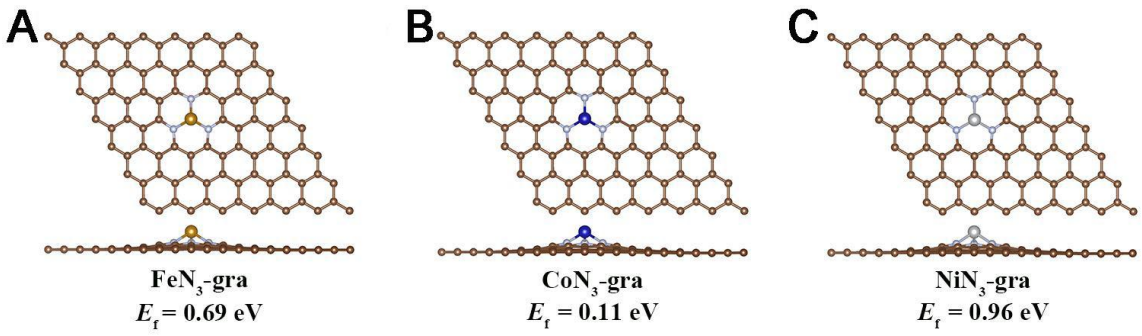
Supplementary Materials

High hydrogen evolution activities of dual-metal atoms incorporated N-doped graphenes achieved by coordination regulation

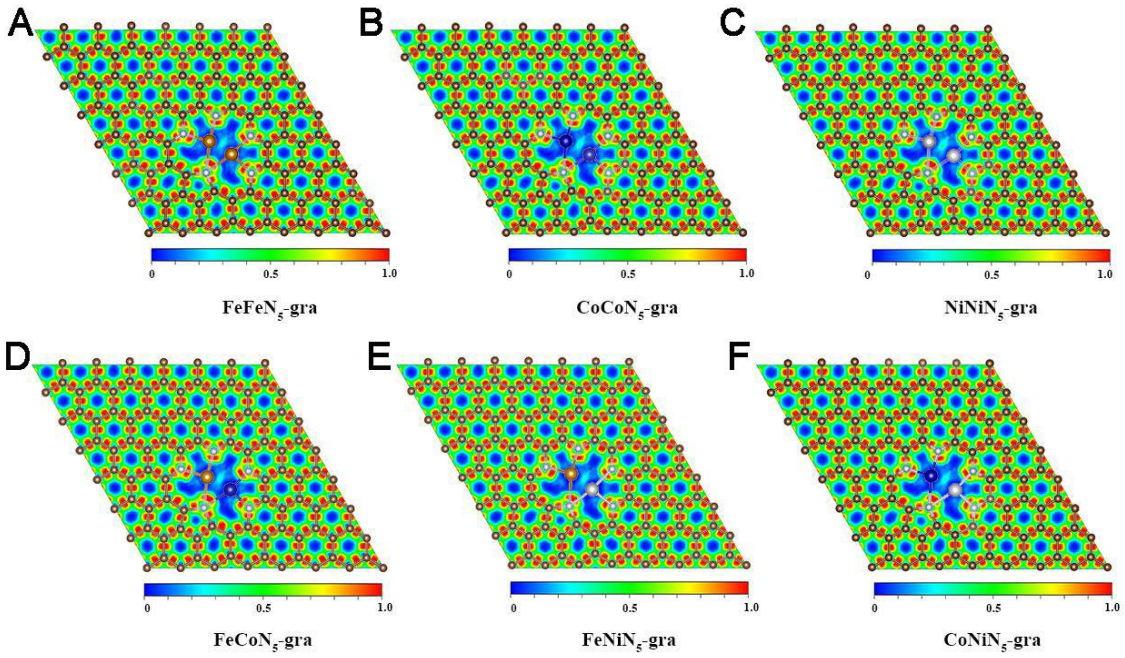
Cunjin Zhang, Shuaibo Qin, Hui Gao, Peng Jin*

School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, China. *E-mail:* pengjin@hebut.edu.cn

