47 | -0.18 |
| Ta | -4.92 | 1.04 |
| W | -3.90 | 1.40 |
| Re | -3.28 | 1.39 |
| Os | -2.84 | 1.19 |
| Ir | -3.09 | 2.19 |
| Pt | -2.75 | 2.56 |
| Au | -1.10 | 1.87 |

**Table S2.** The Gibbs free energy changes of TM@$MoS_2$. (eV)

| TM | $\Delta G_{*NO}$ | $\Delta G_{*NOH}$ | $\Delta G_{*N}$ | $\Delta G_{*NH}$ | $\Delta G_{*NH2}$ | $\Delta G_{*NH3}$ |
|---|---|---|---|---|---|---|
| Sc | | | | | | |
| Ti | -3.11 | -3.07 | -5.62 | -5.43 | -5.06 | -4.27 |
| V | -2.93 | -3.29 | -5.60 | -5.47 | -4.90 | -3.91 |
| Cr | -2.50 | -3.30 | -5.42 | -5.53 | -4.58 | -3.80 |
| Mn | -2.13 | -2.87 | -4.98 | -5.08 | -4.14 | -3.62 |
| Fe | -2.35 | -2.98 | -5.22 | -5.23 | -4.72 | -4.20 |
| Co | -2.26 | -2.59 | -5.12 | -4.96 | -4.81 | -4.23 |
| Ni | -2.28 | -2.51 | -5.02 | -4.82 | -4.90 | -4.16 |
| Cu | -2.38 | -2.67 | -4.94 | -4.95 | -4.95 | -4.25 |
| Zn | -2.16 | -2.45 | -4.71 | -4.71 | -4.88 | -4.29 |
| Y | | | | | | |
| Zr | | | | | | |
| Nb | -2.77 | -3.19 | -5.28 | -5.39 | -4.88 | -3.84 |
| Mo | -2.34 | -3.18 | -4.89 | -5.45 | -4.27 | -3.55 |
| Ru | -2.26 | -2.83 | -4.65 | -5.05 | -4.34 | -3.91 |
| Rh | -2.15 | -2.40 | -4.58 | -4.65 | -4.64 | -4.02 |
| Pd | -2.16 | -2.32 | -4.52 | -4.51 | -4.74 | -4.02 |
| Ag | -2.25 | -2.44 | -4.20 | -4.53 | -4.92 | -4.28 |
| Cd | -2.27 | -2.32 | -3.91 | -4.24 | -5.06 | -4.36 |
| Hf | | | | | | |
| Ta | -2.76 | -3.20 | -5.40 | -5.43 | -4.84 | -3.82 |
| W | -2.29 | -3.19 | -4.91 | -5.48 | -4.19 | -3.47 |
| Re | -2.44 | -3.08 | -4.74 | -5.37 | -4.15 | -3.67 |
| Os | -2.28 | -2.88 | -4.61 | -5.11 | -3.87 | -3.88 |
| Ir | -2.01 | -2.35 | -4.54 | -4.60 | -4.45 | -3.92 |
| Pt | -2.02 | -2.11 | -4.52 | -4.32 | -4.63 | -4.01 |
| Au | -2.21 | -2.30 | -3.80 | -4.32 | -5.02 | -4.43 |

**Table S3.** The adsorption energies of $*NH_2$, $*NH_3$ and *H on TM@$MoS_2$. (eV)

| TM | $E_{*NH2}$ | $E_{*NH3}$ | $E_{*H}$ |
|---|---|---|---|
| Sc | | | |
| Ti | -4.15 | -0.96 | -1.09 |
| V | -3.99 | -0.59 | -1.00 |
| Cr | -3.63 | -0.45 | -0.81 |
| Mn | -3.28 | -0.31 | -0.50 |
| Fe | -3.87 | -0.90 | -0.89 |
| Co | -3.97 | -0.88 | -0.89 |
| Ni | -4.04 | -0.88 | -0.90 |
| Cu | -4.14 | -0.97 | -0.93 |
| Zn | -4.06 | -1.01 | -0.84 |
| Y | | | |
| Zr | | | |
| Nb | -3.98 | -0.53 | -0.99 |
| Mo | -3.29 | -0.22 | -0.57 |
| Ru | -3.50 | -0.57 | -0.70 |
| Rh | -3.81 | -0.72 | -0.81 |
| Pd | -3.90 | -0.75 | -0.86 |
| Ag | -4.06 | -1.01 | -0.83 |
| Cd | -4.21 | -1.07 | -0.93 |
| Hf | | | |
| Ta | -3.90 | -0.50 | -0.98 |
| W | -3.21 | -0.14 | -0.51 |
| Re | -3.17 | -0.35 | -0.51 |
| Os | -2.87 | -0.51 | -0.58 |
| Ir | -3.66 | -0.63 | -0.72 |
| Pt | -3.79 | -0.68 | -0.79 |
| Au | -4.15 | -1.16 | -0.85 |

