Supporting Information

Nitrogen Electroreduction Performance of Transition Metal Dimers Embedded into N-Doped Graphene: A Theoretical Prediction

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Table S1. The calculated entropy correction (*TS*, eV) of different reaction intermediates of NRR on FeRh@NPG and its effects on the free energy change (ΔG_{with} and $\Delta G_{without}$) of each elementary reaction along the distal and alternative mechanisms,.

Adsorption Intermediates	*-TS*	elementary reaction	ΔG_{with}	$\Delta G_{without}$
N_2^*	–0.19	$N_2 \rightarrow N_2^*$	–0.49	–0.30
N_2H^*	–0.13	$N_2^* \rightarrow N_2H^*$	**0.28**	**0.22**
$N\text{-}NH_2^*$	–0.12	$N_2H^* \rightarrow N\text{-}NH_2^*$	0.06	0.05
N^*	–0.04	$N\text{-}NH_2^* \rightarrow N^* + NH_3$	–0.22	–0.30
NH^*	–0.09	$N^* \rightarrow NH^*$	–0.46	–0.41
NH_2^*	–0.14	$NH^* \rightarrow NH_2^*$	–1.39	–1.34
NH_3^*	–0.16	$NH_2^* \rightarrow NH_3^*$	–0.07	–0.05
		$NH_3^* \rightarrow NH_3$	1.30	1.14
$NH\text{-}NH^*$	–0.15	$N_2H^* \rightarrow NH\text{-}NH^*$	0.51	0.53
$NH\text{-}NH_2^*$	–0.17	$NH\text{-}NH^* \rightarrow NH\text{-}NH_2^*$	–1.01	–0.99
$NH_2\text{-}NH_2^*$	–0.25	$NH\text{-}NH_2^* \rightarrow NH_2\text{-}NH_2^*$	0.78	0.86
		$NH_2\text{-}NH_2^* \rightarrow NH_2^* + NH_3$	–2.29	–2.40

Table S2. The comparson between the binding energies of BACs on NPG and the cohesive energies of the relevant individual metal atoms.

M_1M_2	E_b	E_c (exp.)[a]	E_c (calc.)
Fe<u>Fe</u>	-10.72	-4.30/-4.30	-4.83/-4.83
Fe<u>Co</u>	-10.42	-4.30/-4.40	-4.83/-4.85
Fe<u>Ni</u>	-10.55	-4.30/-4.40	-4.83/4.64
Fe<u>Cu</u>	-9.65	-4.30/-3.50	-4.83/-3.86
Fe<u>Rh</u>	-9.47	-4.30/-5.80	-4.83/-5.80
Fe<u>Ru</u>	-9.91	-4.30/-6.70	-4.83/-7.24
Fe<u>Pd</u>	-8.32	-4.30/-3.90	-4.83/4.14
<u>Mo</u>Fe	-9.04	-6.80/-4.30	-6.83/-4.83
<u>Mo</u>Co	-9.20	-6.80/-4.40	-6.83/-4.85
<u>Mo</u>Cu	-7.28	-6.80/-3.50	-6.83/-3.86
<u>Mo</u>Ru	-8.02	-6.80/-6.70	-6.83/-7.24
<u>Mo</u>Mo	-6.99	-6.80/-4.30	-6.83/-6.83

[a)] The present experimental values E_c (exp.) were taken from Kittel and C., *Introduction to solid state physics*, Wiley in 2005.

