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

Supporting Information

Rational design of Fe cluster catalyst for robust nitrogen activation

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Supporting Note 1: The spin of Fe atom

According to the number of unpaired electrons in the d band of Fe, the initial spins of Fe atom were set from 0 to 4, respectively. As results, all the systems were convergence to the same spin of Fe_4 at 10.25 μ_B with the same energy. Therefore, an initial spin of 3 was set to each Fe atom in this work.

Then, different spin configurations are considered, including ferromagnetic state (FS), antiferromagnetic state (AS), and nonmagnetic state (NS). As results, the FS is the most stable spin configuration, whose energy is 2.51 eV lower than NS, and the AS is transformed to FS after geometry optimization. Therefore, only FS configuration is considered in this work.

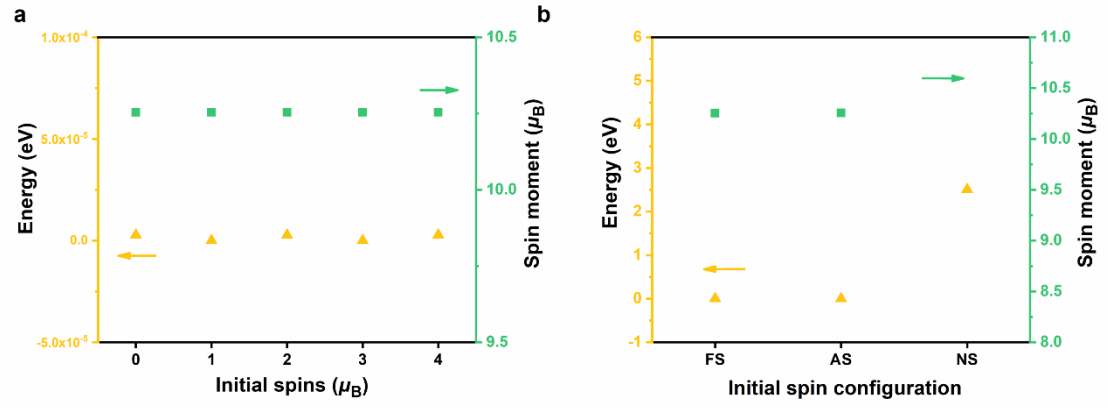

Fig. S1 (a) The corresponding energies (in eV) and spin moments (in μ_B) after geometry optimization with initial spins set from 0 to 4. (b) The energy (in eV) and spin moments (in μ_B) of different spin configurations.

Supporting Note 2: The calculation of threshold potential U_n

The threshold potential U_n for leaching one metal atom from Fe_4/GaS is determined by the methods proposed in reference 82 in the text part.

The leaching process is investigated with differential leaching steps for a Fe_n cluster anchored on the substrate

$$Fe_n/GaS = Fe_{n-1}/GaS + Fe^{2+}(aq) + 2e^- \qquad (1)$$

Thus, the corresponding reaction energies at a certain applied potential U can be written as

$$\Delta E(Fe_n - Fe_{n-1}) = E(Fe_{n-1}/GaS) + E(Fe^{2+}(aq)) - E(Fe_n/GaS) + 2eU \qquad (2)$$

However, the linear coefficient for U dependence and $E(Fe_n/GaS)$ is neglect since the limit potential (U_L) in this work is low. The free energies of solvated cations $E(Fe^{2+}(aq))$ from the experimental standard reduction potentials U_0 and the calculated free energies of bulk metals $E(Fe(s))$ is calculated by

$$E(Fe^{2+}(aq)) = E(Fe(s)) - 2eU_0 \qquad (3)$$

The U_0's of Fe element is from CRC *handbook of chemistry and physic* at − 0.447 V. Combining eqs 2 and 3, one derives

$$\Delta E(Fe_n - Fe_{n-1}) = 2eU + E(Fe_{n-1}/GaS) - E(Fe_n/GaS) + E(Fe(s)) - 2eU_0 \qquad (4)$$

