

Supplementary Materials

Highly Graphitized Fe-N-C Electrocatalysts Prepared from Chitosan Hydrogel Frameworks

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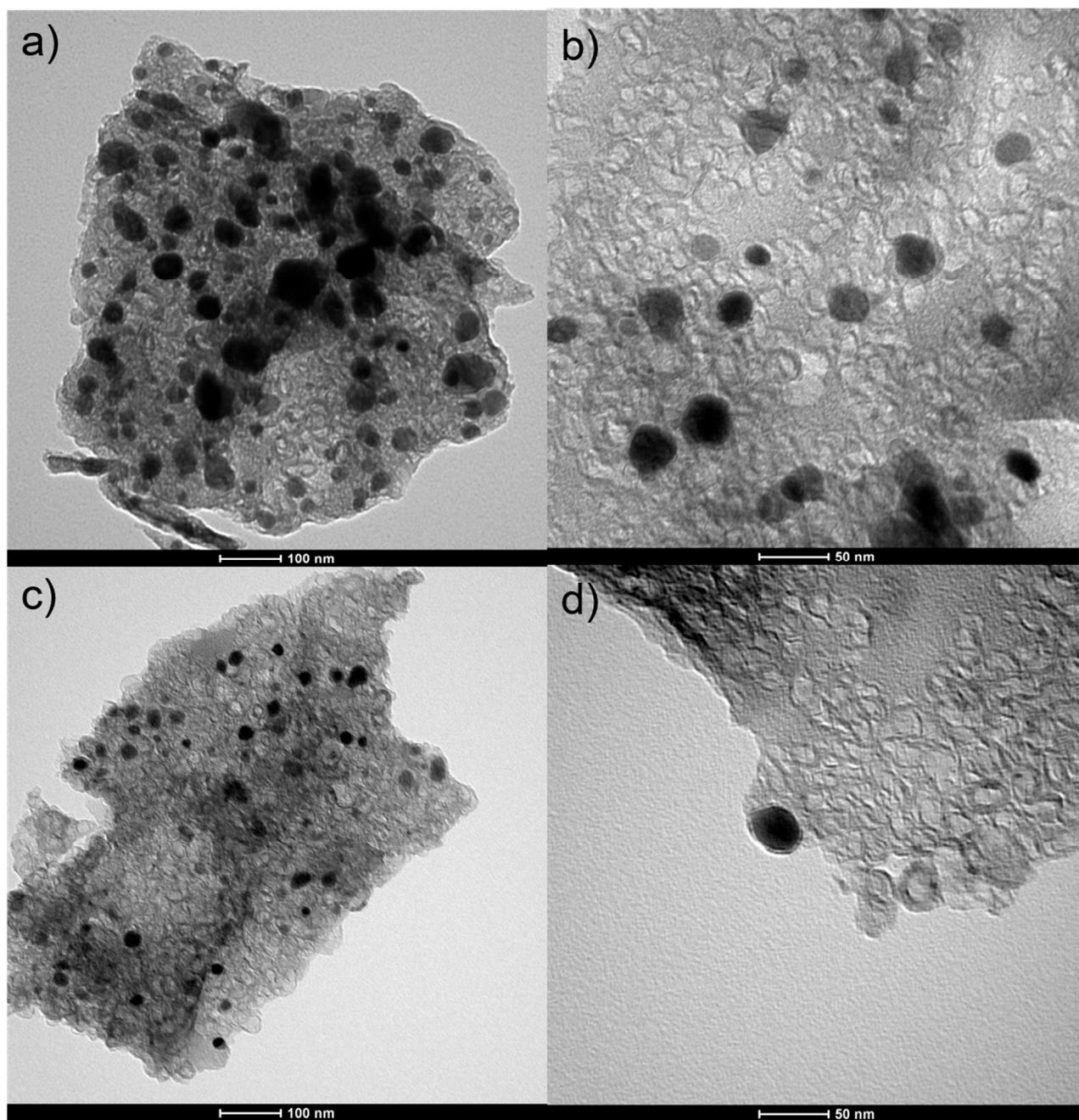


Figure S1: TEM images of Fe-N-C3 before (a,b) and after (c,d) acid treatment.

