Supplementary Information

Enhancing HER Performance via Nitrogen Defects: A Comparative DFT Study of Fe and Ru Single-Atom Catalysts on Graphene

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Supplementary Figures

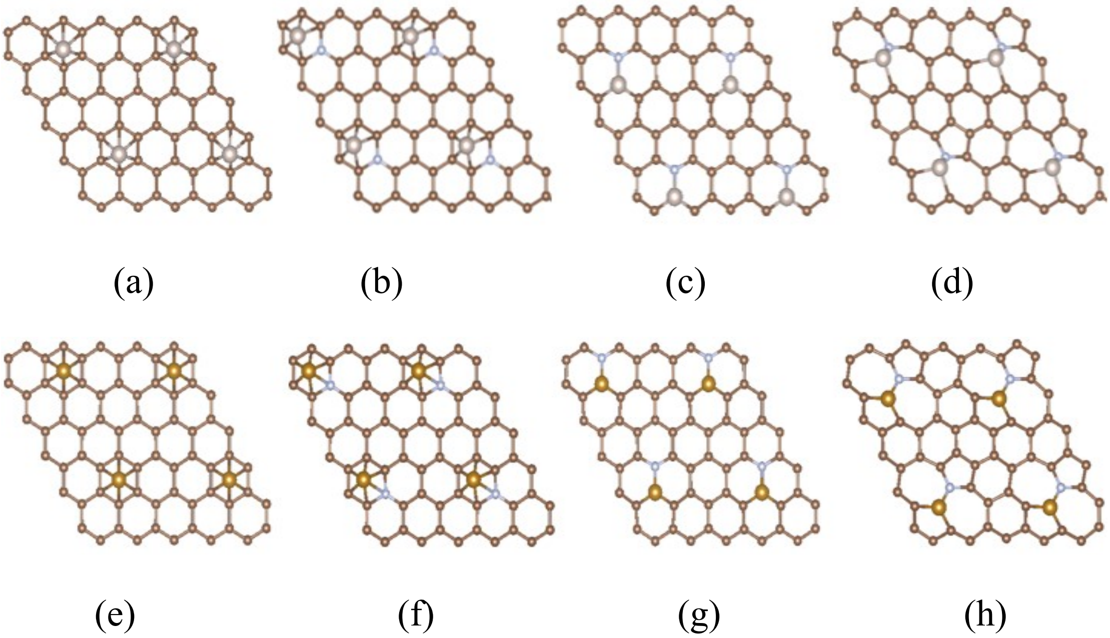
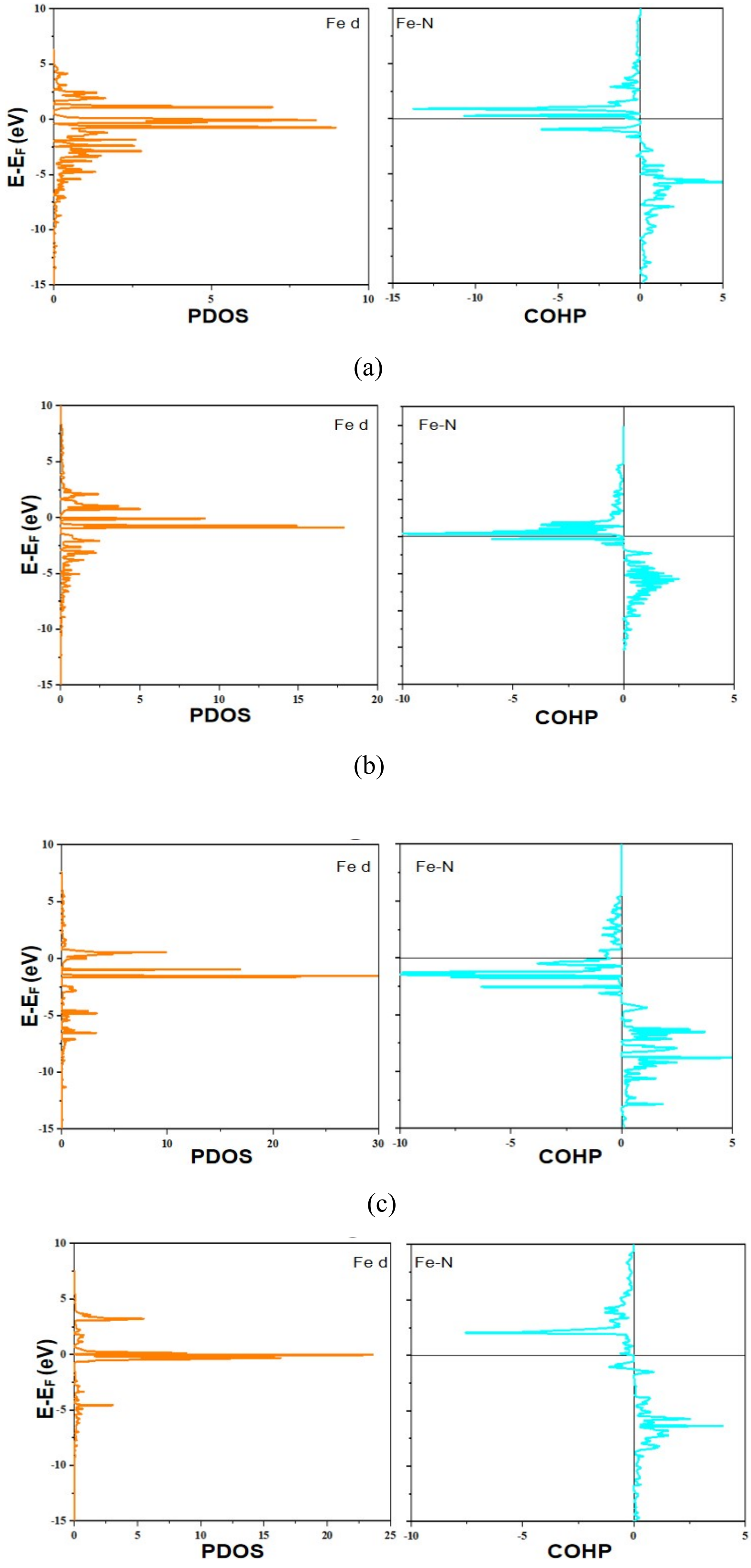