When $\Delta E(Fe_n - Fe_{n-1}) < 0$, the leaching step is taking place spontaneously. Thus, the threshold potential U_n for leaching one metal atom from Fe_n/GaS is

$$U_n = (E(Fe_{n-1}/GaS) + 2eU_0 - E(Fe_n/GaS) - E(Fe(s)) / 2e \qquad (5)$$

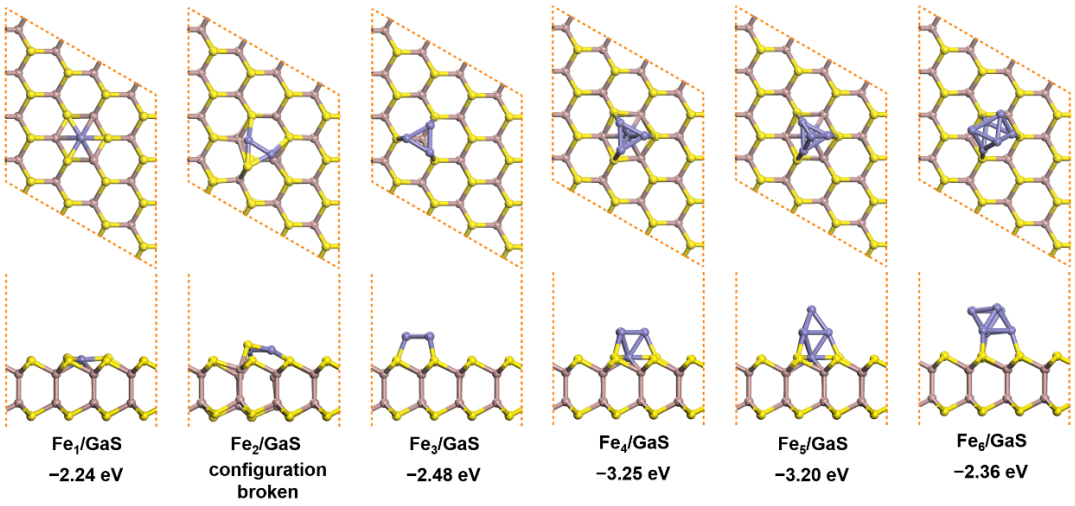

Fig. S2 Optimized structure of Fe_n/GaS (n = 1 ~ 6) with the corresponding binding energies.

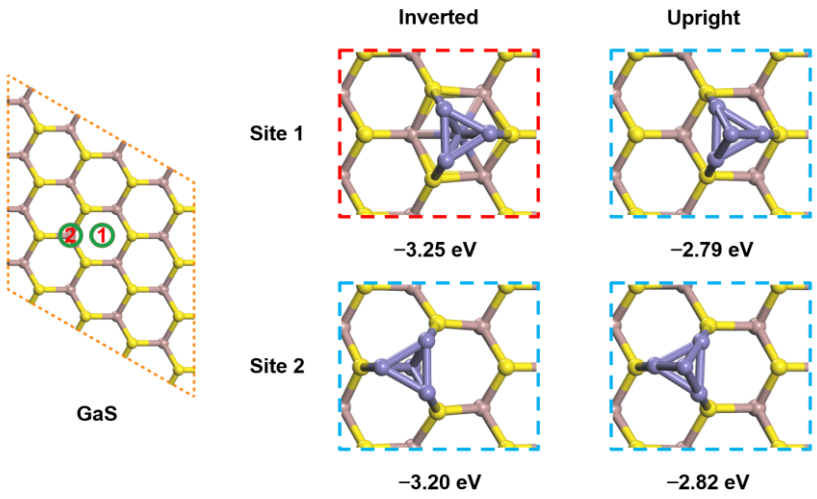

Fig. S3 Different binding configurations of Fe_4 cluster on GaS and the corresponding binding energy values.

