SUPPORTING INFORMATION

1,10-Phenanthroline-Iron Complex-Derived Fe-N-C Electrocatalysts: Enhanced Oxygen Reduction Activity and Stability Through Synthesis Tuning

Table S1: Nominal weight percentages of components in the different synthesized electrocatalyst, varying iron, nitrogen, and carbon sources. All electrocatalysts were pyrolyzed in Ar atmosphere at 1050 °C, for 1.0 h.

Label	Weight percentage / wt.%							Iron-to-nitrogen (nominal atomic ratio)
	Fe	$N_{(Imi)}$	$N_{(Phen)}$	$N_{(total)}$	$C_{(ligand)}$	$C_{(powder)}$	$C_{(total)}$	
Fe-N-C Phen VC	1.0	-	6.6	6.6	33.9	58.5	92.4	1:27
Fe-N-C Imi BP	1.0	6.6	-	6.6	8.5	83.9	92.4	1:27
		-						
Fe-N-C Phen BP	1.0	-	1.0	1.0	5.1	92.9	98.0	1:4
	1.0	-	1.5	1.5	7.7	89.8	97.5	1:6
	1.0	-	3.0	3.0	15.6	80.4	96.0	1:12
	1.0	-	6.6	6.6	33.9	58.5	92.4	1:27

Table S2: BET surface areas of the powders synthesized using different N-containing molecules and carbon sources.

Electrocatalyst	***Surface Area* / $m^2\ g^{-1}$**
$VC_{(after\ pyrolysis\ at\ 1050\ ^oC)}$	230
Fe-N-C Phen VC	255
$BP_{(after\ pyrolysis\ at\ 1050\ ^oC)}$	1700
Fe-N-C Imi BP	730
Fe-N-C Phen BP	840

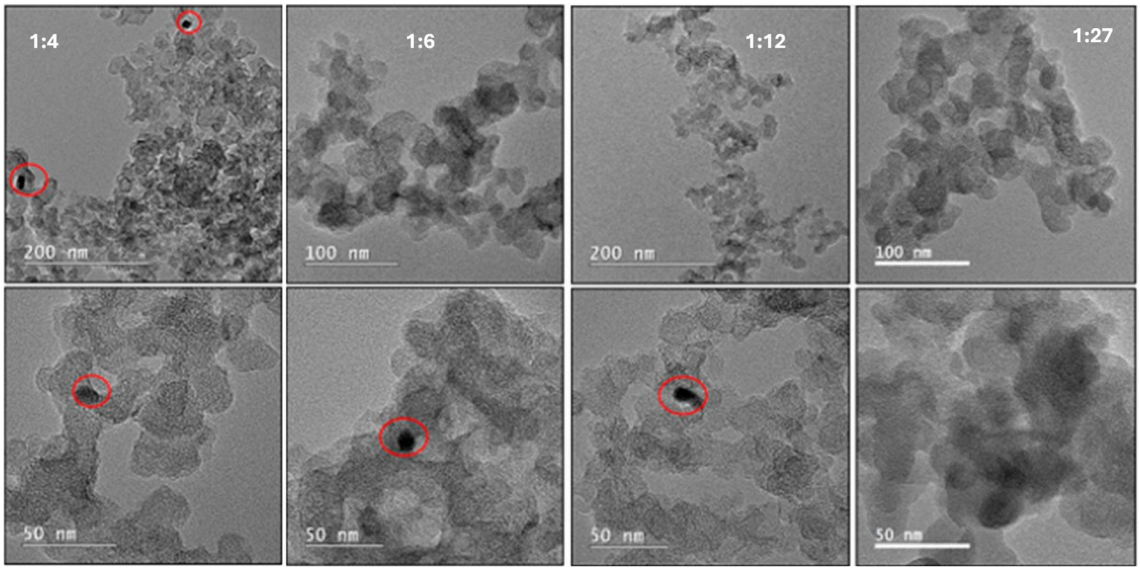


Figure S1. TEM images obtained for the Fe-N-C electrocatalyst synthesized using 1,10-Phenanthroline and Black Pearls with different iron-to-nitrogen ratios.