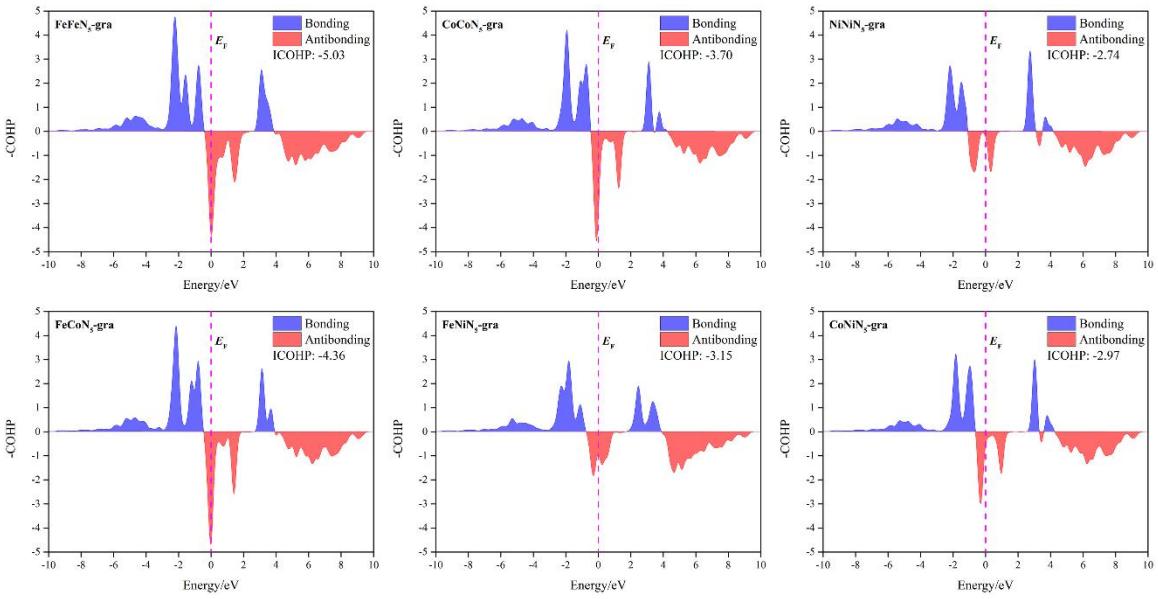
Supplementary Figures



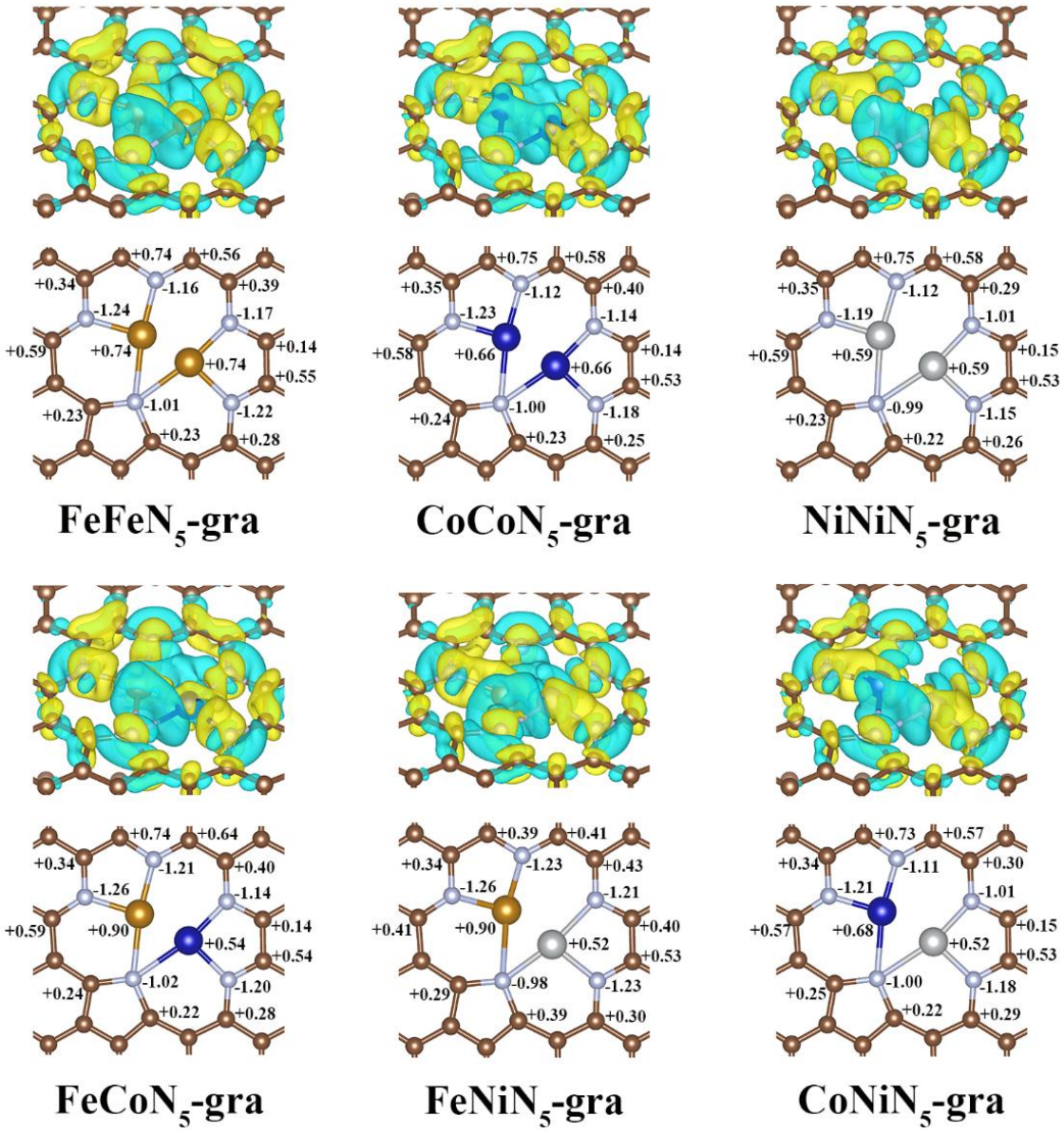
Supplementary Figure 1. Optimized structures (top and side views) and formation energies (E_f) of the three single-atom catalysts. (A)-(C) MN_3-gra (M = Fe, Co, Ni). C: brown; N: light blue; Fe: golden; Co: dark blue; Ni: silvery.



Supplementary Figure 2. Electron localization functions (ELFs) for the N-doped graphene planes of all the catalysts shown in Figure 3 of main text.



Supplementary Figure 3. Crystal orbital Hamilton population (COHP) and integrated-COHP (ICOHP) between the two adjacent metal atoms of MMN_5-gra and $M1M2N_5$-gra.

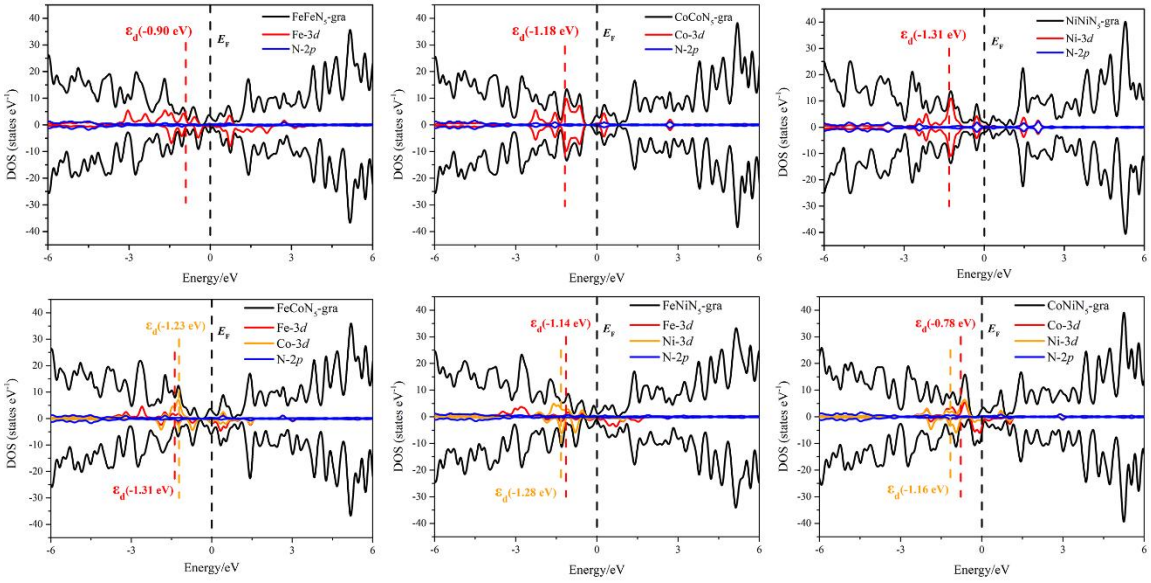


Supplementary Figure 4. Charge density difference (upper) and Bader charges (down) of MMN_5-gra/$M1M2N_5$-gra catalysts. The yellow and cyan colors denote the electron accumulation and depletion, respectively. The charge density difference was calculated as follows:

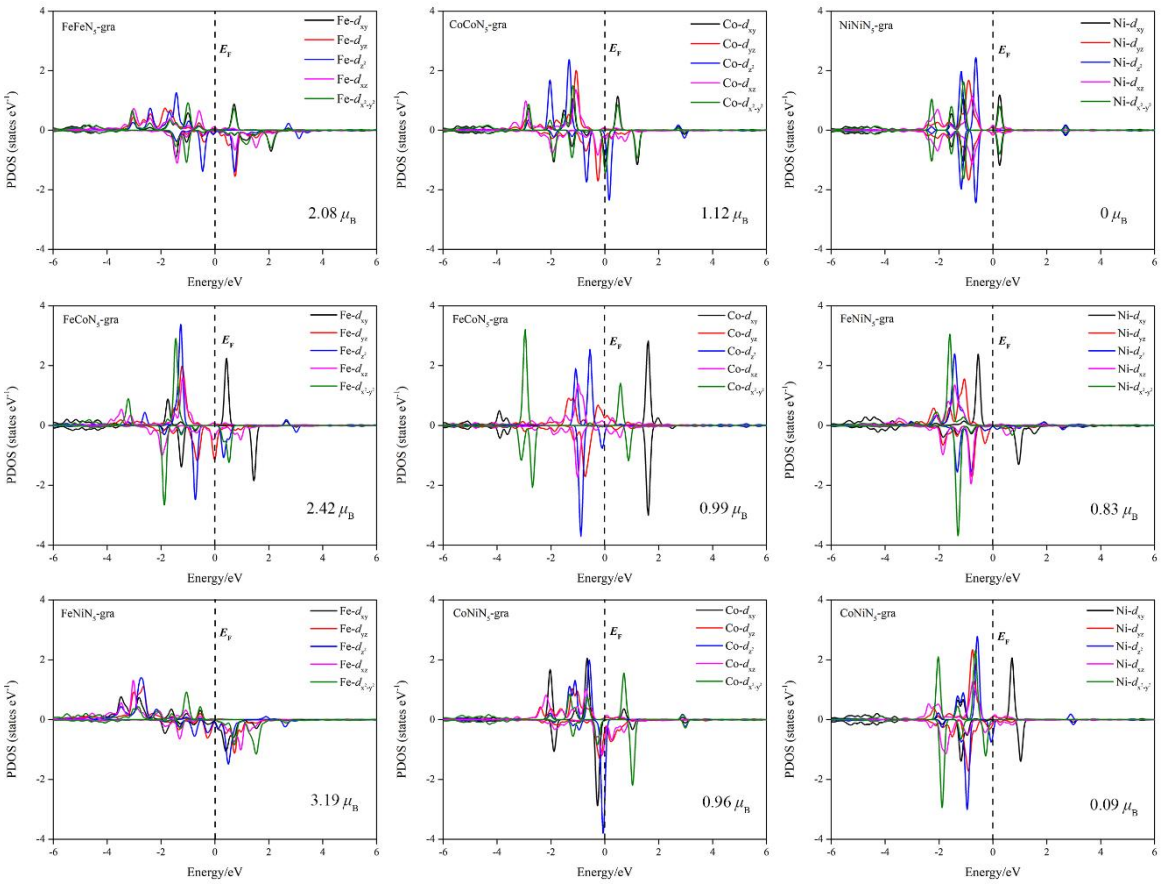
$\Delta\rho(r) = \rho(r)_{MMN5\text{-}gra} - \rho(r)_{MM} - \rho(r)_{N5\text{-}gra}$

