

**Supporting information for**

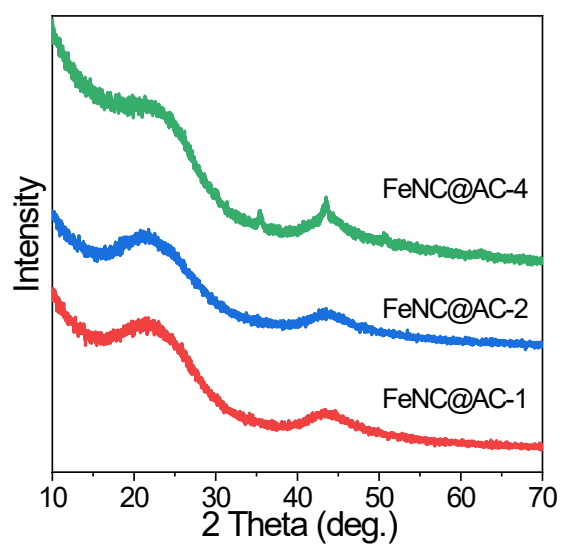
**Formamide-derived “glue” for hundred-gram scale synthesis of atomically dispersed iron-nitrogen-carbon electrocatalysts**

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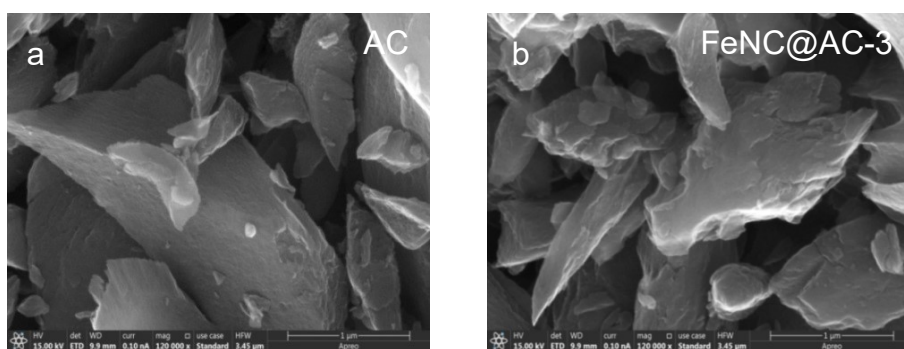
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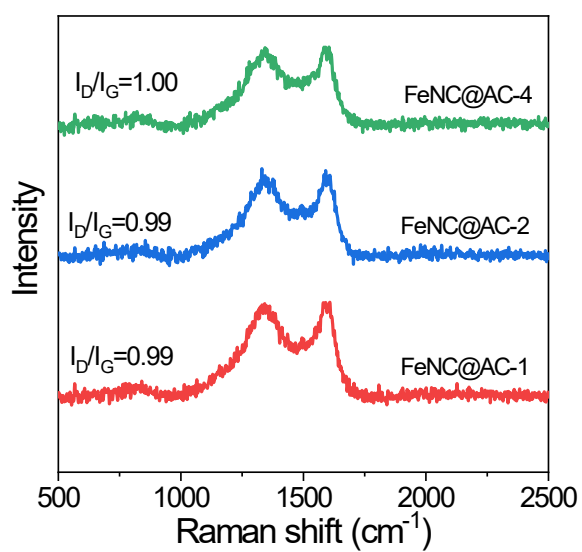
† These authors contribute equally to this work.



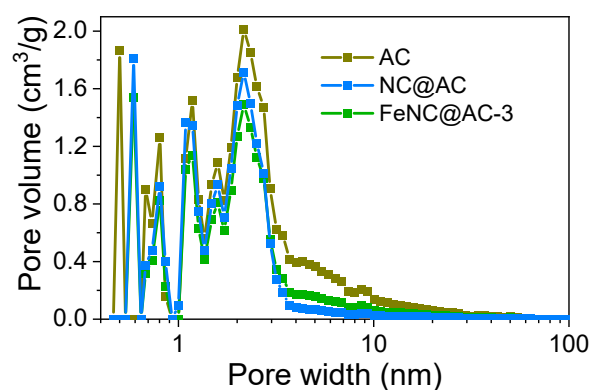
**Figure S1.** XRD curves of FeNC@AC-X, X=1, 2, or 4.



