Supplementary Material

Atomically dispersed NiN_4-Cl active site with axial Ni-Cl coordination for accelerating electrocatalytic hydrogen evolution

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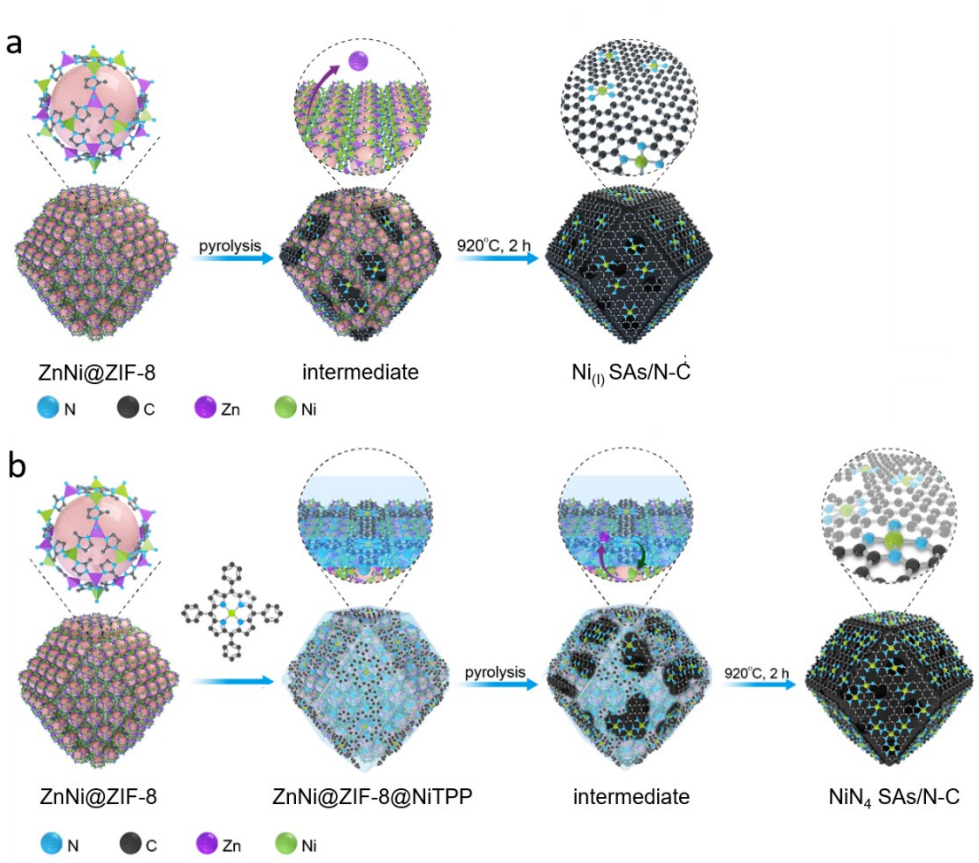


Fig. S1 Preparation process diagram of (a) $Ni_{(I)}$ SAs/N-C, (b) NiN_4 SAs/N-C.

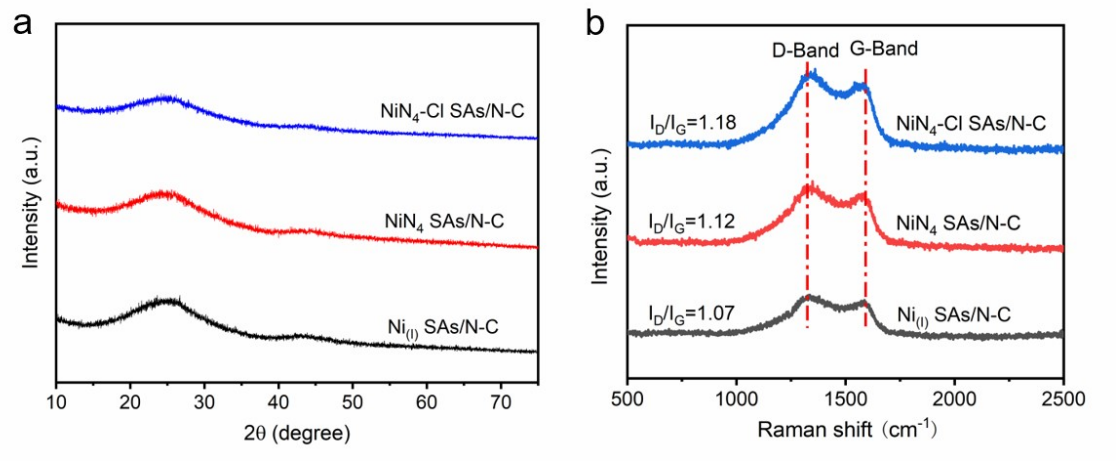


Fig. S2 (a) XRD pattern, (b) Raman diagram of $Ni_{(I)}$ SAs/N-C, NiN_4 SAs/N-C and $NiNi_4$-Cl SAs/N-C.