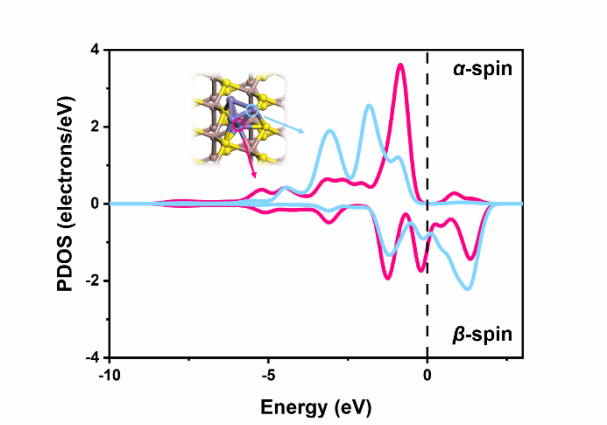

Fig. S4 Partial density of states (PDOS) of Fe atoms in Fe_4/GaS with two type electron structures. The Fermi level is set to zero.

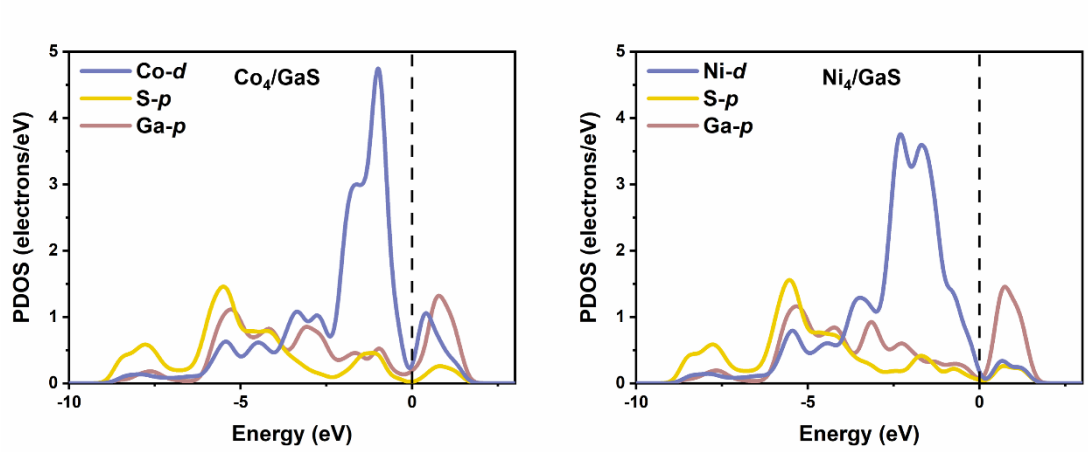

Fig. S5 PDOS of Co_4/GaS and Ni_4/GaS, including the Co/Ni-*d* orbits and adjacent S-*p*, Ga-*p* orbits. The Fermi level is set to zero.

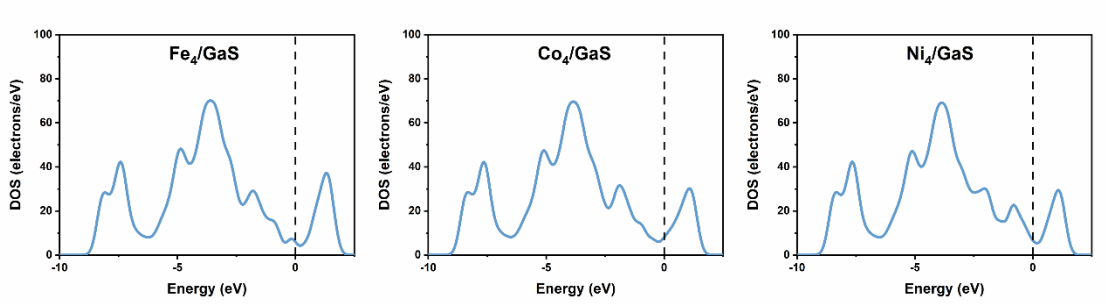

Fig. S6 Density of states (DOS) of M_4/GaS (M = Fe, Co, Ni). The black dotted line indicates the Fermi energy level.

