Electronic Supplementary Information

A DFT Screening of Single Transition Atoms Supported on MoS_2 as Highly Efficient Electrocatalysts for Nitrogen Reduction Reaction†

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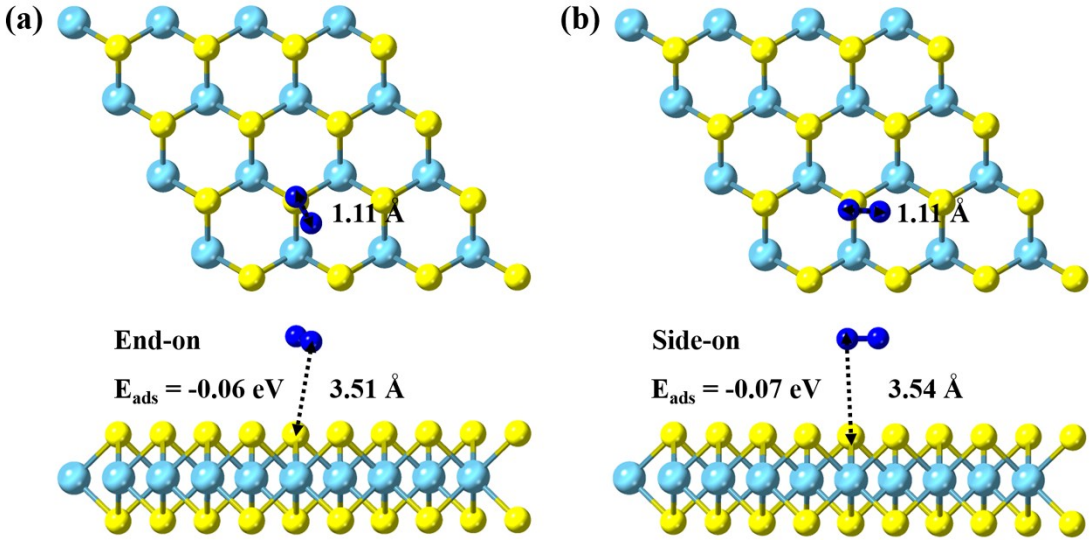

Figure S1. Top and side view of the optimized geometric structures of the adsorption of N_2 on S site of MoS_2 by the (a) end-on and (b) side-on patterns. The adsorption energies of N_2, N-N bond lengths and N-S distances are also presented. The blue, cyan and yellow balls represent N, Mo and S atoms, respectively. The N-S distances are 3.51 Å and 3.54 Å, respectively, for end-on and side-on patterns, indicating that N_2 cannot be effectively activated due to weak interactions between the N_2 and S atom. This was confirmed by the unchanged bond length of N≡N (1.11 Å) and the small adsorption energy of N_2 on S-top-site for end-on and side-on patterns, respectively (-0.06 eV and -0.07 eV).

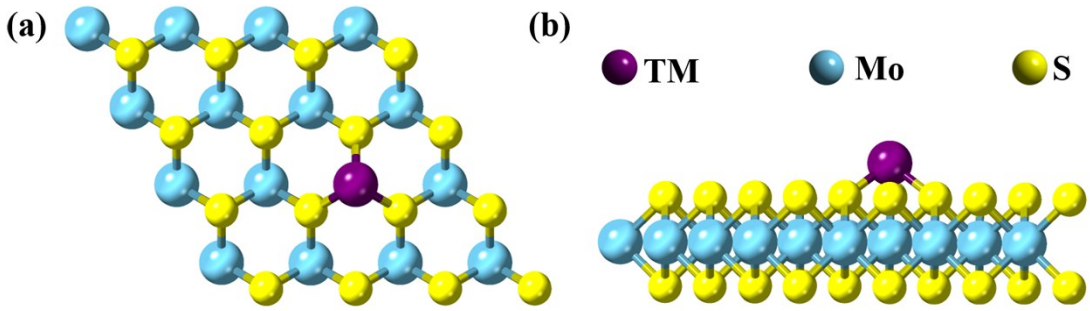

Figure S2. (a) Top and (b) side view of TM@MoS_2, where purple, cyan and yellow balls represent TM, Mo and S atoms, respectively.