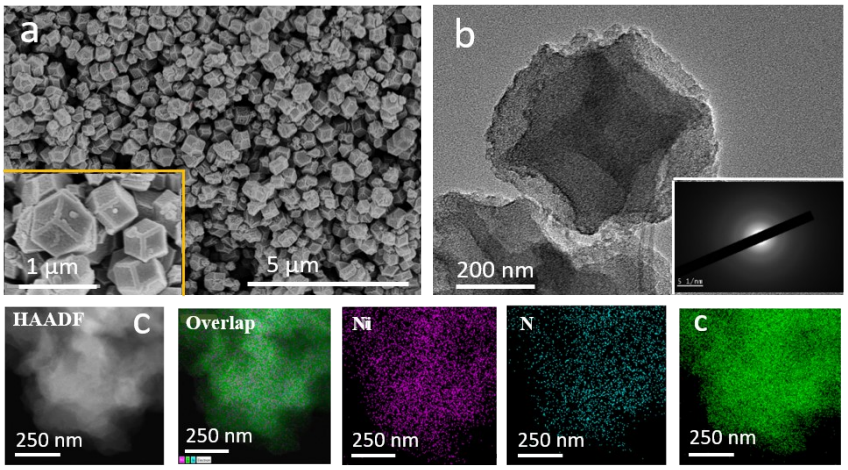


Fig. S3 (a) SEM, (b) TEM, (c) EDS mapping of NiN_4 SAs/N-C.