$\Delta\rho(r) = \rho(r)_{M1M2N5\text{-}gra} - \rho(r)_{M1M2} - \rho(r)_{N5\text{-}gra}$

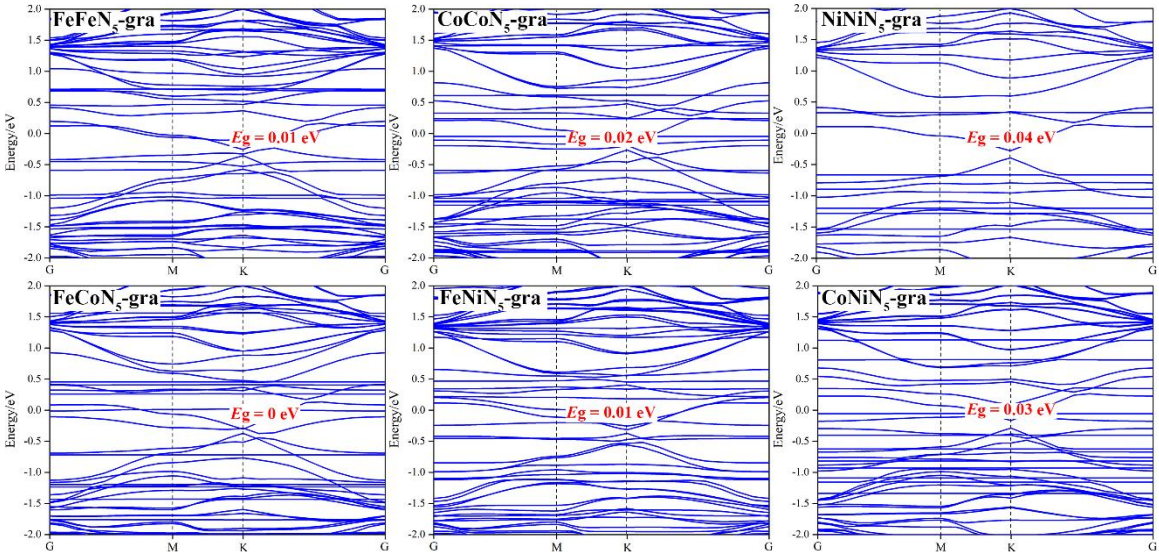
where $\rho(r)_{MMN5\text{-}gra}$ and $\rho(r)_{M1M2N5\text{-}gra}$ are the charge density of the catalysts, $\rho(r)_{N5\text{-}gra}$ is the charge density of the catalysts without metals, and $\rho(r)_{MM}$ and $\rho(r)_{M1M2}$ are the charge density of the metal atoms.



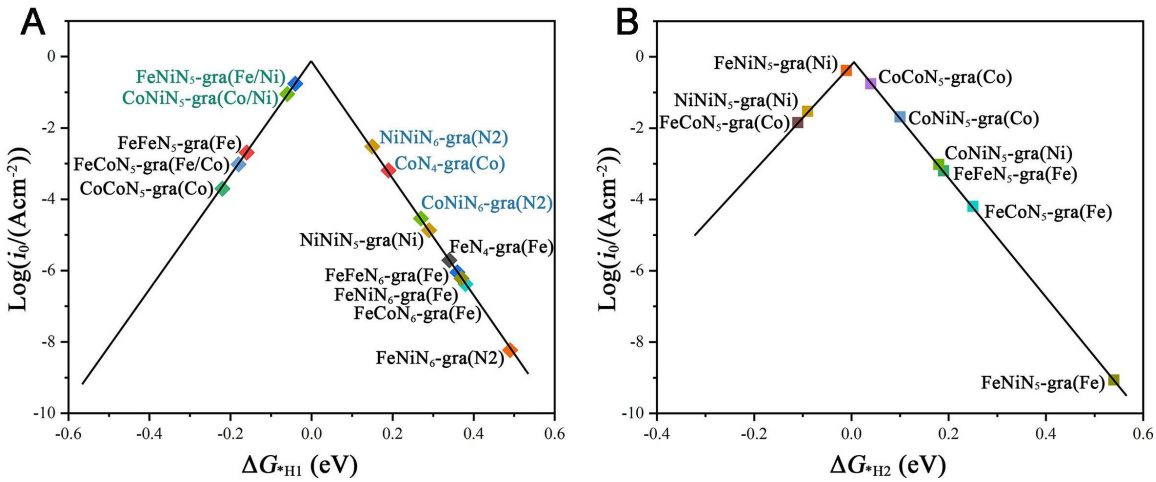
Supplementary Figure 5. Total DOSs and projected M-3*d* and N-2*p* states of all MMN_5-gra/M1M2N_5-gra catalysts with the metal d-band centers (ε_d) calculated from both spin up and spin down states. Fermi levels are set at 0 eV.



Supplementary Figure 6. Projected DOSs of M-3*d* states (both spin up and spin down) and metal spin moment of all MMN_5-gra/M1M2N_5-gra catalysts. Fermi levels are set at 0 eV.



Supplementary Figure 7. Electronic band structures of MMN_5-gra/M1M2N_5-gra catalysts.



Supplementary Figure 8. Volcanic curve of the exchange current (i_0) as a function of the ΔG_{*H} values for the adsorption of (A) first and (B) second hydrogen atoms. In (B) only those with high activity in both (A) and (B) are considered to be promising catalysts following the HMH intermediate mechanism.

The theoretical exchange current was calculated by using the following equations as done in the recent literature[1]:

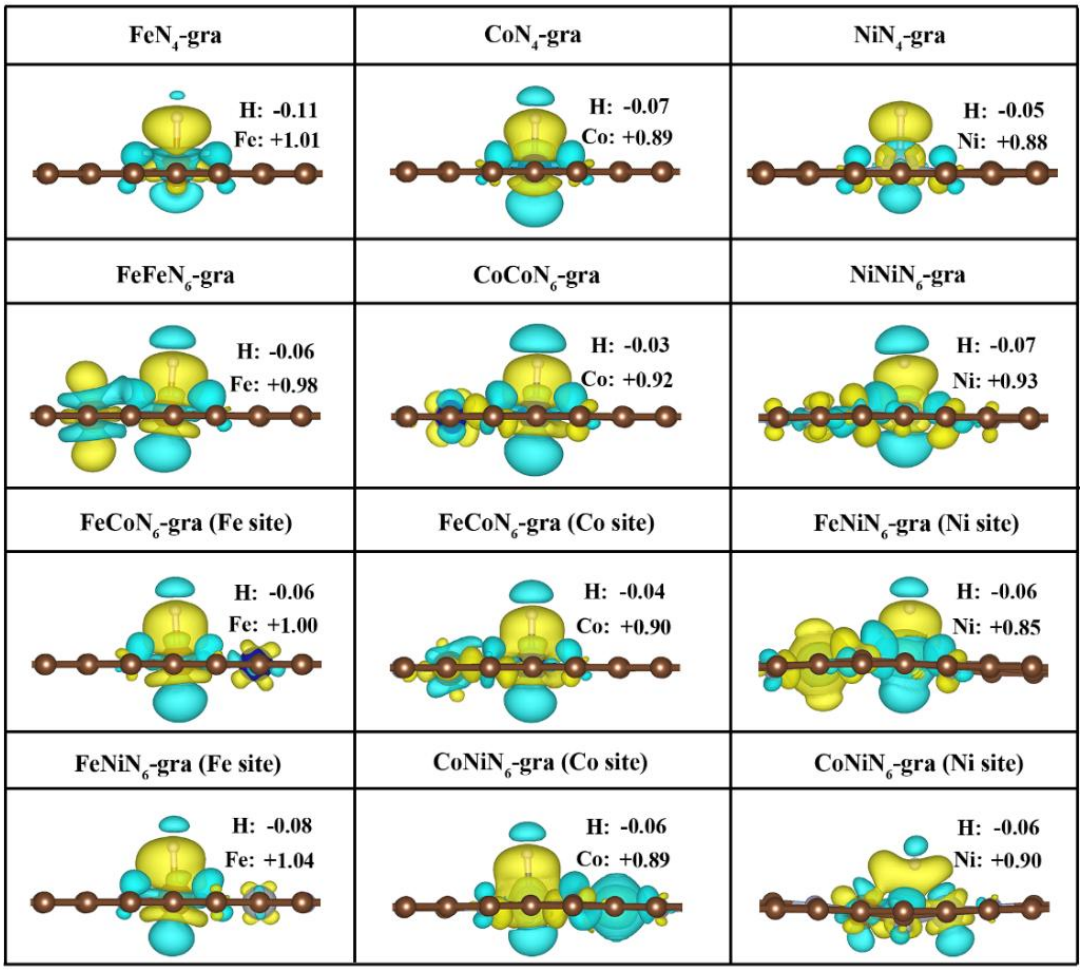
If $\Delta G_{*H} \leq 0$

$$i_0 = -ek_0/(1+\exp(-\Delta G_{*H}/k_B T)) \quad (1)$$

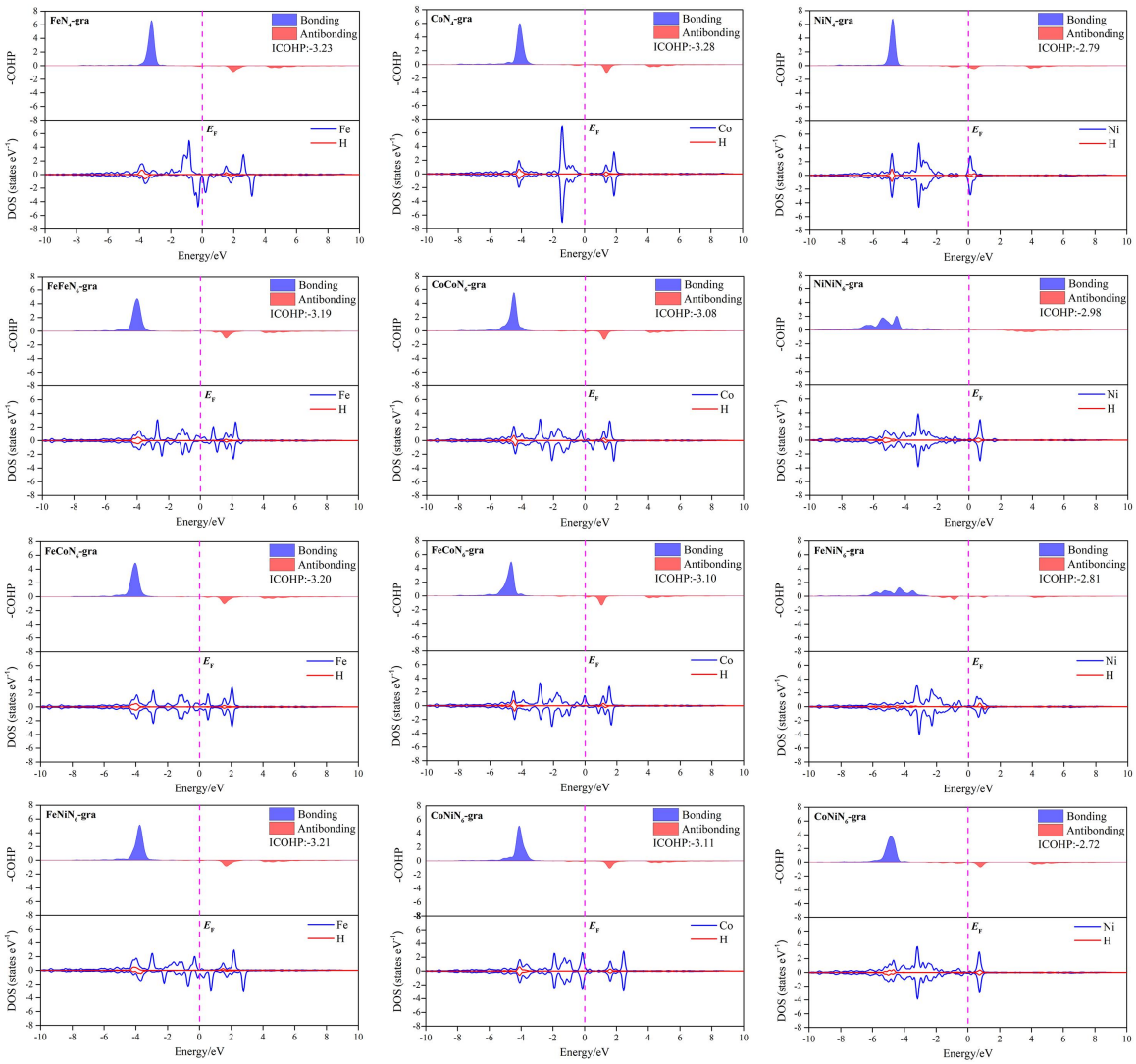
If $\Delta G_{*H} > 0$

$$i_0 = -ek_0/(1+\exp(\Delta G_{*H}/k_B T)) \quad (2)$$

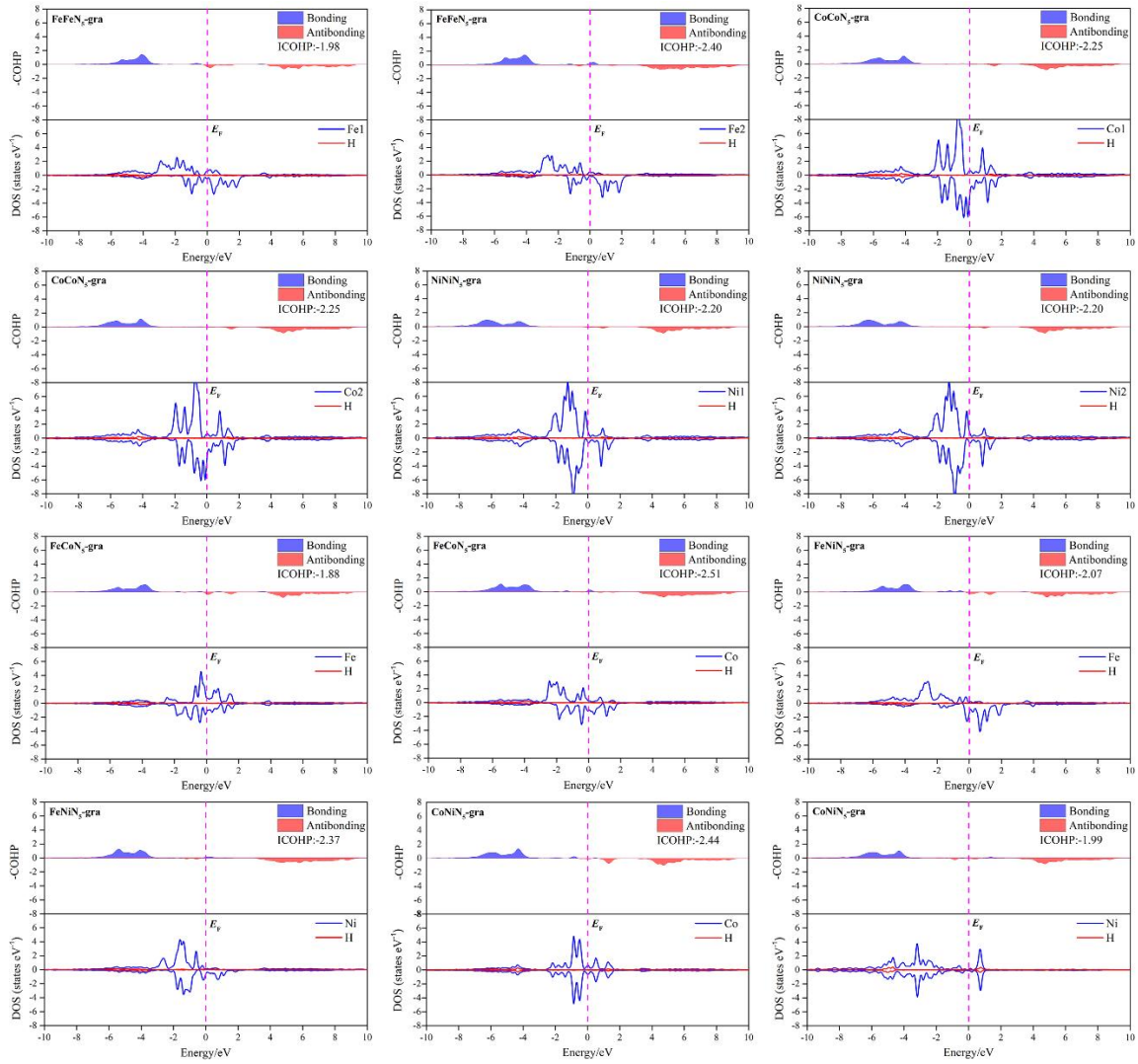
where rate constant (k_0) is set to 1, k_B is the Boltzmann constant (1.38064×10^{-23} J/K) and T is temperature (298.15 K).



