Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Synergy Effect on Atomic Cluster M_4 Supported on MN_4-Graphene (M=Fe, Ni) for Hydrogen Evolution Reaction

Jiake Cui[1], Xiaojing Liu[1], Yongxue Wei[1], Xiangjian Shen*

[1] Engineering Research Center of Advanced Functional Material Manufacturing of Ministry of Education, Zhengzhou University, Zhengzhou 450001, China,

* To whom correspondence should be addressed: xjshen85@zzu.edu.cn

Table of content

Table S1: The binding energies between tetrahedralM_4 clusters and MN_4-Gr substrates in different configurations, including Regular-Tetrahedron (RT), Side-Tetrahedron (ST) and Inverted-Tetrahedron (IT),respectively.

Catalyst	E_b/(eV)		
	RT	ST	IT
Fe_4FeN_4Gr	2.352	2.233	1.158
Fe_4NiN_4Gr	1.292	1.275	1.259
Ni_4FeN_4Gr	2.491	2.306	2.315
Ni_4NiN_4Gr	1.75	1.590	1.590

Table S2: Binding energies of M_4 clusters in a planar form supported on MN_4-Gr substrates.

Catalyst	E_b/(eV)
Flat-Fe_4@FeN_4Gr	2.255
Flat-Fe_4@NiN_4Gr	0.845
Flat-Ni_4@FeN_4Gr	1.603
Flat-Ni_4@NiN_4Gr	0.815

Table S3: Bader charge (BC) of each metal atom and N atom of M_4@MN_4-Gr model catalysts.

Fe_4@FeN_4-Gr		Fe_4@NiN_4-Gr		Ni_4@FeN_4-Gr		Ni_4@NiN_4-Gr	
Element	BC(|e|)	Element	BC(|e|)	Element	BC(|e|)	Element	BC(|e|)
Fe1	-0.76	Ni1	-0.71	Fe1	-0.88	Ni1	-0.75
Fe2	-0.35	Fe1	-0.32	Ni1	-0.24	Ni2	-0.27
Fe3	0.08	Fe2	0.06	Ni2	-0.22	Ni3	-0.22
Fe4	-0.34	Fe3	-0.32	Ni3	0.11	Ni4	0.11
Fe5	-0.34	Fe4	-0.32	Ni4	-0.23	Ni5	-0.23
N1	1.19	N1	1.2	N1	1.18	N1	1.18
N2	1.13	N2	1.22	N2	1.11	N2	1.19
N3	1.21	N3	1.24	N3	1.18	N3	1.22
N4	1.13	N4	1.04	N4	1.18	N4	1.07

Figure S1: The optimized stable structures of the substrates and metal clusters, (a) FeN_4-Gr, (b) NiN_4-Gr, (c) Fe_4 cluster, (d) Ni_4 cluster.

