Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

CoN_3 embedded graphene, a potential catalyst for oxygen reduction reaction from theoretical perspective

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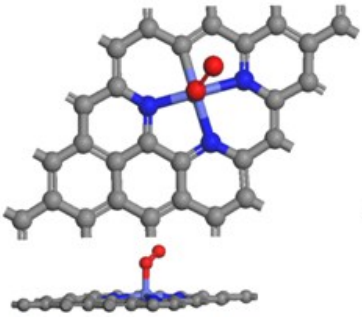
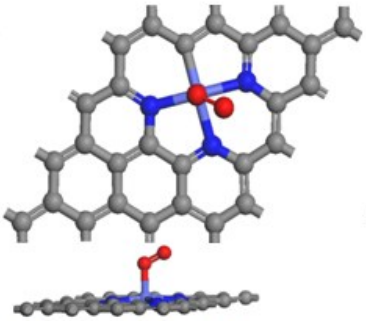
Optimization structures—O_2



E_{ads}= -0.42 eV



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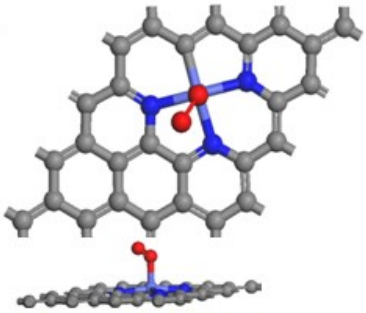
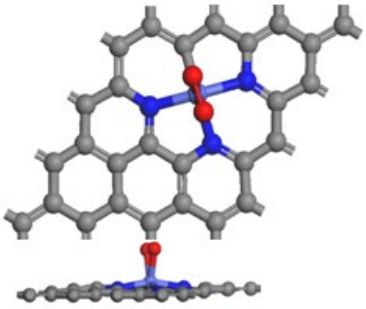


E_{ads}= -0.42 eV



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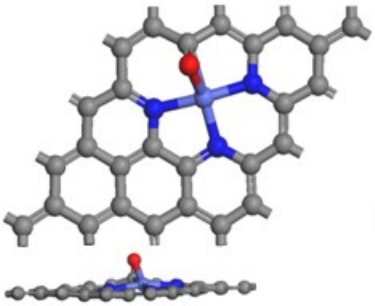
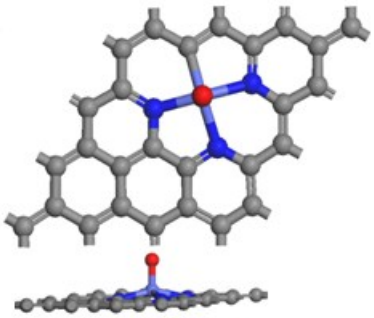
Optimization structures—O