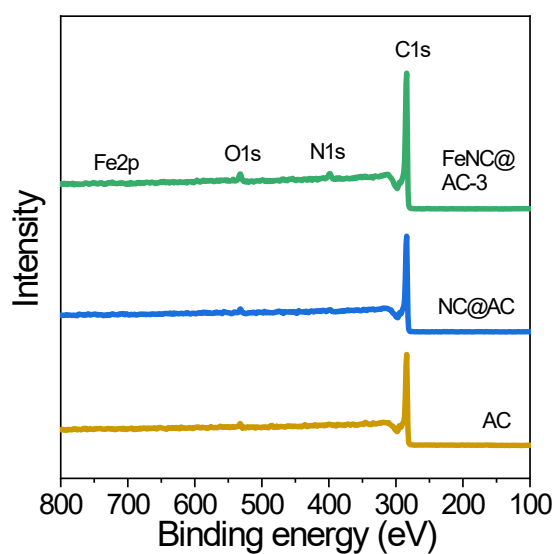
**Figure S2.** SEM images of (a) activated carbon black (AC) and (b) FeNC@AC samples.



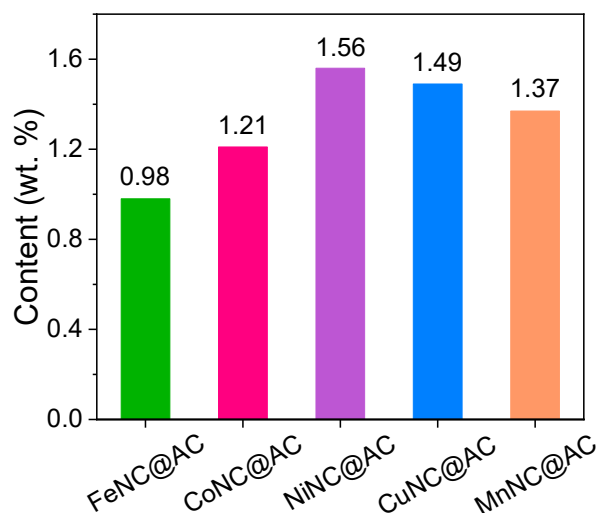
**Figure S3.** Raman spectra of FeNC@AC-X, X=1, 2, or 4.



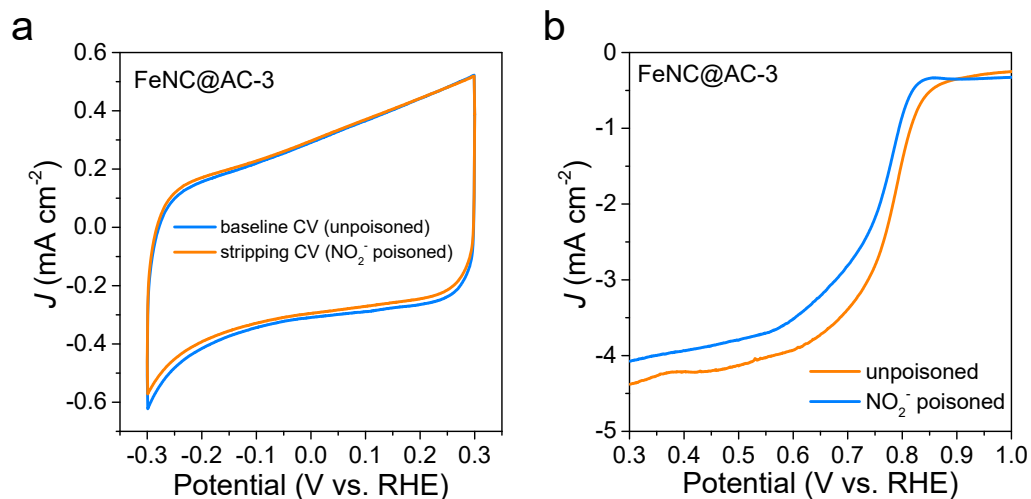
**Figure S4.** Pore distribution curves of AC, NC@AC, and FeNC@AC-3.