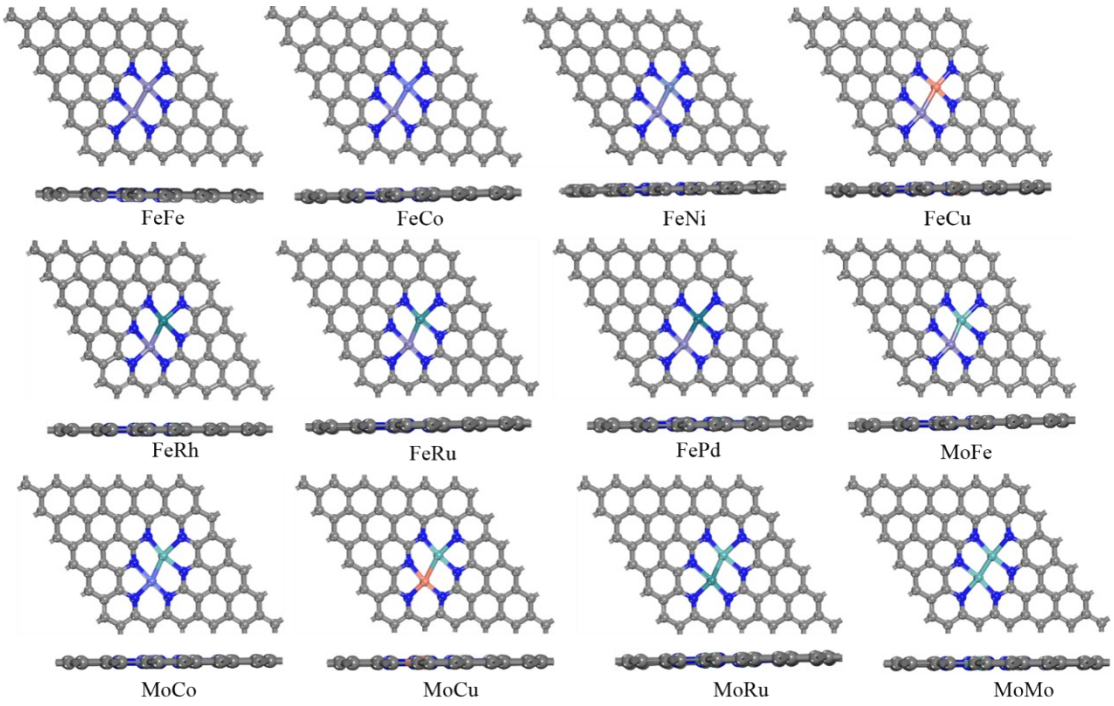


Fig. S1. The optimized configurations of metal dimers embedded into N-doped porous graphene. Both top and side views were provided.