Figure S1. The optimized structures Ru on the substrate of (a)graphene, (b)N_graphitic, (c)N_pyridinic and (d)N_pyrrolic doped graphene; The optimized structures of Fe SA on the substrate of (e)graphene, (f)N_graphitic, (g)N_pyridinic and (h)N_pyrrolic doped graphene. the C, N, Ru and Fe atoms are represented by dark brown, blue, gray and yellow balls, respectively.



(a)

(b)

(c)

(d)

Figure S2. PDOS and COHP analysis for Fe SACs on the (a) N_pyrrolic, (b) 2N, (c) 3N and (d) 4N-doped graphene substrates.

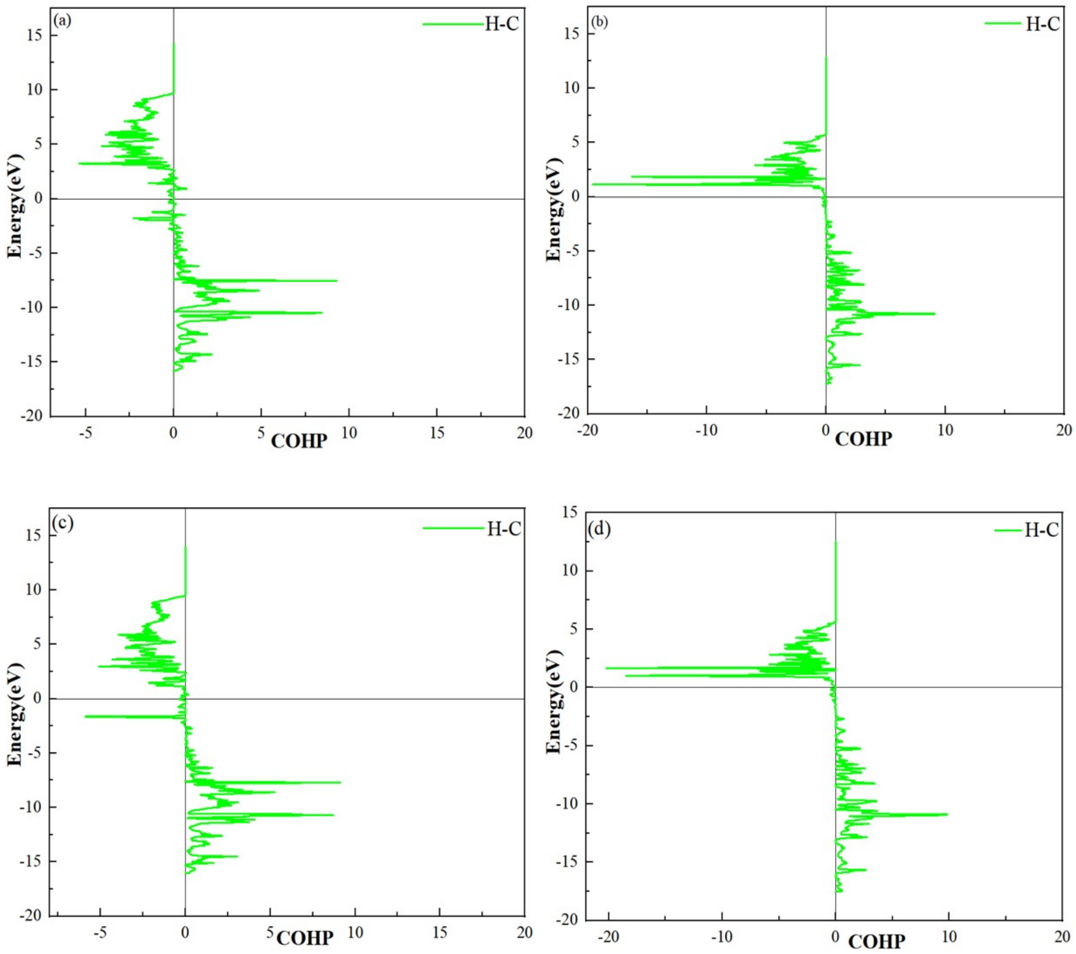


Figure S3. COHP of C-H bonds for (a) Ru SAC@N_pyrrolic, (b) Ru SAC@3N, (c)Fe SAC@N_pyrrolic and (d)Fe SAC@3N doped graphene

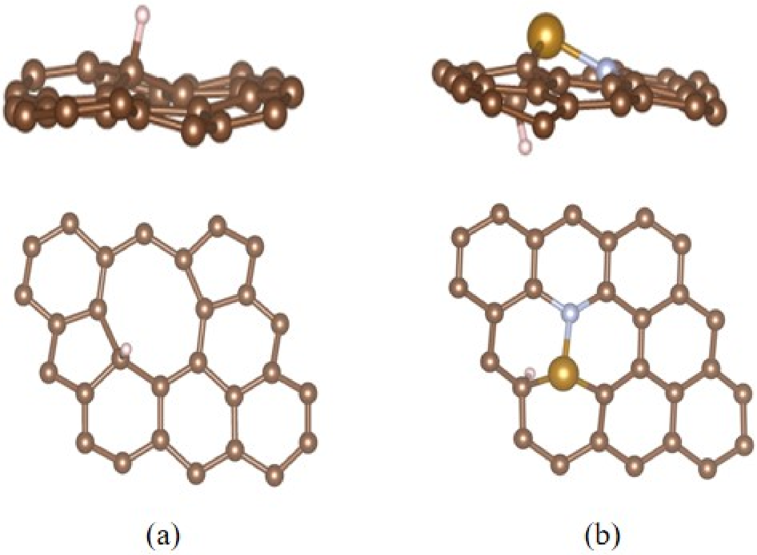


Figure S4. The optimized hydrogen adsorption configurations for (a)Vac$_2$_C and (b)Fe SAC@N_pyridinic doped graphene. Dark brown, blue, yellow and white represent C, N, Fe and H, respectively.

