

A First-Principles Investigation of Substrate Oxidation Effects on the Catalytic Activity of Co Single-Atom Supported on C₂N for Oxygen Evolution Reaction

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Computational Details

First-principles calculations are performed by using spin-polarized density functional theory (DFT) in the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA) as implemented in the Vienna ab initio simulation package (VASP).¹⁻³ The DFT + U calculations were performed and the value of U-J is 3.5 for Co.⁴⁻⁶ The projected augmented wave method is used with a kinetic energy cutoff of 400 eV. The DFT-D3 method was used to describe van der Waals interactions.⁷ The solvent effect was considered via implicit solvent model (VASPsol).⁸ 3 × 3 × 1 k-point grid with Monkhorst-Pack sampling model is used for all structural optimization work.⁹ The energy convergence limit is set to 10⁻⁵ eV/atom, with a force convergence criterion of 0.02 eV/Å. Structures are relaxed at the same initial guess of overall magnetic moments, and the resulting minimum energy structures are used for all analyses.

The Gibbs free energy (ΔG) was defined as $\Delta G = \Delta E + \Delta ZPE - T\Delta S - eU + \Delta G_{pH}$, where ΔE , ΔZPE and ΔS represented the reaction energy, the difference in zero-point energies (ZPE), the difference in entropy obtained from vibrational frequency

calculations, respectively. eU represents the effect of the electrode potential measured against the standard hydrogen electrode (SHE). ΔG_{pH} is the correction of free energy of H^+ with respect to concentration, which can be determined as $\Delta G_{pH} = 2.303 \times k_B T \times pH$, where k_B is the Boltzmann constant. Our current calculations are all based on standard conditions ($T = 298.15$ K, $P = 1$ bar, $pH = 0$). The entropies of gas phase H_2 , and H_2O were obtained from the NIST database (Computational Chemistry Comparison and Benchmark Database. <http://cccbdb.nist.gov/>) with standard condition.

Under ideal conditions, the OER reaction with a total energy change of 4.92 eV can be driven at 1.23 V, while the ΔG of each elementary reaction would be equally divided into 1.23 eV.¹⁰ Therefore, the overpotential η is introduced to represent additional required potential and measure the catalytic activity of materials, which is defined in theoretical calculations as $\eta = \Delta G_{max}/e - 1.23$ V.

The polarization curves simulation of OER

For a given electrochemical process $O + ne \rightleftharpoons R$ under one electric potential U , it can be used the well-known Nerst equation to link the concentrations of the reactant and the product by the following equation:¹¹

$$U = U_0 + \frac{RT}{nF} \ln \left(\frac{C_O}{C_R} \right)$$

Here, U_0 refers to the equilibrium potential of the reaction at the standard state, R refers to the universal gas constant, T refers to the temperature, n refers to the electron transfer number, F refers to the Faraday constant, and C_O/C_R refers to the concentration of the reactant/product in this reaction.¹² Therefore, the exchange current density j_0 can be calculated by the following equation:

$$j_0 = nFkC_O \exp \left[-\frac{\alpha F}{RT} (U_{eq} - U_0) \right] = nFkC_O^{1-\alpha} C_R^\alpha$$

where k refers to the reaction rate constant, U_{eq} refers to the equilibrium potential, and α refers to the transfer coefficient. So, the electrochemical polarization equation can be defined by equation:

$$j = j_0 \left[\exp\left(-\frac{\alpha F}{RT}\eta\right) - \exp\left(\frac{(1-\alpha)F}{RT}\eta\right) \right]$$

where $\eta = U - U_{eq}$ refers to the overpotential deviated from the equilibrium potential and j of the overall current density. The exchange current density j_0 can be used to evaluate the catalytic activity of one catalyst. Following the electrochemical catalysis mode developed by Nørskov¹⁰, the reaction rate constant k can be defined as follows:

$$k = k_0 \exp\left[-\frac{\Delta G_{max}}{k_b T}\right]$$

where k_b and ΔG_{max} refers to the Boltzmann constant and the Gibbs free energy change of the potential-determining step, respectively. In the electrochemical polarization model¹³, k_0 is defined as the equation:

$$k_0 = \frac{k_b T}{h}$$

where h refers to the Planck constant. Therefore, the exchange current density j_0 of the electrochemical reaction when the reaction approaches its equilibrium state can be described as the following equation:

$$j_0 = nFC_0 \frac{k_b T}{h} \exp\left[-\frac{\Delta G_{max}}{k_b T}\right]$$

Hence, the overall current density j can be calculated by the follows equation according to the overpotential η ¹⁰:

$$j = nFC_0 \frac{k_b T}{h} \exp\left[-\frac{\Delta G_{max}}{k_b T}\right] \left[\exp\left(-\frac{\alpha F}{RT}\eta\right) - \exp\left(\frac{(1-\alpha)F}{RT}\eta\right) \right] \approx nFC_0 \frac{k_b T}{h} \exp\left[-\frac{\Delta G_{max}}{k_b T} - \frac{\alpha F}{RT}\eta\right]$$