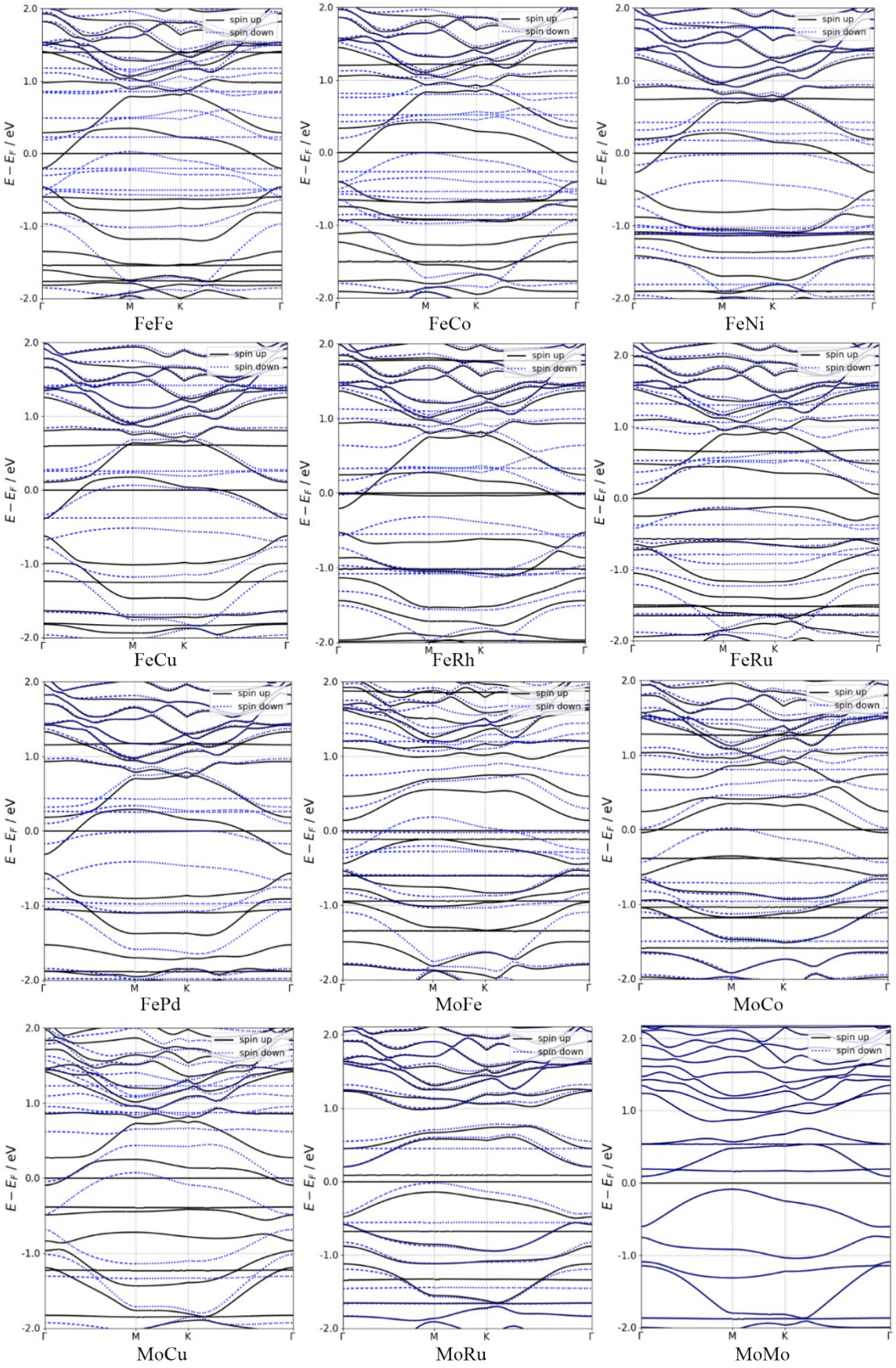


Fig. S2. The computed band structures of various BACs@NPG. The Fermi level was set to zero.

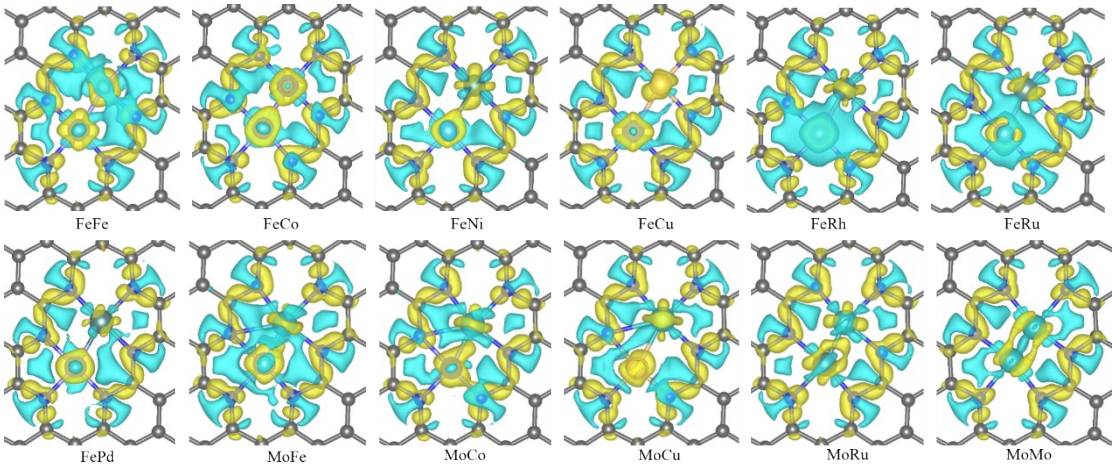


Fig. S3. The differential charge density distribution of BACs@NPG at isosurfaces of ±0.01 e/Å^3. The charge accumulation and depletion are denoted by cyan and yellow colors, respectively.