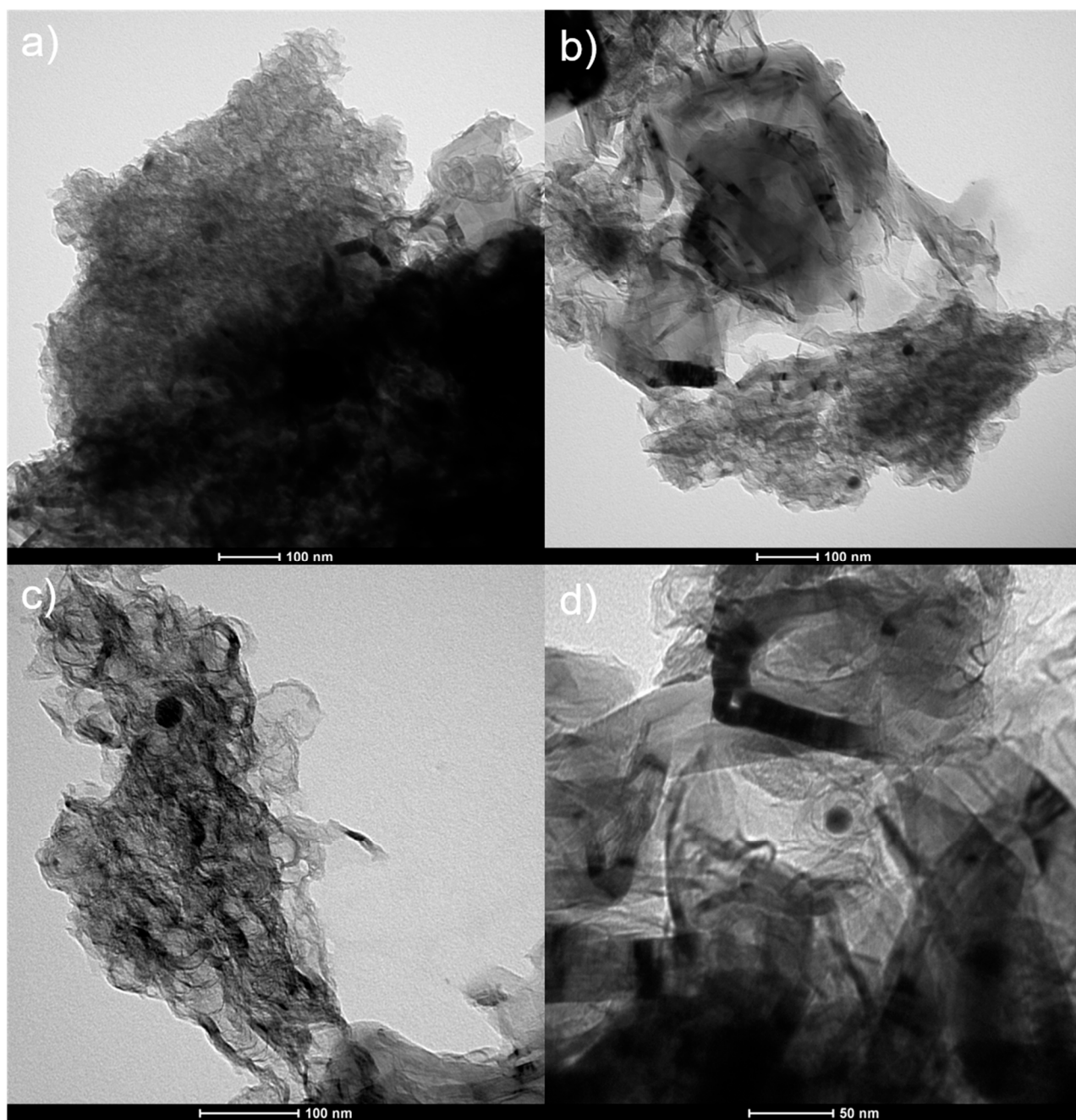


Figure S2: TEM images of Fe-N-C5 before (a,b) and after (c,d) acid treatment.

