Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Optimizing reaction intermediate adsorption by engineering the coordination structure of single-atom Fe–N_5–C electrocatalysts for efficient oxygen reduction

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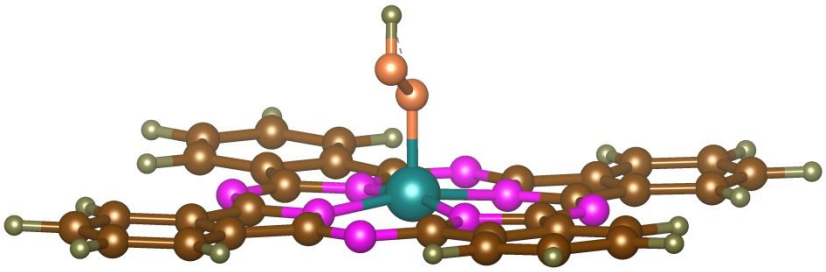

Fig. S1 Reaction intermediate OOH* adsorbed on FeN_4 structure.

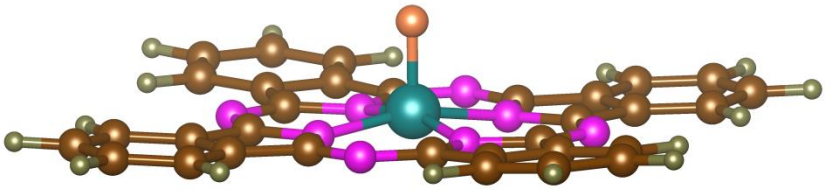

Fig. S2 Reaction intermediate O* adsorbed on FeN_4 structure.

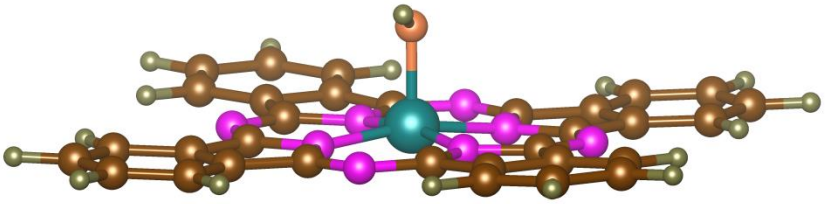

Fig. S3 Reaction intermediate OH* adsorbed on FeN_4 structure.

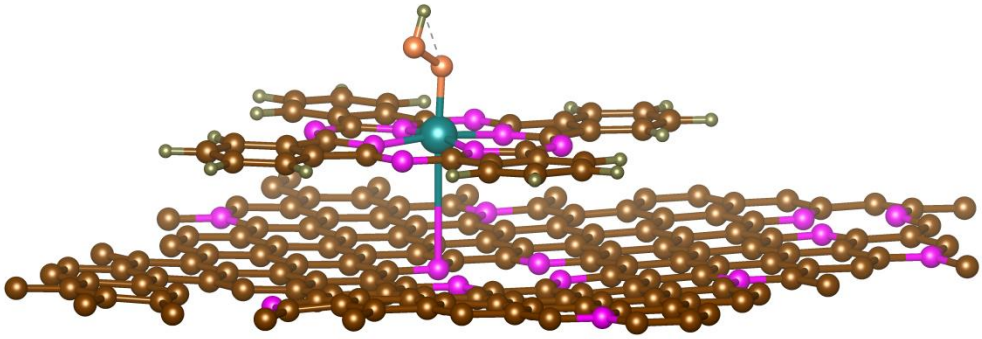

Fig. S4 Reaction intermediate OOH* adsorbed on FeN_5 structure.

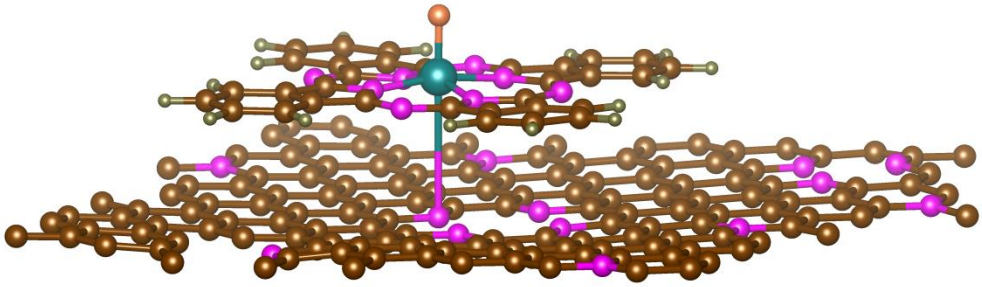

Fig. S5 Reaction intermediate O* adsorbed on FeN_5 structure.