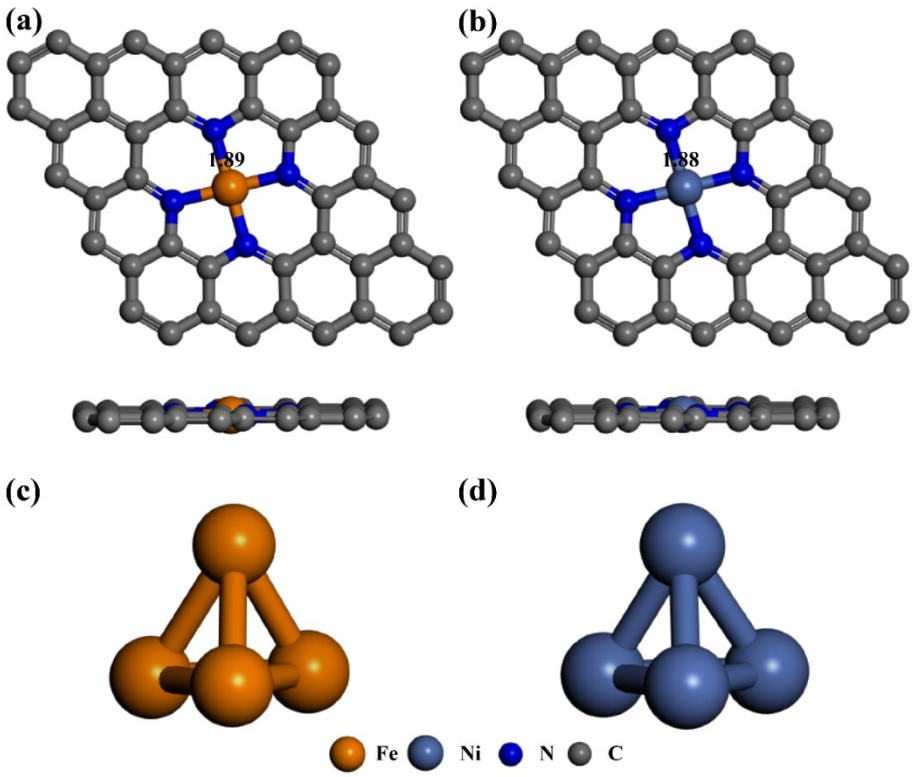
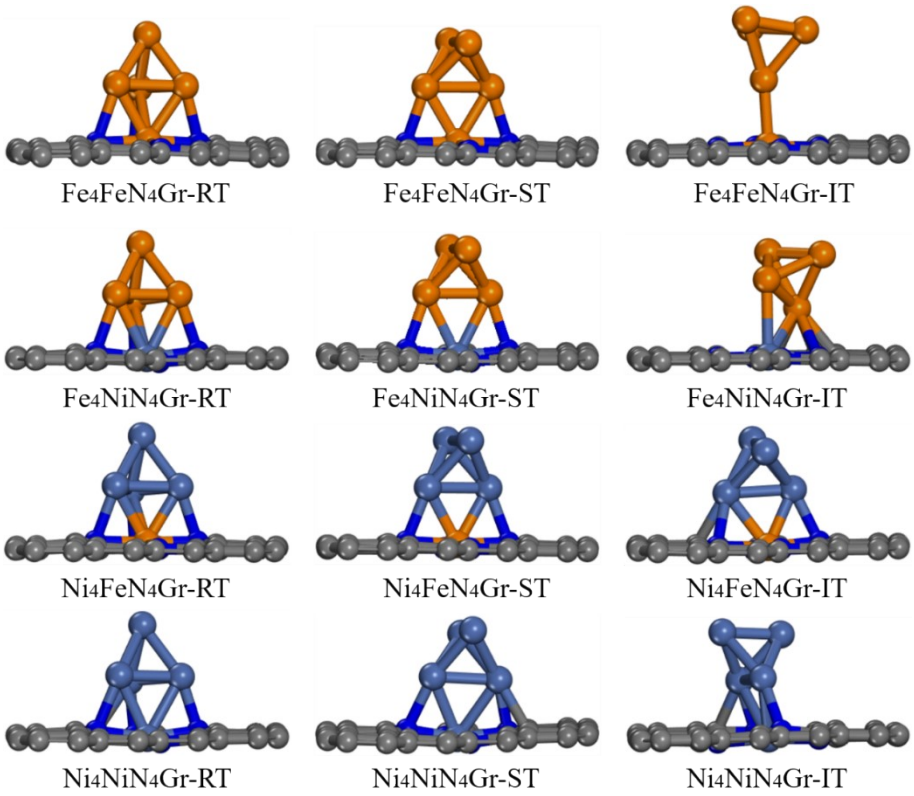


Figure S2: Three basic configurations of optimized $M_4@MN_4$-Grmodel catalysts: Regular-Tetrahedron (RT), Side-Tetrahedron (ST) and Inverted-Tetrahedron (IT).



It can be clearly seen from Figure S2 andTable S1that the Regular-Tetrahedron is the

most stable in the three configurations, while the Inverted-Tetrahedron tends to be deformed.In the Inverted-Tetrahedronconfiguration, one vertex atom of the M_4 cluster interacts with the substrate,and the other three atoms are far away from the substrate, which is unstable.When more metal atoms in the M_4 cluster interact with the substrate like Side-Tetrahedron and Regular-Tetrahedronconfigurations, there will be more electron transfer between the cluster and the substrate, which will make the M_4 cluster stably bind to the MN_4-Gr substrate.

Figure S3: Final configurations of planar M_4 clusters initially bounded to MN_4-Gr substrates. (a)-(d) are shown for Fe_4@FeN_4Gr, Fe_4@NiN_4Gr, Ni_4@FeN_4Gr and Ni_4@NiN_4Gr, respectively.