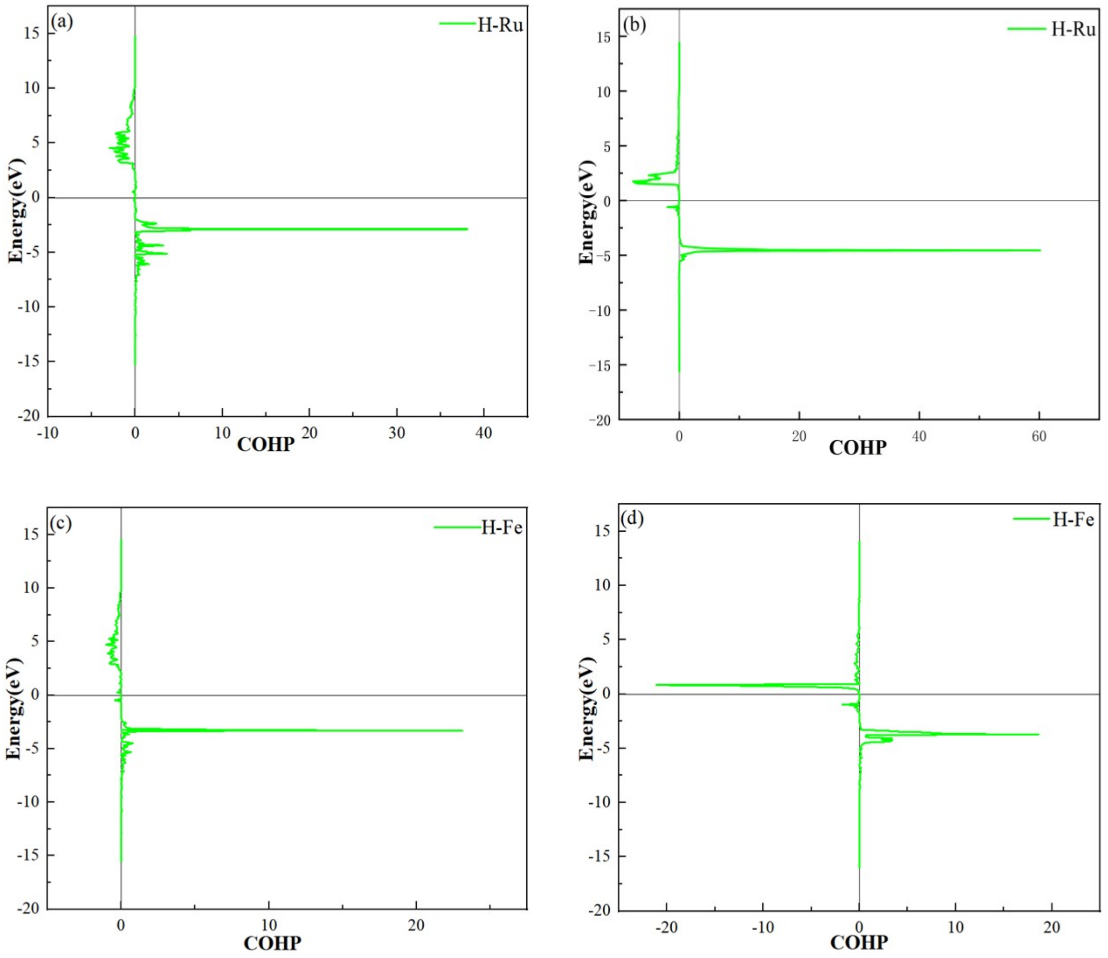


Figure S5. COHP of Ru-H bonds for (a)Ru SAC@2N, (b)Ru SAC@4N; COHP of Fe-H bonds for (a)Fe SAC@2N, (b)Fe SAC@4N doped graphene