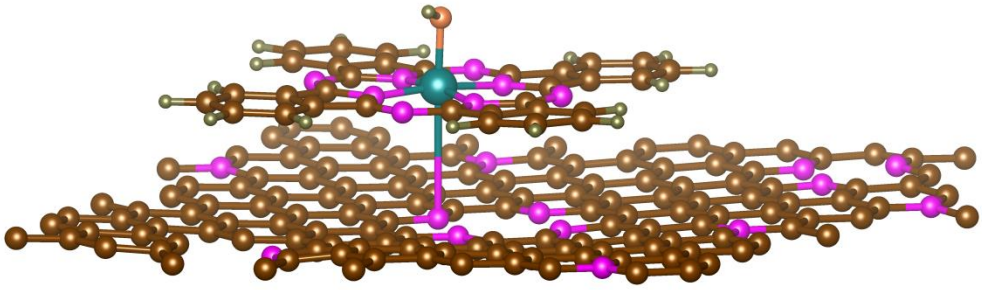

Fig. S6 Reaction intermediate OH* adsorbed on FeN_5 structure.

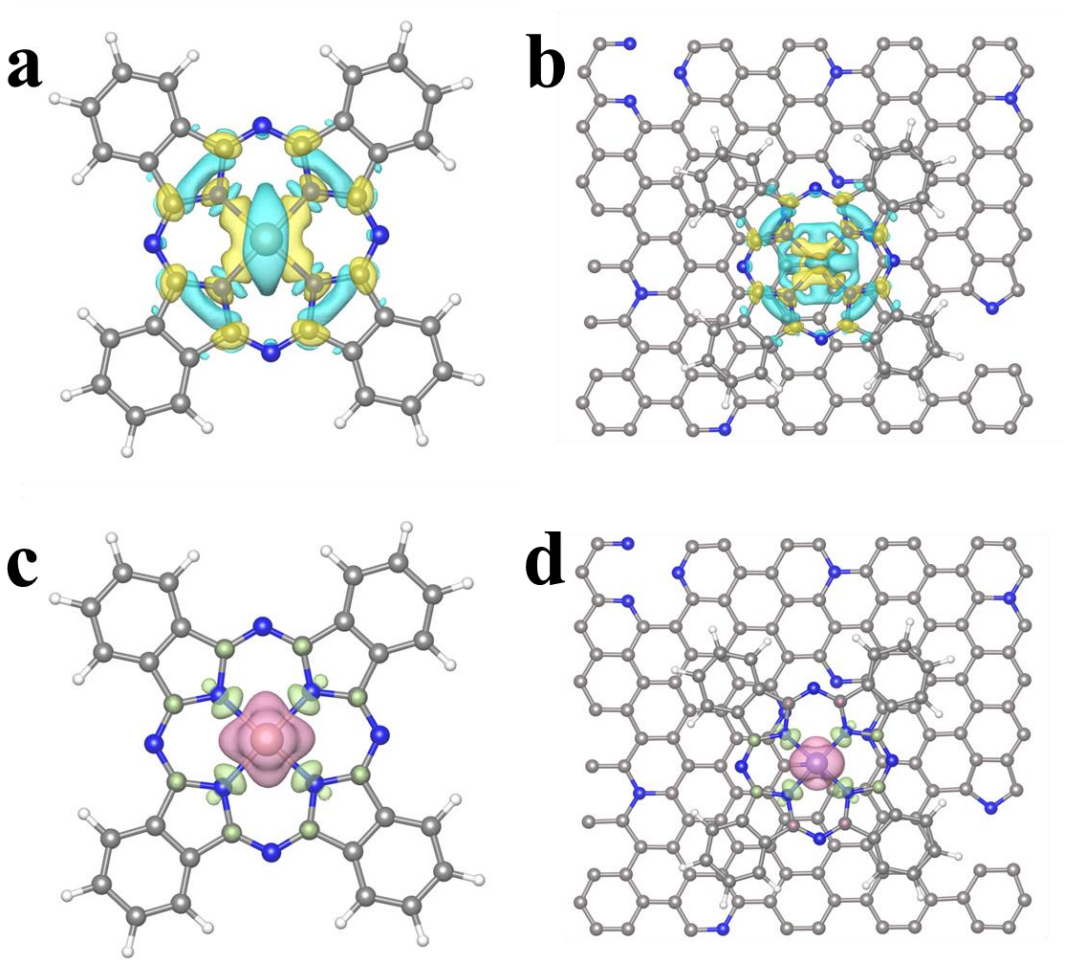

Fig. S7 DFT calculation study of differential charge density diagram for (a) FeN_4 and (b) FeN_5, yellow and cyan isosurfaces represent charge accumulation and depletion. DFT calculation study of spin density diagram for (c) FeN_4 and (d) FeN_5, red and green isosurfaces represent upspin and downspin. The gray spheres represent carbon atoms, the blue spheres represent nitrogen atoms, the pink spheres represent iron atoms and the white spheres represent hydrogen atoms.