The OER need to overcome the reaction kinetic energy barriers, and the onset potential generally represents the reaction potential at which the current begins to deviate from the baseline.¹⁴ In this work, the calculated polarization curves for the OER was calculated as literature reported.¹⁵

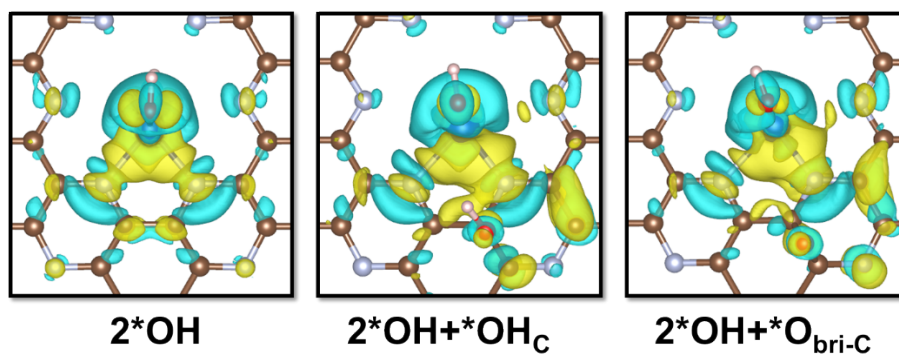


Fig. S1. The differential charge density maps of Co@C₂N adsorbing different intermediates. The presence of Co atoms alters the electronic structure of the C sites, and conversely, when the C sites are occupied by *O_{bri-C} species, they significantly affect the electronic structure of the Co atoms.

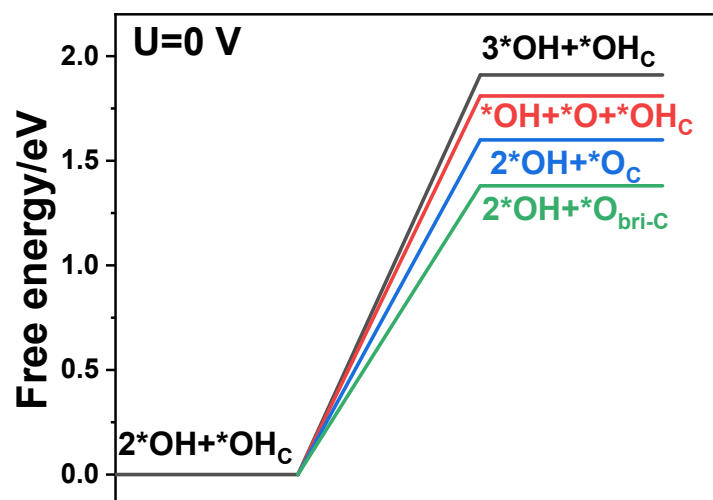


Fig. S2. The possible evolution of intermediates $2^*OH+^*OH_C$ and the corresponding free energy change.