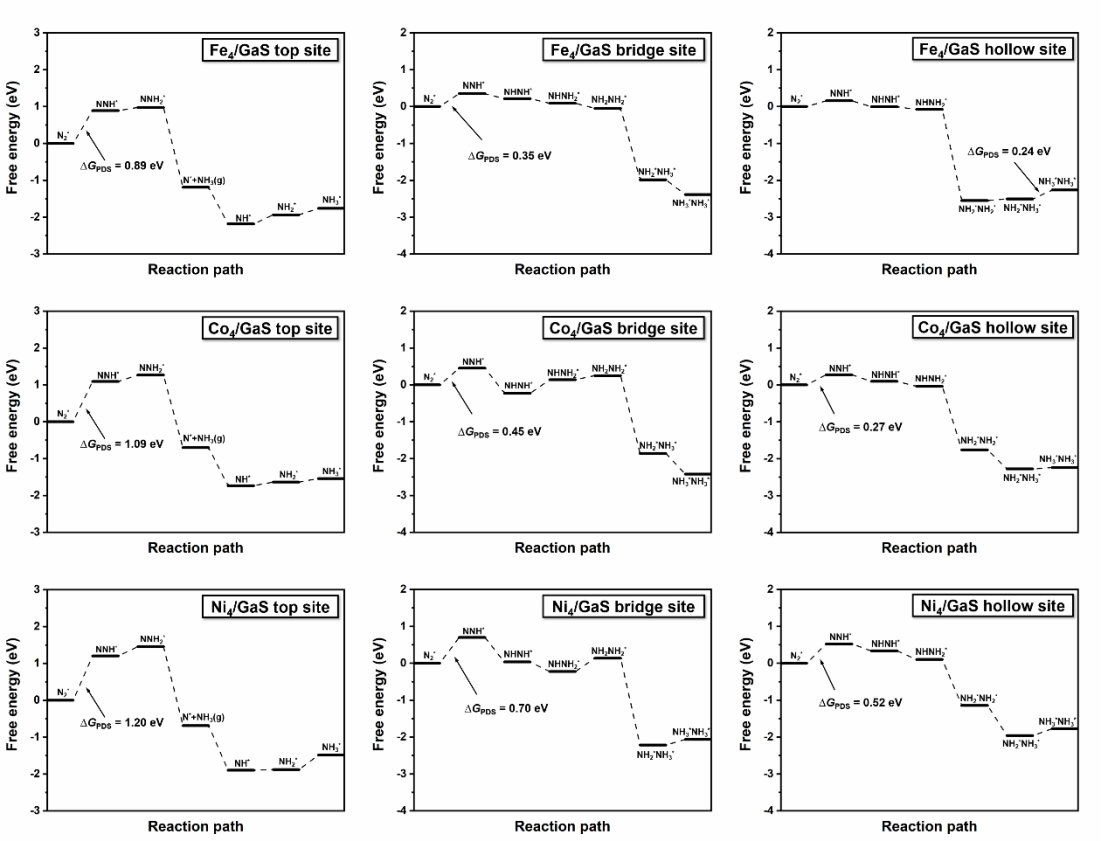

Fig. S7 The reaction path for NRR on M_4/GaS (M = Fe, Co, Ni). The free energy profiles and the potential determining step (PDS) are shown.

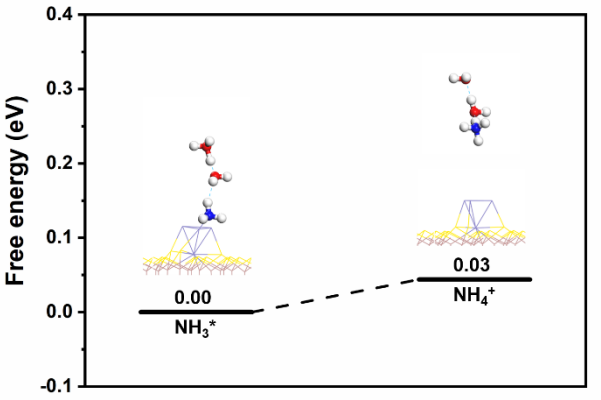

Fig. S8 Desorption process of NH_3^* to NH_4^+ on Fe_4/GaS with the free energy profile. The proton comes from $H_5O_2^+$. The solvation model is used with a dielectric constant of 78.54.

