SUPPLEMENTARY INFORMATION

Surface Diels-Alder adducts on multilayer graphene for the generation of edge-enriched single-atom FeN_4 sites for ORR and OER electrocatalysis

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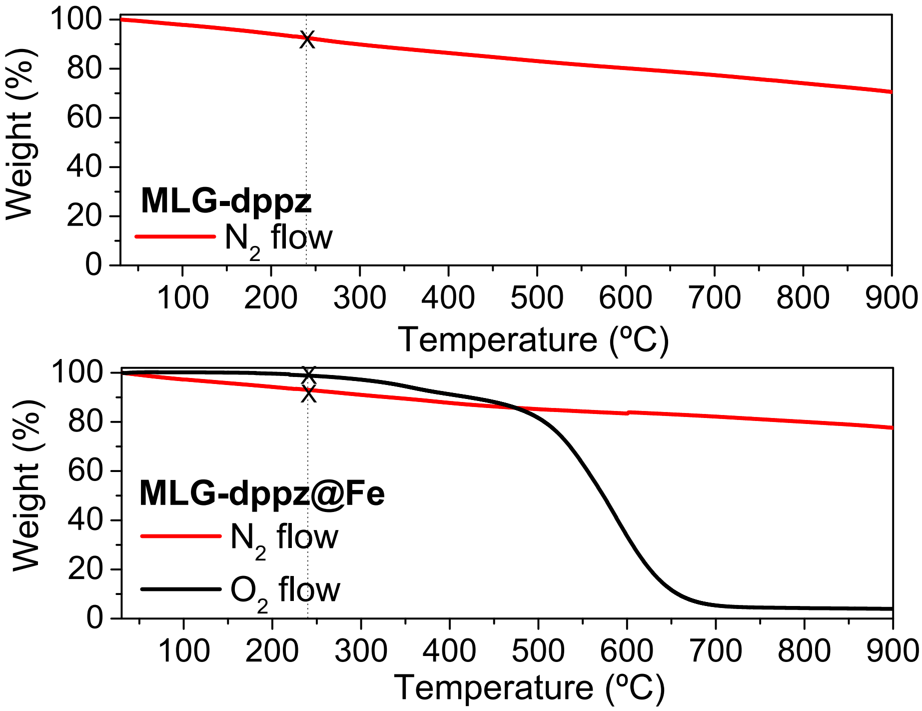

Fig. S1 TGA curves of MLG-dppz (under a nitrogen atmosphere) and MLG-dppz@Fe (in nitrogen and oxygen atmospheres).

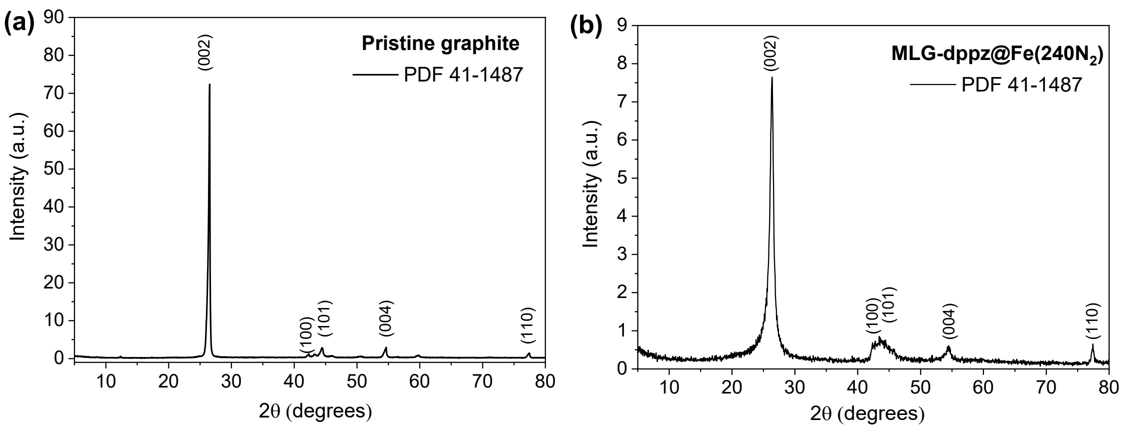

Fig. S2 XRD patterns of (a) pristine graphite powder and (b) MLG-dppz@Fe(240N_2) materials.