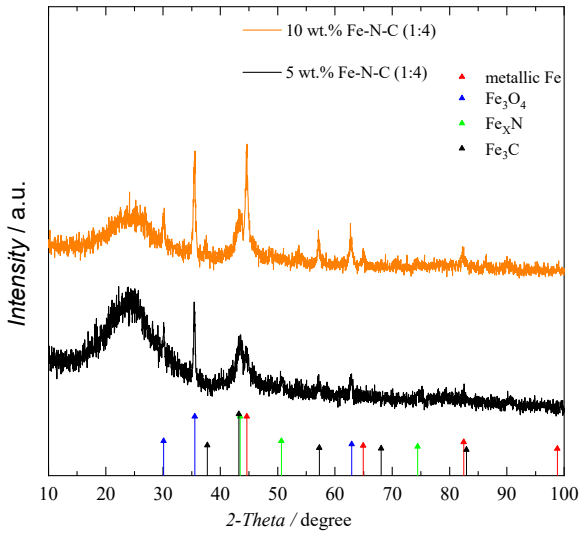


Figure S2. X-ray powder diffraction of the Fe-N-C electrocatalysts synthesized using 1,10-Phenanthroline and Black Pearls carbon, with different loadings of iron.

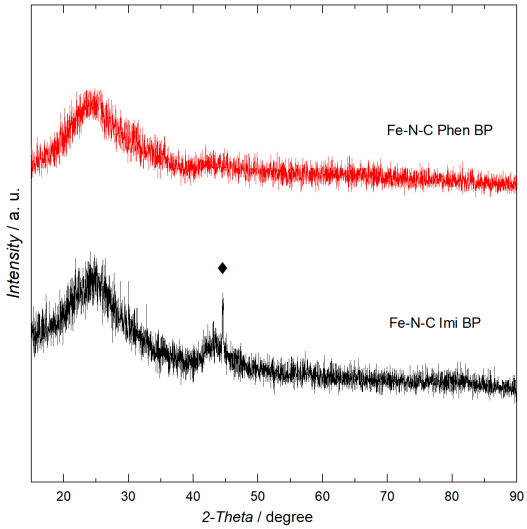


Figure S3. X-ray powder diffraction for the Fe-N-C electrocatalysts synthesized using Phenanthroline (red) or imidazole (black).

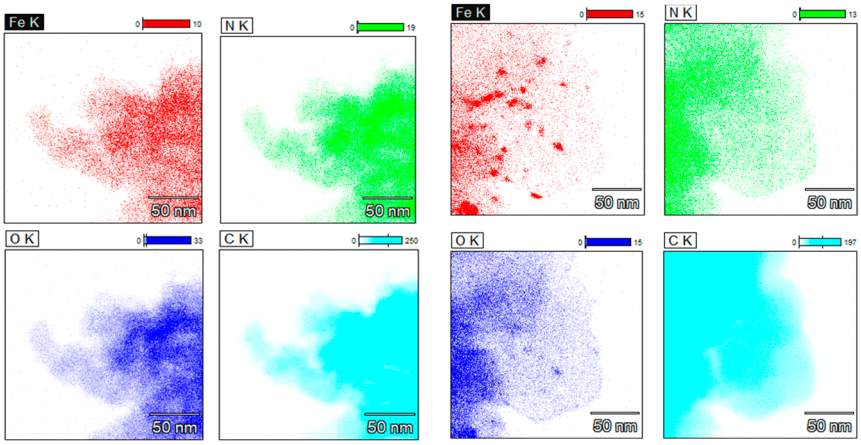
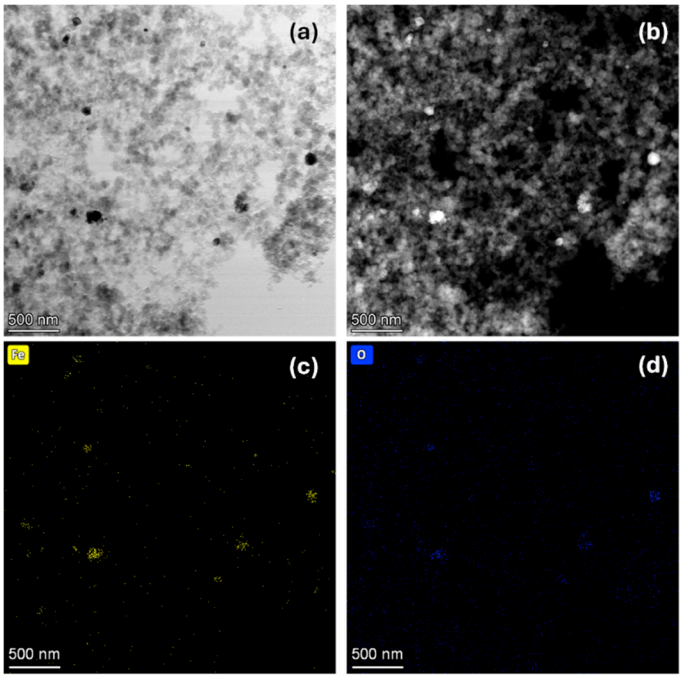