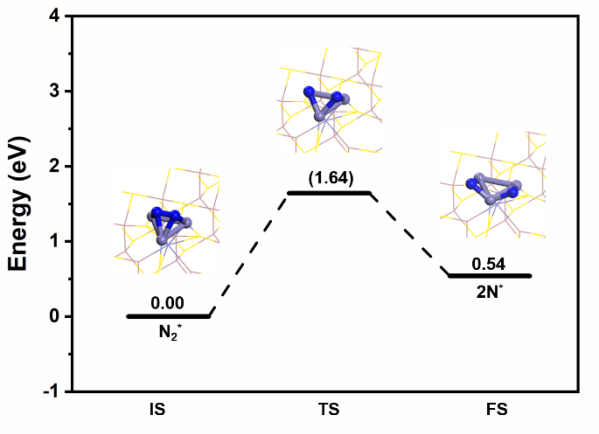

Fig. S9 Energy profile of the dissociation of adsorbed N_2 into two separate N atoms on the hollow site of Fe_4/GaS.

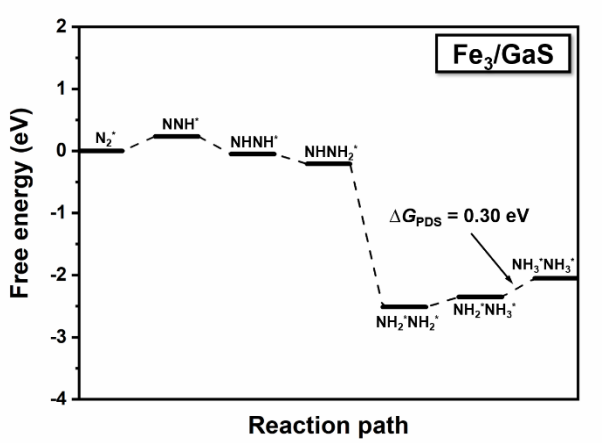

Fig. S10 The reaction path for NRR on Fe_3/GaS. The free energy profiles and the potential determining step (PDS) are shown.

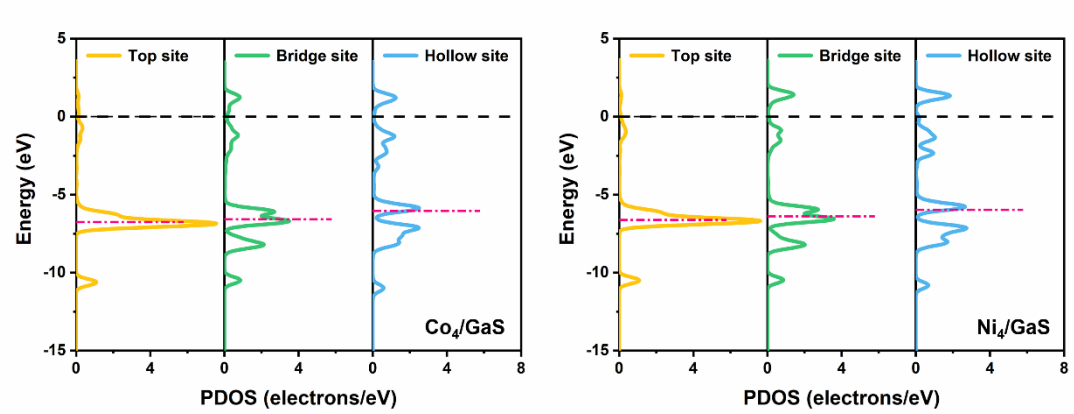

Fig. S11 PDOS of N_2 adsorbed on different sites of Co_4/GaS and Ni_4/GaS with N-*p* orbitals. The Fermi level is set to zero.