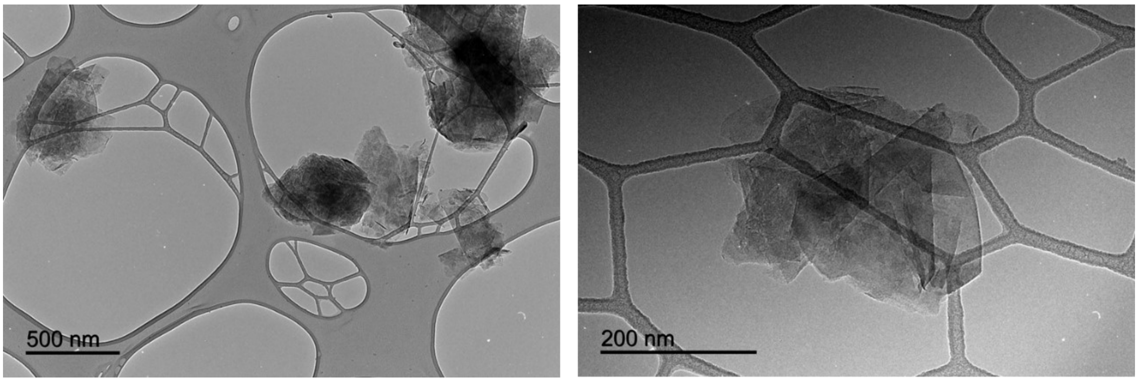

Fig. S3 TEM images of MLG-dppz@Fe(240N_2).

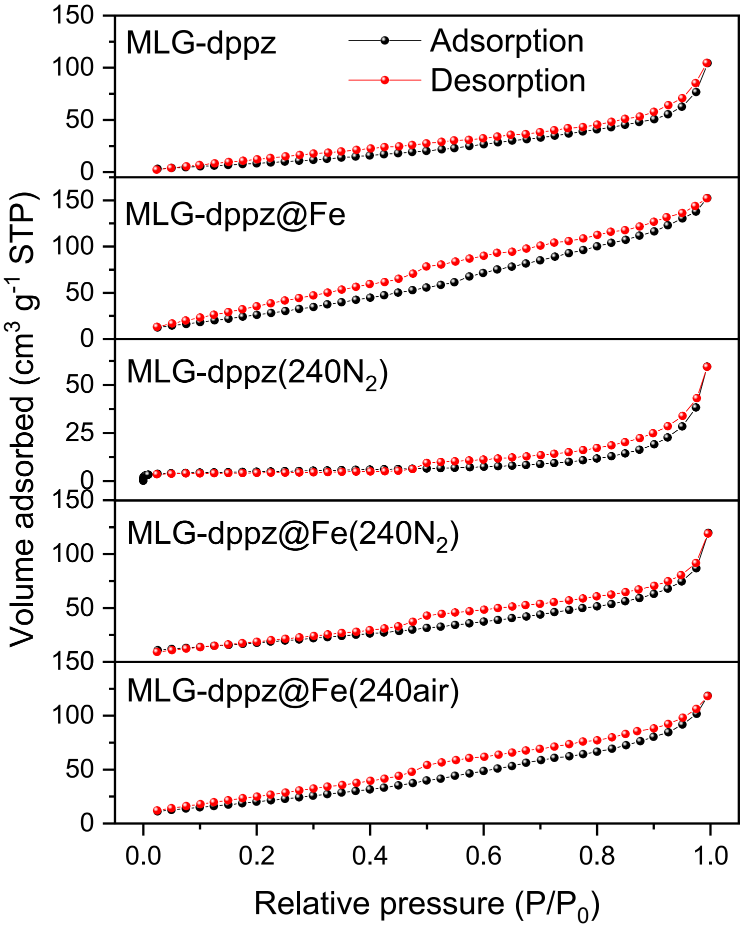

Fig. S4 N_2 adsorption/desorption isotherms of MLG-dppz materials.