**Table S4.** The calculated novel descriptor **Ω**.

| TM | **Ω** |
|---|---|
| Sc | |
| Ti | 4.28 |
| V | 4.40 |
| Cr | 4.00 |
| Mn | 3.47 |
| Fe | 3.87 |
| Co | 3.98 |
| Ni | 4.05 |
| Cu | 4.10 |
| Zn | 3.89 |
| Y | |
| Zr | |
| Nb | 4.45 |
| Mo | 3.64 |
| Ru | 3.63 |
| Rh | 3.90 |
| Pd | 4.01 |
| Ag | 3.88 |
| Cd | 4.06 |
| Hf | |
| Ta | 4.38 |
| W | 3.58 |
| Re | 3.33 |
| Os | 2.94 |
| Ir | 3.75 |
| Pt | 3.90 |
| Au | 3.84 |

**Table S5.** The calculated Δ*ZPE* and TΔ*S* values of TM@$MoS_2$. (eV)

| TM | *NO<br>ΔZPE/TΔS | *NOH<br>ΔZPE/TΔS | *N<br>ΔZPE/TΔS | *NH<br>ΔZPE/TΔS | *$NH_2$<br>ΔZPE/TΔS | *$NH_3$<br>ΔZPE/TΔS |
|---|---|---|---|---|---|---|
| Sc | | | | | | |
| Ti | 1.92/2.26 | 2.17/2.29 | 1.81/2.23 | 2.09/2.24 | 2.41/2.25 | 2.73/2.33 |
| V | 1.92/2.25 | 2.18/2.34 | 1.82/2.23 | 2.11/2.24 | 2.41/2.25 | 2.73/2.35 |
| Cr | 1.87/2.31 | 2.19/2.27 | 1.81/2.23 | 2.13/2.22 | 2.39/2.28 | 2.72/2.38 |
| Mn | 1.87/2.32 | 2.19/2.31 | 1.80/2.25 | 2.12/2.24 | 2.43/2.28 | 2.71/2.36 |
| Fe | 1.87/2.35 | 2.18/2.33 | 1.78/2.23 | 2.11/2.25 | 2.44/2.26 | 2.72/2.36 |
| Co | 1.90/2.32 | 2.16/2.37 | 1.78/2.22 | 2.09/2.28 | 2.44/2.26 | 2.71/2.40 |
| Ni | 1.89/2.34 | 2.19/2.34 | 1.79/2.25 | 2.08/2.28 | 2.43/2.27 | 2.70/2.32 |
| Cu | 1.87/2.37 | 2.17/2.37 | 1.74/2.34 | 2.06/2.31 | 2.40/2.32 | 2.68/2.42 |
| Zn | 1.84/2.44 | 2.14/2.44 | 1.74/2.37 | 2.04/2.36 | 2.38/2.37 | 2.67/2.47 |
| Y | | | | | | |
| Zr | | | | | | |
| Nb | 1.93/2.26 | 2.18/2.35 | 1.82/2.22 | 2.12/2.23 | 2.41/2.25 | 2.74/2.35 |
| Mo | 1.88/2.30 | 2.20/2.27 | 1.81/2.24 | 2.14/2.21 | 2.38/2.29 | 2.73/2.35 |
| Ru | 1.88/2.33 | 2.19/2.32 | 1.78/2.31 | 2.12/2.25 | 2.44/2.28 | 2.72/2.41 |
| Rh | 1.89/2.34 | 2.17/2.37 | 1.79/2.27 | 2.09/2.29 | 2.44/2.27 | 2.71/2.36 |
| Pd | 1.88/2.36 | 2.17/2.38 | 1.78/2.30 | 2.07/2.30 | 2.43/2.29 | 2.70/2.35 |
| Ag | 1.84/2.46 | 2.14/2.46 | 1.73/2.39 | 2.04/2.40 | 2.37/2.39 | 2.67/2.47 |
| Cd | 1.85/2.43 | 2.14/2.45 | 1.73/2.39 | 2.05/2.37 | 2.39/2.37 | 2.67/2.45 |
| Hf | | | | | | |
| Ta | 1.92/2.27 | 2.18/2.36 | 1.82/2.25 | 2.12/2.26 | 2.38/2.29 | 2.72/2.37 |
| W | 1.87/2.33 | 2.19/2.29 | 1.81/2.26 | 2.13/2.24 | 2.38/2.30 | 2.72/2.36 |
| Re | 1.88/2.32 | 2.18/2.31 | 1.80/2.27 | 2.12/2.26 | 2.39/2.32 | 2.73/2.36 |
| Os | 1.88/2.34 | 2.19/2.34 | 1.79/2.31 | 2.12/2.27 | 2.38/2.34 | 2.72/2.40 |
| Ir | 1.89/2.36 | 2.17/2.40 | 1.80/2.26 | 2.10/2.32 | 2.45/2.28 | 2.72/2.42 |
| Pt | 1.89/2.36 | 2.17/2.40 | 1.79/2.29 | 2.09/2.31 | 2.44/2.30 | 2.71/2.43 |
| Au | 1.84/2.46 | 2.13/2.45 | 1.73/2.43 | 2.06/2.37 | 2.37/2.39 | 2.68/2.47 |