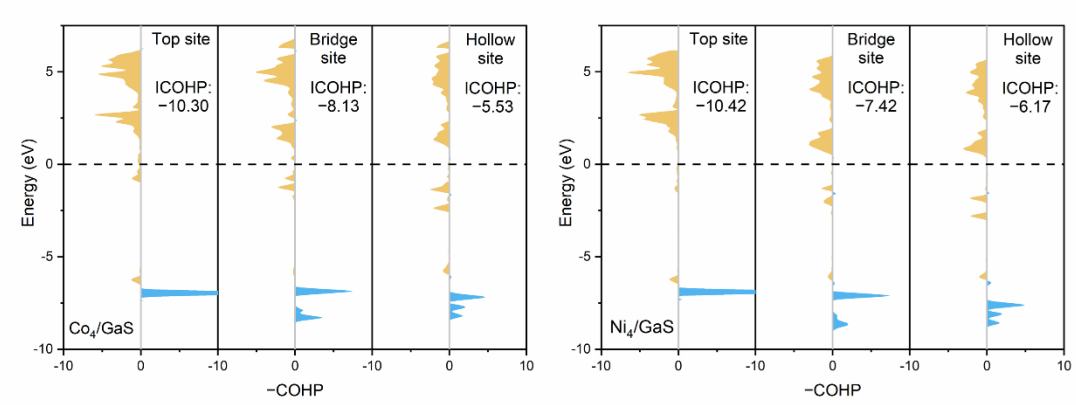

Fig. S12 Crystal orbital Hamilton population (COHP) between N–N bond on Co_4/GaS and Ni_4/GaS with the integrated crystal orbital Hamilton population (ICOHP).

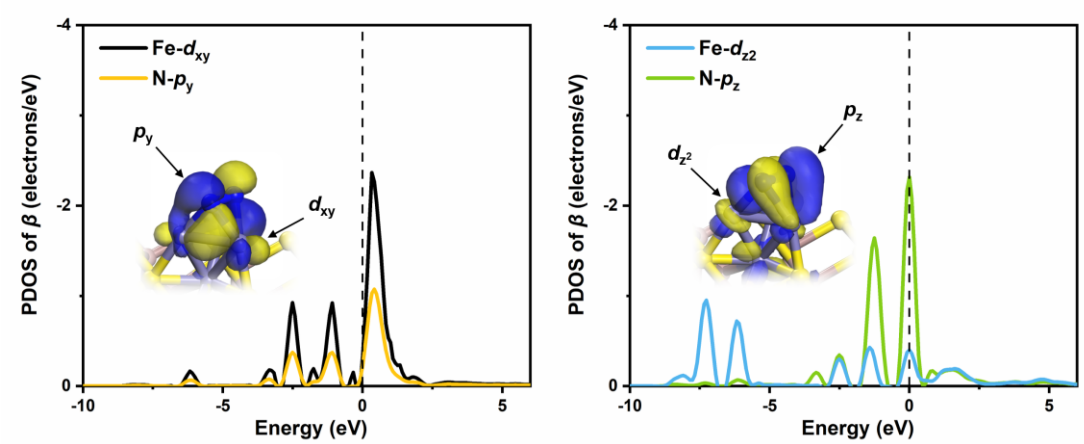

Fig. S13 PDOS of β-spin Fe-d_{xy} and N_2-p_y orbitals, and β-spin Fe-d_{z2} and N_2-p_z orbitals. The inserts are the illustration of the orbital hybridization.

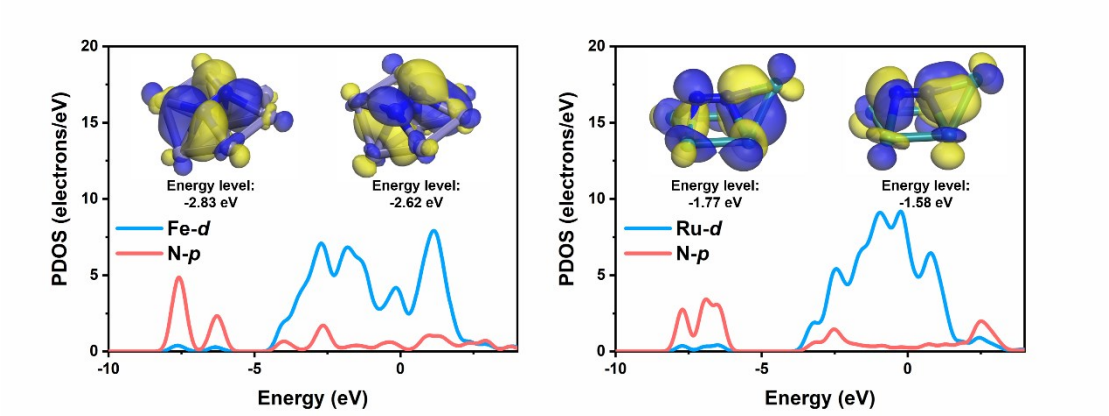

Fig. S14 The PDOS of N_2 adsorbed on the C7 site of Fe(211) and B5 site of Ru(0001). The inserts are illustration of the orbital hybridization between the N_2-π^* orbitals and the frontier orbitals of the active sites.