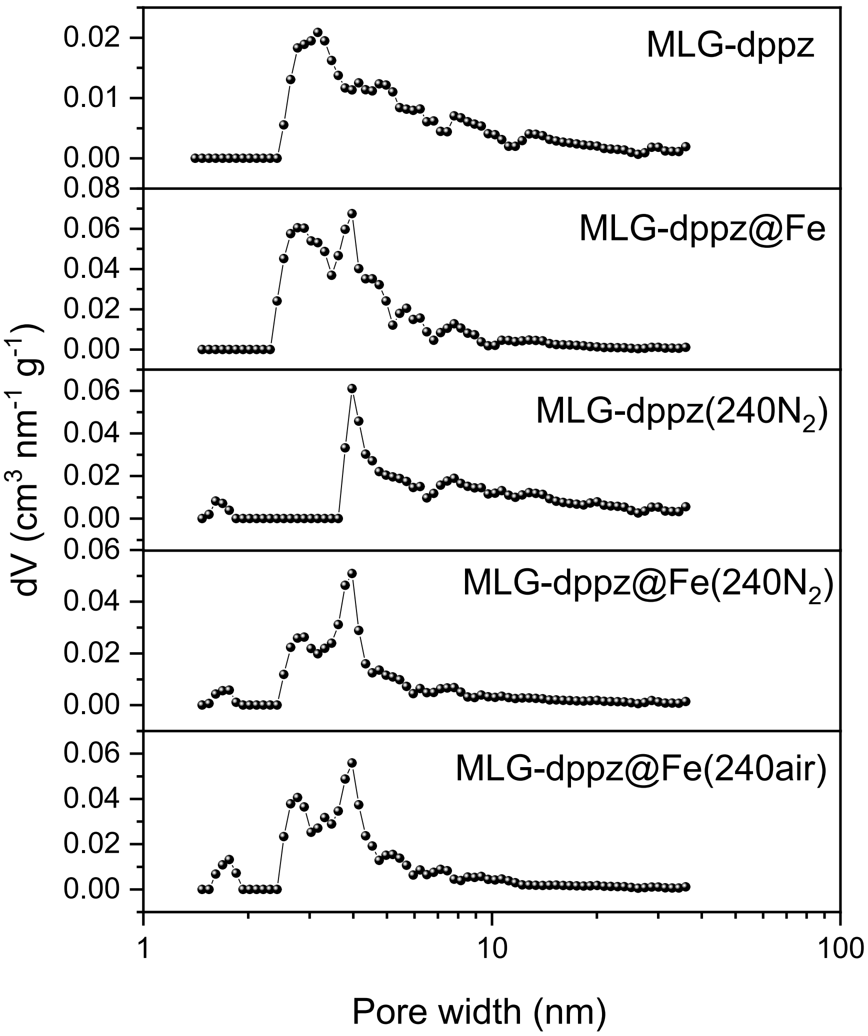

Fig. S5 Pore size distribution of MLG-dppz materials.

Table S1 Textural data of MLG-dppz materials.

Samples	**S_{BET} (m^2 g^{-1})**	**V_T (cm^3 g^{-1})**	**D_{pore} (nm)**
MLG-dppz	50	0.161	13
MLG-dppz@Fe	128	0.236	7
MLG-dppz(240N_2)	18	0.092	21
MLG-dppz@Fe(240N_2)	74	0.185	10
MLG-dppz@Fe(240air)	92	0.183	8

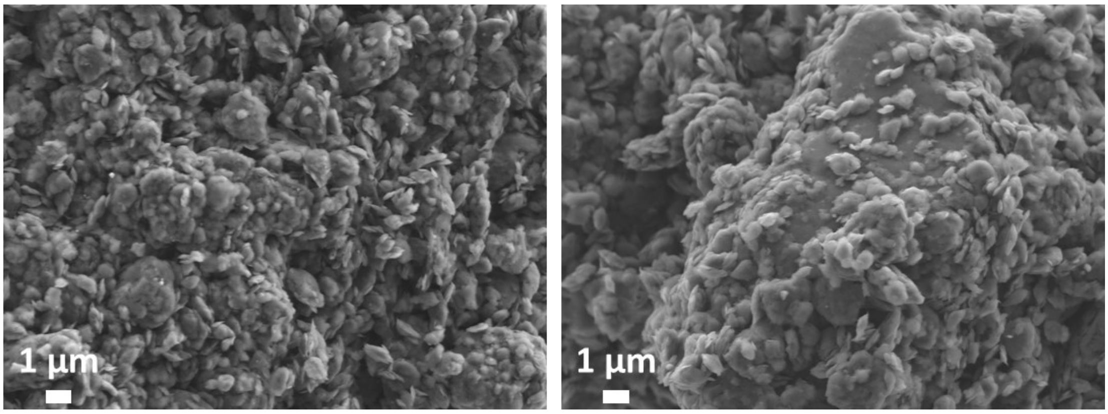

Fig. S6 SEM representative images of MLG-dppz@Fe(240N_2).