Figure S4. STEM images and the corresponding elemental mapping, as indicated in the figure inset, for the Fe-N-C electrocatalysts synthesized using 1,10-Phenanthroline and Black Pearls (Fe-N-C Phen BP; (left)) or Vulcan carbon (Fe-N-C Phen VC; (right)).

(A)



(B)

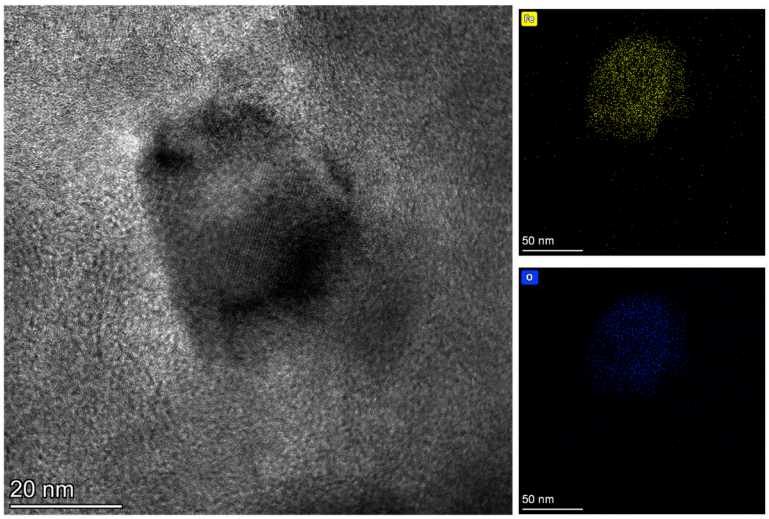


Figure S5. (A) HR-TEM (a), STEM (b) images and the corresponding elemental mapping for iron and oxygen (c and d) obtained for the Fe-N-C electrocatalyst synthesized using 1,10-Phenanthroline and Vulcan carbon (Fe-N-C Phen VC 1050), and (B) HR-TEM and the corresponding elemental mapping of iron (top) and oxygen (bottom) of an individual iron-oxide nanoparticle.

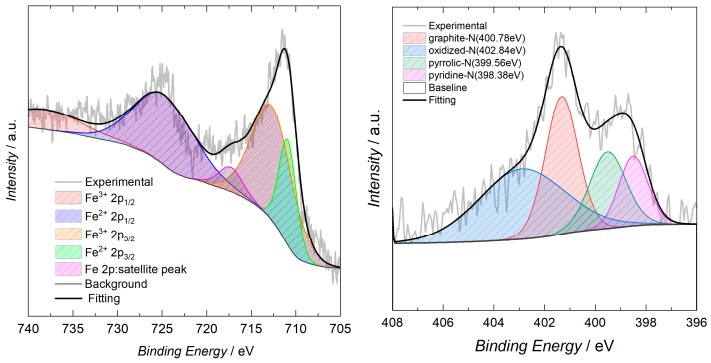
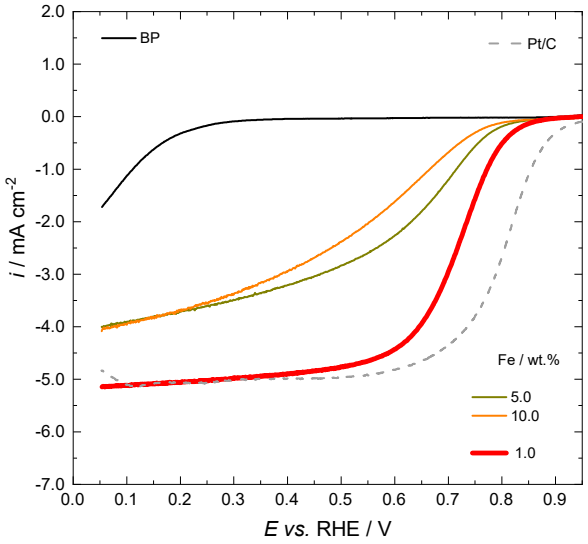