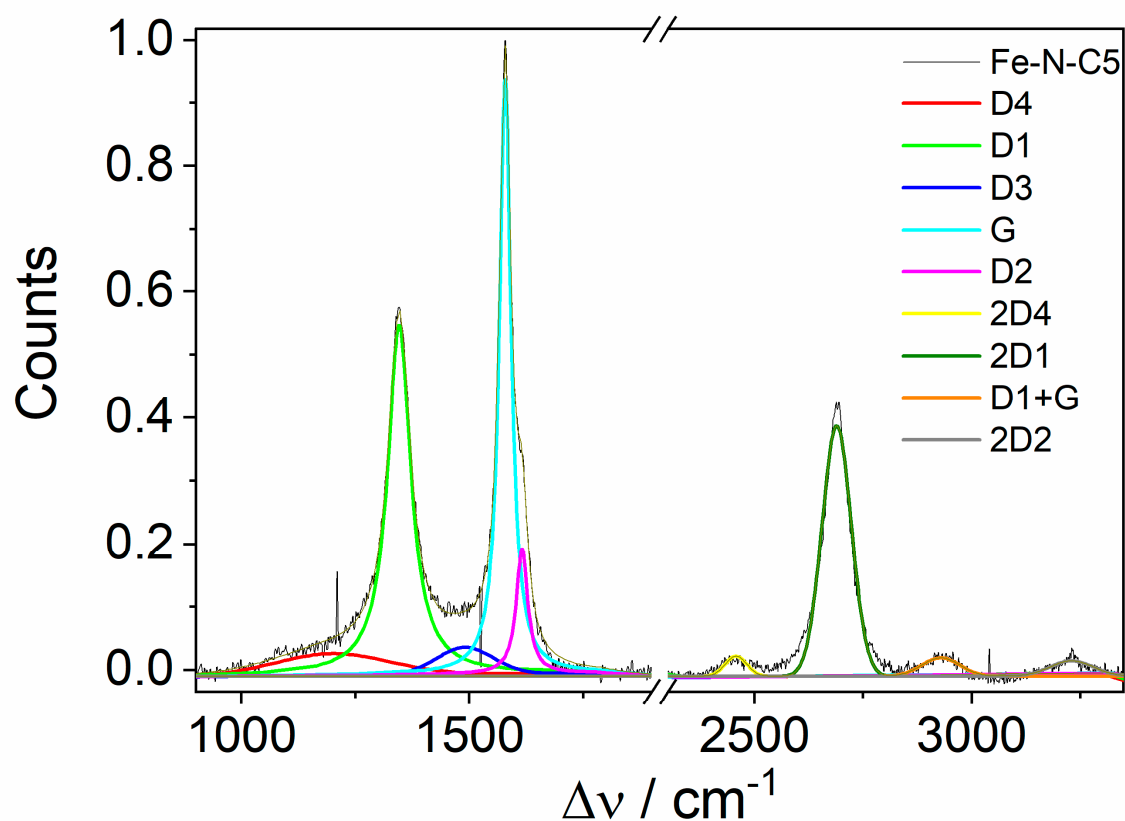


Figure S3: Example of Raman spectrum deconvolution.