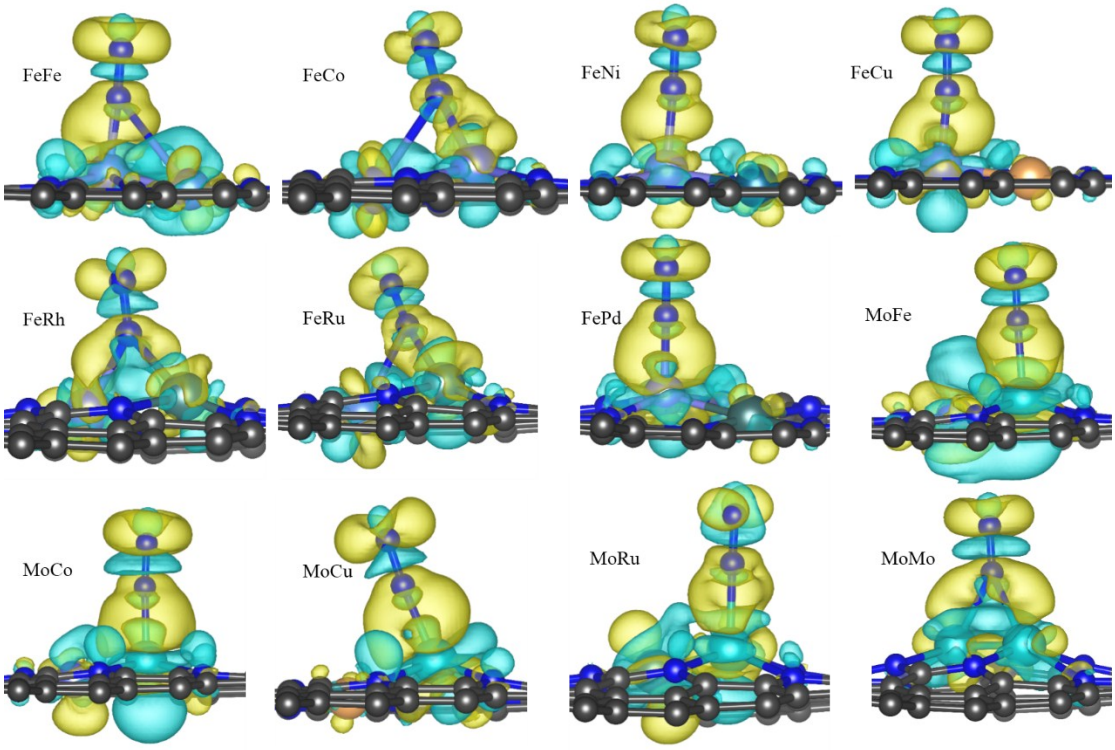


Fig. S4. The differential charge density distribution of N_2 molecule adsorbed on these BACs@NPG at isosurfaces of ±0.01 e/Å^3. The charge accumulation and depletion are denoted by cyan and yellow colors, respectively.