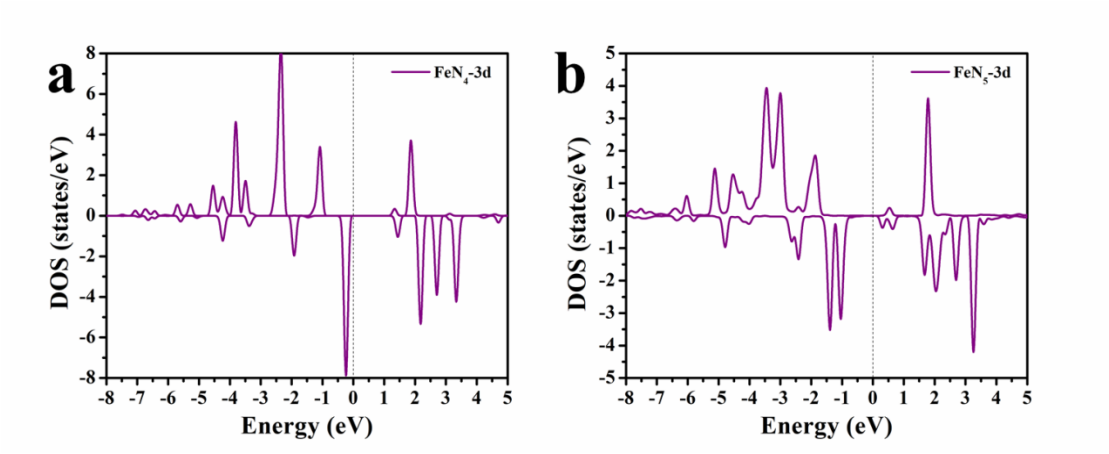

Fig. S8 The density of states (DOS) plots of (a) FeN_4 and (b) FeN_5.

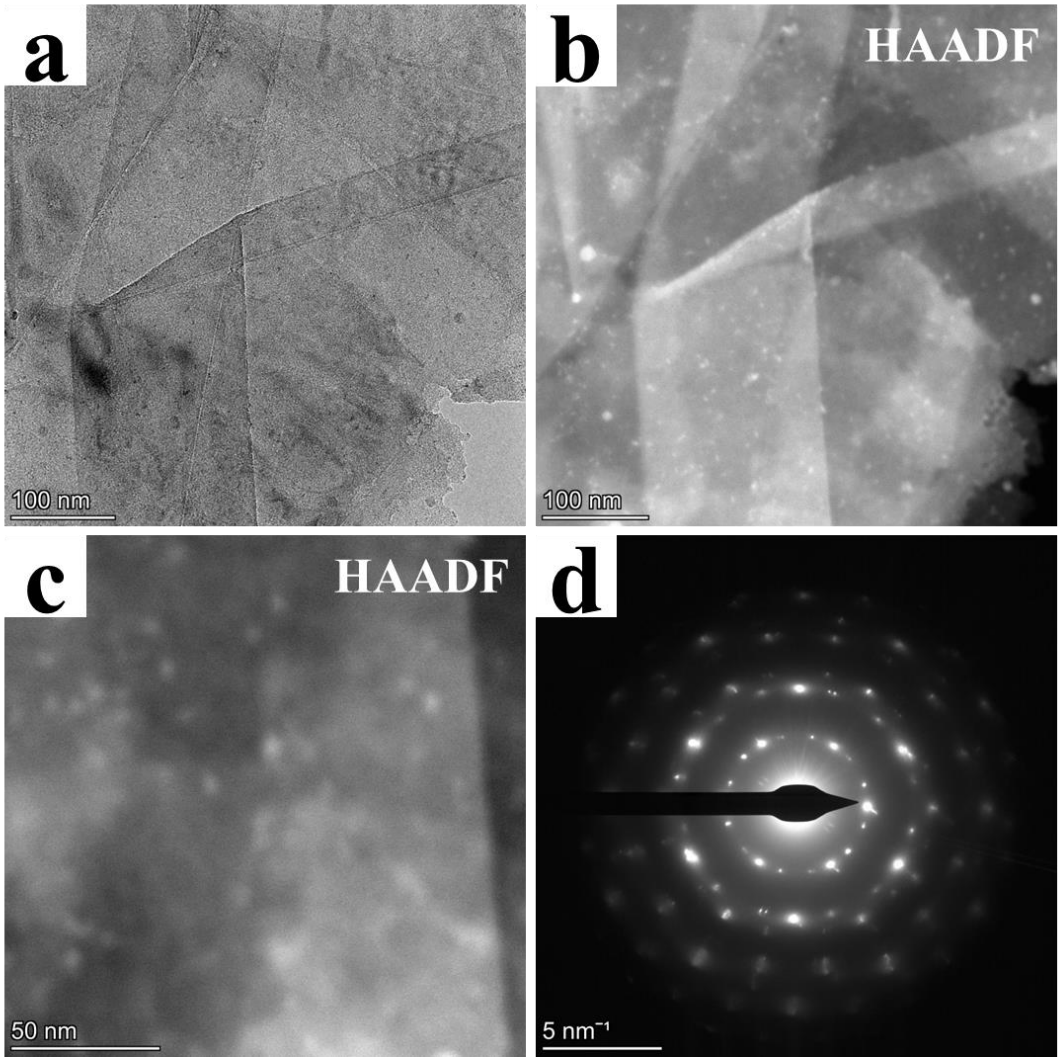

Fig. S9 (a) TEM image, (b-c) HAADF-STEM images at different magnifications and (d) SAED pattern of FePc-c-CG-N.