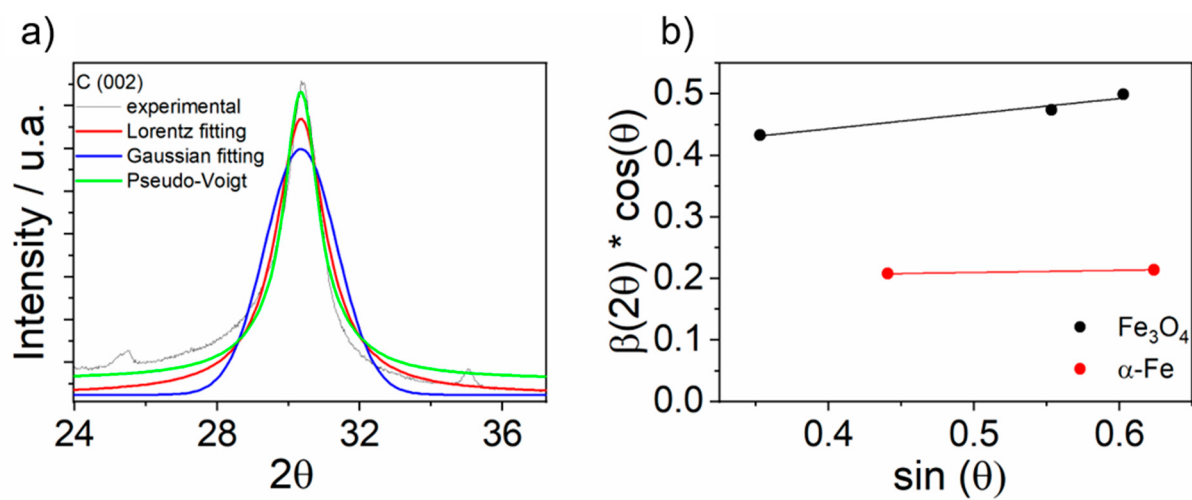


Figure S4: (a) Pseudo-Voigt fitting on graphite peak obtained from XRD technique. (b) Williamson-Hall (W-H) plot of magnetite and $\alpha\text{-Fe}$.

