Supporting Information:

Graphyne-based single atom catalysts for oxygen reduction reaction: a constantpotential first-principles study

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The Grand canonical potential (GCP) Formulation

The grand canonical potential is defined as:^{1, 2}

$$G(n;U) = F(n) - ne(U_{SHE} - U)$$
⁽¹⁾

Where G is the grand canonical free energy, n is the number of electrons, e is unit electronvolt in energy, F is the total free energy as a function of n, and $U_{SHE} = \mu_{e,SHE}/e$ is the electronic energy at the standard hydrogen electrode. When employing the grand potential G(n;U) as a thermodynamic descriptor, the system's electron count must self-consistently adapt to the applied electrode potential U. This potential-dependent electron population is achieved through Fermi level alignment, where the occupation of electronic states is systematically adjusted to maintain equilibrium with the external potential, thereby modifying the total electron number in the simulation cell.

$$\mu_e = \frac{dF(n)}{dn} = e\left(U_{SHE} - U\right)_{\text{or}} \frac{dG(n;U)}{dn} = 0$$
(2)

Then, the thermodynamic Grand Canonical Potential (GCP) is defined as:

$$GCP(U) = minG(n;U) = min [F(n) - ne(U_{SHE} - U)]$$
(3)

F(n) is as quadratic and minimizing G(n;U) leads to a quadratic form in GCP(U). The F(n) can be expanded as:

$$F(n) = a(n - n_0)^2 + b(n - n_0) + c$$
(4)

The parameters a, b, and c were determined through least-squares fitting, with their optimal values obtained by minimizing the error function in Equation (4), yielding the following analytical expression:

$$GCP(U) = -\frac{1}{4a} (b - \mu_{e,SHE} + eU)^2 + c - n_0 \mu_{e,SHE} + n_0 eU$$
(5)

The physical quantities of parameters are as follows:

The differential capacitance, $C_{diff} = \frac{\partial n}{\partial U} = -\frac{1}{2a}$. Thus, $a = -\frac{1}{2C_{diff}}$

When the system at the potential of zero charge, $n(U_{PZC}) = n_0$

$$n(U) = -\frac{1\partial GCP(U)}{e} = n_0 - \frac{1}{2ae}(b - \mu_{e,SHE} + eU)$$

Then,
$$b = \mu_{e,SHE} - eU$$
.

When the system is neutral, $F(n = n_0) = c$. Put these parameters into formulas (4) and (5). We can obtain:

$$F(n) = -\frac{1}{2C_{diff}} (n - n_0)^2 + (\mu_{e,SHE} - eU_{PZC})(n - n_0) + F_0$$
(6)

$$GCP(U) = \frac{e^2 C_{diff}}{2} (U - U_{PZC})^2 + n_0 eU + F_0 - n_0 \mu_{e,SHE}$$
(7)

Where n_0 is the number of electrons at zero net charge, $\mu_{e,SHE}$ is the chemical potential of an electron vs standard hydrogen electrode (SHE).

pH effect

The pH of the electrolyte critically governs electrochemical reaction through its influence on proton-coupled electron transfer processes and interfacial charge

distributions. In conventional CHE model, pH effect is considered via an energy correction term $\Delta G_{pH} = k_B T \times pH \times ln10$. However, When the electrode potential is referenced to the reversible hydrogen electrode (RHE) scale, the pH-dependent correction becomes inherently incorporated through the Nernstian relationship ($E_{RHE} =$ $E + 0.0592 \times pH$ at 298 K)., this pH correction is cancelled out, so conventional computational models typically neglect pH considerations at RHE level. In CPM model, the electrode potential is regulated by the number of charges in the system. In experimental electrochemistry, potentials are conventionally referenced to the RHE scale, which relates to the standard hydrogen electrode (SHE):

$$U_{RHE} = U_{SHE} + 0.0592 \times \text{pH} \text{ (at 298 K)}$$

This fundamental relationship enables precise pH determination when maintaining a constant RHE potential (U_{RHE}) through systematic charge state modulation of the electrochemical system. By computationally varying the total electron count while fixing U_{RHE} , we establish a correspondence between the charge state and pH, thereby providing an accurate computational framework for pH-dependent electrochemical studies.



Fig. S1 The atomic structure model of (a) Mn-GY, (b) *OOH, (c) *O and (d) *OH adsorption configurations on Mn-GY.