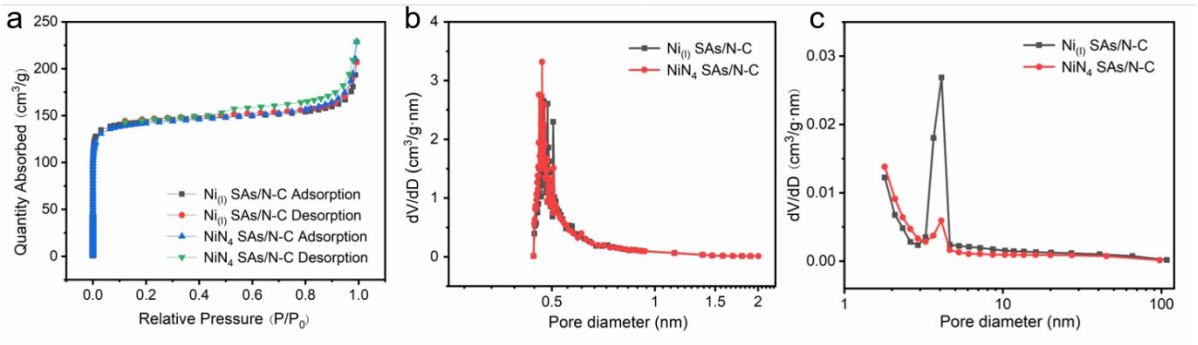
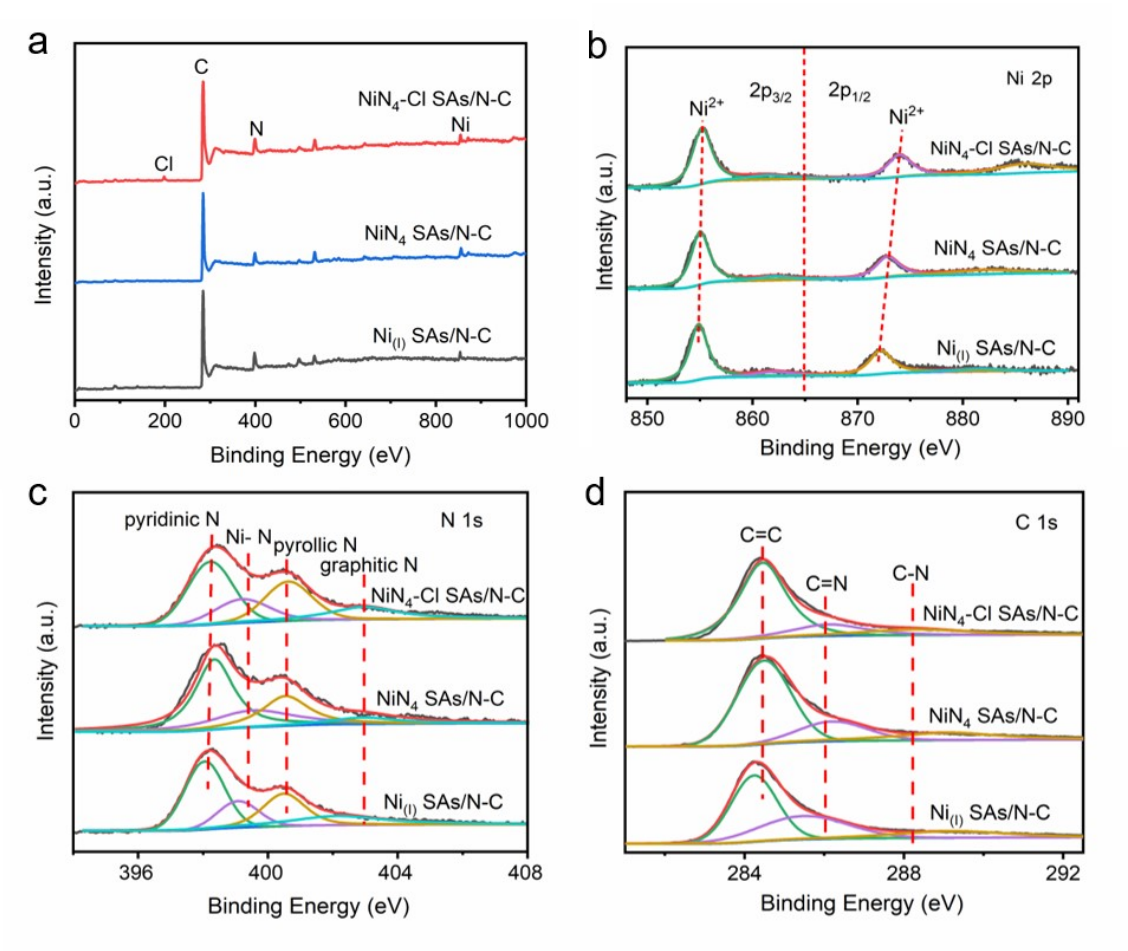


Fig. S4 BET analysis of $Ni_{(I)}$ SAs/N-C, NiN_4 SAs/N-C (a) N_2 absorption/desorption curve, (b, c) Aperture distribution curve.



Fi. S5 XPS spectra of $Ni_{(I)}$ SAs/N-C, NiN_4 SAs/N-C and NiN_4-Cl SAs/N-C (a) Survey, (b) Ni 2p, (c) N 1s, (d) C 1s.

