Supporting information for

Computational and Experimental Evidence for a New TM-N₃/C Moiety Family in Non-PGM Electrocatalysts

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Experimental Details:

Computational

Detailed computational parameters are E_{cut}=800 eV, slight broadening of the Fermi level using Fermi-Dirac distribution function with width (0.025 eV), and a Γ-centered 4x4x1 k-point grid for the determination of the equilibrium geometry follow previous work.[28-30] . It was modelled as a **4x4 orthorhombic single-layer graphene supercell with lattice parameters a=9.842 Å, b=8.524 Å (containing 32 atoms). Artificial interactions between the sheet and its periodic images perpendicular to the modelled sheet were eliminated by introducing a 14 Å vacuum region. The in-plane nitrogen coordinated $Fe-N_x$ defects in graphene were generated by modifying the graphene sheet (Fig. S1 for DV-TM-N_2 (C1,C2) and DV-TM-N_4; for DV-TM-N_3 and V-TM-N_3, see Fig. 1 main text). The energies of Fe, Co and N_2 in the gas phase were computed by placing the species of interest in a orthorhombic box of dimensions of at least 10 Å x 11 Å x 12 Å. Other computational parameters remained the same as for the computations of the defective structures.**

a)   b)   c)
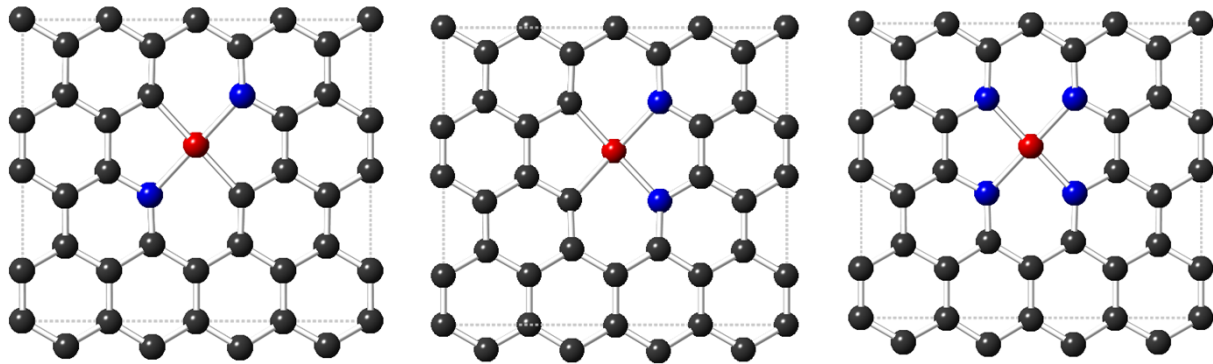
Fig. S1 Top view of computed defect configurations considered in this study: a) TM-N_2/C(1), b) TM-N_2/C(2), c) TM-N_4/C. Gray: Carbon; Blue: Nitrogen; Red: Fe.

The binding energies (BE) for the N 1s orbitals of TM-N$_x$ defects were calculated using single electronic excitations in the final state approximation for a Γ-centered 8x8x1 K point grid, following previous work. For binding energy calculations, we follow the convention that a positive (negative) CLS corresponds to a higher (lower) BE. Test calculations with denser k-point show that the precision of the computed CLS is ~50 meV, well within our experimental uncertainties, which are ~0.1 eV.