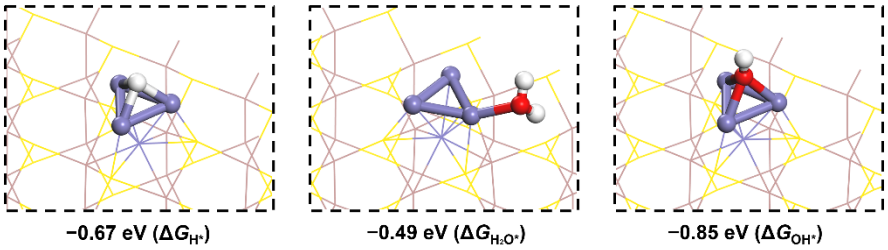

Fig. S15 The adsorption configuration of H^*, H_2O^* and OH^* on the Fe_4/GaS with the adsorption free energy values.

Calculation details are listed below:

DFT adsorption free energies:

$$\Delta G_{ad} = \Delta E_{ad} + \Delta ZPE - T\Delta S$$

DFT adsorption energies are calculated as:

$$\Delta E_{H^*} = E_{H^*} - E_* - 0.5E_{H_2(g)}$$

$$\Delta E_{H_2O^*} = E_{H_2O^*} - E_* - E_{H_2O(g)}$$

$$\Delta E_{OH^*} = E_{OH^*} - E_* - [E_{H_2O(g)} - 0.5E_{H_2(g)}]$$

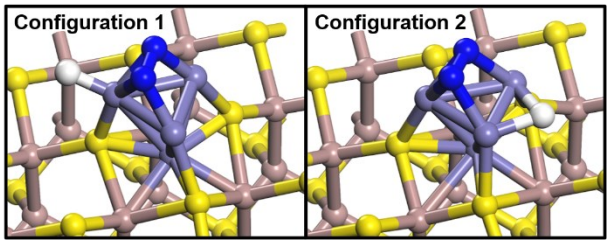

Fig. S16 The co-adsorption configurations of H^* and N_2^* on the Fe_4/GaS.

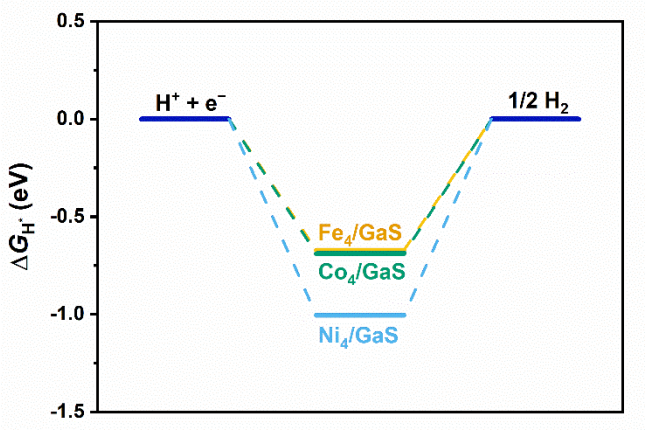

Fig. S17 Gibbs free energy diagram for HER process of Fe_4/GaS, Co_4/GaS and Ni_4/GaS.

Table S1 Calculated potentials (*U*) for NRR on different systems

Catalysts	*U*(V) *vs*. RHE	References
Fe_4/GaS	−0.24	This work
Fe_3-GDY/Gra	−0.37	33
Mo-embedded BN	−0.35	64
$Mo_1(Cr_1)/N_3$-G	−0.50 (−0.75)	65
MoS_2	−0.68	66
B-graphene	−0.31	67
B_4C(110)	−0.34	68
Au(310)	−1.50	69
Several MXene materials	> −0.63	70
Several SACs	> −0.33	71
Several metal surfaces	> −0.70	72