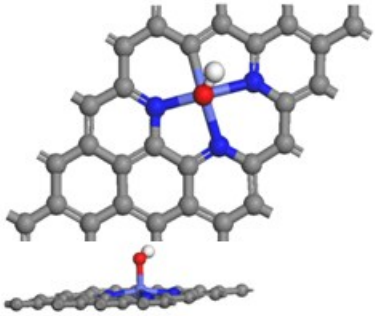


E_{ads}= -4.97eV



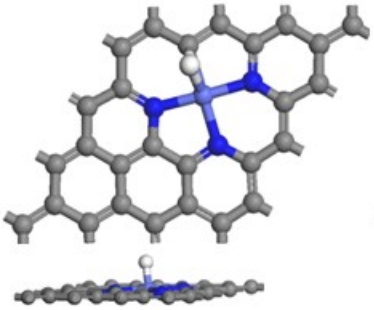
E_{ads}= -4.17 eV

Optimization structures—OH

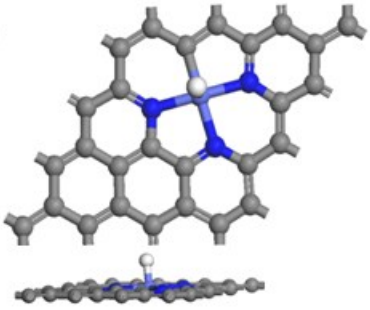


E_{ads}= -2.78 eV

Optimization structures—H

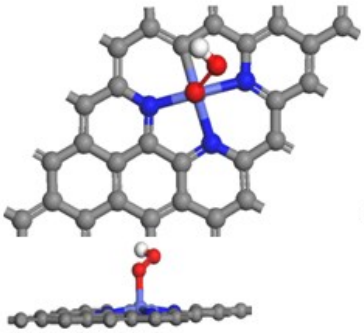


E_{ads}= -2.88 eV

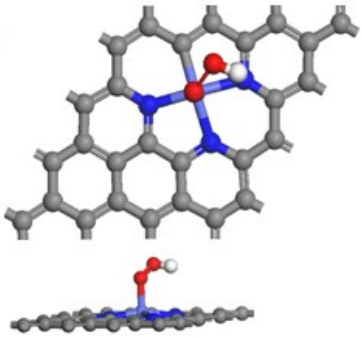


E_{ads}= -2.78 eV

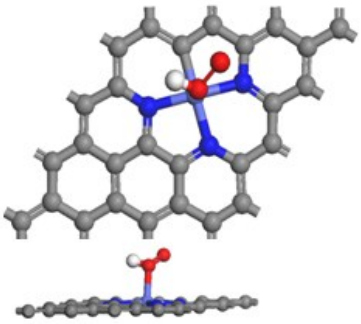
Optimization structures—OOH