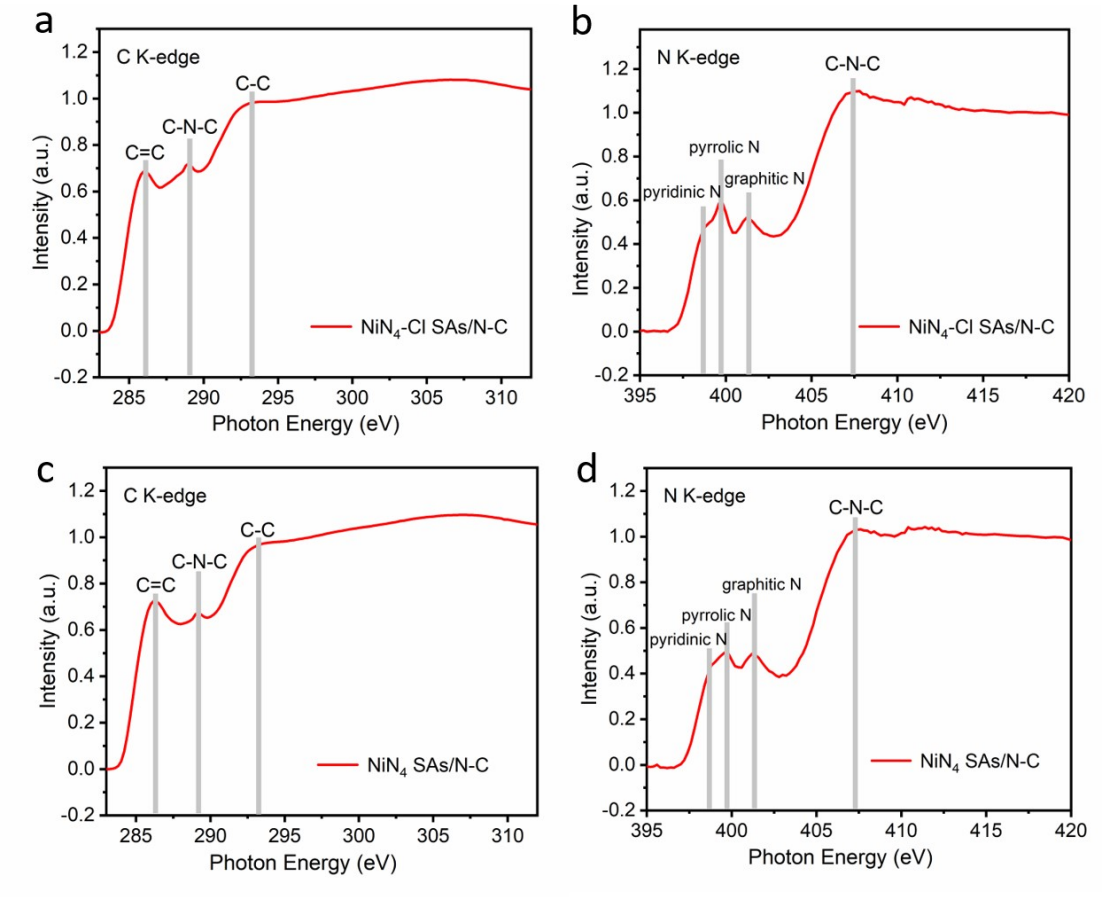


Fig. S6 (a) C K-edge XANES spectrum, (b) N K-edge XANES spectrum of NiN_4-Cl SAs/N-C, (c) C K-edge XANES spectrum, (d) N K-edge XANES spectrum of NiN_4 SAs/N-C.