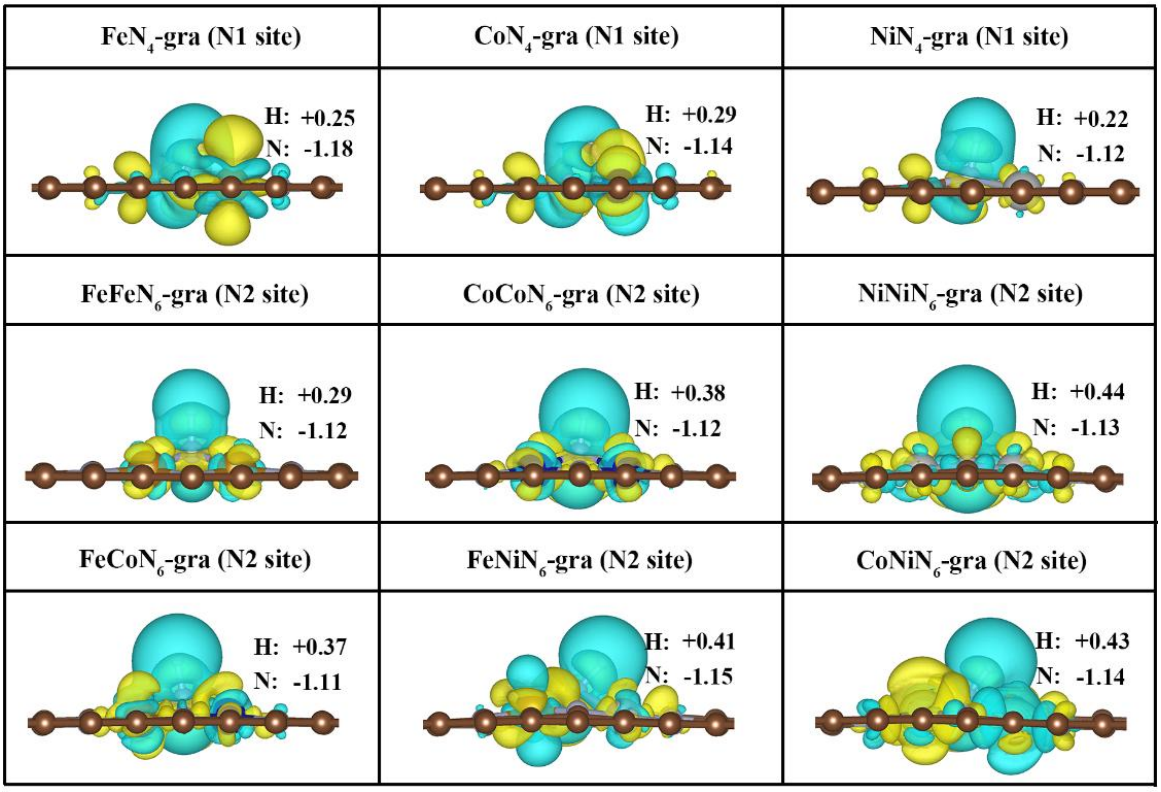
Supplementary Figure 9. The charge density difference and Bader charge when the hydrogen evolution reaction occurs on the metal site for MN_4-gra/MMN_6-gra/$M1M2N_6$-gra.



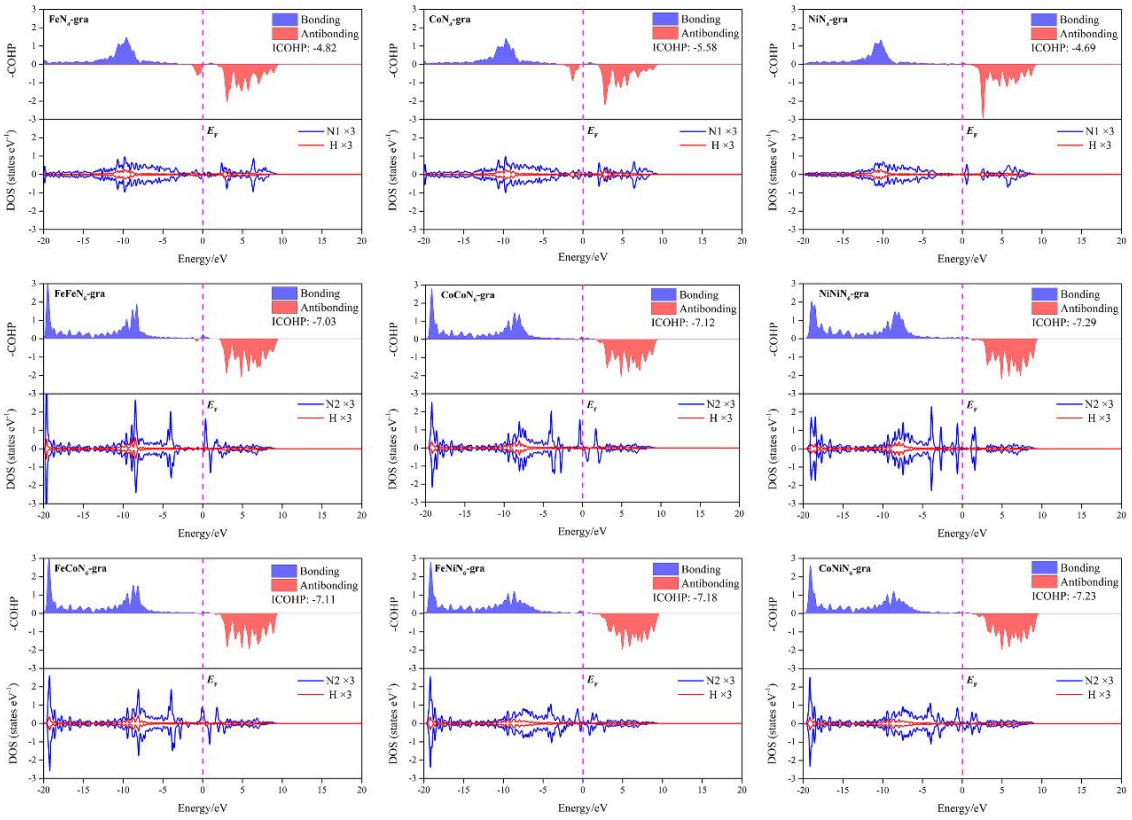
Supplementary Figure 10. Crystal orbital Hamiltonian population (COHP) between M-H in *H for MN_4-gra/MMN_6-gra/$M1M2N_6$-gra.



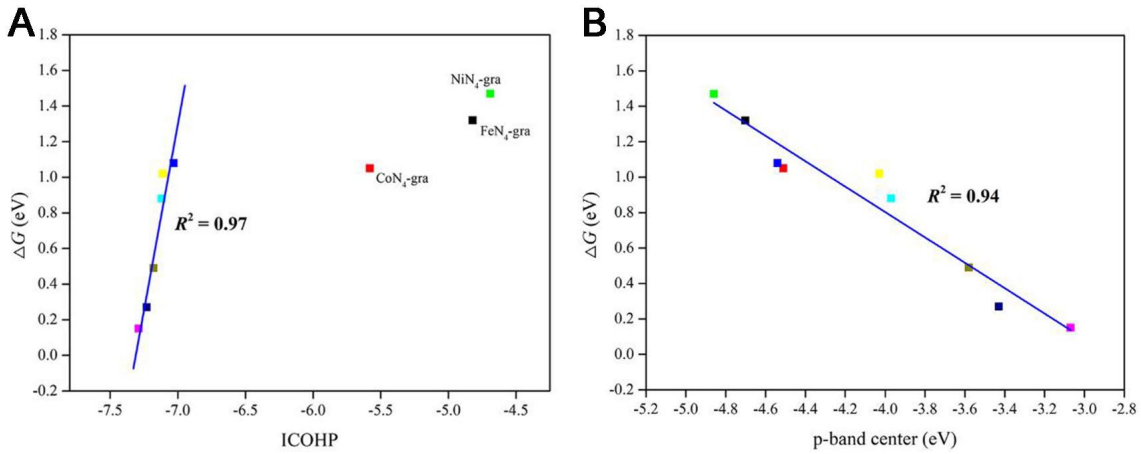
Supplementary Figure 11. Crystal orbital Hamiltonian population (COHP) between M-H in *H for MMN_5-gra/M1M2N_5-gra.