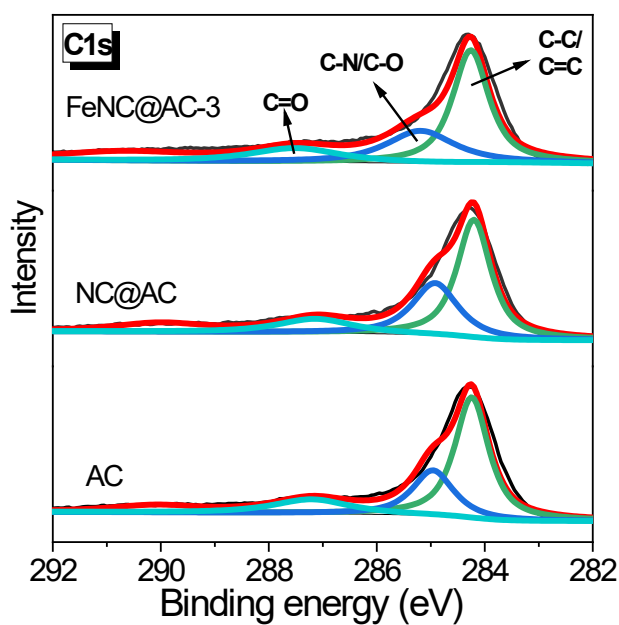
**Figure S5.** XPS survey curves of AC, NC@AC, and FeNC@AC-3.



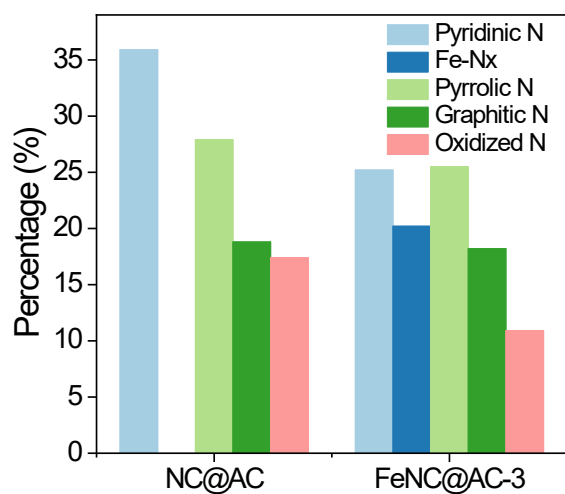
**Figure S6.** ICP element weight percentages of FeNC@AC, and other four types of as-made MNC@AC materials.



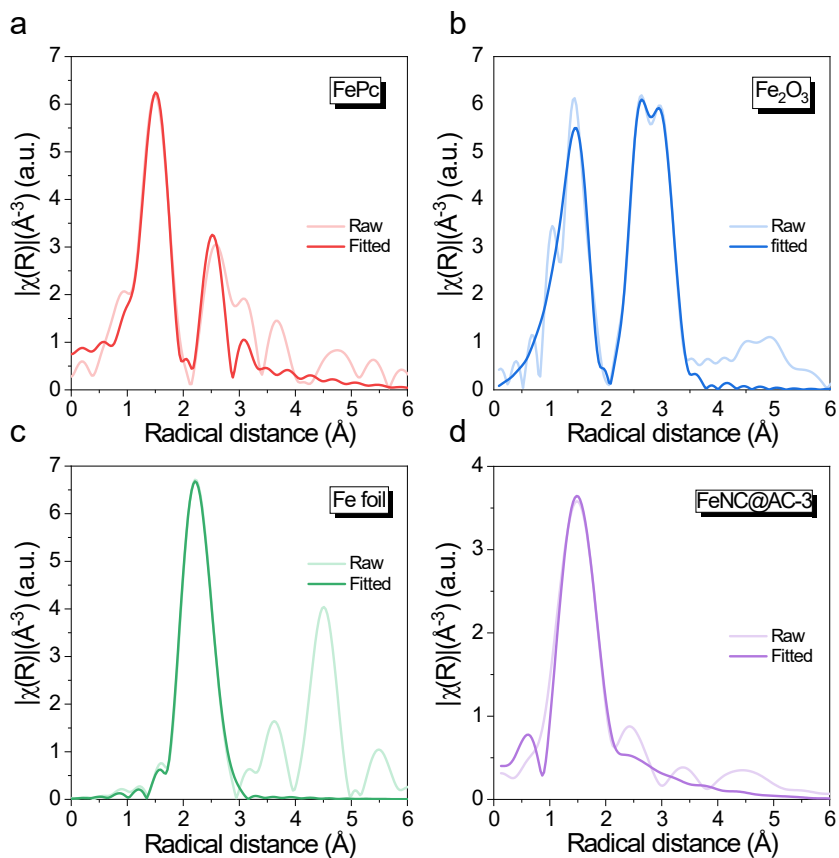
**Figure S7.** Determination of site density of FeNC@AC-3 through reversible nitrite poisoning. (a) CV curves and (b) ORR LSV curves before and after nitrite adsorption in a 0.5 M acetate buffer at pH 5.2.