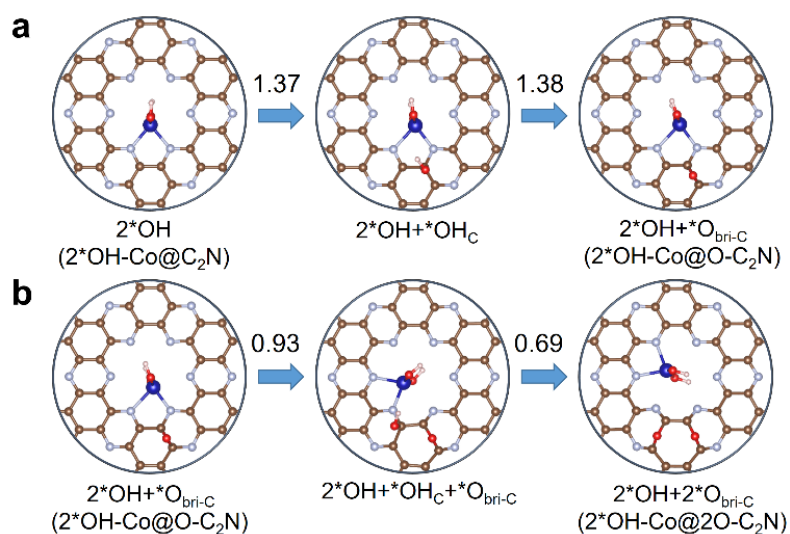


Fig. S3. The formation steps of a) the first $*O_{bri-C}$ and b) the second $*O_{bri-C}$. Their corresponding energy requirements (eV) are also given out.

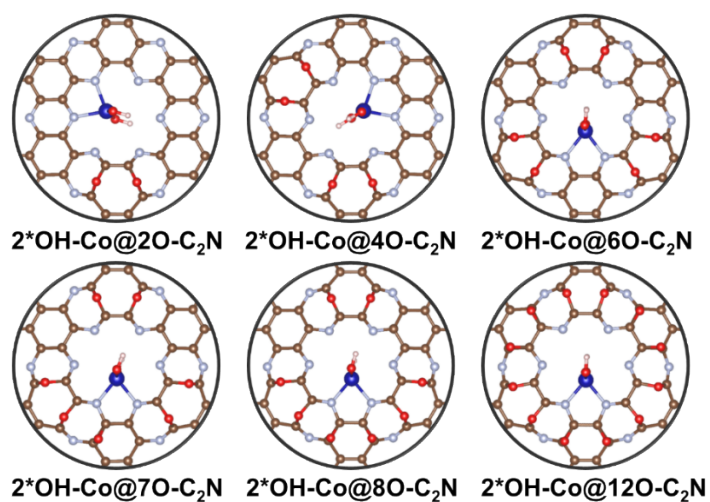


Fig. S4. The optimized structure of $2^*OH-Co@xO-C_2N$ ($x = 4, 6, 7, 8, 12$). When $x \leq 6$, $*O_{bri-C}$ exists in the form of ether oxygen. When $x > 6$, the additional $*O_{bri-C}$ exists in the form of epoxy oxygen.

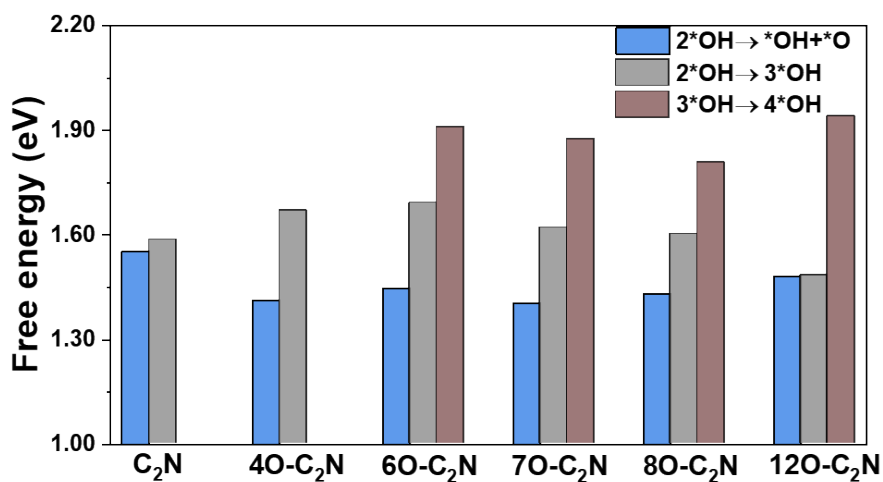


Fig. S5. The free energy required for the evolution of intermediates on the Co single atom.