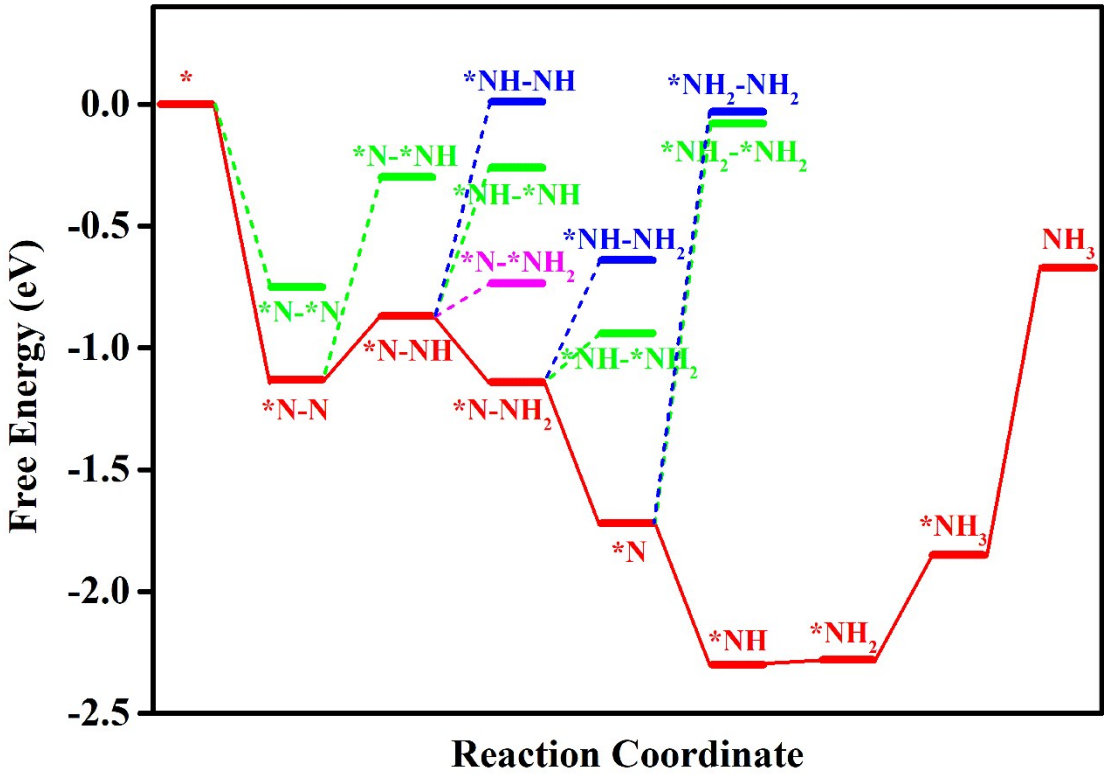

Figure S3. Gibbs energy profiles of NRR processes at U = 0 V for Re@MoS_2. The solid red line indicates the favorable pathway.