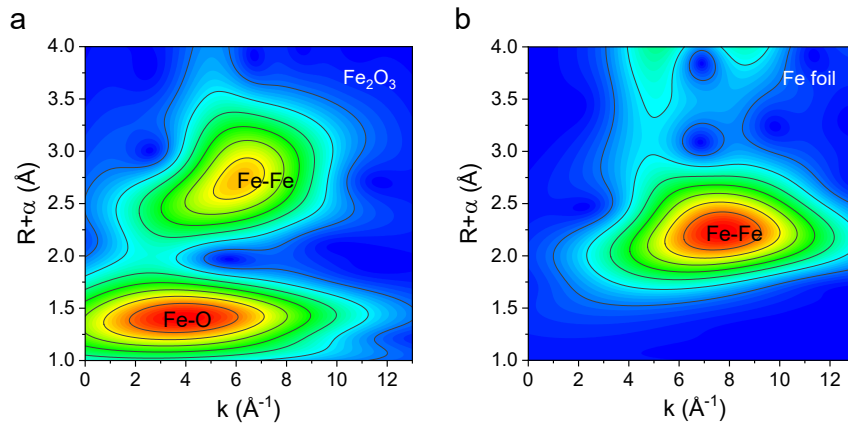
**Figure S8.** (a) XPS survey curves and (b) C1s spectra of AC, NC@AC, and FeNC@AC-3.



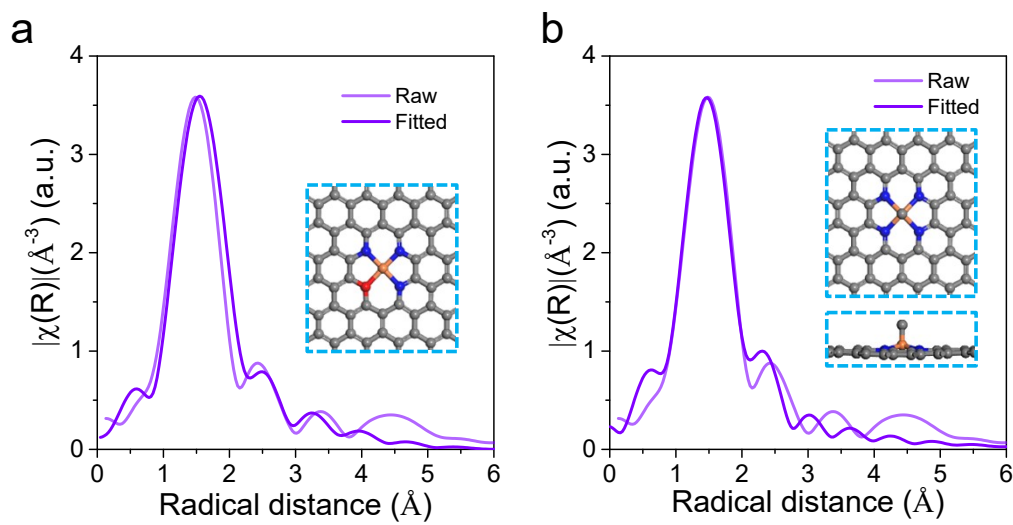
**Figure S9.** Percentages of different N species in NC@AC and FeNC@AC-3.