Figure S6. Deconvolution of the XPS spectra for the Fe 2p and nitrogen N 1s of the Fe-N-C Phen BP electrocatalyst.



(a)

Figure S7: Linear sweep voltammetry (LSV) curves for the oxygen reduction on Fe-N-C Phen BP 1050 electrocatalysts synthesized with 5.0 and 10.0 wt.% Fe, obtained in O_2-saturated 0.5 mol L^{-1} H_2SO_4 electrolyte, with scan rate of 1.0 mV s^{-1} and rotation rate of 1600 rpm.

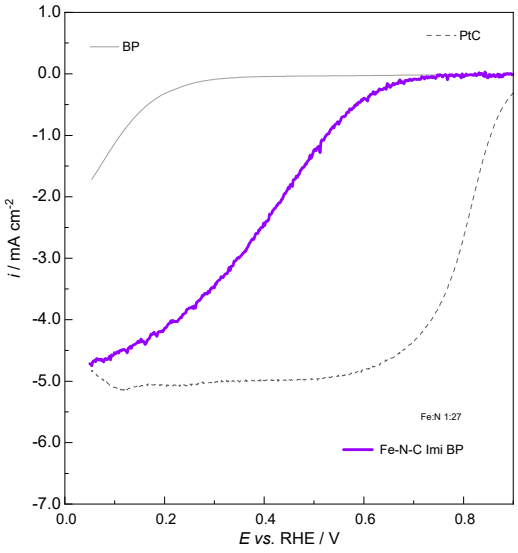


Figure S8. Linear sweep voltammetry (LSV) curves for the oxygen reduction on Fe-N-C synthesized using imidazole (instead of Phen) and BP carbon, obtained in O_2-saturated 0.5 mol L^{-1} H_2SO_4 electrolyte, with scan rate of 1.0 mV s^{-1} and rotation rate of 1600 rpm.

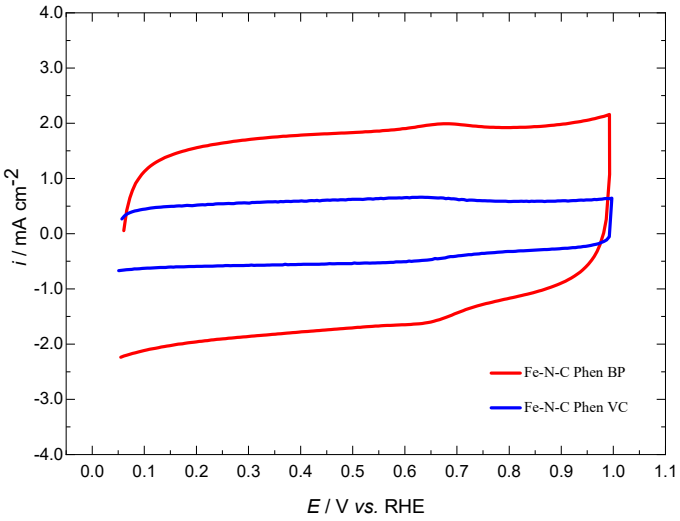


Figure S9. Cyclic voltammetry (CV) curves for Fe-N-C Phen BP (red) and Fe-N-C Phen VC (blue), obtained in Ar-saturated 0.5 mol L^{-1} H_2SO_4 electrolyte, with scan rate of 50 mV s^{-1}.