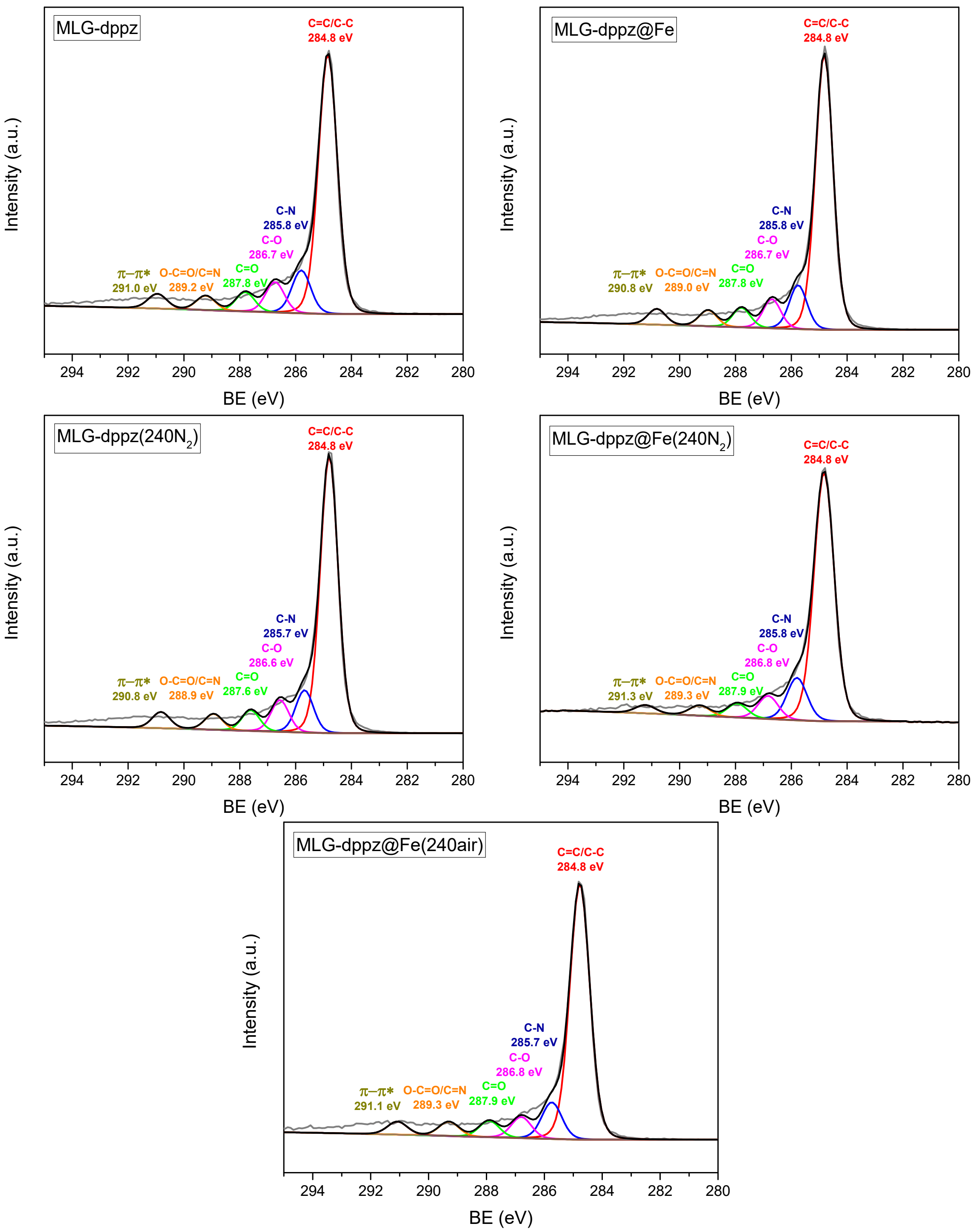

Fig. S7 XPS spectra for the C1s photoemission peak of MLG-dppz materials.

Table S2 Contribution of the six components used in the fitting of the C 1s core level signal.

C1s	***MLG-dppz***		***MLG-dppz@Fe***		***MLG-dppz(240N$_2$)***		***MLG-dppz@Fe(240N$_2$)***		***MLG-dppz@Fe(240air)***	
Surface groups	***BE (eV)***	***Atom %***	***BE (eV)***	***Atom %***	***BE (eV)***	***Atom %***	***BE (eV)***	***Atom %***	***BE (eV)***	***Atom %***
C=C/C-C	284.8	68.1	284.8	68.9	284.8	68.6	284.8	71.7	284.8	71.6
C-N	285.8	11.3	285.8	11.0	285.7	10.5	285.8	12.2	285.7	10.3
C-O	286.7	8.0	286.7	7.3	286.6	7.9	286.8	6.7	286.8	5.9
C=O	287.8	5.1	287.8	4.9	287.6	5.1	287.9	4.0	287.9	4.6
O-C=O/C=N	289.2	3.8	289.0	4.0	288.9	3.9	289.3	3.0	289.3	4.0
π-π*	291.0	3.9	290.8	4.0	290.8	4.0	291.3	2.4	291.1	3.7