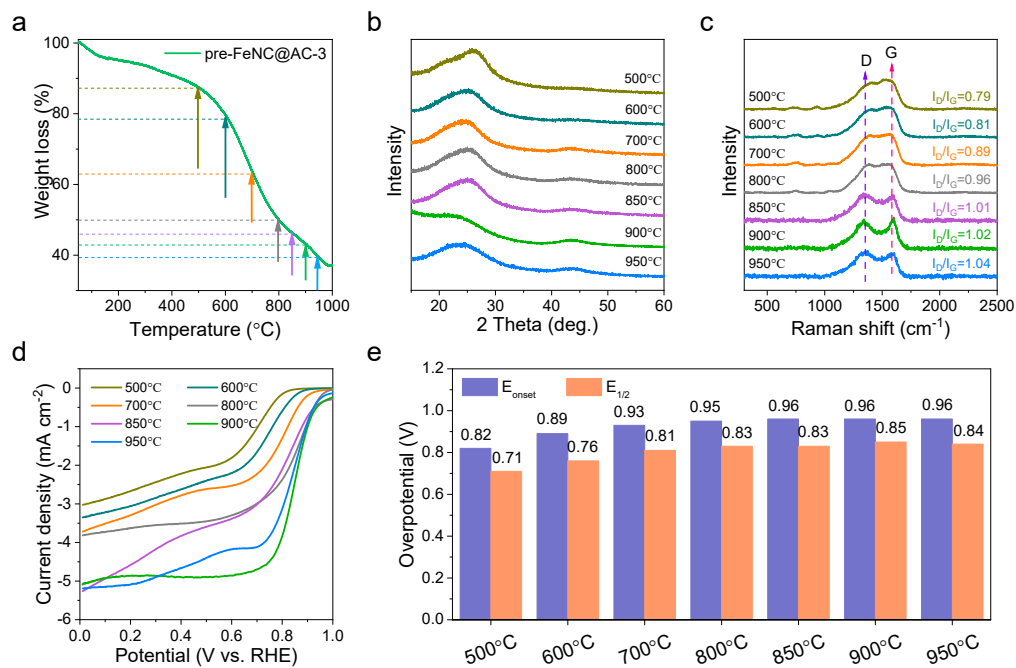
**Figure S10.** Fe K-edge EXAFS fitting curves of (a) FePc, (b) Fe<sub>2</sub>O<sub>3</sub>, (c) Fe foil, and (d) FeNC@AC-3 in R-space.



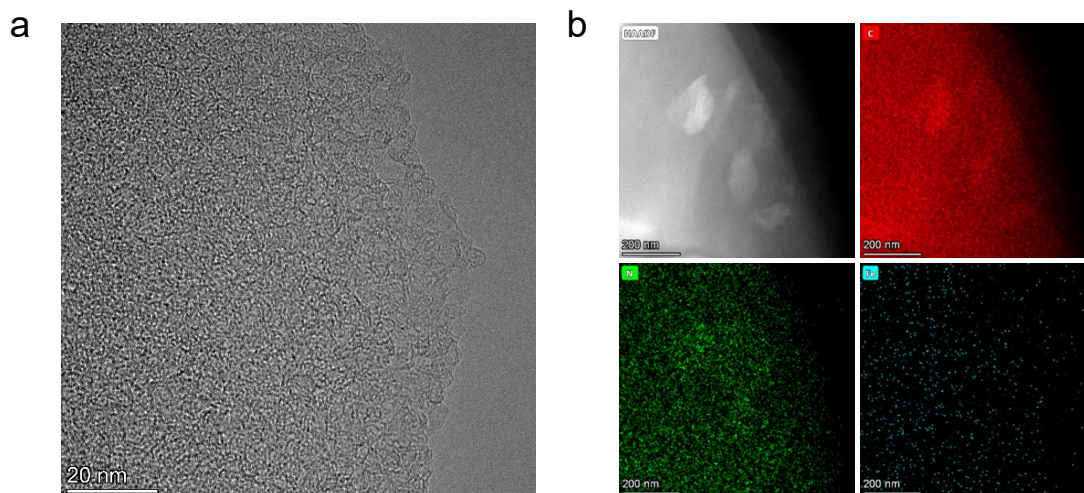
**Figure S11.** Wavelet transformed (WT) EXAFS spectra of (a)  $\text{Fe}_2\text{O}_3$  and (b) Fe foil.