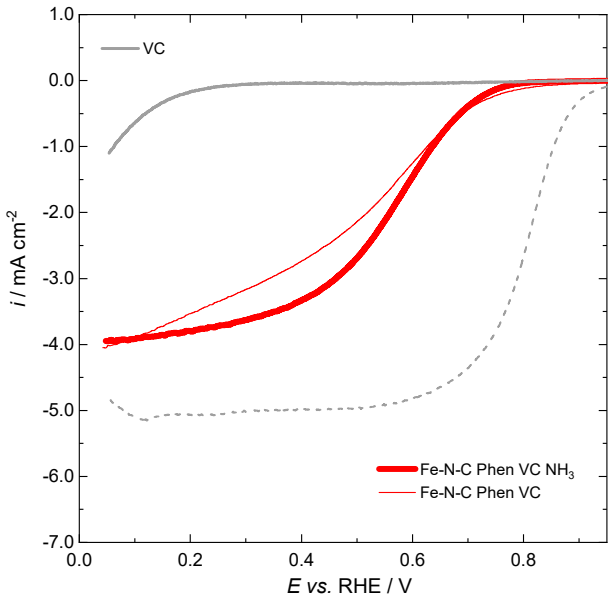


Figure S10. Linear sweep voltammetry (LSV) curves for the oxygen reduction on Fe-N-C Phen VC before (thin red line) and after treatment in NH_3, at 900 °C (thick red line), obtained in O_2-saturated 0.5 mol L^{-1} H_2SO_4 electrolyte, with scan rate of 1.0 mV s^{-1} and rotation rate of 1600 rpm (the curves for the ORR on pure Vulcan Carbon and Pt/C were included for comparison).

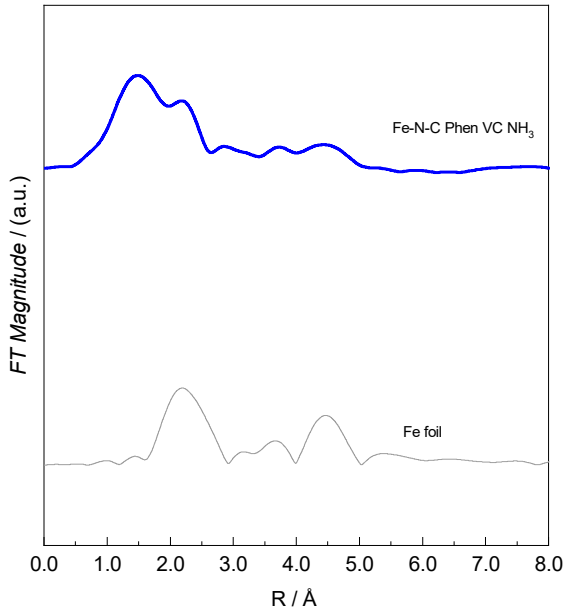


Figure S11. Fourier Transform of the EXAFS oscillations, K^3-weighted, at the Fe (7112 eV) K edge, for the Fe-N-C Phen VC electrocatalyst further step of treatment in NH_3 at 900 °C. The reference spectrum for Fe foil was included for comparison.