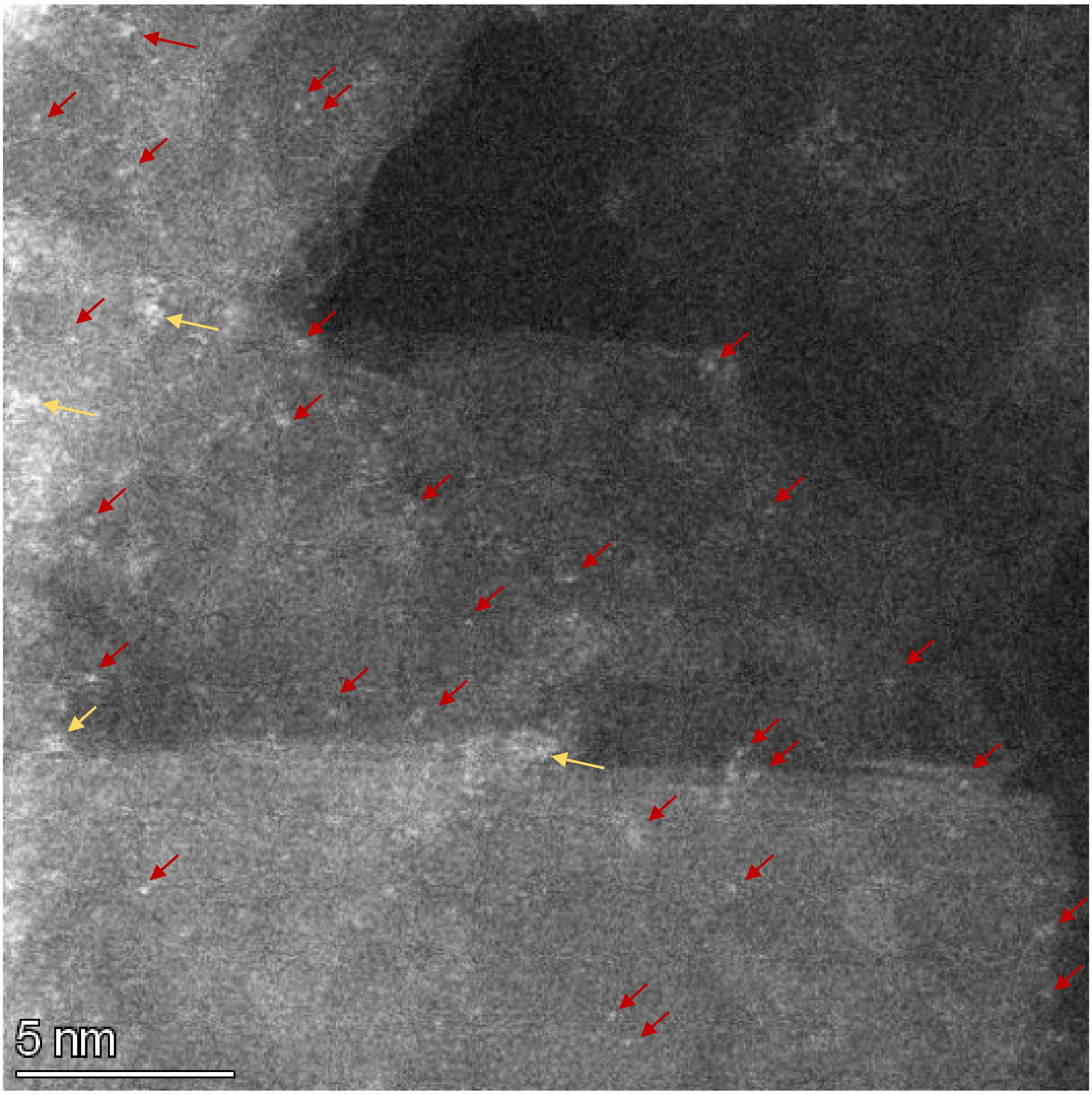

Fig. S8 Aberration corrected HAADF-STEM image of MLG-dppz@Fe(240N_2) sample (showed in **Fig. 4D**).