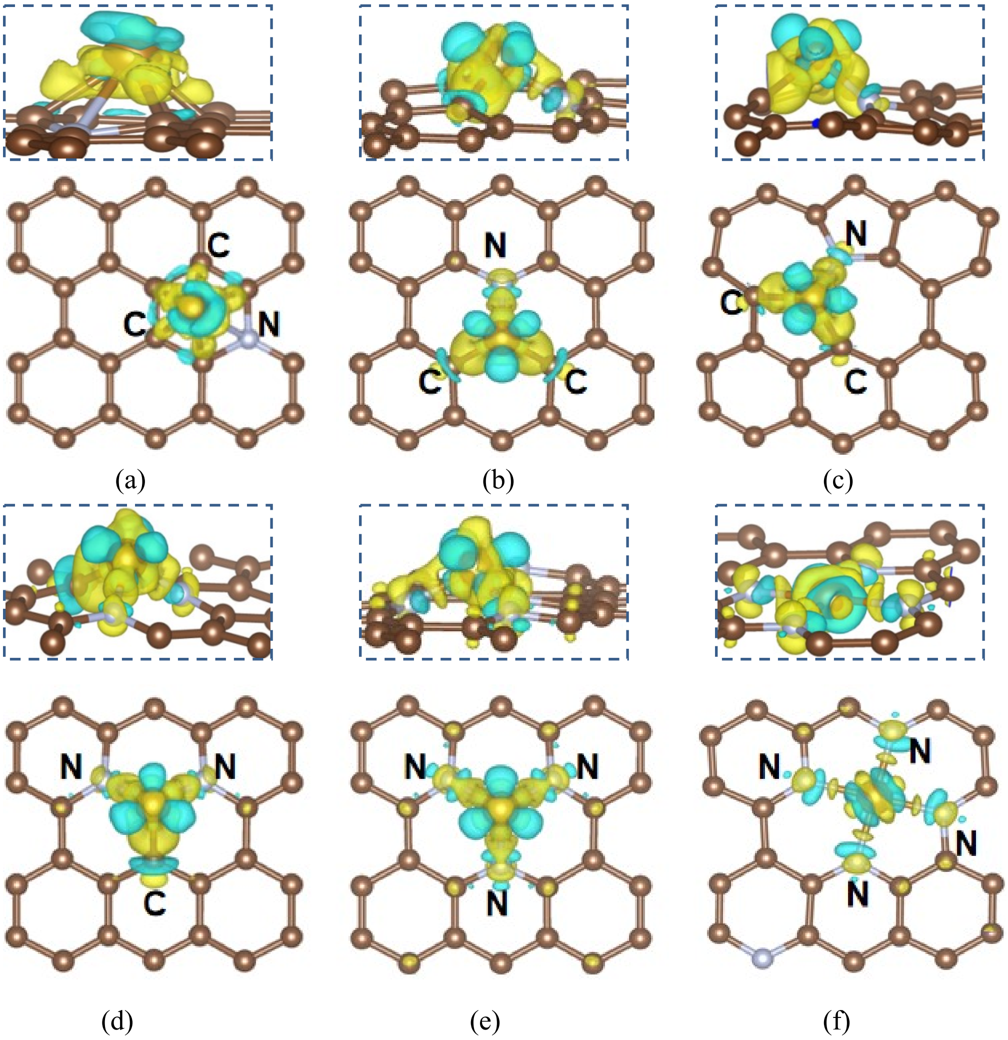


Figure S6. Electron Density Difference mapping for Fe deposition on the substrates (a)N_graphitic, (b)N_pyridinic, (c)N_pyrrolic, (d)2N_Vac, (e)3N_Vac and (f)4N_Vac. The yellow and blue areas denote electron accumulation and depletion, respectively.