Supplementary Figure 12. The charge density difference and Bader charge when the hydrogen evolution reaction occurs on the N site for MN_4-gra/MMN_6-gra/$M1M2N_6$-gra.



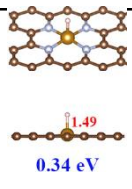
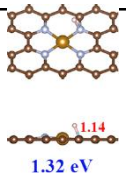
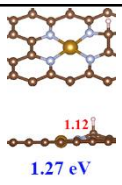
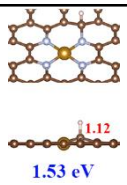
Supplementary Figure 13. Crystal orbital Hamiltonian population (COHP) between N-H in *H for MN_4-gra/MMN_6-gra/$M1M2N_6$-gra.



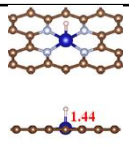
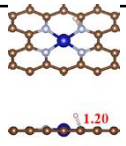
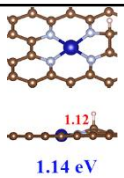
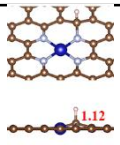
Supplementary Figure 14. (A) Linear relationship between N-H crystal orbital Hamiltonian population integral (ICOHP) and free energy of H adsorption for MN_4-gra/MMN_6-gra/$M1M2N_6$-gra; (B) Linear relationship between the p-band centers of the nitrogen atom and free energy of H adsorption.

Supplementary Tables

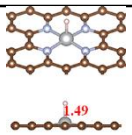
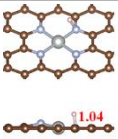
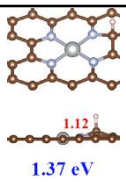
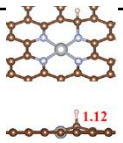
Supplementary Table 1. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on FeN_4-gra.

Fe-H	N1-H	C1-H	C2-H
 0.34 eV	 1.32 eV	 1.27 eV	 1.53 eV

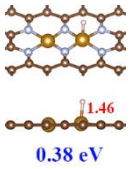
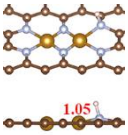
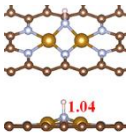
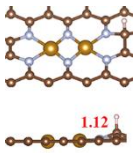
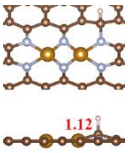
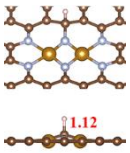
Supplementary Table 2. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on CoN_4-gra.

Co-H	N1-H	C1-H	C2-H
 0.19 eV	 1.05 eV	 1.14 eV	 1.51 eV

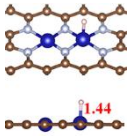
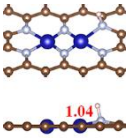
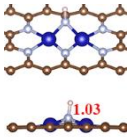
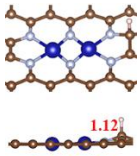
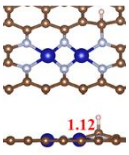
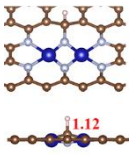
Supplementary Table 3. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on NiN_4-gra.

Ni-H	N1-H	C1-H	C2-H
 1.67 eV	 1.47 eV	 1.37 eV	 1.59 eV

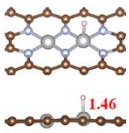
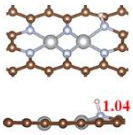
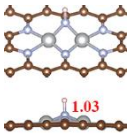
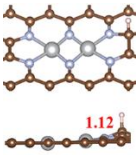
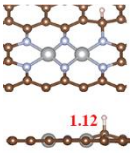
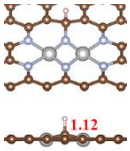
Supplementary Table 4. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $FeFeN_6$-gra.

Fe-H	N1-H	N2-H
 0.38 eV	 1.32 eV	 1.08 eV
C1-H	**C2-H**	**C3-H**
 1.23 eV	 1.46 eV	 1.38 eV

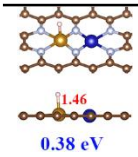
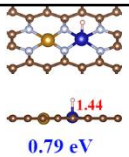
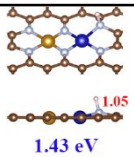
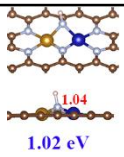
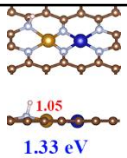
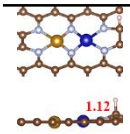
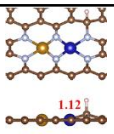
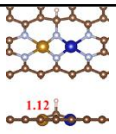
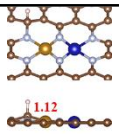
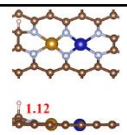
Supplementary Table 5. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $CoCoN_6$-gra.

Co-H	N1-H	N2-H
 0.84 eV	 1.33 eV	 0.88 eV
C1-H	**C2-H**	**C3-H**
 1.37 eV	 1.57 eV	 1.58 eV

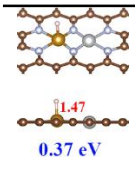
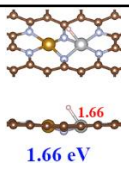
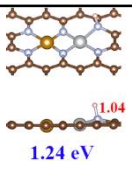
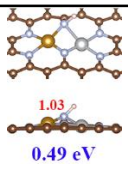
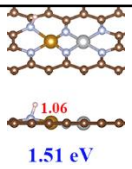
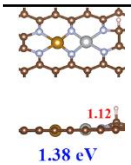
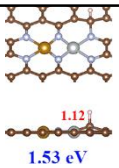
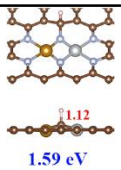
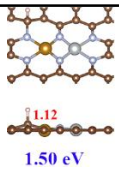
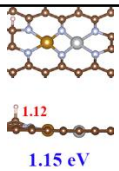
Supplementary Table 6. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $NiNiN_6$-gra.

Ni-H	N1-H	N2-H
 1.34 eV	 1.24 eV	 0.15 eV
C1-H	**C2-H**	**C3-H**
 1.25 eV	 1.75 eV	 1.79 eV

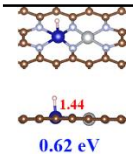
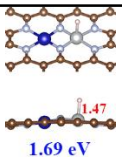
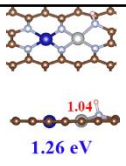
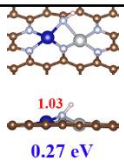
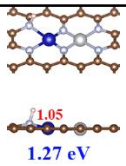
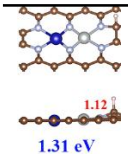
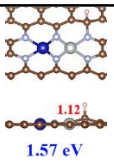
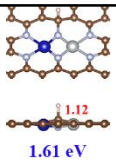
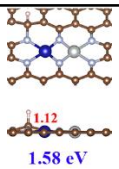
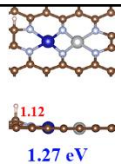
Supplementary Table 7. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $FeCoN_6$-gra.

Fe-H	Co-H	N1-H	N2-H	N3-H
 0.38 eV	 0.79 eV	 1.43 eV	 1.02 eV	 1.33 eV
C1-H	**C2-H**	**C3-H**	**C4-H**	**C5-H**
 1.40 eV	 1.53 eV	 1.40 eV	 1.50 eV	 1.29 eV

Supplementary Table 8. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $FeNiN_6$-gra.

Fe-H	Ni-H	N1-H	N2-H	N3-H
 0.37 eV	 1.66 eV	 1.24 eV	 0.49 eV	 1.51 eV
C1-H	C2-H	C3-H	C4-H	C5-H
 1.38 eV	 1.53 eV	 1.59 eV	 1.50 eV	 1.15 eV

Supplementary Table 9. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $CoNiN_6$-gra.