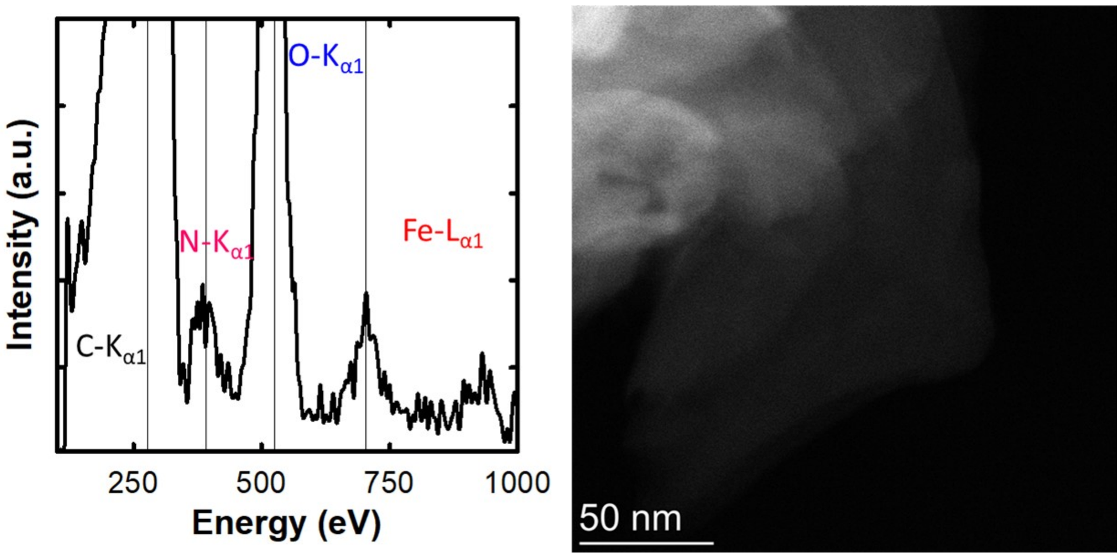

Fig. S9 Sum EDX spectrum of the area included in the HAADF image.