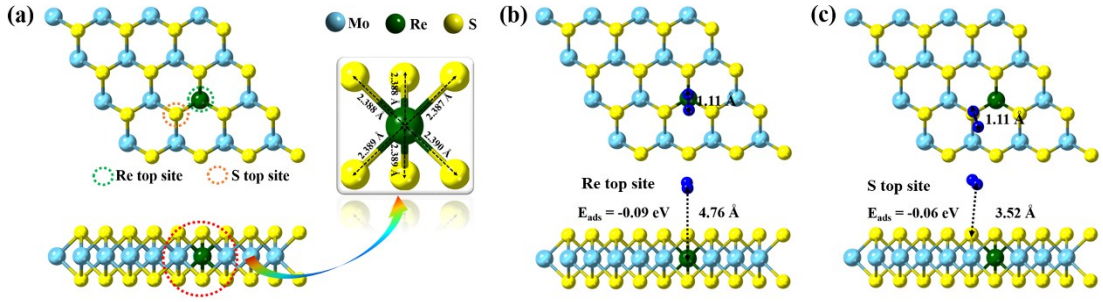

Figure S4. (a) Top and side view of the optimized geometric structures of the Re substitutionally doped MoS_2. The Re-S bond lengths and possible active sites (Re top site and S top site) are presented. Top and side view of the optimized geometric structures of the adsorption of N_2 on Re substitutionally doped MoS_2 by the (b) Re-top-site and (c) S-top-site patterns. The adsorption energies of N_2, N-N bond lengths and N-S distances are also presented. The green, blue, cyan and yellow balls represent Re, N, Mo and S atoms, respectively. The structure of Re substitutionally doped MoS_2 are shown in Figure S4. The Re-top-site and S-top-site were considered as possible active sites for N_2 activation. The long N-Re distance (4.76 Å) and N-S distance (3.52 Å) indicate that N_2 cannot be effectively activated due to weak interactions between N_2 and the substrate. This was also confirmed by the unchanged bond length of N≡N (1.11 Å) and the low adsorption energy of N_2 at the Re-top-site (-0.09 eV) and S-top-site (-0.06 eV), respectively.

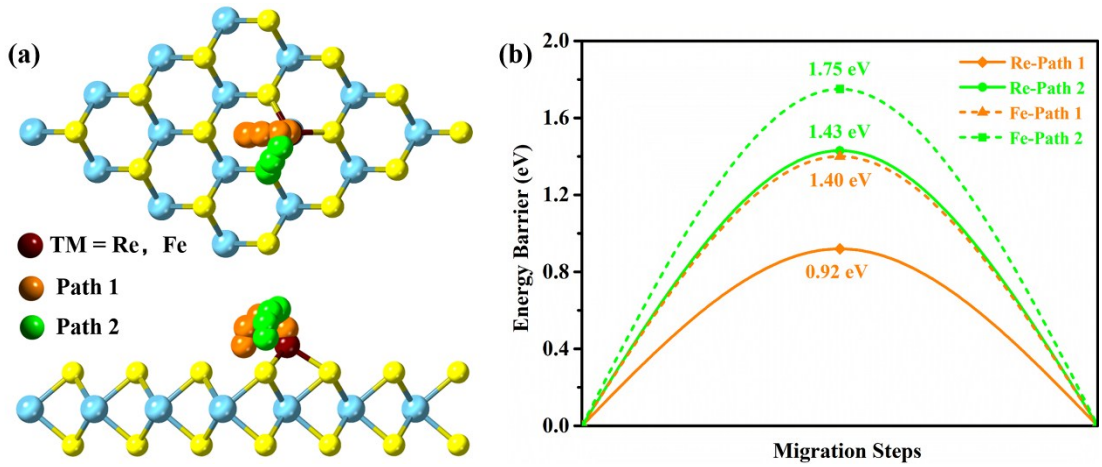

Figure S5. (a) Top and side views of the migration paths for Re and Fe atoms on MoS_2 surface and (b) corresponding migration energy barrier profiles. Two possible migration paths (Figure S5) of Re atom are considered, i.e., path 1 and path 2. The path1 and path 2 are the migration process of TM (TM = Re and Fe) atom from Mo-top-site to hollow and S site, respectively. The migration energy barriers of recently synthesized Fe supported on MoS_2 were also calculated for comparison on same migration paths.

Table S1. The calculated ZPE and TS value of different species, where the label * denotes the status of adsorption.

Adsorbed species (Re@MoS_2)	E_{ZPE} (eV)	TS (eV)
N_2	0.15	0.59
*N-N	0.21	0.08
*N-NH	0.47	0.12
*N-NH_2	0.81	0.13
*N	0.08	0.08
*NH	0.35	0.08
*NH_2	0.67	0.11
*NH_3	1.04	0.13
*NH-NH	0.81	0.08
*NH-NH_2	1.14	0.17
*NH_2-NH_2	1.49	0.18
*N-*N	0.19	0.07
*N-*NH	0.49	0.08
N-NH_2	0.84	0.10
*NH-*NH	0.77	0.06
NH-NH_2	1.15	0.13
NH_2-NH_2	1.48	0.09
H_2	0.27	0.40
NH_3	0.91	0.60

Adsorbed species (Ti@MoS_2)	E_{ZPE} (eV)	TS (eV)
N_2	0.15	0.59
*N-*N	0.18	0.16
*N-*NH	0.48	0.16
*NH-*NH	0.74	0.14
NH-NH_2	1.14	0.13
NH_2-NH_2	1.47	0.24
*NH_2	0.63	0.17
*NH_3	1.02	0.17
H_2	0.27	0.40
NH_3	0.91	0.60