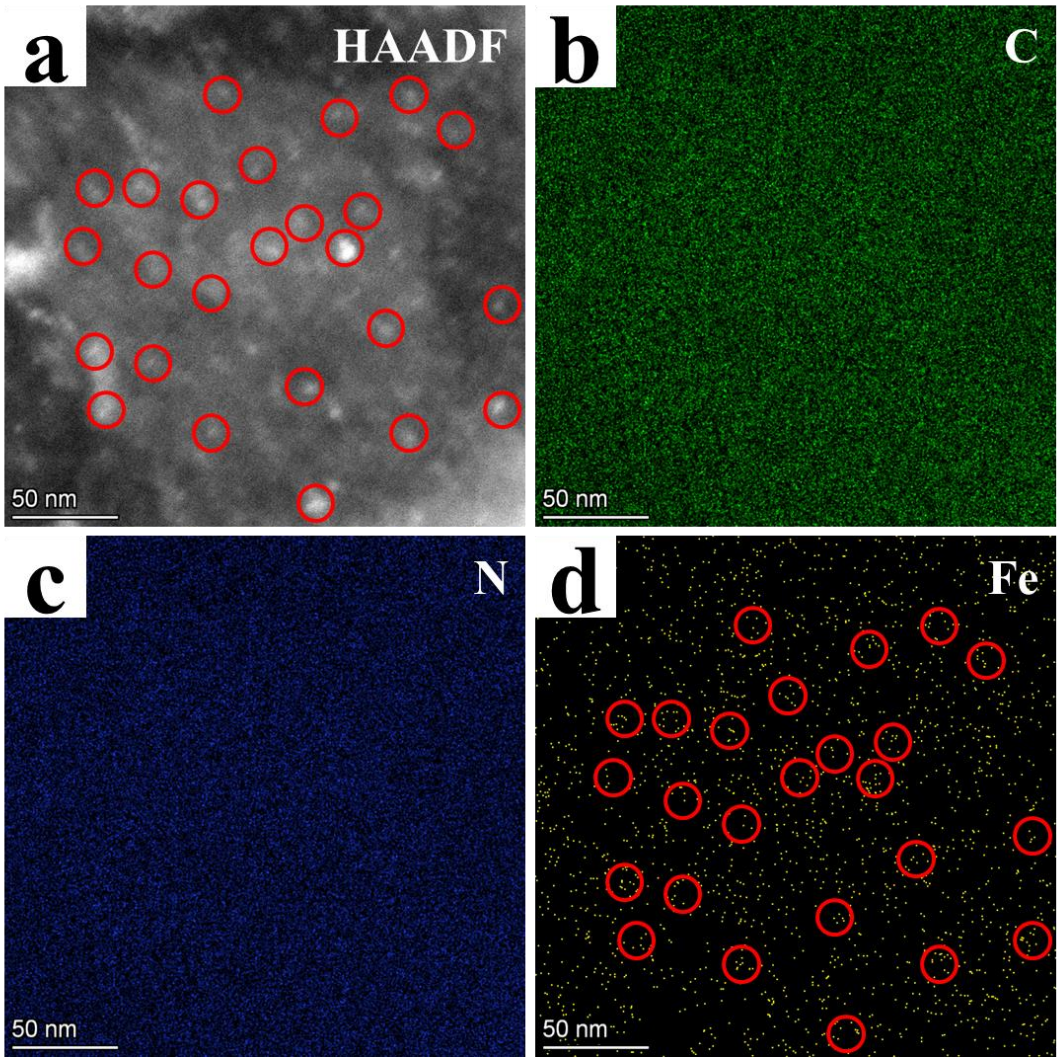

Fig. S10 HAADF-STEM image and EDS elemental mappings of FePc-c-CG-N.