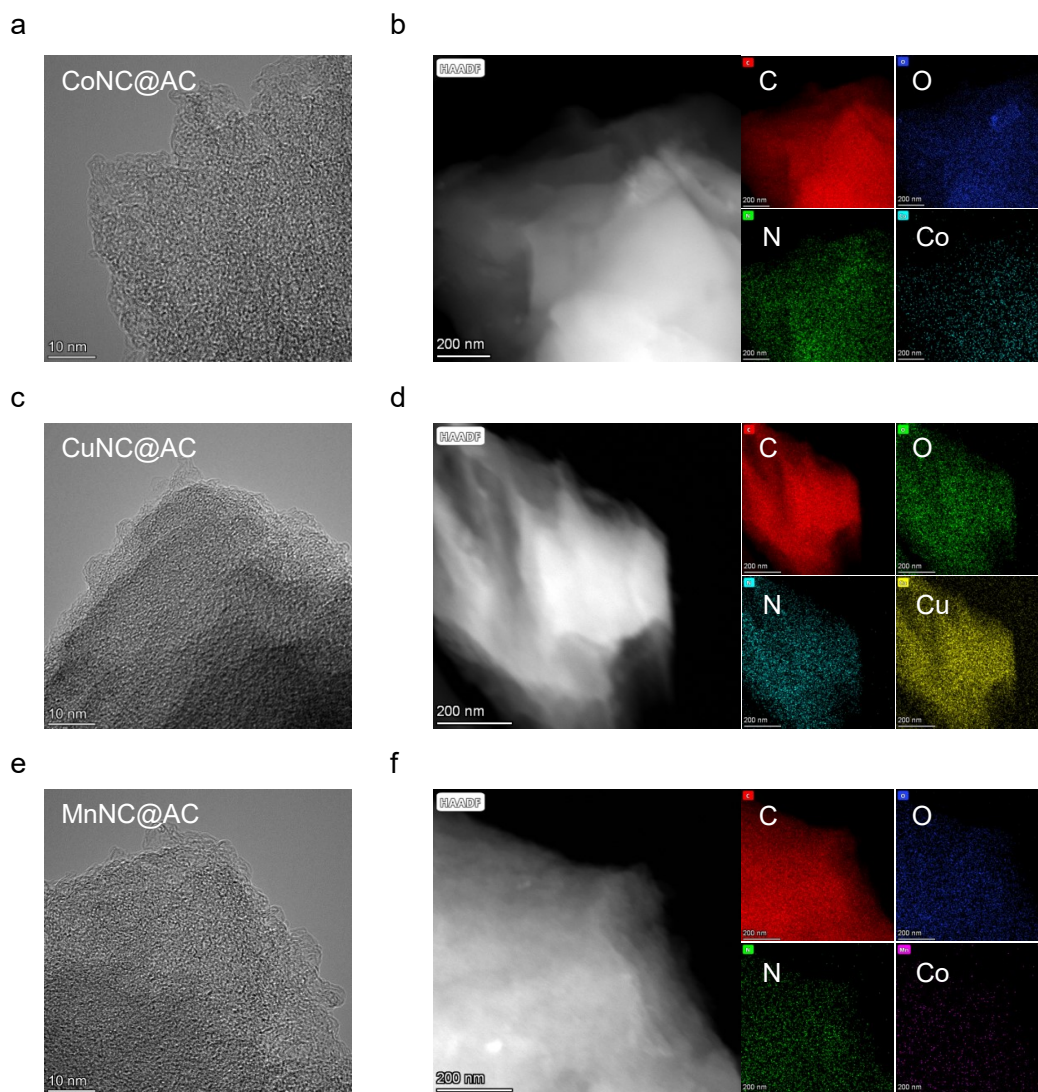
**Figure S12.** Fe k-edge EXAFS fitting curves of (a)  $\text{Fe-N}_3\text{O}_1$  and (b)  $\text{C-Fe-N}_4$  in R-space, insets show their corresponding proposed coordination structures.



**Figure S13.** (a) TGA curve of pre-FeNC@AC-3. (b) XRD curves and (c) Raman spectra of Fe-NC@AC-3 synthesized at different temperatures. (d) ORR polarization curves of FeNC@AC-3 synthesized at different temperatures. Panel (e) shows a summary of onset potentials and half-wave potentials of Fe-NC@AC-3 synthesized at different temperatures.