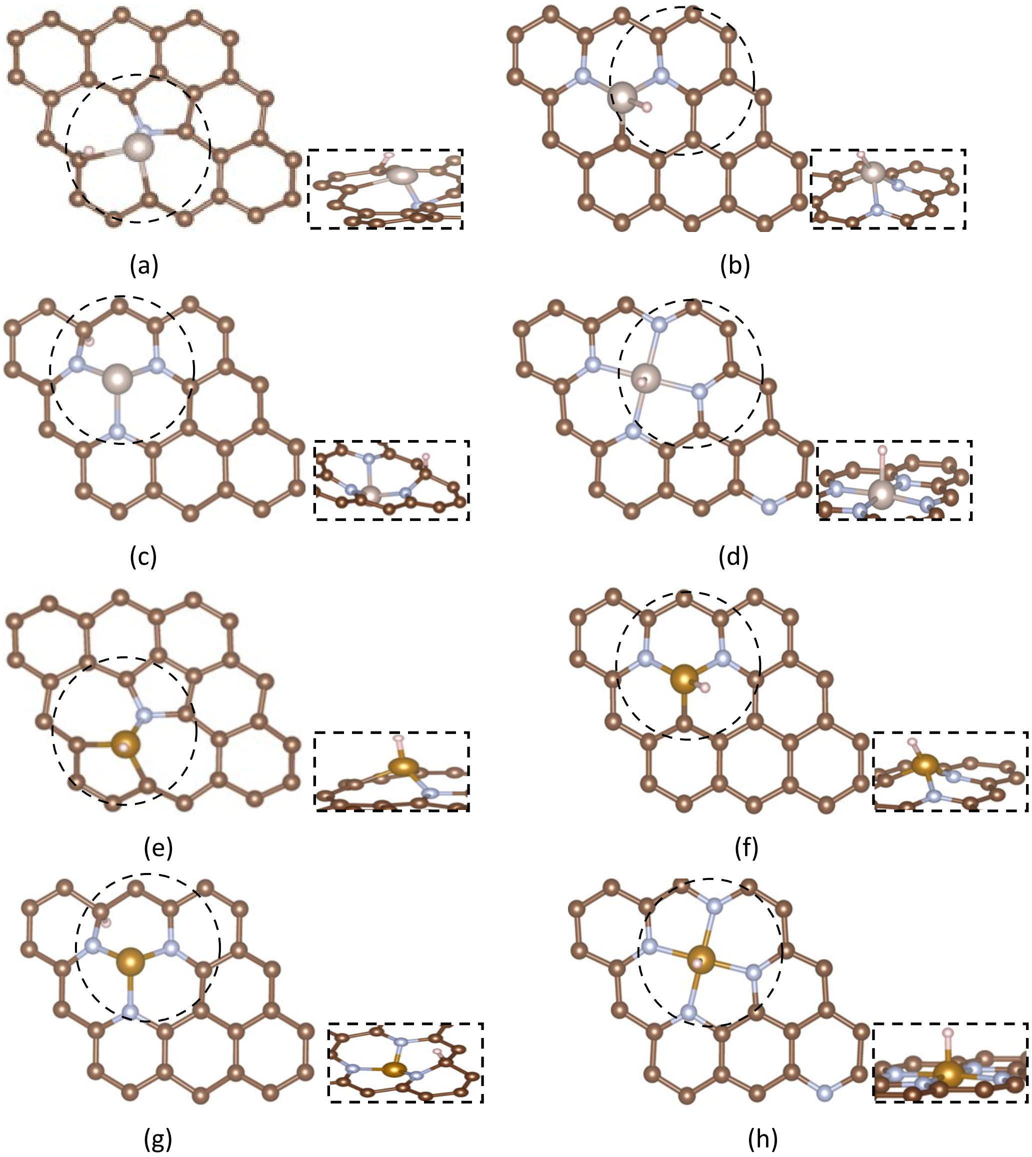
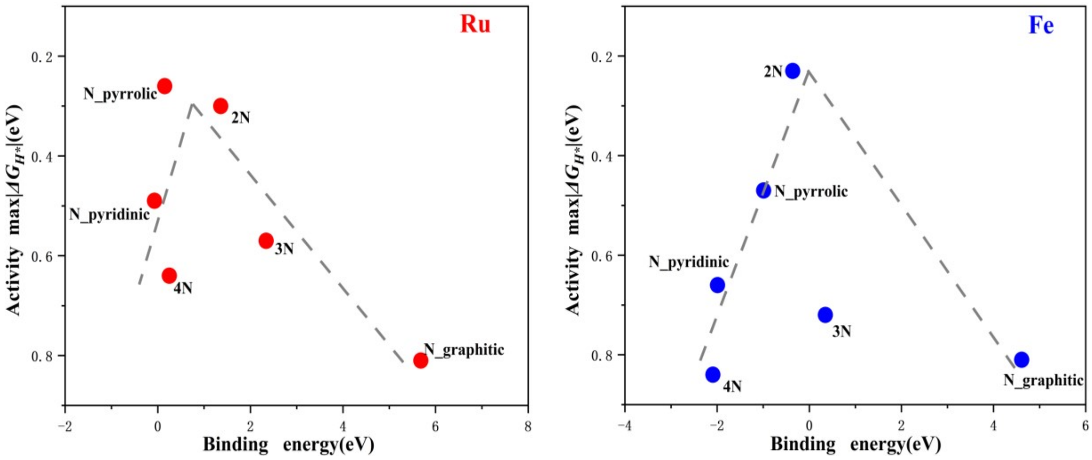


Figure S7. The optimized hydrogen adsorption configurations for (a)Ru SAC @N_pyrrolic, (b)Ru SAC@2N, (c)Ru SAC@3N, (d)Ru SACs@4N,(e)Fe SAC @N_pyrrolic, (f)Fe SAC@2N,(g)Fe SAC@3N and (h)Fe SACs@4N doped graphene. Dark brown, blue, gray, yellow and white represent C, N, Ru, Fe and H, respectively.



(a) (b)

Figure S8. volcano plots of max|ΔG_{H*}| vs binding energy (E_{bind}) of (a) Ru SACs and (b) Fe SACs on N doped graphene substrates. The worst absorption case represented by the maximum |ΔG_{H*}| is considered as the most limiting step of HER reaction in the acidic condition. Note that, the zigzag site nitrogen in metal SAC@N_pyridinic and 3N show very strong deprotonation tendency (ΔG_{H*}>1.4eV) , these sites are considered as non-active sites during HER.