Co-H	Ni-H	N1-H	N2-H	N3-H
 0.62 eV	 1.69 eV	 1.26 eV	 0.27 eV	 1.27 eV
C1-H	C2-H	C3-H	C4-H	C5-H
 1.31 eV	 1.57 eV	 1.61 eV	 1.58 eV	 1.27 eV

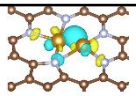
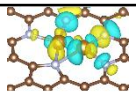
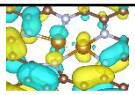
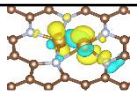
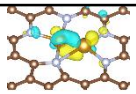
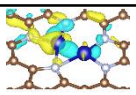
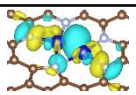
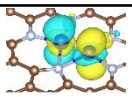
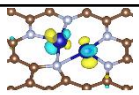
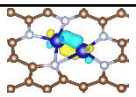
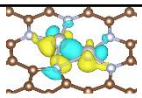
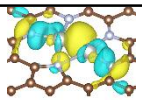
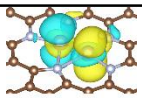
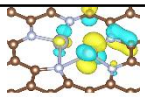
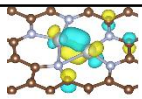
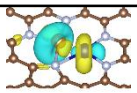
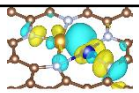
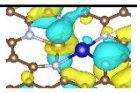
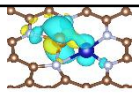
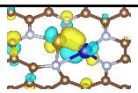
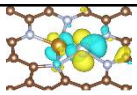
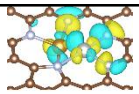
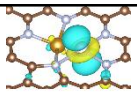
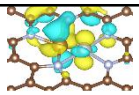
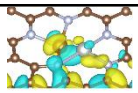
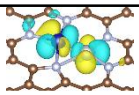
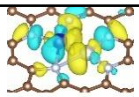
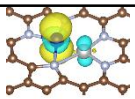
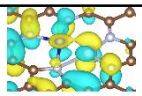
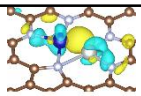
Supplementary Table 10. The d-band centers (eV) of metal sites on MN_4-gra, MMN_6-gra, and $M1M2N_6$-gra catalysts.

Model	Fe	Co	Ni
FeN_4-gra	-0.98	N/A	N/A
CoN_4-gra	N/A	-1.08	N/A
NiN_4-gra	N/A	N/A	-2.02
$FeFeN_6$-gra	-1.26	N/A	N/A
$CoCoN_6$-gra	N/A	-1.67	N/A
$NiNiN_6$-gra	N/A	N/A	-1.73
$FeCoN_6$-gra	-1.25	-1.56	N/A
$FeNiN_6$-gra	-1.17	N/A	-2.08
$CoNiN_6$-gra	N/A	-1.42	-2.20

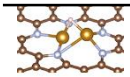
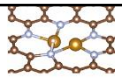
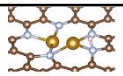
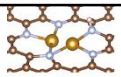
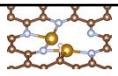
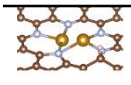
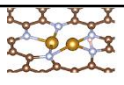
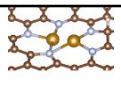
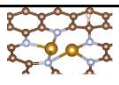
Supplementary Table 11. Average distances ($d_{M\text{-}N}$, Å) vs. sum of covalent radii ($r_M + r_N$, Å) of the metal and N atoms, and the distances ($d_{M\text{-}M}$, Å) vs. sum of covalent radii ($r_M + r_M$, Å) of two adjacent metal atoms.

Model	$d_{M\text{-}N}$	$r_M + r_N$	$d_{M\text{-}M}$	$r_M + r_M$
$FeFeN_5$-gra	2.07	2.38	1.92	3.34
$CoCoN_5$-gra	2.05	1.97	1.97	2.52
$NiNiN_5$-gra	2.03	1.88	2.06	2.34
$FeCoN_5$-gra	2.05/2.05	2.38/1.97	1.93	2.93
$FeNiN_5$-gra	2.14/2.05	2.38/1.88	2.09	2.84
$CoNiN_5$-gra	2.03/2.03	1.97/1.88	2.05	2.43

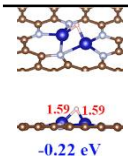
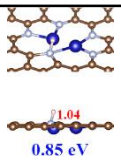
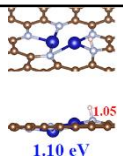
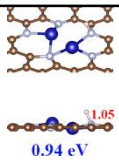
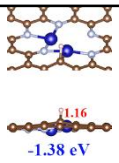
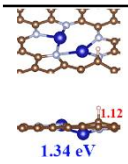
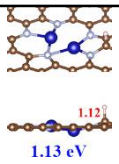
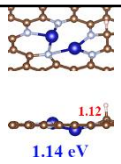
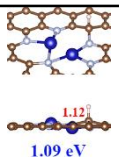
Supplementary Table 12. Crystal orbital overlaps between the two adjacent metal atoms of MMN_5-gra and $M1M2N_5$-gra. The isovalues are given in a.u.

Model	d_{x2-y2}	d_{xy}	d_{z2}	d_{yz}	d_{xz}
$FeFeN_5$-gra	 4.0×10⁻⁷	 2.0×10⁻⁷	 5.0×10⁻⁸	 2.0×10⁻⁷	 3.0×10⁻⁷
$CoCoN_5$-gra	 2.0×10⁻⁷	 2.0×10⁻⁷	 2.0×10⁻⁷	 2.0×10⁻⁷	 2.0×10⁻⁷
$NiNiN_5$-gra	 3.0×10⁻⁷	 2.0×10⁻⁷	 5.0×10⁻⁸	 2.0×10⁻⁷	 2.0×10⁻⁷
$FeCoN_5$-gra	 2.0×10⁻⁷	 2.0×10⁻⁷	 5.0×10⁻⁸	 5.0×10⁻⁷	 2.0×10⁻⁷
$FeNiN_5$-gra	 2.0×10⁻⁷	 2.0×10⁻⁷	 5.0×10⁻⁸	 2.0×10⁻⁷	 1.0×10⁻⁷
$CoNiN_5$-gra	 2.0×10⁻⁷	 2.0×10⁻⁷	 2.0×10⁻⁷	 2.0×10⁻⁷	 2.0×10⁻⁷

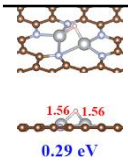
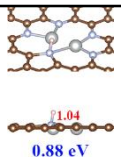
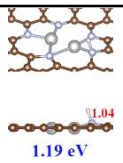
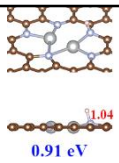
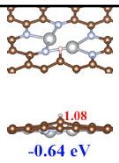
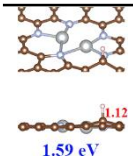
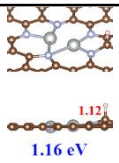
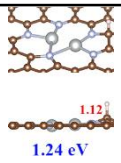
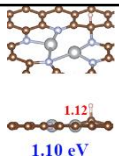
Supplementary Table 13. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $FeFeN_5$-gra.

Fe-H	N1-H	N2-H	N3-H	C1-H
 -0.16 eV	 1.02 eV	 1.14 eV	 1.17 eV	 -1.19 eV
C2-H	C3-H	C4-H	C5-H	
 1.15 eV	 1.14 eV	 1.13 eV	 1.22 eV	

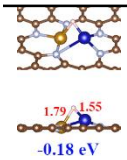
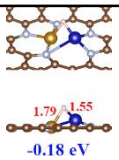
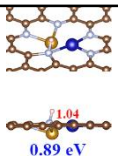
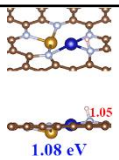
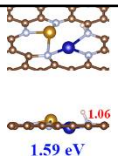
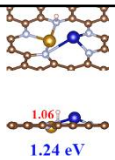
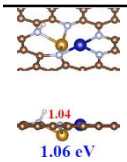
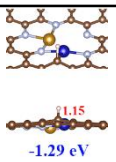
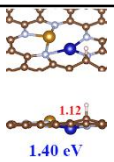
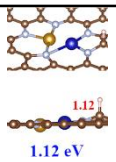
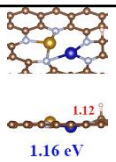
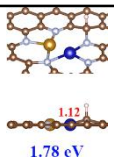
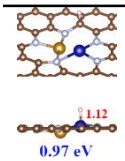
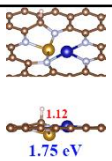
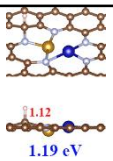
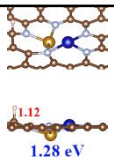
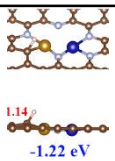
Supplementary Table 14. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $CoCoN_5$-gra.