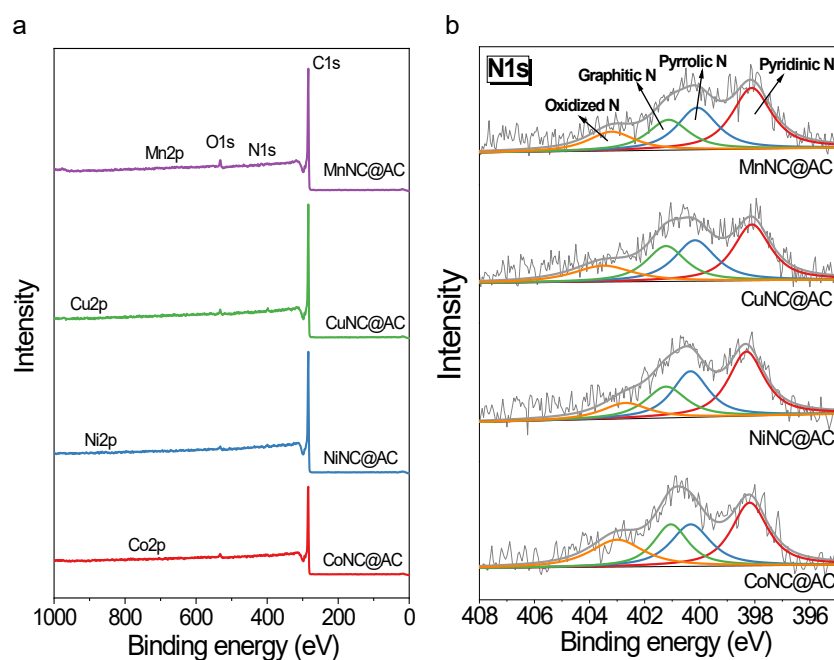


**Figure S14.** HRTEM image and EDS mapping images of FeNC@AC-3 after durability test.

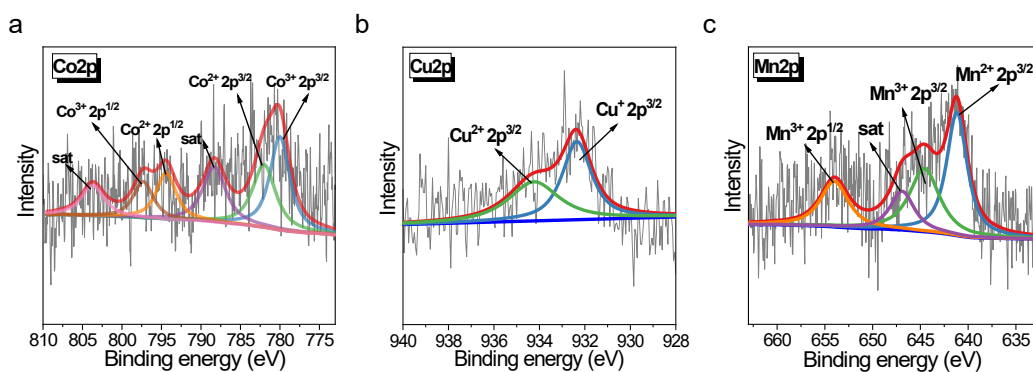


**Figure S15.** (a) HRTEM and (b) elemental mapping images of CoNC@AC sample. (c) HRTEM and (d) elemental mapping images of CuNC@AC sample. (e) HRTEM and (f) elemental mapping images of MnNC@AC sample.