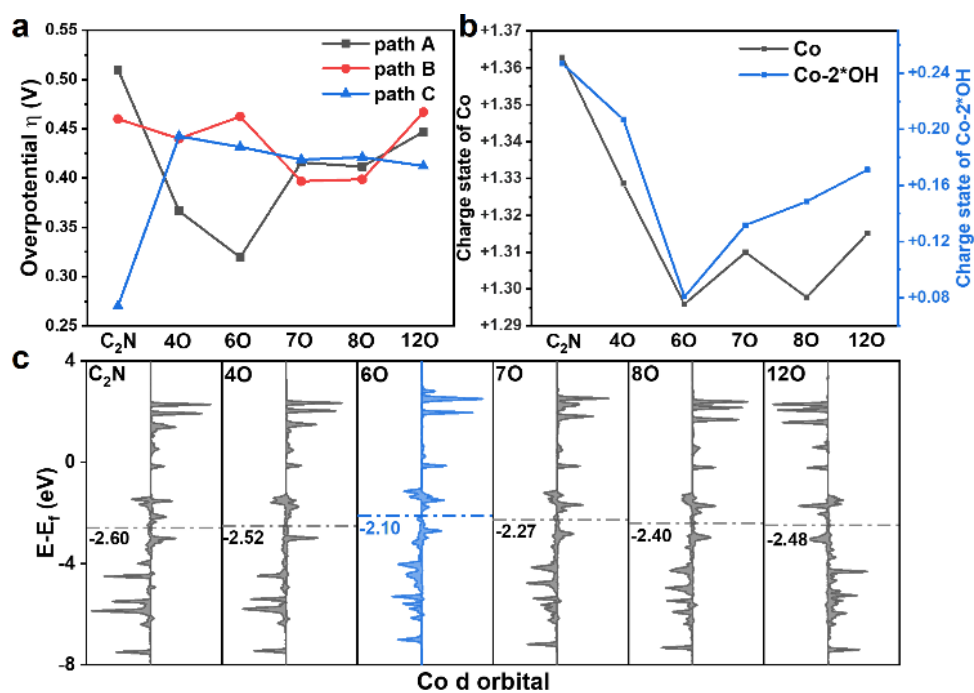


Fig. S6. a) The variation in overpotentials for different pathways as the coverage of *O_{bri-C} increases. b) Changes in the charge state of the Co atom and the overall charge state of the Co-2*OH cluster. c) Showing the *d*-orbital of the Co center in the 2*OH-Co@*x*O-C₂N system (*x* = 0, 4, 6, 7, 8, 12). The auxiliary lines in the figure show the changes in the *d*-band center of the Co atom.

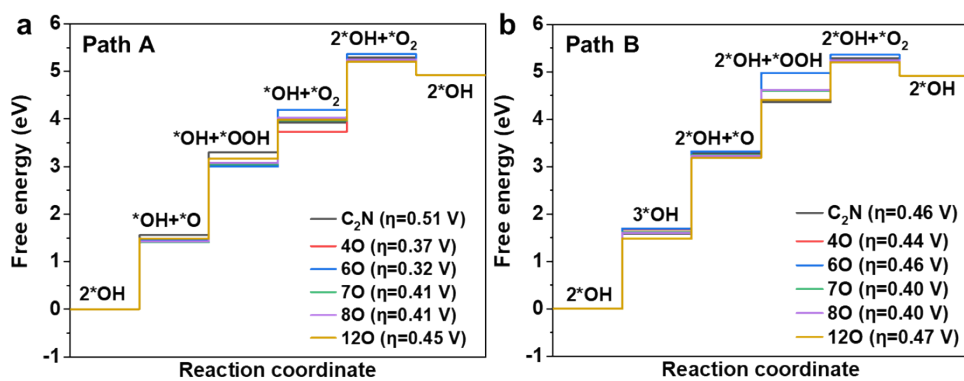


Fig. S7. The energy profile of a) path **A** and b) path **B** in the $2^*OH-Co@xO-C_2N$ system ($x = 0, 4, 6, 7, 8, 12$).