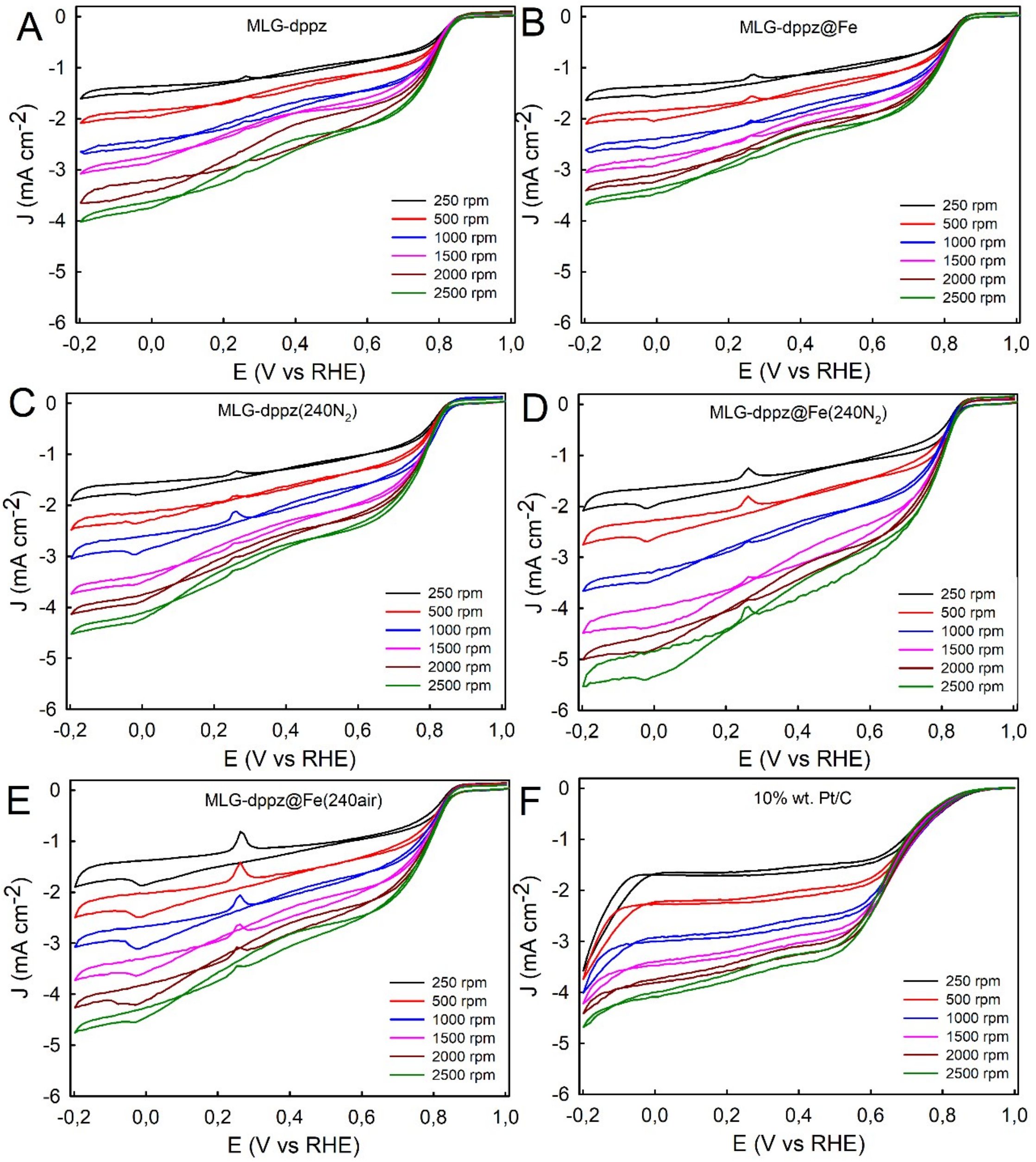

Fig. S10 Rotating-disk voltammograms at different rotation rates for (A) MLG-dppz, (B) MLG-dppz@Fe, (C) MLG-dppz(240N_2), (D) MLG-dppz@Fe(240N_2), (E) MLG-dppz@Fe(240air) and (F) 10 % wt. Pt/C in O_2 saturated 0.5 M KOH at scan rate of 10 $mV \cdot s^{-1}$.

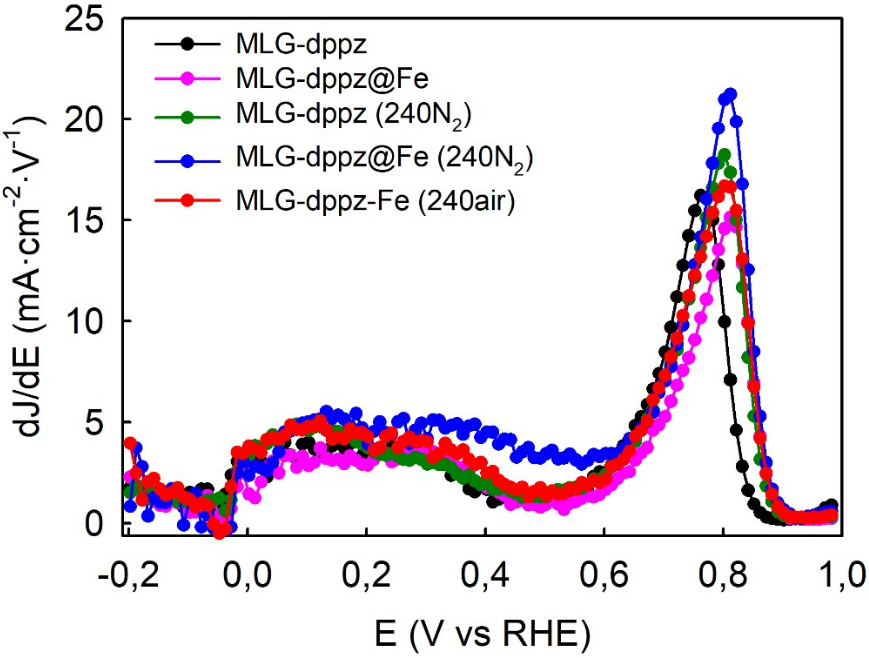

Fig. S11 Derivatives of the ORR data shown in **Fig. 5C** to obtain the half-wave potentials.

Table S3 Summary table of ORR electrocatalysts based on NC and Fe-NC materials.

C/Fe based electrocatalyst	Fe Wt%	J (mA·cm^{-2}) and ω (rpm)	E_{onset} (V)	J_k (mA·cm^{-2})	n	Potential (V)	Electrolyte	Reference electrode	Working electrode	Ref.
BINOL-CTF-10-500	-	-3.00 and 2400	0.79	9.00	4.04	0.23	0.1M KOH	RHE (SCE)	GC	[1]
Fe_2O_3-NPCS	21.00	-5.80 and 2500	1.06	31.8	3.85	0.90	0.1M KOH	RHE (Ag/AgCl)	GC	[2]
CNT/PC	2.90	-6.00 and 1600	0.95	4.3	3.98	0.90	0.1M KOH	RHE (Ag/AgCl)	GC	[3]
Fe-N-CNT@RGO	30.00	-4.44 and 1600	0.93	1.85	4.00	0.85	0.1M KOH	RHE (SCE)	GC	[4]
Co,N-PCL	-	-5.20 and 1600	0.93	-	3.99	0.30	0.1M KOH	RHE (Ag/AgCl)	GC	[5]
Fe_3C/NG-800	0.81	-6.40 and 2500	1.03	100	3.70	0.70	0.1M KOH	RHE (SCE)	GC	[6]
Fe-N-C-800acid	2.20	-4.30 and 1600	0.93	-	3.70	0.56	0.1M KOH	RHE (Ag/AgCl)	GC	[7]
$Fe_{1.6}$-N-HCNS/rGO-900	1.60	-5.70 and 1600	0.7-0.9	-	4.02	0.70	0.1M KOH	RHE (SCE)	GC	[8]
Fe_3C/C-800	15.00	-5.50 and 2500	1.05	-	3.80-4.00	0.99	0.1M KOH	RHE (SCE)	GC	[9]
Fe-N-C-800	0.24	-4.90 and 2025	0.98	-	3.95	0.75	0.1M KOH	RHE (Ag/AgCl)	GC	[10]
Fe−N−C/rGO	0.15 (atom)	-4.50 and 2025	0.94	-	4.00	0.60	0.1M KOH	RHE (Ag/AgCl)	GC	[11]
Fe@C-	0.42	-5.00 and 1600	0.93	-	4.00	0.80	0.1M KOH	RHE (SCE)	GC	[12]*