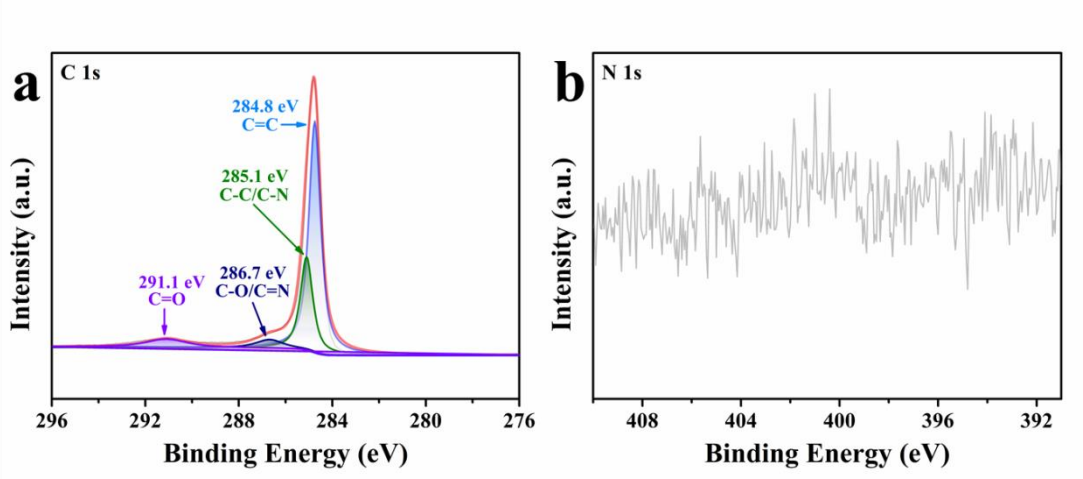

Fig. S11 (a) High-resolution XPS spectrum for C 1s and (b) High-resolution XPS spectrum for N 1s of CG-N.

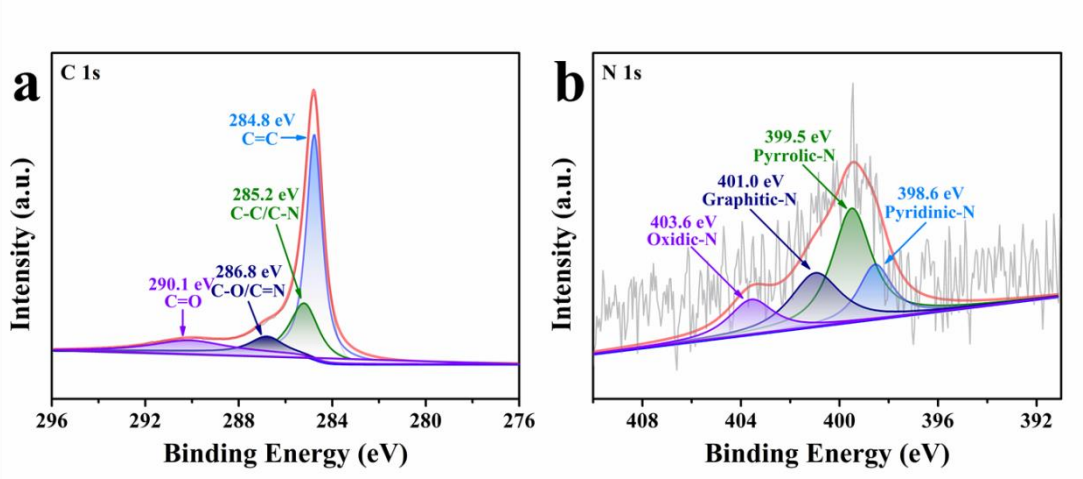

Fig. S12 (a) High-resolution XPS spectrum for C 1s and (b) High-resolution XPS spectrum for N 1s of NG.