XPS

The base pressure was about 2x10–10 torr, and operating pressure was around 2x10–9 torr. N 1s spectra from polypyridine were acquired for 3 minutes with default charge-neutralization settings of –3.1 V bias voltage, -1.0 V filament voltage and filament current of 2.1 A. Au 4f spectra acquired from the reference Au powder deposited on the polypyridine sample was used for charge referencing. N 1s spectra from Fe-carbendazim catalyst were acquired for 20 minutes without charge compensation. Data analysis and quantification were performed using CasaXPS software. A linear background subtraction was used for quantification of N 1s spectra. A 70% Gaussian/30% Lorentzian line shape was utilized in the curve-fit of spectra.
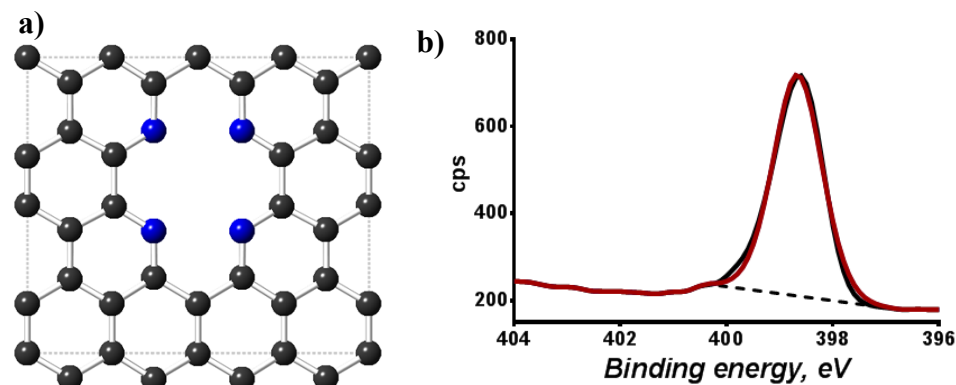
Fig. S2 a) $C_{26}N_4$ – reference structure and corresponding XPS N 1s spectrum.; Gray: carbon; blue: nitrogen; b) N-Pyridinic.

Fig. S2 (b) shows a high resolution N 1s spectrum acquired from polypyridine representing this reference structure. After charge correcting the position of the N 1s spectra by the position of the Au 4f spectrum obtained from the reference gold powder deposited on the sample, the position of pyridinic nitrogen is determined to be 398.8 eV. Thus, the absolute defect specific N 1s BE can be obtained by adding the DFT-CLS to this reference BE.
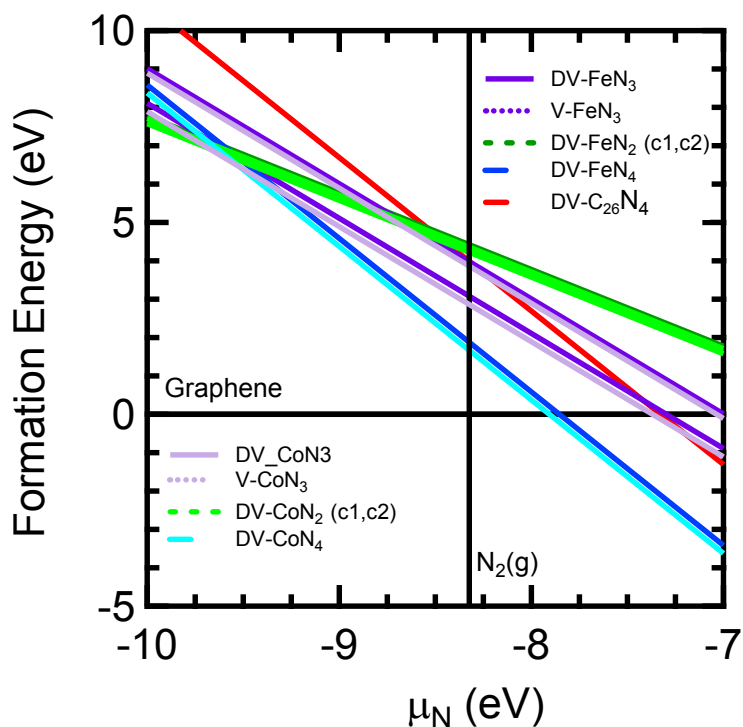
Fig. S3 Comparison of formation energies for TM-N_x/C (TM=Fe, Co) defects, for explanation see main text (Fig. 3).