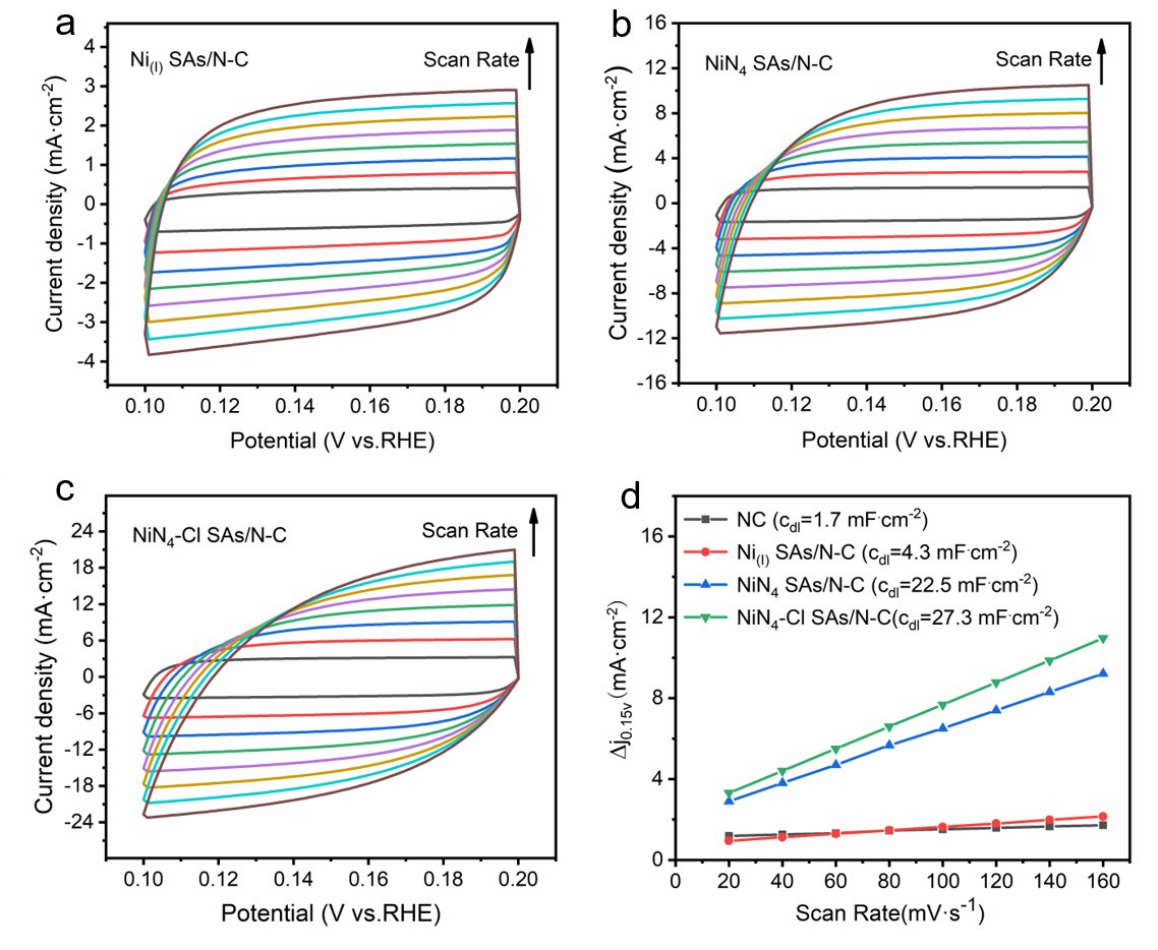


Fig. S7 CV curves of (a) $Ni_{(I)}$ SAs/N-C, (b) NiN_4 SAs/N-C, (c) NiN_4-Cl SAs/N-C in 1 M KOH, (d) C_{dl} diagram.