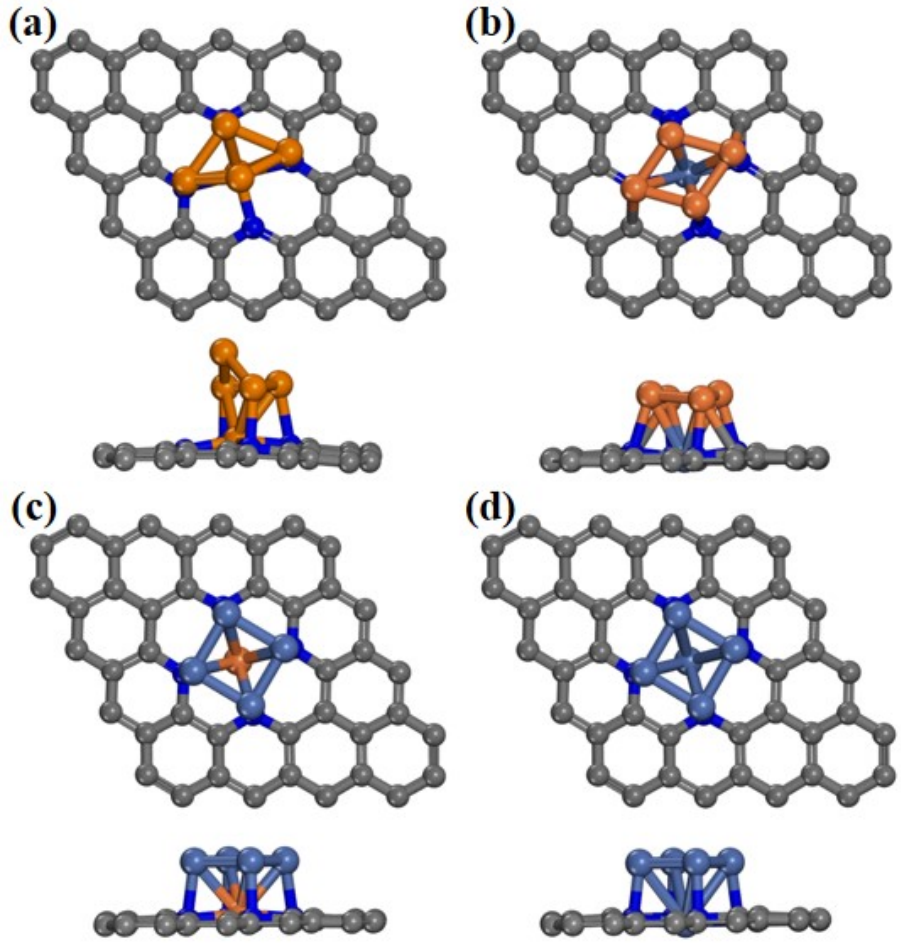


Figure S4: Schematic diagram of metal and N atoms labelling: (a)-(d) are shown for Fe_4FeN_4Gr, Fe_4NiN_4Gr, Ni_4FeN_4Gr and Ni_4NiN_4Gr, respectively.