Fig. S2 The atomic structure model of (a) Fe-GY, (b) OOH, (c) Oand (d) OH adsorption configurations on Fe-GY.



g. S3 Free energy changes of ORR on (a) Mn-GY and (b) Fe-GY at pH = 1 as a function of electrode potential. Free energy changes of ORR on (c) Mn-GY and (d) Fe-GY at pH = 13 as a function of electrode potential.



Fig. S4 The atomic structure model of (a) N_1 -Co-GY, (b) *OOH, (c) *O and (d) *OH adsorption configurations on N_1 -Co-GY.



Fig. S5 The atomic structure model of (a) N_{13} -Co-GY, (b) *OOH, (c) *O and (d) *OH adsorption configurations on N_{13} -Co-GY.



Fig. S6 The atomic structure model of (a) N_{16} -Co-GY, (b) *OOH, (c) *O and (d) *OH adsorption configurations on N_{16} -Co-GY.



Fig. S7 The atomic structure model of (a) N_{135} -Co-GY, (b) *OOH, (c) *O and (d) *OH adsorption configurations on N_{135} -Co-GY.



Fig. S8 Free energy changes of ORR on N_1 -Co-GY and at (a) pH = 1 and (b) pH = 13 as a function of electrode potential.



Fig. S9 Free energy changes of ORR on (a) N_{13} -Co-GY and (b) N_{16} -Co-GY at pH = 1 as a function of electrode potential. Free energy changes of ORR on (c) N_{13} -Co-GY and (d) N_{16} -Co-GY at pH = 13 as a function of electrode potential.



Fig. S10 Free energy changes of ORR on N_{135} -Co-GY and at (a) pH = 1 and (b) pH = 13 as a function of electrode potential.



Fig. S11 Volcano plots of the limiting potential of ORR as a function of the *OH adsorption energy under (a) charge-neutral condition, (b) constant-potential condition at pH=1 and (c) constant-potential condition at pH=13, respectively.



Fig. S12 Molecular dynamics simulations of Co-GY under electrochemical working conditions at pH=1. Total energy of (a)Co-GY, (b) Co-GY-*OOH, (c) Co-GY-*O, (d) Co-GY-*OH as a function of MD time at 0.77 V vs RHE at pH=1. Inset: snapshots of atomic configurations of Co-GY-*OOH, Co-GY-*O, and Co-GY-*OH at the end of AIMD simulations. The optimized atomic structures are displayed in the top and side views.



Fig. S13 Molecular dynamics simulations of Co-GY under electrochemical working conditions at pH=13.Total energy of (a) Co-GY, (b) Co-GY-*OOH, (c) Co-GY-*O, (d) Co-GY-*OH as a function of MD time at 0.87 V vs RHE at pH=13. Inset: snapshots of atomic configurations of Co-GY, Co-GY-*OOH, Co-GY-*O, and Co-GY-*OH at the end of AIMD simulations. The optimized atomic structures are displayed in the top and side views.



Fig. S14 Molecular dynamics simulations of N_0 -Co-GY under electrochemical working conditions at pH=1. Total energy of (a) N_0 -Co-GY, (b) N_0 -Co-GY-*OOH, (c) N_0 -Co-GY-*O, (d) N_0 -Co-GY-*OH as a function of MD time at 0.97 V vs RHE at pH=1. Inset: snapshots of atomic configurations of N_0 -Co-GY, N_0 -Co-GY-*OOH, N_0 -Co-GY-*O, and N_0 -Co-GY-*OH at the end of AIMD simulations. The optimized atomic structures are displayed in the top and side views.



Fig. S15 Molecular dynamics simulations of N_0 -Co-GY under electrochemical working conditions at pH=13.Total energy of (a) N_0 -Co-GY, (b) N_0 -Co-GY-*OOH, (c) N_0 -Co-GY-*O, (d) N_0 -Co-GY-*OH as a function of MD time at 0.90 V vs RHE at pH=13. Inset: snapshots of atomic configurations of N_0 -Co-GY, N_0 -Co-GY-*OOH, N_0 -Co-GY-*O, and N_0 -Co-GY-*OH at the end of AIMD simulations. The optimized atomic structures are displayed in the top and side views.



Fig. S16 Project density of states (PDOS) of Co atom in (a) N_1 -Co-GY, (b) N_{13} -Co-GY, (c) N_{16} -Co-GY and (d) N_{135} -Co-GY.

- 1. M. D. Hossain, Y. Huang, T. H. Yu, W. A. Goddard, III and Z. Luo, *Nat. Commun.*, 2020, **11**, 2256.
- Y. Huang, R. J. Nielsen and W. A. Goddard, 3rd, J. Am. Chem. Soc., 2018, 140, 16773-16782.