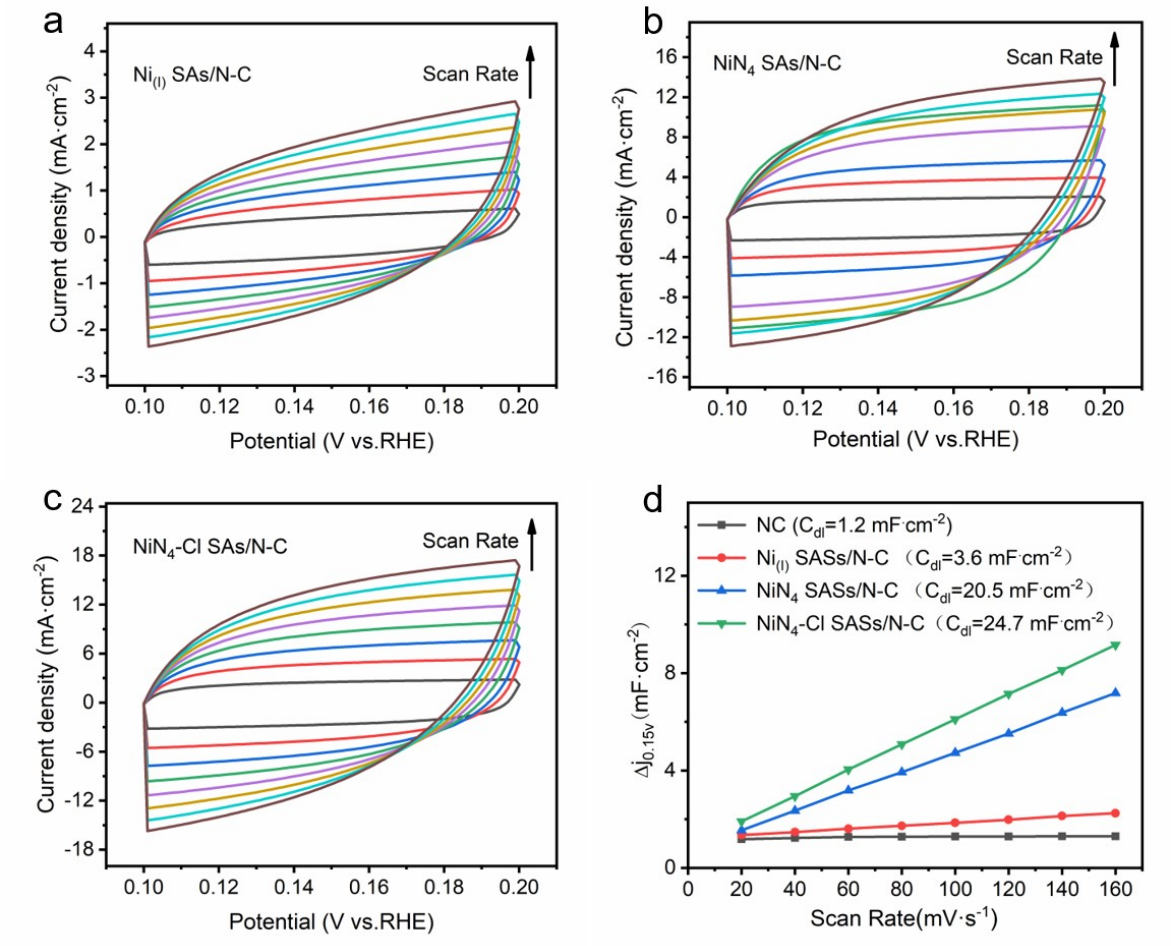


Fig. S8 CV curves of (a) $Ni_{(I)}$ SAs/N-C, (b) NiN_4 SAs/N-C, (c) NiN_4-Cl SAs/N-C in 0.5 M H_2SO_4, (d) C_{dl} diagram.

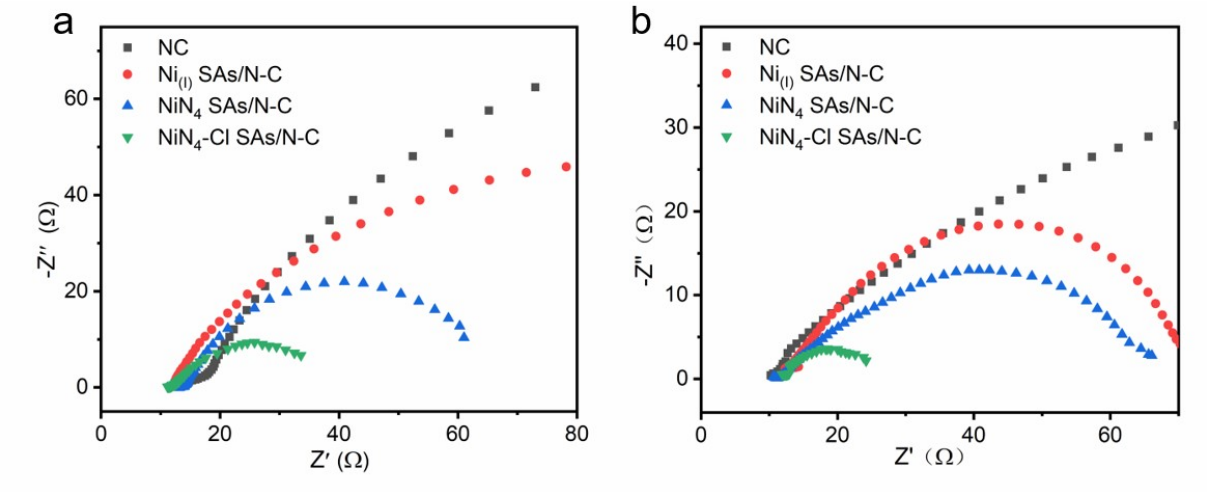


Fig. S9 EIS curves in (a) 1 M KOH (b) 0.5 M H_2SO_4 of $Ni_{(I)}$ SAs/N-C, NiN_4 SAs/N-C, NiN_4-Cl SAs/N-C and NC catalysts.