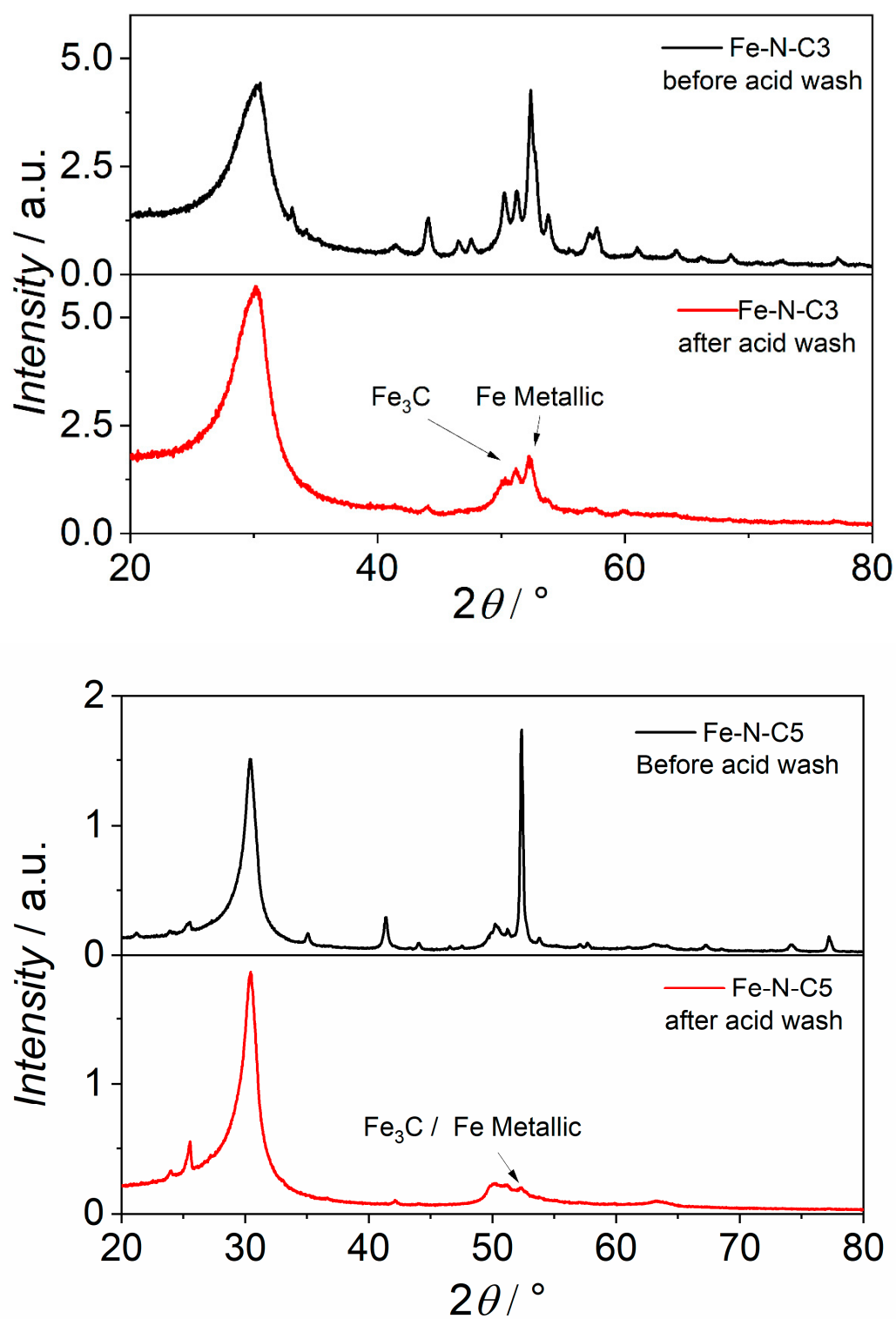


Figure S5: XRD spectra of Fe-N-C3 and Fe-N-C5 before and after acid washing.