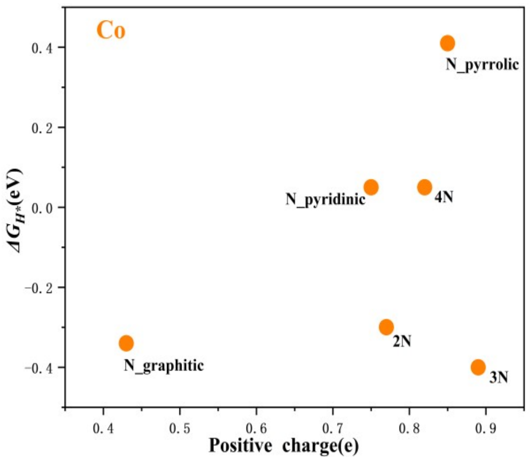


Figure S9. volcano plots of ΔG_{H^*} varies with the positive charge of supported Co SACs.

Supplementary Tables

Table S1. Calculated energetic results for various substrate models of N doped graphene. E_{DEF} represents the defect formation energy.

Structure	*E/atom* (eV)	E_{DEF} (eV)
Gra_C	-9.22	/
Vac_C	-8.76	7.89
Vac_2_C	-8.88	**5.47**
N_graphitic	-9.12	**0.91**
N_pyridinic	-8.80	6.19
N_pyrrolic	-8.66	8.64
2N_Vac	-8.83	**4.73**
3N_Vac	-8.85	**3.67**
4N_Vac	-8.82	**3.18**
N_Vac_2_C	-8.81	5.75
2N_Vac_2	-8.66	7.19
3N_Vac_2	-8.72	5.34
4N_Vac_2	-8.77	3.51

Table S2. Calculated energetic and bond formation results of Fe SACs on the various models of defect containing graphene substrates. E_{bind}[Fe] represents the binding energy of Fe. ΔE represents the total formation energy of Fe SACs@N_x moieties. i.e. $\Delta E = E_{DEF} + E_{bind}$[Fe]. $d_{\text{Fe-N}}$ represents the distance between the Fe and N atoms. $d_{\text{Fe-C}}$ represents the distance between the Fe and neighboring C atoms. Q_{Fe} represents the positive charge of Fe atoms on the N doped substrate derived from Bader charge analysis.

Structure	E_{bind}[Fe] (eV)	ΔE (eV)	$d_{\text{Fe-N}}$ (Å)	$d_{\text{Fe-C}}$ (Å)	Q_{Fe} (eV)	ICOHP Fe-N (eV)
Gra_C	4.61	4.61	/	2.07	+0.43	/
Vac_C	-2.58	5.31	/	1.76	+0.71	/
Vac_2_C	1.03	6.50	/	1.85	+0.91	/
N_Vac_2_C	3.06	8.81	1.85	1.84	+0.74	-2.48
N_graphitic	4.61	5.52	2.41	2.01	+0.60	-0.10
N_pyridinic	-1.99	4.20	1.77	1.76	+0.53	-3.47
N_pyrrolic	-0.99	7.65	1.73	1.83	+0.75	-3.70
2N	-0.36	4.37	1.78	1.74	+0.84	-3.37
3N	0.35	4.02	1.78	/	+1.03	-3.28
4N	-2.09	1.42	1.88	/	+0.99	-2.68

Table S3. Calculated energetic and bond formation results of Ru SACs on the various models of defect containing graphene substrates. E_{bind}[Ru] represents the binding energy of Ru. ΔE represents the total formation energy for the Fe SACs@Nx moieties, i.e. $\Delta E = E_{DEF} + E_{bind}$[Ru]. $d_{\text{Ru-N}}$ represents the distance between the Ru and N atoms. $d_{\text{Ru-C}}$ represents the distance between the Ru and neighboring C atoms. Q_{Ru} represents the positive charge of Ru atoms on the N doped substrate derived from Bader charge analysis.