NG/NCNTs										
C-COP-C-Fe	4.95	-5.70 and 2025	0.89	4.00	3.93	0.75	0.1M KOH	RHE (SCE)	GC	[13]
Fe_3C-Co/NC	1.70	-5.50 and 1600	0.94	-	3.9	0.80	0.1M KOH	RHE (Ag/AgCl)	GC	[14]*
N-doped CoCx/FeCo@ C/rGO	-	-7.00 and 2500	1.02	-	3.84	0.46	0.1M KOH	RHE (SCE)	GC	[15]*
M-2	-	-7.90 and 2500	0.97	-	-	-	0.1M KOH	RHE (Ag/AgCl)	GC	[16]*
FeCo/N-DNC	52.80 (atom)	-6.20 and 1600	0.89	-	3.92	0.2	0.1M KOH	RHE (Ag/AgCl)	GC	[17]*
FeS/Fe_3C@N-S -C-800	2.17	-6.80 and 2500	1.02	-	3.9	0.2	0.1M KOH	RHE (Ag/AgCl)	GC	[18]*
MLG-dppz@Fe (240N_2)	0.73	-5.50 and 2500	0.89	86.59	3.92	1.00	0.5M KOH	RHE (Ag/AgCl)	GC	This work*

*Materials with bi- or tri-functional character.

Table S4 Summary table of OER electrocatalysts based on NC and Fe-NC materials.

C/Fe based catalyst	Fe Wt%	η10 (mV)	Tafel Slope (mV/dec)	Electrolyte	Reference electrode	Working electrode	Ref.
Fe/Fe_3C-MC	2.40	320	51.0	1M KOH	RHE	GC	[19]*
Fe@C-NG/NCNTs	0.42	450	163.0	1M KOH	RHE (SCE)	GC	[12]*
Fe_3C-Co/NC	1.70	340	108.8	1M KOH	RHE (Ag/AgCl)	GC	[14]*
Fe_3O_4/NiS@CC	1.18	310	82.0	1M KOH	RHE (Ag/AgCl)	GC	[20]
N-doped CoCx/FeCo@C/rGO	-	390	77.1	0.1M KOH	RHE (SCE)	GC	[15]*
PNG-NiCo	-	564	156.0	0.1M KOH	RHE (Ag/AgCl)	Hybrid films	[21]
M-2	-	710	54.0	0.1M KOH	RHE (Ag/AgCl)	GC	[16]*
N-doped SWNT	-	430	-	0.1M KOH	RHE	GC	[22]
FeCo/N-DNC	52.80 (atom)	390	68.0	0.1M KOH	RHE (Ag/AgCl)	GC	[17]*
FeS/Fe_3C@N-S-C-800	2.17	570	81.0	1M KOH	RHE (Ag/AgCl)	GC	[18]*
Fe_3C@C–N	3.50	608	89.0	0.1M KOH	RHE (SCE)	GC	[23]
Ni1.95Fe-MOP@CNTs	2.69	256	58.0	1M KOH	RHE (Ag/AgCl)	GC	[24]
Co_3O_4/N–C	-	390	44.0	1M KOH	RHE (Ag/AgCl)	GC	[25]
Fe/C-doped-MoS_2/Ni_3S_2-450	-	273	66.0	1M KOH	RHE (SCE)	GC	[26]
MLG-dppz@Fe (240N_2)	0.73	500	100.5	0.5M KOH	RHE (Ag/AgCl)	GC	This work*

*Materials with bi- or tri-functional character.

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