Co-H	N1-H	N2-H	N3-H	C1-H
 -0.22 eV	 0.85 eV	 1.10 eV	 0.94 eV	 -1.38 eV
C2-H	**C3-H**	**C4-H**	**C5-H**	
 1.34 eV	 1.13 eV	 1.14 eV	 1.09 eV	

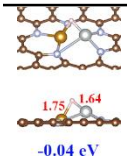
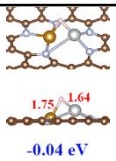
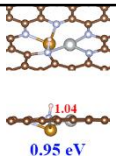
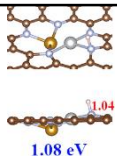
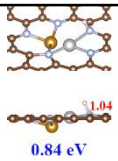
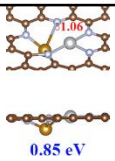
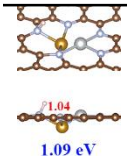
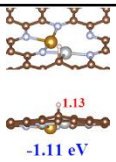
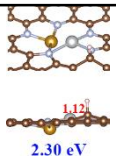
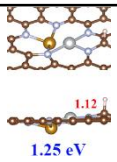
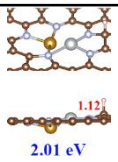
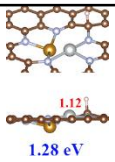
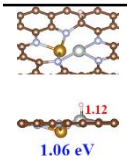
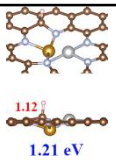
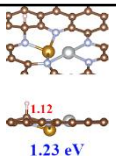
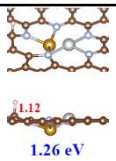
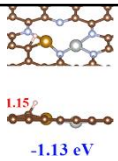
Supplementary Table 15. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $NiNiN_5$-gra.

Ni-H	N1-H	N2-H	N3-H	C1-H
 0.29 eV	 0.88 eV	 1.19 eV	 0.91 eV	 -0.64 eV
C2-H	**C3-H**	**C4-H**	**C5-H**	
 1.59 eV	 1.16 eV	 1.24 eV	 1.10 eV	

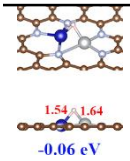
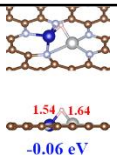
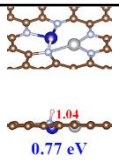
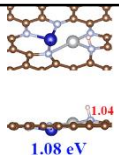
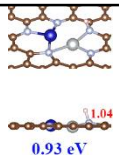
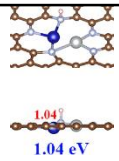
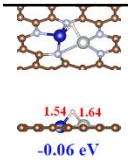
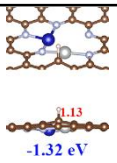
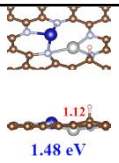
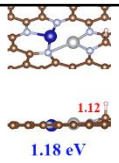
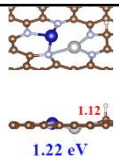
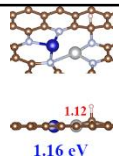
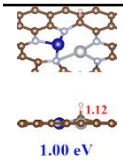
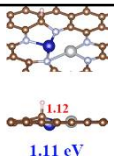
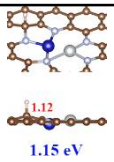
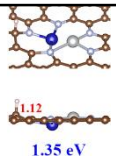
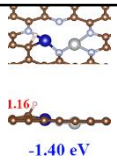
Supplementary Table 16. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $FeCoN_5$-gra.

Fe-H	Co-H	N1-H	N2-H	N3-H	N4-H
 -0.18 eV	 -0.18 eV	 0.89 eV	 1.08 eV	 1.59 eV	 1.24 eV
N5-H	C1-H	C2-H	C3-H	C4-H	C5-H
 1.06 eV	 -1.29 eV	 1.40 eV	 1.12 eV	 1.16 eV	 1.78 eV
C6-H	C7-H	C8-H	C9-H	C10-H	
 0.97 eV	 1.75 eV	 1.19 eV	 1.28 eV	 -1.22 eV	

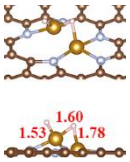
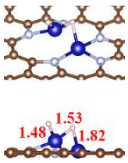
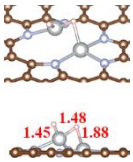
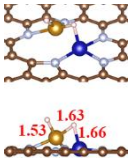
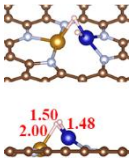
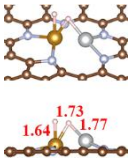
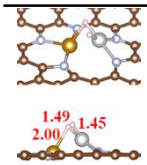
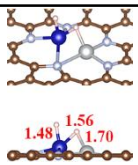
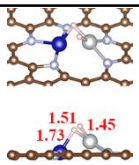
Supplementary Table 17. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $FeNiN_5$-gra.

Fe-H	Ni-H	N1-H	N2-H	N3-H	N4-H
 -0.04 eV	 -0.04 eV	 0.95 eV	 1.08 eV	 0.84 eV	 0.85 eV
N5-H	C1-H	C2-H	C3-H	C4-H	C5-H
 1.09 eV	 -1.11 eV	 2.30 eV	 1.25 eV	 2.01 eV	 1.28 eV
C6-H	C7-H	C8-H	C9-H	C10-H	
 1.06 eV	 1.21 eV	 1.23 eV	 1.26 eV	 -1.13 eV	

Supplementary Table 18. Potential *H adsorption structures (distance unit: Å) and adsorption free energies on $CoNiN_5$-gra. The adsorption on N5 site is unstable and leads to the same structure as metal site.

Co-H	Ni-H	N1-H	N2-H	N3-H	N4-H
 -0.06 eV	 -0.06 eV	 0.77 eV	 1.08 eV	 0.93 eV	 1.04 eV
N5-H	C1-H	C2-H	C3-H	C4-H	C5-H
 -0.06 eV	 -1.32 eV	 1.48 eV	 1.18 eV	 1.22 eV	 1.16 eV
C6-H	C7-H	C8-H	C9-H	C10-H	
 1.00 eV	 1.11 eV	 1.15 eV	 1.35 eV	 -1.40 eV	

Supplementary Table 19. Possible HMH structures (distance unit: Å) on MMN_5-gra/$M1M2N_5$-gra.

$FeFeN_5$-gra	$CoCoN_5$-gra	$NiNiN_5$-gra
		
$FeCoN_5$-gra (Fe)	$FeCoN_5$-gra (Co)	$FeNiN_5$-gra (Fe)
		
$FeNiN_5$-gra (Ni)	$CoNiN_5$-gra (Co)	$CoNiN_5$-gra (Ni)
		

Supplementary Table 20 The adsorption free energies (unit: eV) of the first and second H and the distance (unit: Å) between two H atoms in the HMH structures.

Model	**ΔG_{*H1}**	**ΔG_{*H2}**	**d_{H-H}**
$FeFeN_5$-gra	-0.16	0.19	1.86
$CoCoN_5$-gra	-0.22	0.04	1.71
$NiNiN_5$-gra	0.29	-0.09	1.66
$FeCoN_5$-gra (Fe site)	-0.18	0.25	1.78
$FeCoN_5$-gra (Co site)	-0.18	-0.11	1.80
$FeNiN_5$-gra (Fe site)	-0.04	0.54	0.99
$FeNiN_5$-gra (Ni site)	-0.04	-0.01	1.70
$CoNiN_5$-gra (Co site)	-0.06	0.10	1.45
$CoNiN_5$-gra (Ni site)	-0.06	0.18	1.71

Reference:

[1] Du J, Chen J, Zhang C, Jiang G. Screening out the transition metal single atom supported on onion-like carbon (OLC) for the hydrogen evolution reaction. *Inorg Chem* 2023; 62: 1001-1006. [DOI: 10.1021/acs.inorgchem.2c03922]