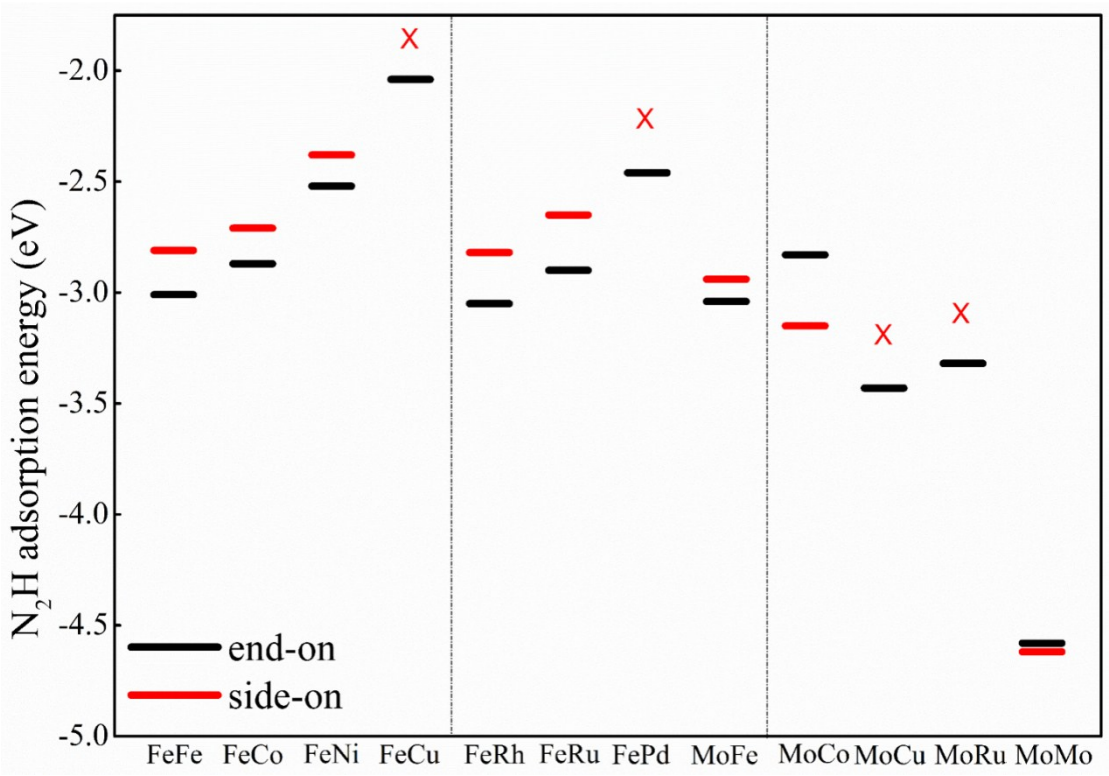


Fig. S5. The computed adsorption energies of N_2H^* species on various BACs@NPG via end-on and side-on patterns. X represents the unstable adsorption configurations.

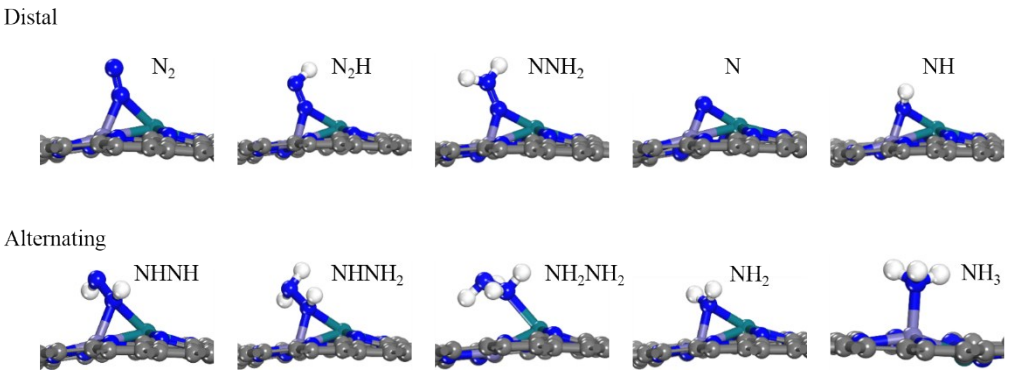


Fig. S6. The involved eNRR intermediates along distal and alternating pathways.