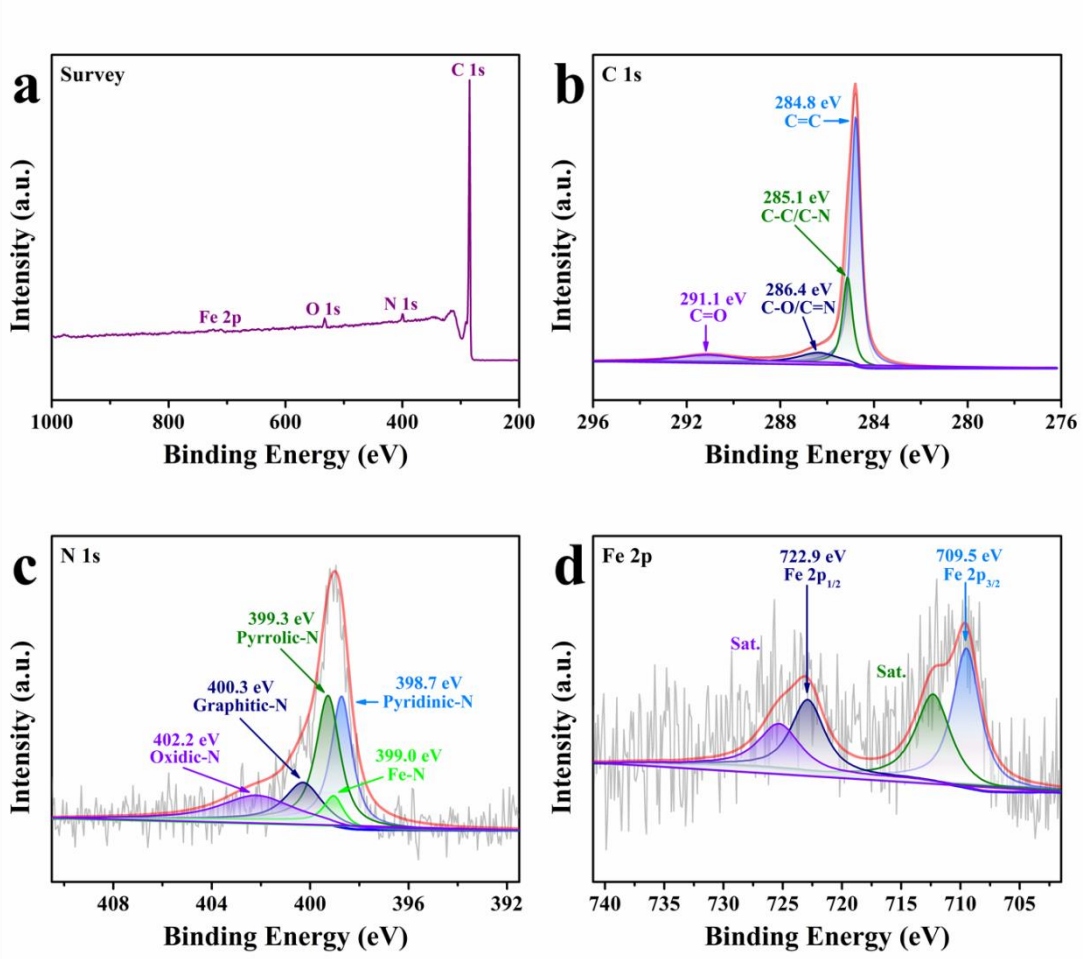

Fig. S13 (a) XPS survey spectrum, (b) High-resolution XPS spectrum for C 1s, (c) High-resolution XPS spectrum for N 1s and (d) High-resolution XPS spectrum for Fe 2p of FePc-c-CG-N.

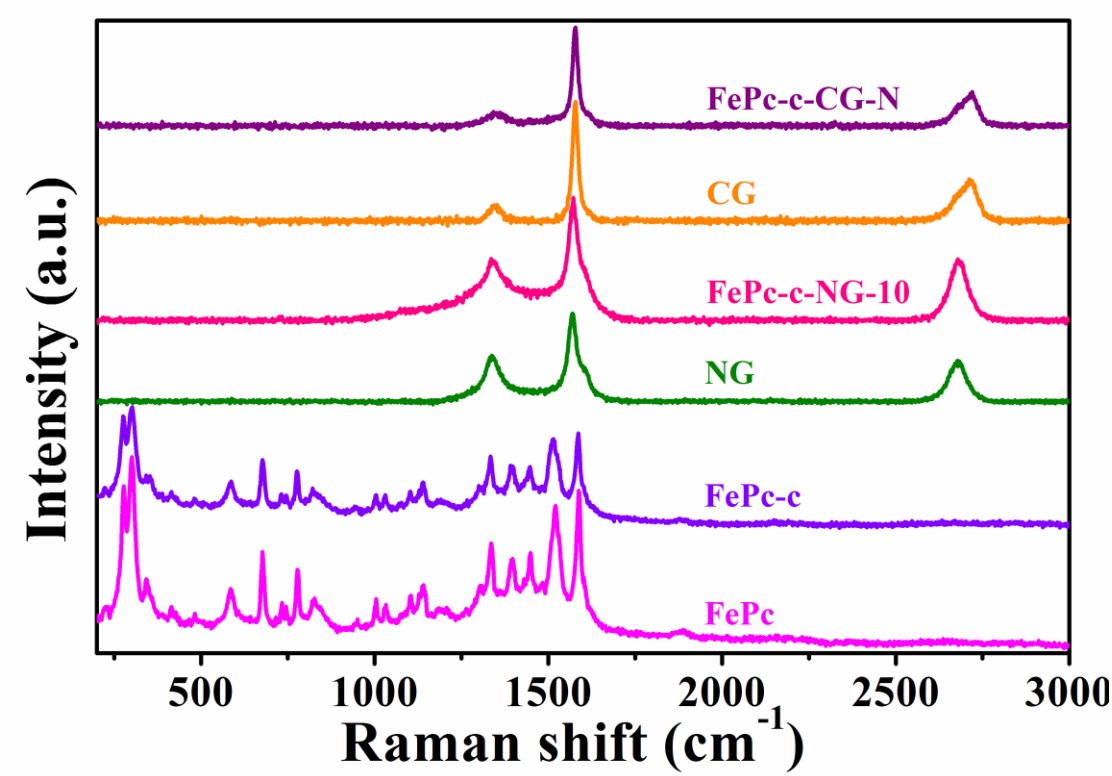

Fig. S14 Raman spectra of FePc, FePc-c, CG, NG, FePc-c-CG-N and FePc-c-NG-10.