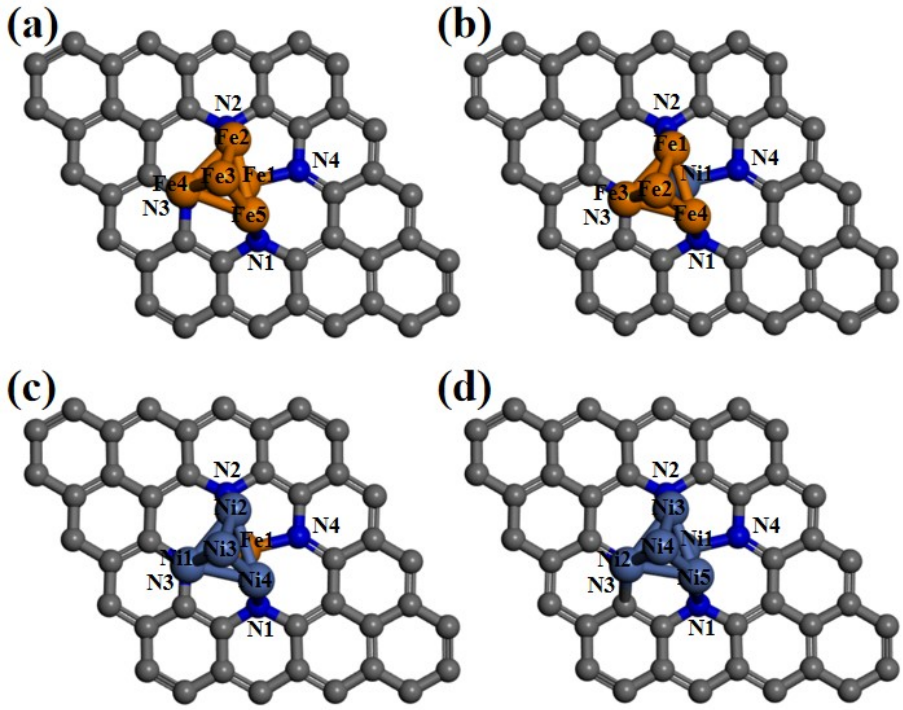


Figure S5: Schematic illustration of different adsorption sites on M_4 clusters supported on MN_4-Gr substrates.

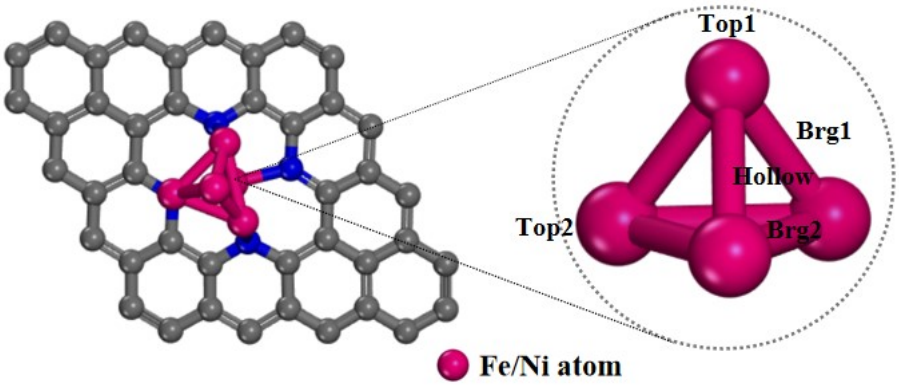


Figure S6: TheGibbs free energies of hydrogen adsorption ($^{\Delta G_{H*}}$) inimplicit solvation model.

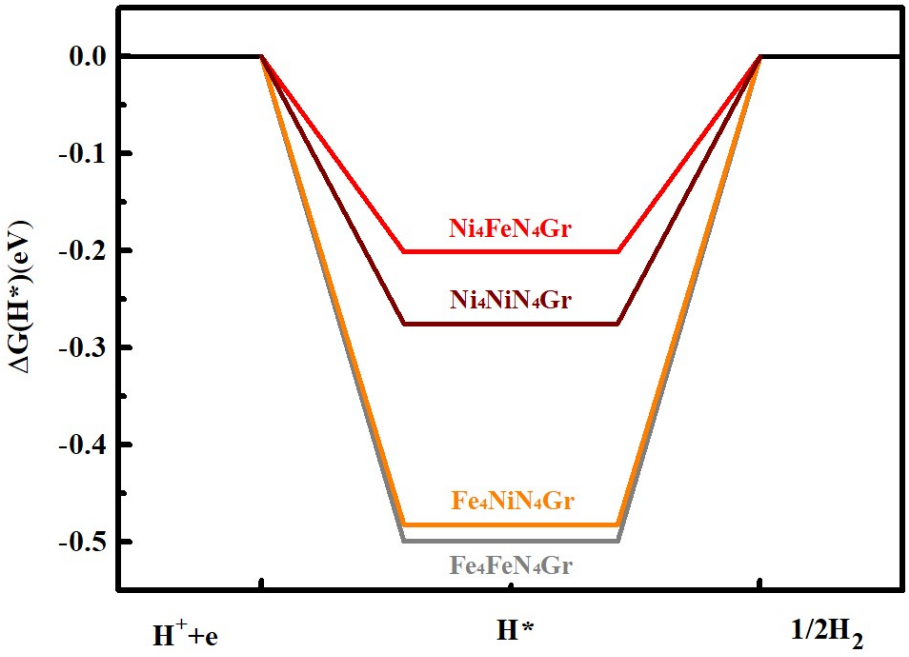


Figure S7: Configuration diagrams of the HER mechanism on four model catalysts. (a)-(d) are Fe_4FeN_4Gr, Fe_4NiN_4Gr, Ni_4FeN_4Gr and Ni_4NiN_4Gr, respectively,