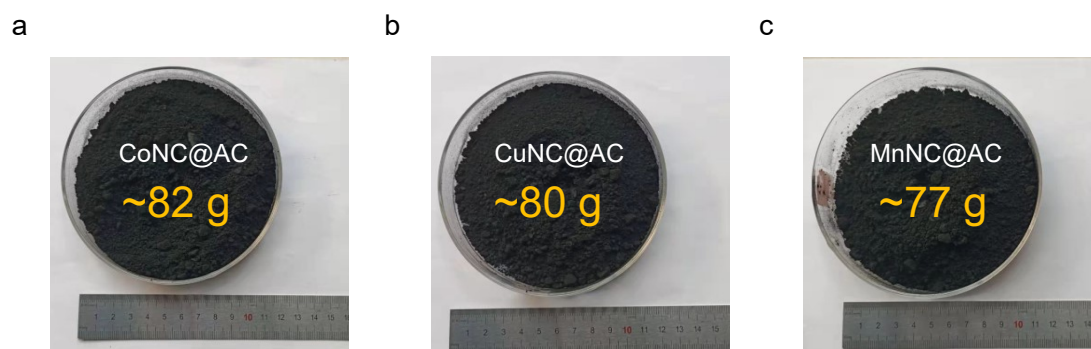




**Figure S16.** (a) XPS survey curves and (b) C1s spectra of CoNC@AC, NiNC@AC, CuNC@AC, and MnNC@AC.



**Figure S17.** (a) Co2p spectra of CoNC@AC, (b) Cu2p spectra of CoNC@AC, and (c) Mn2p spectra of MnNC@AC



**Figure S18.** Digital image of appearance of (a) CoNC@AC, (b) CuNC@AC, and (c) MnNC@AC.



**Table S1.** XPS elemental analysis of AC, NC@AC, and FeNC@AC-3.

Sample	%C	%N	%O	%Fe
AC	97.33	0.39	2.28	-
NC@AC	95.25	2.1	2.65	-
FeNC@AC-3	93.99	1.45	4.38	0.19

**Table S2.** A summary of site density (SD), turnover of frequency (TOF), and Fe utilization rate of FeNC@AC-3 before and after long-term use (10,000 s).

Sample	Site density (SD)/site g <sup>-1</sup>	Turnover of frequency (TOF)/s <sup>-1</sup>	Utilization rate (%)
FeNC@AC-3	1.49×10 <sup>19</sup>	1.69	16.0% (based on XPS) 14.9% (based on ICP)
FeNC@AC-3 after long-term use (10,000 s)	1.36×10 <sup>19</sup>	1.57	14.6% (based on XPS) 12.9% (based on ICP)

**Table S3.** EXAFS fitting parameters at the Fe K-edge for the FeNC@AC-3 sample with comparison to standard references of Fe foil, Fe<sub>2</sub>O<sub>3</sub>, and FePc. Comparison of Fe-N<sub>3</sub>O<sub>1</sub> and C-Fe-N<sub>4</sub> to Fe-N<sub>4</sub> coordination are also shown.

Sample	Shell	N <sup>a</sup>	R(Å) <sup>b</sup>	σ <sup>2</sup> ×10 <sup>3</sup> (Å <sup>2</sup> ) <sup>c</sup>	ΔE <sub>0</sub> (eV) <sup>d</sup>	R factor
Fe foil	Fe-Fe	8*	2.47±0.01	4.8±0.8	6.7±1.3	0.001
	Fe-Fe	6*	2.85±0.01	6.0±1.7	5.4±2.6	
Fe <sub>2</sub> O <sub>3</sub>	Fe-O	6.1±1.1	1.93±0.02	11.7±2.7	-6.5±3.0	0.014
	Fe-Fe	2.6±1.4	2.99±0.05	9.8±4.9	-4.1±6.2	
	Fe-Fe	8.4±4.1	3.42±0.02	10.3±3.3	-7.9±3.3	
FePc	Fe-N	4.1±0.5	1.99±0.02	8.0±3.0	8.1±3.2	0.012
	Fe-C	4.8±2.1	2.98±0.02	6.7±3.4	7.4±3.3	
Fe in Fe-N <sub>4</sub> for FeNC@AC-3	Fe-N	3.8±0.5	1.98±0.02	5.7±4.4	-3.8±2.9	0.016
Fe in FeN <sub>3</sub> O structure	Fe-N	3.1±0.3	1.97±0.05	6.8±4.6	-3.7±0.8	0.214
	Fe-O	1.2±0.3	2.03±0.09			
Fe in C-FeN <sub>4</sub> structure	Fe-C	4.9±0.6	1.99±0.06	3.3±2.7	-4.5±1.2	0.158

<sup>a</sup>CN: coordination numbers; <sup>b</sup>R: bond distance; <sup>c</sup>σ<sup>2</sup>: Debye-Waller factors; <sup>d</sup> ΔE<sub>0</sub>: the inner potential correction. R factor: goodness of fit. S<sub>0</sub><sup>2</sup> was set to 0.729 (Fe), according to the experimental EXAFS fit of metal foil reference by fixing CN as the known crystallographic value.

**Table S4.** XPS elemental analysis of CoNC@AC, NiNC@AC, CuNC@AC, and MnNC@AC.

<b>Sample</b>	<b>%C</b>	<b>%N</b>	<b>%O</b>	<b>%M (M=Co, Ni, Cu, and Mn)</b>
CoNC@AC	96.72	1.16	1.90	0.22
NiNC@AC	95.95	1.34	2.5	0.21
CuNC@AC	95.8	1.54	2.49	0.16
MnNC@AC	94.56	1.12	4.1	0.22