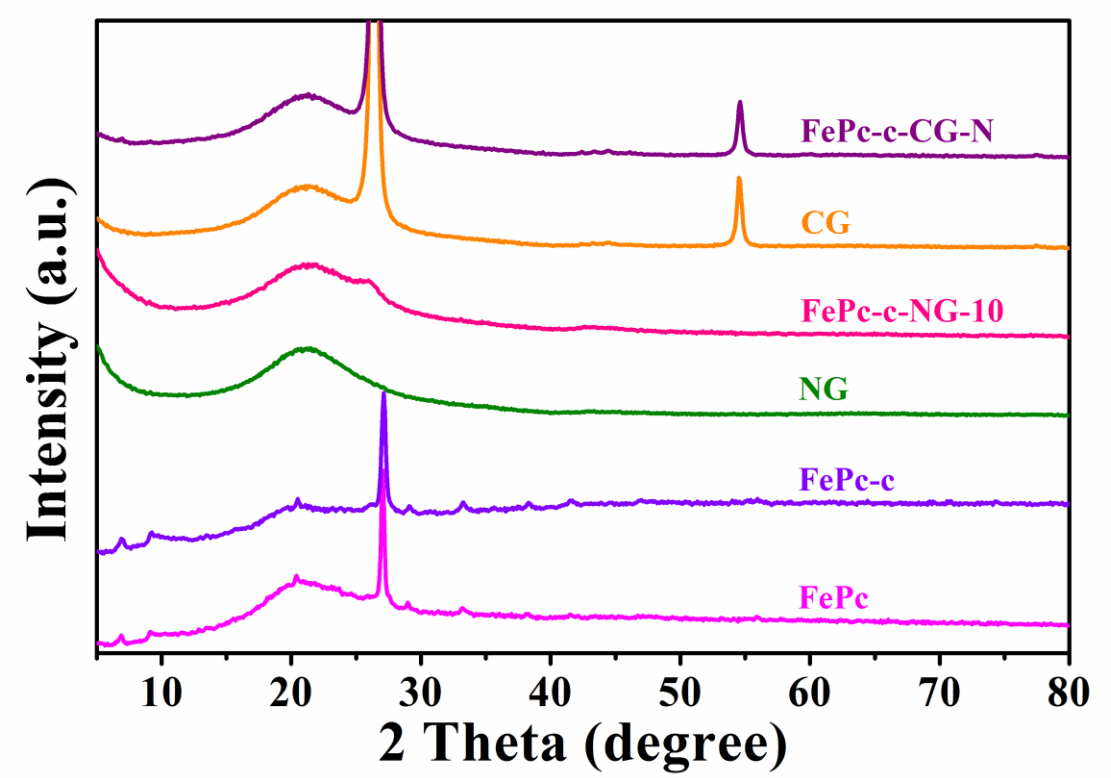

Fig. S15 XRD patterns of FePc, FePc-c, CG, NG, FePc-c-CG-N and FePc-c-NG-10.

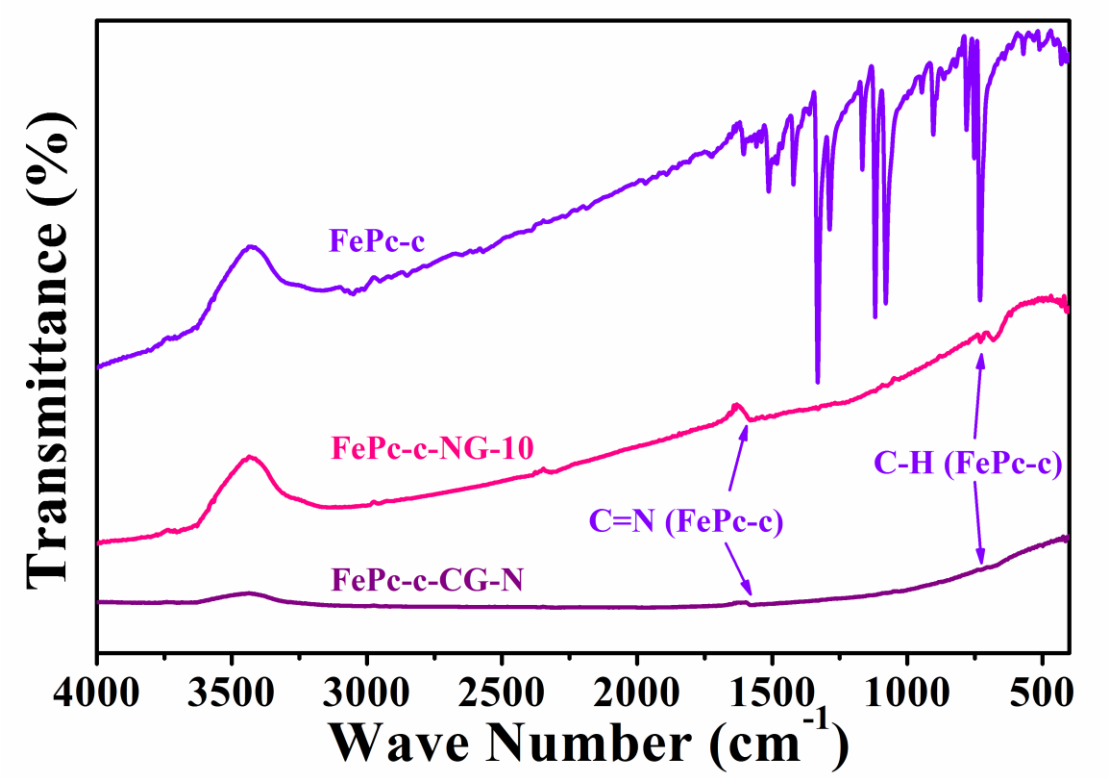

Fig. S16 IR spectra of FePc-c, FePc-c-CG-N and FePc-c-NG-10.

