**Text S5. Theoretical calculation methods.**

Spin-polarized density functional theory (DFT) in the Vienna ab initio Simulation Package (VASP) software was used to calculate the key parameters in this work[1]. The exchange-correlation functionals were treated using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) to achieve structure relaxation and energy minimization[2]. Pseudopotentials were described using the projector augmented wave (PAW) method[3]. The van der Waals interactions between reactants and support were corrected using the DFT-D3 method in Grimme's scheme. The Kohn-Sham valence states expand in the plane-wave basis set with a kinetic energy cutoff of 500 eV. The model taken in this work is a 5 × 5 × 1 graphene supercell. By hollowing out two adjacent C atoms and replacing the remaining four C atoms at the defect with N atoms, a single Co atom was fixed as an active site on the vacancy to bond with the four N atoms to obtain the Co SACs model. Co NPs are nanoparticles containing 38 Co atoms placed on a nitrogen-doped carbon substrate. To avoid interlayer interactions, a 20 Å vacuum layer was inserted in the Z-direction. The Brillouin zone was sampled using a 3 × 3 × 1 Monkhorst–Pack mesh, and an 8 × 8 × 1 grid was used for electronic structure computations. In all relaxations, the maximum residual force for structure optimization is set to 0.03 eV/Å, and the energy convergence is $10^{-5}$ eV per atom. Bader charge analysis was employed to describe charge changes quantitatively. The projected density of states (PDOS) was employed to reveal the nature of bonding between catalysts and intermediates[4]. Adsorption energies ($\Delta E_{ads}$) were computed as:

$$E_{ads} = E_{total} - E_{substrate} - E_{adsorbate}$$

Where $E_{total}$, $E_{substrate}$, and $E_{adsorbate}$ denote energies of the composite system, pristine substrate, and isolated adsorbate. Gibbs' free energy changes ($\Delta G$) incorporated vibrational contributions:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_{pH} + \Delta G_{U}$$

Where $\Delta E$ is the adsorption energy, and $\Delta ZPE$ and $T\Delta S$ are respectively the zero-point energy difference and entropy change between the absorbed state and the gas phase form. $\Delta G_{pH} = -k_B T \ln[H^+]$, where $k_B$ is the Boltzmann constant, and $T$ is the temperature (set to 298.15 K). $\Delta G_U = -eU$ is the free energy contribution due to electrode potential $U$, where e is the elementary charge transferred.

The Gibbs free energy for $NO_3^-$ adsorption ($\Delta G_{*NO3}$) was referenced to gaseous $HNO_3$, thereby circumventing the direct calculation of the charged $NO_3^-$ species. This approach is described by the following equation [5,6].

$$\Delta G_{*NO3} = G_{*NO3} - G_{*} - G_{HNO3(g)} + 1/2G_{H2(g)} + \Delta G_{correct}$$

Where $G_{*NO3}$ and $G_{*}$ denote the Gibbs free energies of the catalyst with adsorbed $NO_3$ and the clean catalyst, respectively. The terms $G_{HNO3}$ (g) and $G_{H2}$ (g) correspond to the Gibbs free energies of gaseous $HNO_3$ and $H_2$. A constant correction $\Delta G_{correct}$ was set at 0.392 eV applied to the adsorption energy.

To evaluate the $NO_3$RR performance of Co-N-C catalysts, the limiting potential ($U_L$) is calculated by the

following equation.

$$U_L = -\Delta G_{max}/e$$

Where $\Delta G_{max}$ represents the maximum free energy change among all protonation steps of $NO_3RR$. A lower $U_L$ value corresponds to superior catalytic performance.

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