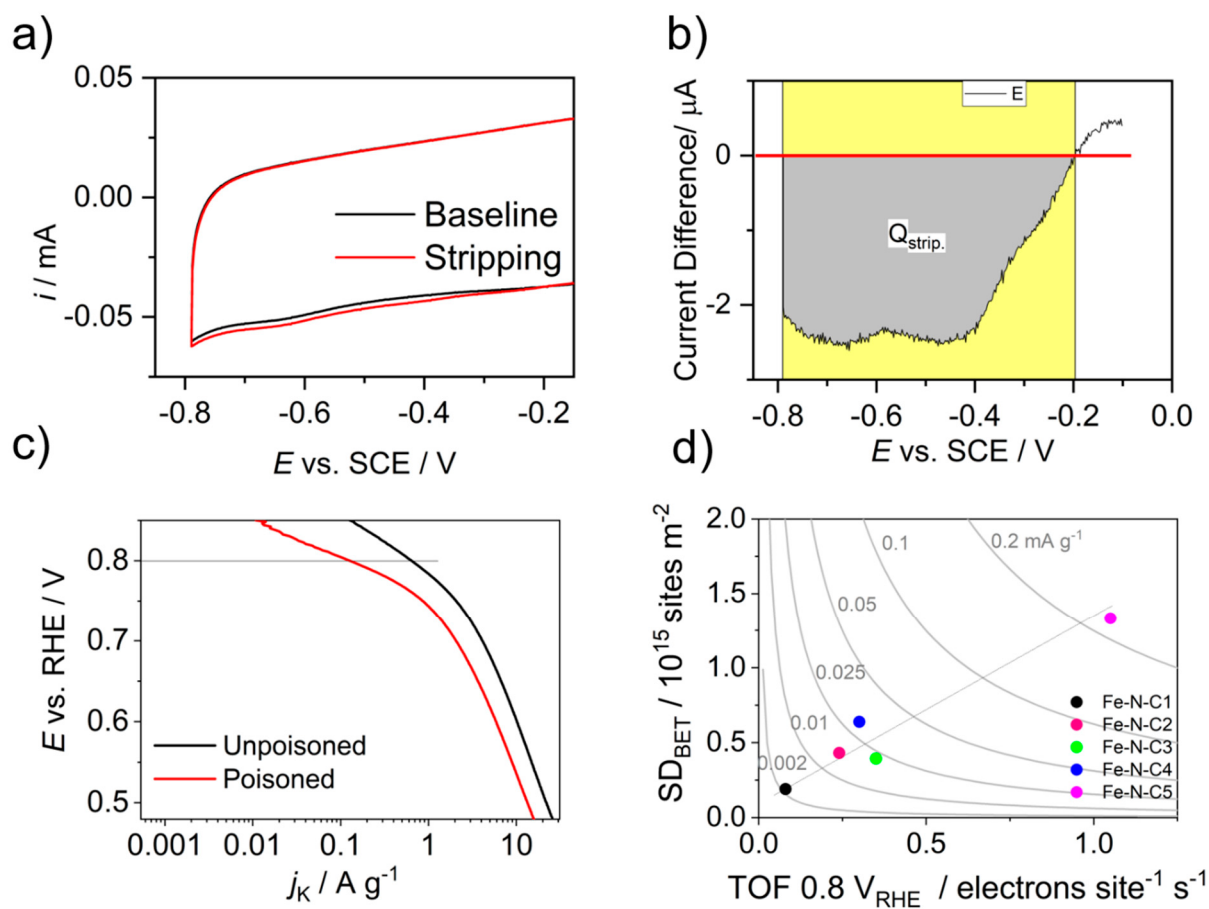


Figure S6: (a) nitrite stripping and recovered CVs of Fe-N-C5 recorded in Ar-saturated electrolyte at 10 mV s^{-1} , (b) magnification of the stripping area integrated for the site density determination, (c) Tafel plot recorded before and after poisoning in O_2 -saturated electrolyte, and (d) Activity map of all catalysts.

Table S1: Raman parameters obtained from deconvolution spectra.

Sample	Raman										
	D1	G	A _{D3}	I _{D1} /I _G	R2	2D4	2D1	2D1 _{Area}	D1+G	2D2	I _{2D1} /I _{D1}
	cm ⁻¹	cm ⁻¹				cm ⁻¹	cm ⁻¹		cm ⁻¹	cm ⁻¹	
Fe-N-C1	1347	1589	40	1.2	0.55	2489	2685	27	2906	-	0.19
Fe-N-C2	1347	1597	76	1.3	0.57	-	2689	23	2915	-	0.19
Fe-N-C3	1342	1588	36	1.5	0.60	2480	2675	35	2905	-	0.22
Fe-N-C4	1343	1583	41	1.3	0.57	2500	2684	20	2920	-	0.21
Fe-N-C5	1346	1577	15	1.1	0.45	2457	2689	34	2929	3230	0.92

Table S2: Line profile analysis results for α -Fe in sample Fe-N-C5.

sample	Reflection	Pos. [°2 θ .]	d-spacing [Å]	Sample IB [°2 θ .]	size [nm]
Fe-N-C5	011	52.305	2.029	0.231	49
	002	77.183	1.434	0.274	48

Table S3: Surface chemistry determined from XPS spectra fitting.

Sample	XPS									
	C 1s	O 1s	N 1s	Fe 2p _{3/2}	N _{imine}	N _{pyridinic}	N _x	N _{pyrrolic}	N _{graphitic}	N-O
	wt. %				%					
					397.8 ^a	398.8 ^a	399.9 ^a	400.7 ^a	401.7 ^a	402.7 ^a
Fe-N-C1	80.56	15.08	2.12	2.23	20.7	19.4	18.9	33.4	7.5	-
Fe-N-C2	88.07	7.55	1.62	2.45	9.8	5.7	27.5	40.3	13.1	3.6
Fe-N-C3	87.56	9.68	2.04	0.72	17.6	12.4	19.2	37.4	7.6	6
Fe-N-C4	82.69	14.60	1.33	1.37	26.1	21.9	29.1	19.7	3.2	-
Fe-N-C5	90.19	7.47	0.76	1.58	17	20.4	20.9	23.2	18.5	-

^a Binding Energy expressed in eV**Table S4:** Electrochemical data from RRDE characterization in 0.5 M H₂SO₄.

Sample	Electrochemistry								
	E _{1/2}	j _L ^a	j _K	n		H ₂ O ₂		SD	TOF
			0.65 V _{RHE}	RRDE ^a	K-L	0.7 V _{RHE}	0.2 V _{RHE}		
	V _{RHE}	mA cm ⁻²	mA cm ⁻²			%		sites g ⁻¹	s ⁻¹
Fe-N-C1	0.353	3.14	0.155	3.79	3.42	8	6	1.2E17	0.08
Fe-N-C2	0.453	3.94	0.334	3.75	3.78	10	6	1.1E17	0.24
Fe-N-C3	0.482	3.87	0.472	3.86	3.88	10	5	1.4E17	0.35
Fe-N-C4	0.539	4.15	0.991	3.93	3.89	9	2	2.3E17	0.3
Fe-N-C5	0.570	4.09	1.472	3.94	3.95	7	2	3.1E17	1.05

^a 0.0 V vs RHE.