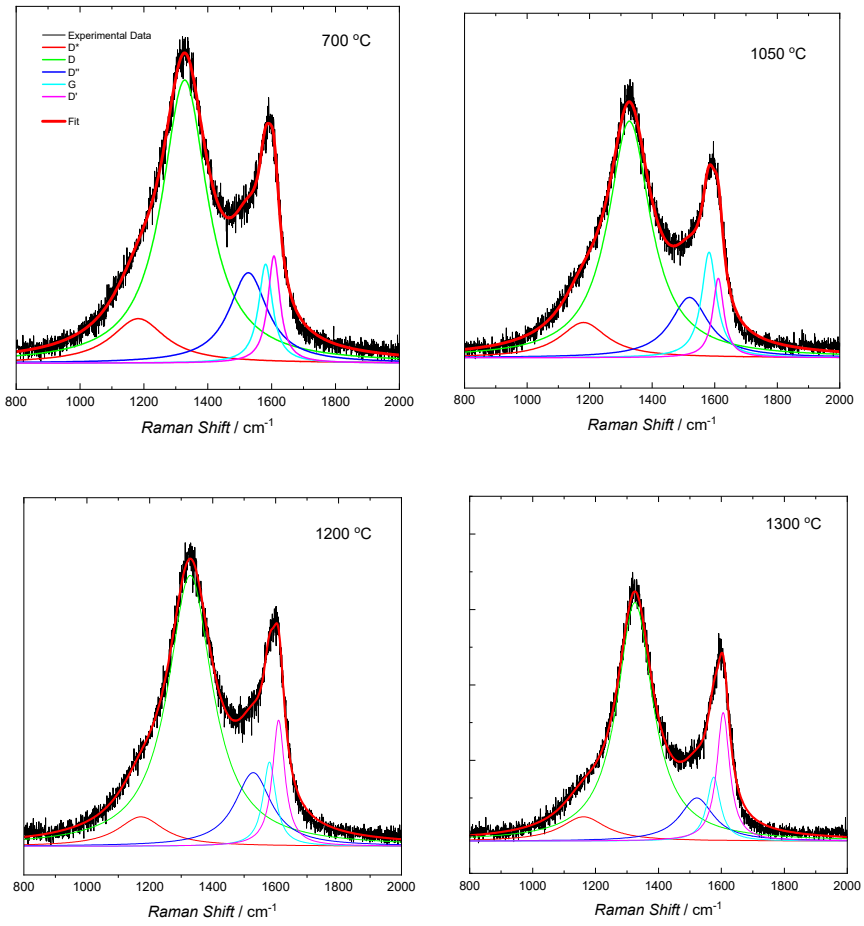


Figure S12. Deconvoluted Raman spectra of Fe-N-C Phen BP electrocatalysts prepared at different pyrolysis temperatures. The band assignments are provided in the figure inset legend.

(a) (b)

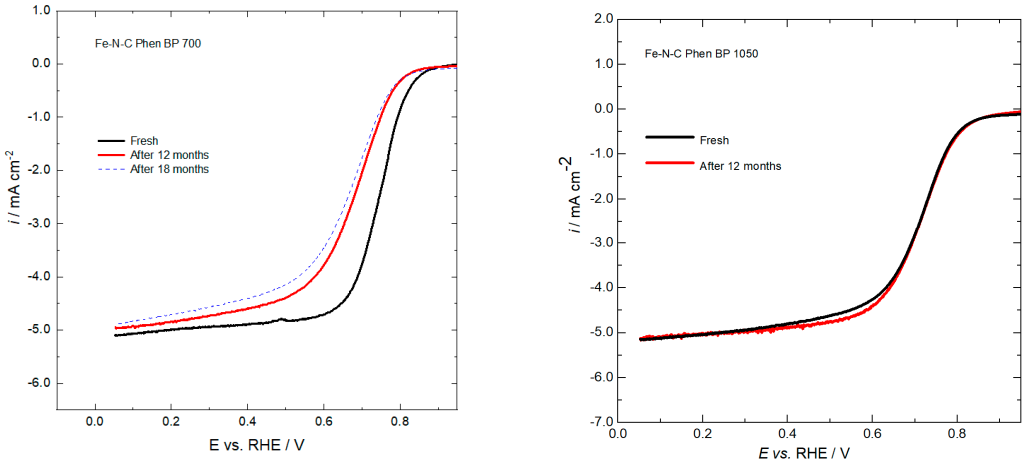


Figure S13: LSV curves recorded before and after the Fe-N-C Phen BP electrocatalyst storage (shelf-life), for different periods of time, as indicated in the figure inset legend, synthesized at pyrolysis temperatures of 700 (a) 1050 (b), obtained in O_2-saturated 0.5 mol L^{-1} H_2SO_4 electrolyte, with scan rate of 1.0 mV s^{-1} and rotation rate of 1600 rpm.