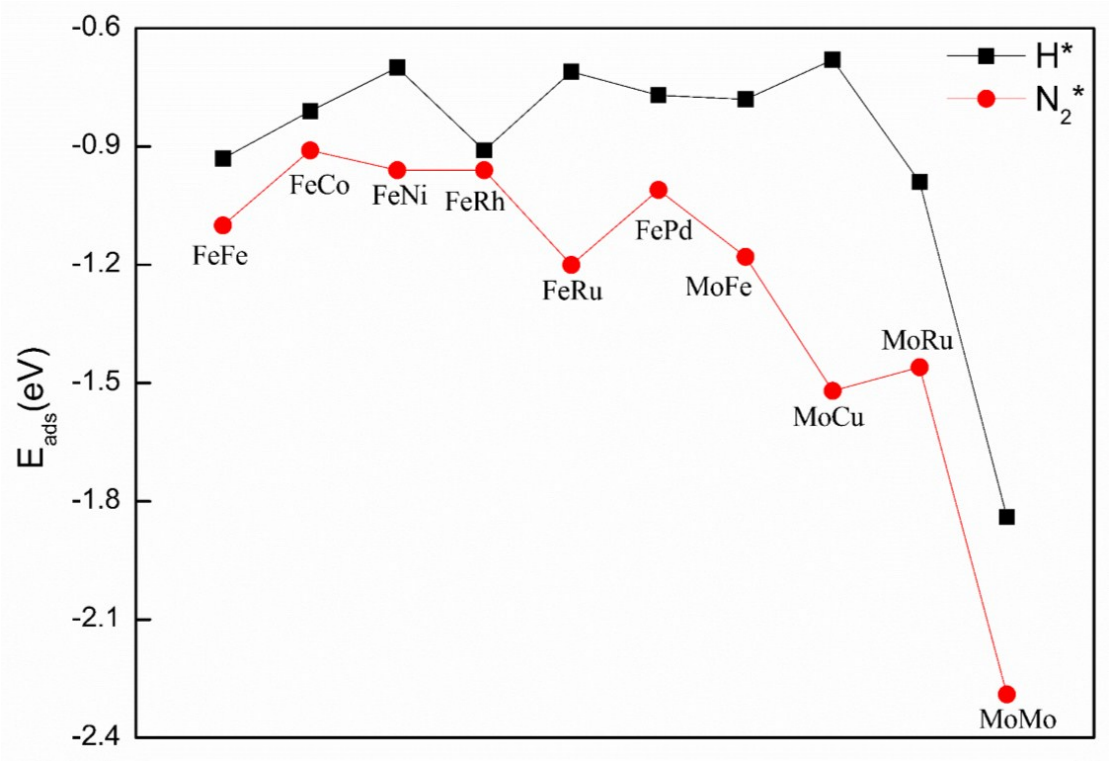


Fig. S7. The computed adsorption energies of H^* and N_2 on BACs@NPG.

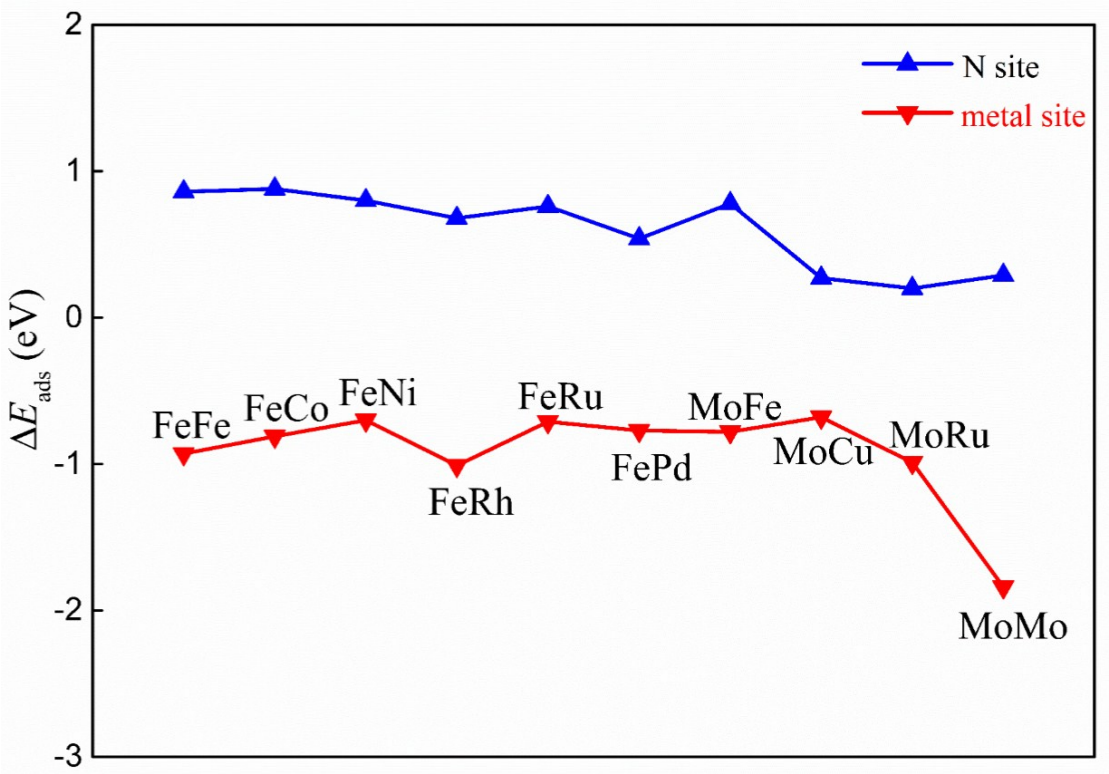


Fig. S8. The computed adsorption energies of H^* on N and metal sites of various BACs@NPG.