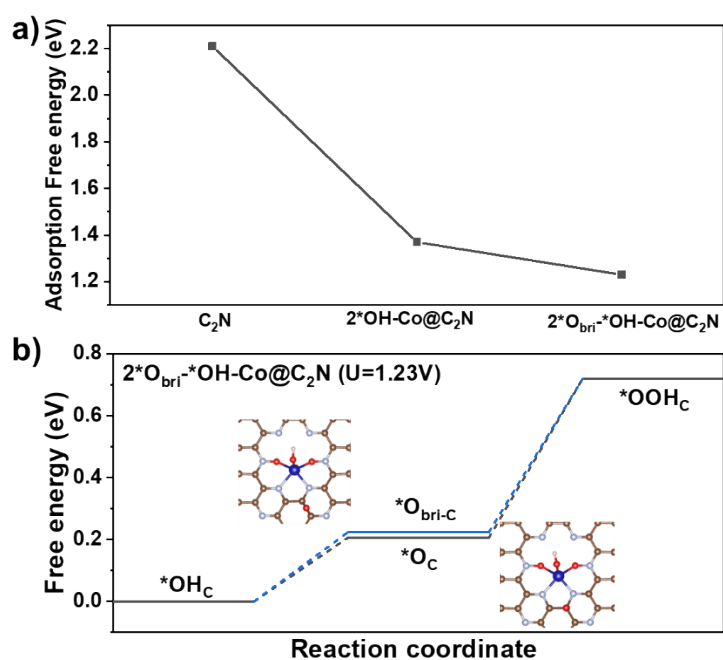


Fig. S8. a) The adsorption free energy of $*OH$ on the C site ($*OH_C$). b) The evolution of $*OH_C$ at a voltage of 1.23V.

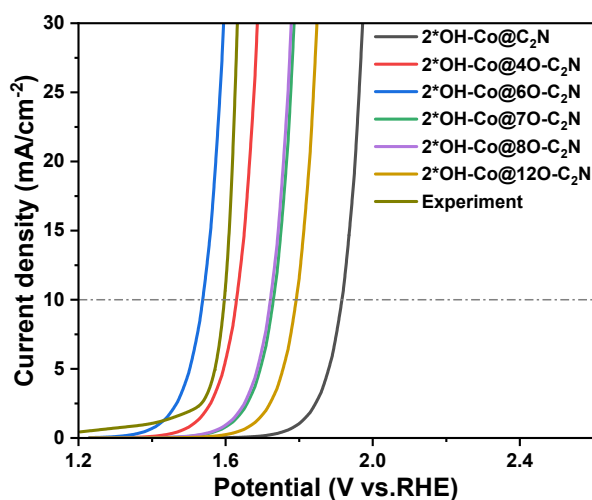


Fig. S9. The theoretical OER polarization curves of the $2^*\text{OH-Co}@x\text{O-C}_2\text{N}$ system.

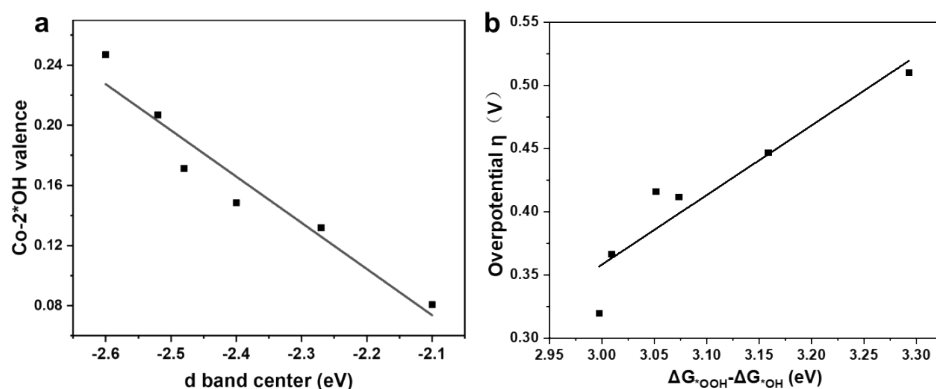


Fig. S10. a) The linear relationship between the d-band center of Co atoms and the oxidation state of the Co-2*OH cluster. b) The positive correlation between the difference in adsorption free energy of intermediates *OOH and *OH ($\Delta G_{^*\text{OOH}} - \Delta G_{^*\text{OH}}$) and the overpotential η in the OER cycle of Path A.

Table S1. The overpotentials for different pathways as the coverage of $^*\text{O}_{\text{bri-C}}$ increases.

$2^*\text{OH-Co}@x\text{O-C}_2\text{N}$	Path A	Path B	Path C
$x=0$	0.51	0.46	0.27
$x=4$	0.37	0.44	0.44
$x=6$	0.32	0.46	0.43
$x=7$	0.42	0.40	0.42
$x=8$	0.41	0.40	0.42
$x=12$	0.45	0.47	0.41

Table S2. The adsorption free energies between the intermediates *OOH and *OH ($\Delta G^*_{\text{OOH}} - \Delta G^*_{\text{OH}}$) of Path A in the 2*OH-Co@xO-C₂N system.

2*OH-Co@xO-C ₂ N	$\Delta G^*_{\text{OOH}} - \Delta G^*_{\text{OH}}$
x=0	3.29
x=4	3.01
x=6	3.00
x=7	3.05
x=8	3.07
x=12	3.16

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