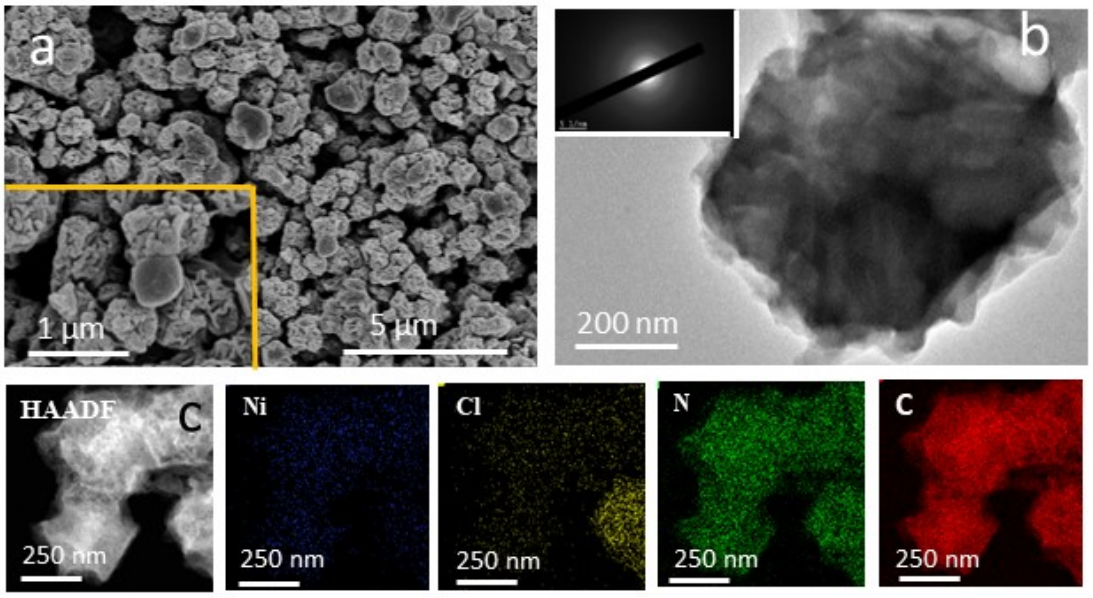


Fig. S10 (a) SEM, (b) TEM, (c) EDS mapping of NiN_4-Cl SAs/N-C after stability test of 24 h.

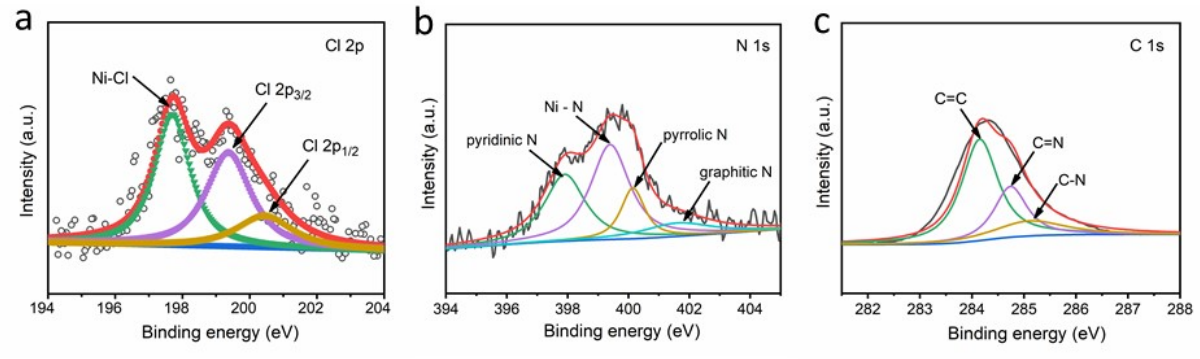


Fig. S11 XPS spectra of NiN_4-Cl SAs/N-C after stability test of 24 h (a) Cl 2p, (b) N 1s, (c) C 1s.

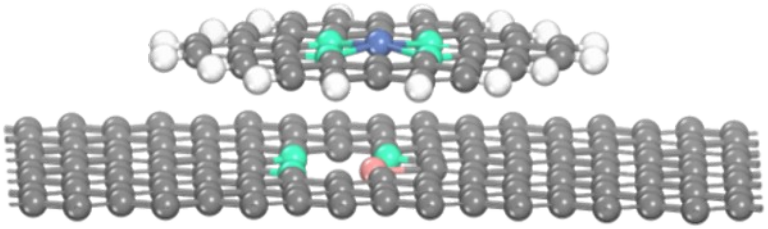


Fig. S12 Model: the pyridinic_NiN_4 supported on optimized isolated graphene substrate substituted by one C and three N atoms (pyrrolic Cl-N_3, named as NiN_4-Cl/N-C).