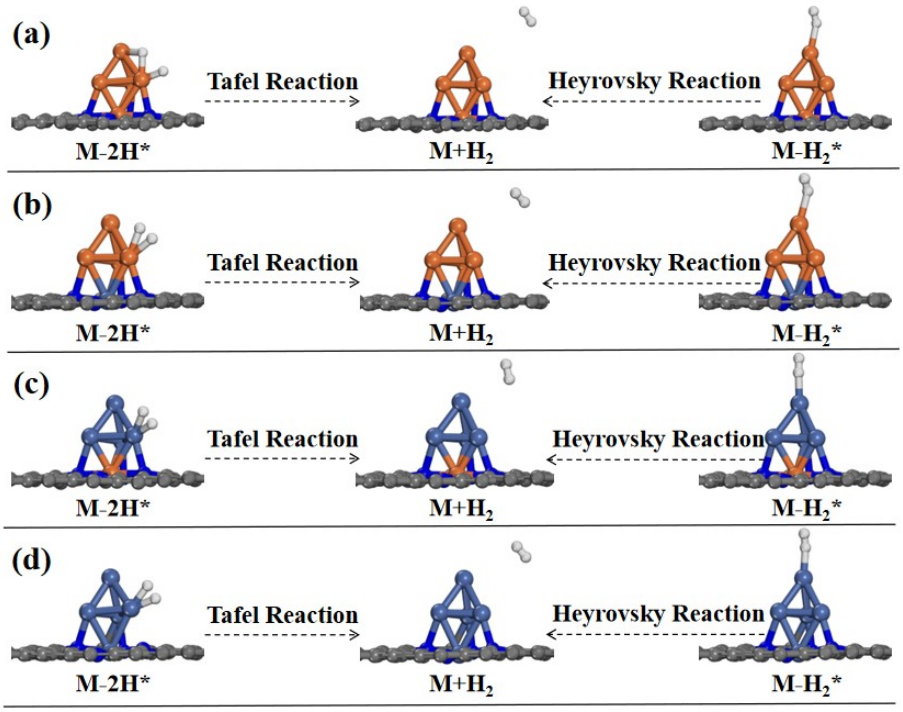


Figure S8: The free energy diagrams of HER inimplicit solvation model, following the Volmer-Heyrovsky pathway (dotted lines) and Volmer-Tafel pathway (solid lines) on various modelcatalysts.

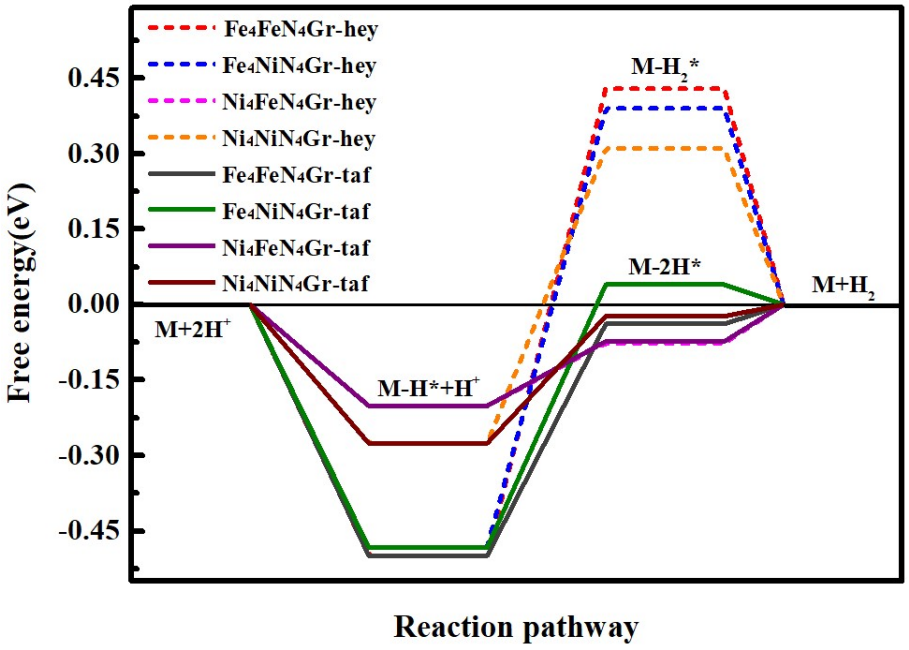


Figure S9: Configuration diagram of two hydrogen atoms adsorbed on the M_4@MN_4-Gr catalyst.