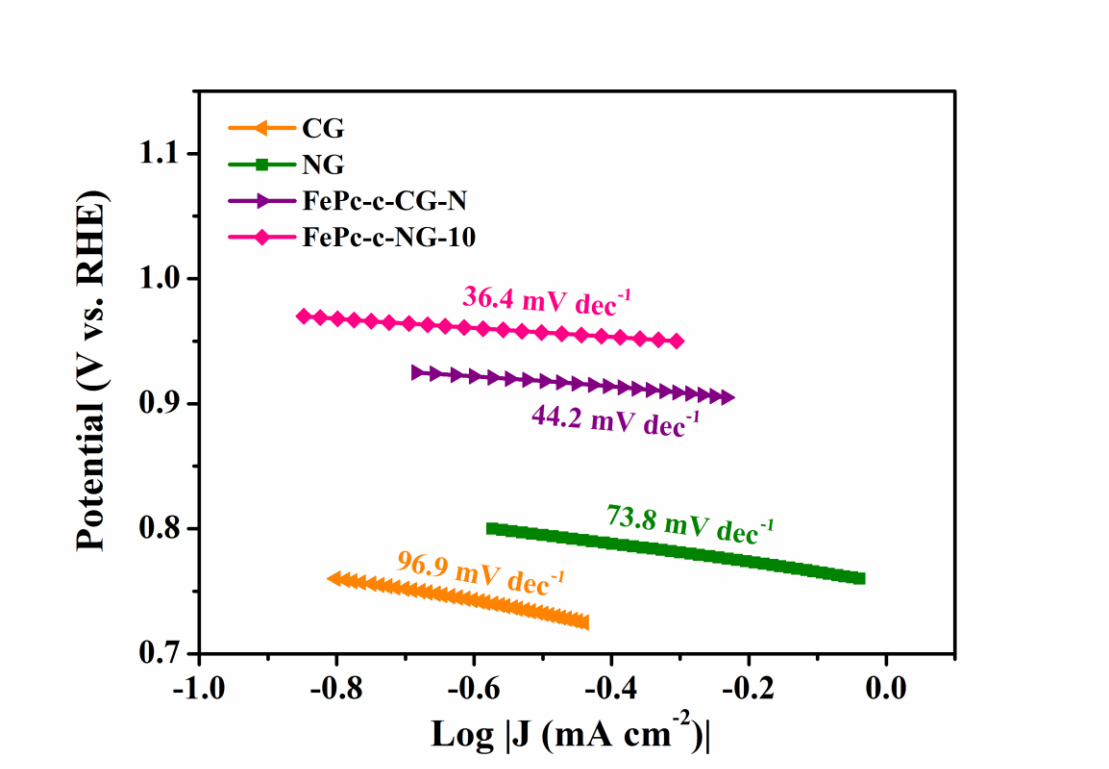

Fig. S17 The corresponding Tafel plots of CG, NG, FePc-c-CG-N and FePc-c-NG-10.

Table S1 The concentration (at %) of chemical elements for CG-N, NG, FePc-c-CG-N and FePc-c-NG-10 by XPS analysis

Samples	C	O	N	Fe
CG-N	**98.80**	**1.20**	**-**	**-**
NG	**91.99**	**7.04**	**0.97**	**-**
FePc-c-CG-N	**94.84**	**2.10**	**2.56**	**0.50**
FePc-c-NG-10	**89.56**	**5.83**	**3.94**	**0.67**

Table S2 Fitting parameters for Fe K-edge EXAFS for the samples

Samples	Shell	CN[a]	R(Å)[b]	σ^2(Å^2)[c]	ΔE_0(eV)[d]	S_0^2	R factor
Fe foil	Fe-Fe	8(set)	2.47	0.006	6.3±0.3	0.8441	0.008
	Fe-Fe2	6(set)	2.84	0.007			
FePc-c-NG-10	Fe-N	5.4±0.2	2.02	0.012	-1.0±0.5	0.8441(set)	0.015

[a]*CN*, coordination number; [b]*R*, the distance to the neighboring atom; [c]σ^2, the Mean Square Relative Displacement (MSRD); [d]ΔE_0, inner potential correction; *R* factor indicates the goodness of the fit. S_0^2 was fixed to 0.7211, according to the experimental EXAFS fit of the sample foil by fixing *CN* as the known crystallographic value. This value was fixed during EXAFS fitting, based on the known structure of Fe foil. Data ranges $3.0 \leq k \leq 12.0$ Å^{-1}, $1.0 \leq R \leq 2.0$ Å. The Debye-Waller factors and Δ*R*s are based on the *guessing* parameters and constrained for Fe-N.

Table S3 The concentration of Fe element for FePc-c-NG-10 by ICP-OES analysis

Chemical Element	**Fe**	**Others**
Concentration (wt %)	**1.67**	**98.33**