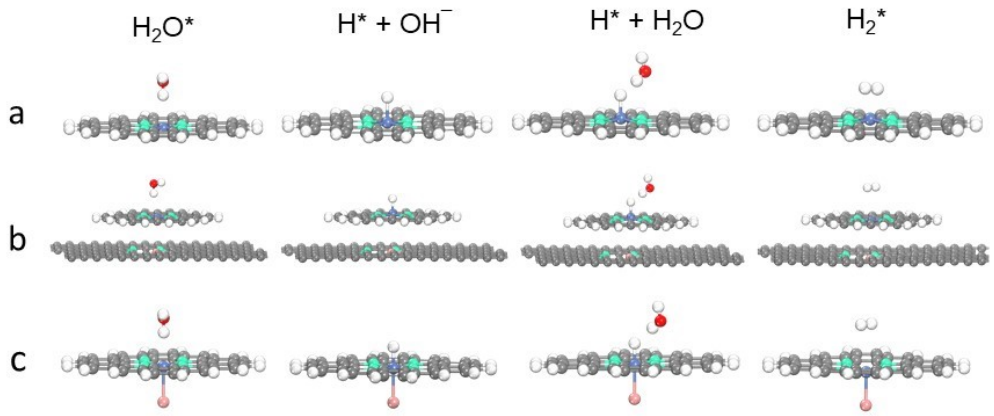


Fig. S13 The intermediate structures involved in the Volmer-Heyrovsky mechanism on (a) pyridinic_NiN_4, (b) NiN_4-Cl/N-C and (c) pyridinic_NiN_4-Cl.

Table S1 The ICP element content data of of $Ni_{(I)}$ SAs/N-C, NiN_4 SAs/N-C and NiN_4-Cl SAs/N-C.

Catalysts	Element	Atomic (%)
$Ni_{(I)}$SAs/N-C	Ni	0.48
NiN_4 SAs/N-C	Ni	1.38
NiN_4-Cl SAs/N-C	Ni	1.37

Table S2 BET analysis data of $Ni_{(I)}$ SAs/N-C, NiN_4 SAs/N-C and NiN_4-Cl SAs/N-C.

Catalysts	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Size (nm)
$Ni_{(I)}$ SAs/N-C	475.5	0.41	3.41
NiN_4 SAs/N-C	522.7	0.35	2.43
NiN_4-Cl SAs/N-C	528.5	0.32	2.72

Table S3 Structural parameters fitted by EXAFS (S_0^2=0.85) of NiN_4 SAs/N-C and NiN_4-Cl SAs/N-C.

Catalysts	Scattering pair	CN	R（Å）	σ^2（$10^{-3}Å^2$）	E_0 (eV)	R factor
NiN_4 SAs/N-C	Ni-N	4.1	1.81	4.9	-8.4	0.02
NiN_4-Cl SAs/N-C	Ni-N	4.2	1.85	5.1	-8.3	
	Ni-Cl	1.0	2.34	6.4	-8.3	

Table S4 The calculated values of ECSA of all catalysts in 1 M KOH.

Catalysts	C_{dl} (mF·cm^{-2})	C_s (mF·cm^{-2} per·cm^2)	ECSA (cm^{-2})
NC	1.7	0.04	42.5
$Ni_{(I)}$ SAs/N-C	4.3	0.04	107.5
NiN_4 SAs/N-C	22.5	0.04	562.5
NiN_4-Cl SAs/N-C	27.3	0.04	682.5

Table S5 The calculated values of ECSA of all catalysts in 0.5 M H_2SO_4.

Catalysts	C_{dl} (mF·cm^{-2})	C_s (mF·cm^{-2} per·cm^2)	ECSA (cm^{-2})
NC	1.2	0.035	30.0
$Ni_{(I)}$ SAs/N-C	3.6	0.035	90.0
NiN_4 SAs/N-C	20.5	0.035	512.5
NiN_4-Cl SAs/N-C	24.7	0.035	617.5

Table S6 Calculated Bader charges of relative atoms on Pyridinic_NiN_4, NiN_4-Cl/N-C and Pyridinic_NiN_4-Cl.

Atom	Pyridinic_NiN_4		NiN_4–Cl/N-C		Pyridinic_NiN_4-Cl	
	Clean surface	H* adsorption	Clean surface	H* adsorption	Clean surface	H* adsorption
N_1	-1.19	-0.67	-1.10	-1.09	-1.21	-0.68
N_2	-1.22	-0.68	-1.10	-1.09	-1.05	-0.69
N_3	-1.16	-0.60	-1.20	-1.16	-1.04	-0.69
N_4	-1.14	-0.59	-1.20	-1.16	-1.20	-0.67
Ni	0.87	0.59	0.84	0.79	0.96	0.61
H	-	-0.14	-	-0.10	-	0.04
Cl	-	-	0.19	0.19	-0.59	-0.53