Structure	E_{bind}[Ru] (eV)	ΔE (eV)	$d_{\text{Ru-N}}$ (Å)	$d_{\text{Ru-C}}$ (Å)	Q_{Ru} (eV)	ICOHP Ru-N (eV)
Gra_C	5.98	5.98	/	2.22	+0.39	/
Vac_C	-1.41	6.48	/	1.87	+0.66	/
Vac_2_C	1.49	6.96	/	2.02	-0.56	/
N_graphitic	5.68	6.59	2.60	2.13	+0.38	-0.03
N_pyridinic	-0.07	6.12	1.91	1.87	+0.32	-3.75
N_pyrrolic	0.15	8.79	1.97	1.98	+0.49	-3.02
N_Vac_2_C	4.37	10.12	2.05	1.96	+0.74	-2.38
2N	1.36	5.79	1.92	1.86	+0.70	-3.68
3N	2.34	6.01	1.91	/	+0.81	-3.68
4N	0.25	3.35	1.94	/	+0.96	-3.46

Table S4 The calculated bonding information for H adsorption on the N-doped graphene.

	Ru			Fe		
	Adsorption sites Bond	Distance (Å)	ICOHP (eV)	Adsorption sites Bond	Distance (Å)	ICOHP (eV)
N_pyrrolic	C-H	1.20	-5.45	Fe-H	1.55	-2.84
2N	Ru-H	1.68	-2.93	Fe-H	1.57	-2.70
3N	C-H	1.12	-5.77	C-H	1.12	-5.77
4N	Ru-H	1.58	-2.93	Fe-H	1.63	-2.08

Table S5 Calculated charge state of Ru and Fe SACs and energetic results for hydrogen adsorption. All possible H* adsorption sites on the substrates have been considered. Q_M denotes the positive charge of metal SACs on the N doped substrate (derived from Bader charge analysis).

Substrate Structure	$\mathbf{Q_{Ru}}$	$\mathbf{\Delta G_{H^*}}$ **@Ru**	$\mathbf{|\Delta G_{H^*}|_{min}}$ **(eV)**	$\mathbf{|\Delta G_{H^*}|_{max}}$ **(eV)**	$\mathbf{Q_{Fe}}$	$\mathbf{\Delta G_{H^*}}$ **@Fe**	$\mathbf{|\Delta G_{H^*}|_{min}}$ **(eV)**	$\mathbf{|\Delta G_{H^*}|_{max}}$ **(eV)**
N_graphitic	0.38	-0.42	(-)0.42	0.81	0.60	-0.39	(-)0.39	0.81
N_pyridinic	0.32	-0.49	0.34	(-)0.49	0.53	-0.38	(-)0.14	0.66
N_pyrrolic	0.49	0.21	0.01	0.26	0.75	0.02	0.02	0.47
2N	0.70	-0.10	(-)0.10	(-)0.30	0.84	-0.01	(-)0.01	(-)0.23
3N	0.81	-0.41	0.19	0.57	1.03	-0.28	0.26	0.72
4N	0.96	-0.64	0.59	(-)0.64	0.99	-0.18	(-)0.18	0.84

Table S6 Calculated charge state of Co SACs and energetic results for hydrogen adsorption. All possible H* adsorption sites on the substrates have been considered. Q_M denotes the positive charge of Co SACs on the N doped substrate (derived from Bader charge analysis).

Substrate Structure	**E_{bind}[Co] (eV)**	**Q_{Co}**	**ΔG_{H^*} @Co**	**$\lvert\Delta G_{H^*}\rvert_{min}$ (eV)**	**$\lvert\Delta G_{H^*}\rvert_{max}$ (eV)**
N_graphitic	4.06	0.43	-0.34	(-)0.34	0.84
N_pyridinic	-1.59	0.75	0.05	0.05	0.80
N_pyrrolic	-1.42	0.85	0.41	0.20	(-)0.50
2N	-0.13	0.77	-0.3	(-)0.30	(-)0.46
3N	0.67	0.89	-0.4	0.30	0.54
4N	-2.65	0.82	0.05	0.05	0.82

Table S7 Ru and Fe SACs substitution on the edge sites of N doped graphene. ***ΔE*** represents the energy required to replace 2H on the substrate with metal ions.

Substrate Structure	*ΔE[Ru] (eV)	*ΔE [Fe] (eV)
N_graphitic-2H	2.83	1.95
N_pyridinic-2H	2.99	2.75
N_pyrrolic-2H	3.89	2.89
2N-2H	4.05	2.54
3N-2H	4.34	2.57
4N-2H	2.83	0.72