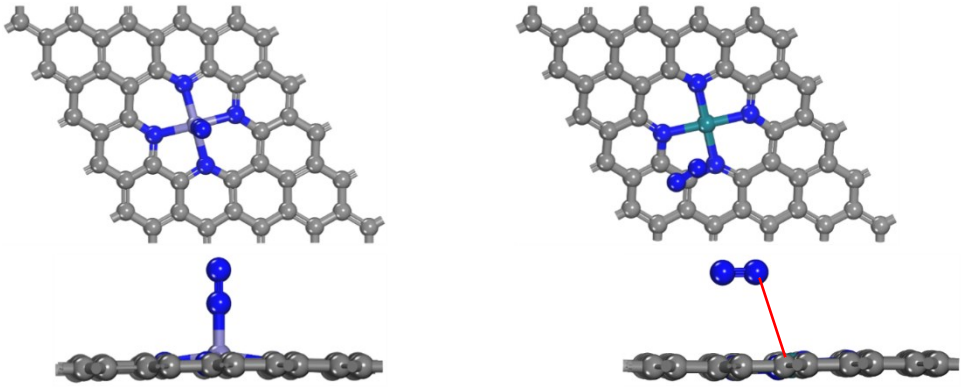


Fig. S9. The optimized adsorption configurations of N_2 molecule on single (a) Fe and (b) Rh atom supported on N-doped graphene.

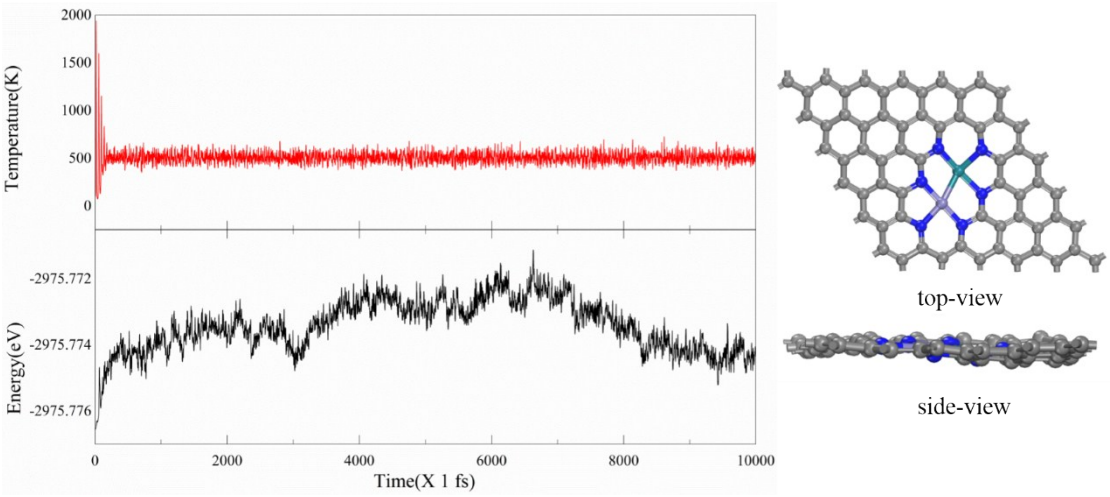
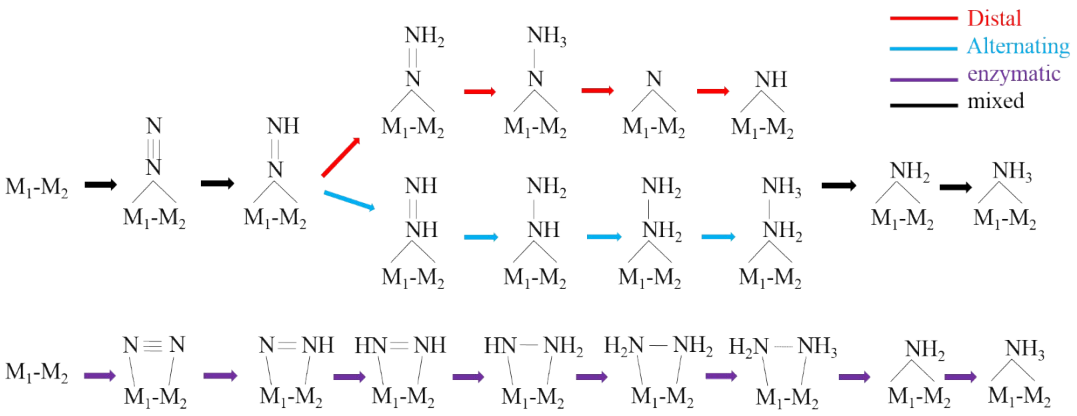


Fig. S10. Variations of temperature and energy against time for MD simulations of the FeRh@NPG, and the insets show top and side views of the snapshot of the atomic configuration. The simulation is run at 500 K for 10 ps with a time step of 1 fs.



Scheme S1. The possible reaction mechanisms for eNRR on DACs@NPG