E_{ads}= -0.89eV



E_{ads}= -0.85eV



E_{ads}= 0.10eV

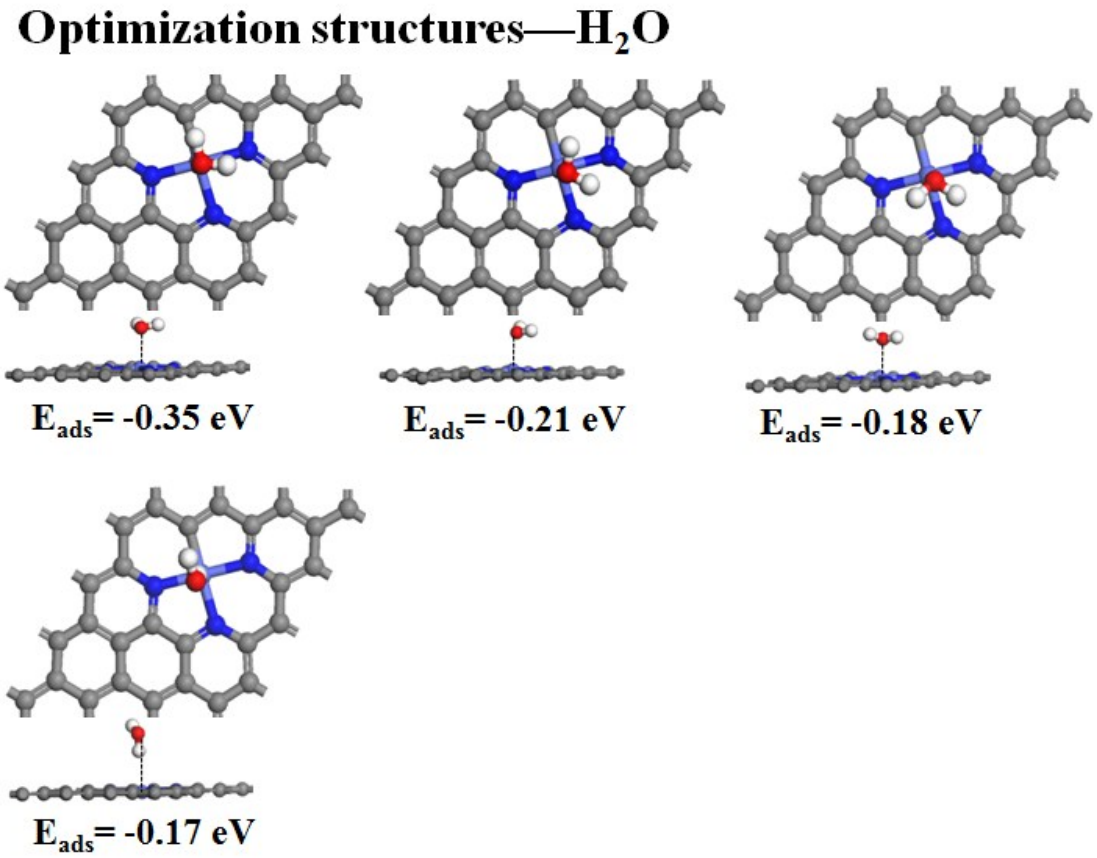
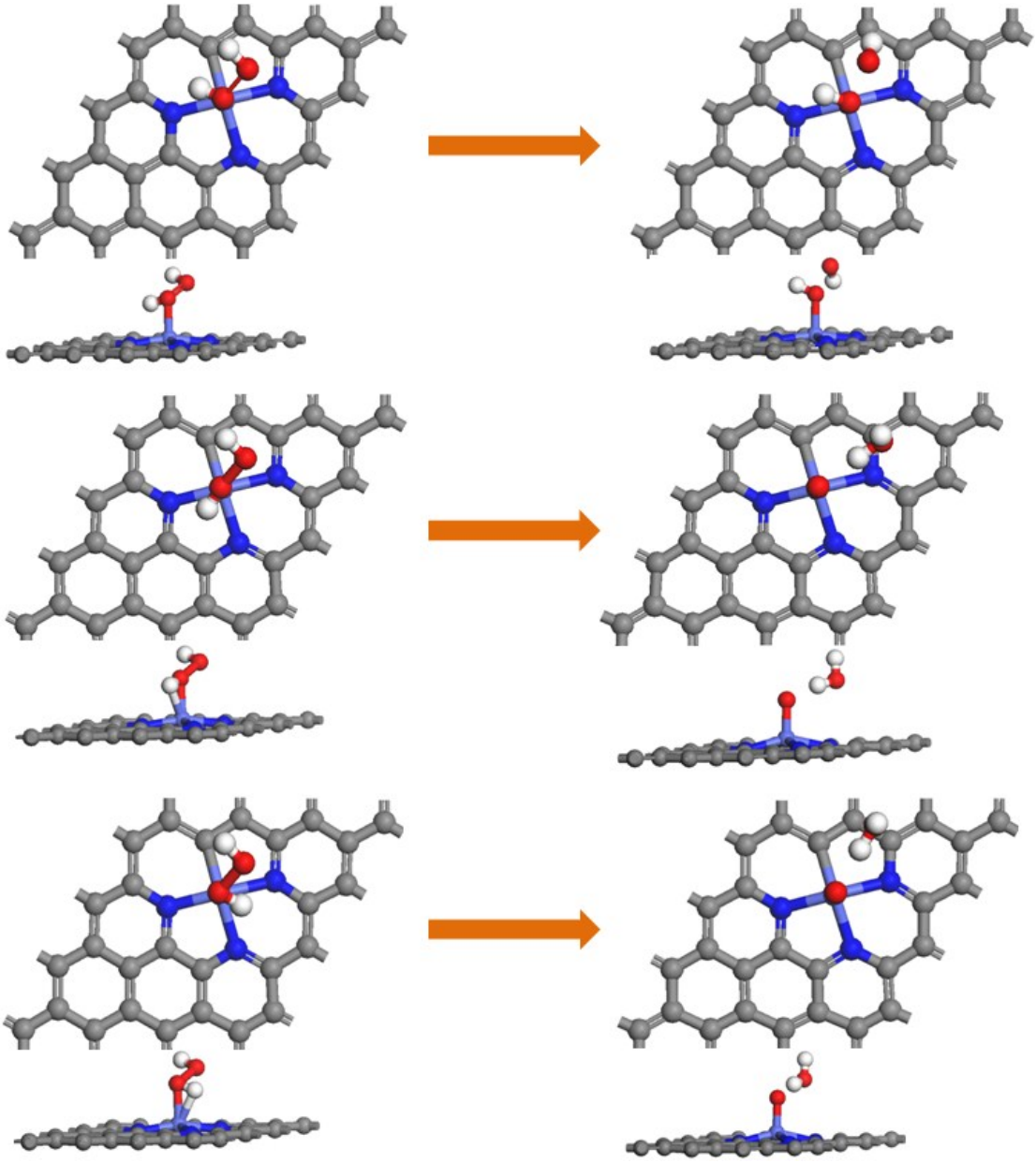


Fig. S1. Possible configurations for each adsorbed species (end-on O_2, side-on O_2, O, H, OH, OOH, H_2O) involved in the ORR on CoN_3 embedded graphene. E_{ads} represents the adsorption energy (eV). The gray, blue, dark blue, red, and white balls represent C, Co, N, O, and H atoms, respectively.



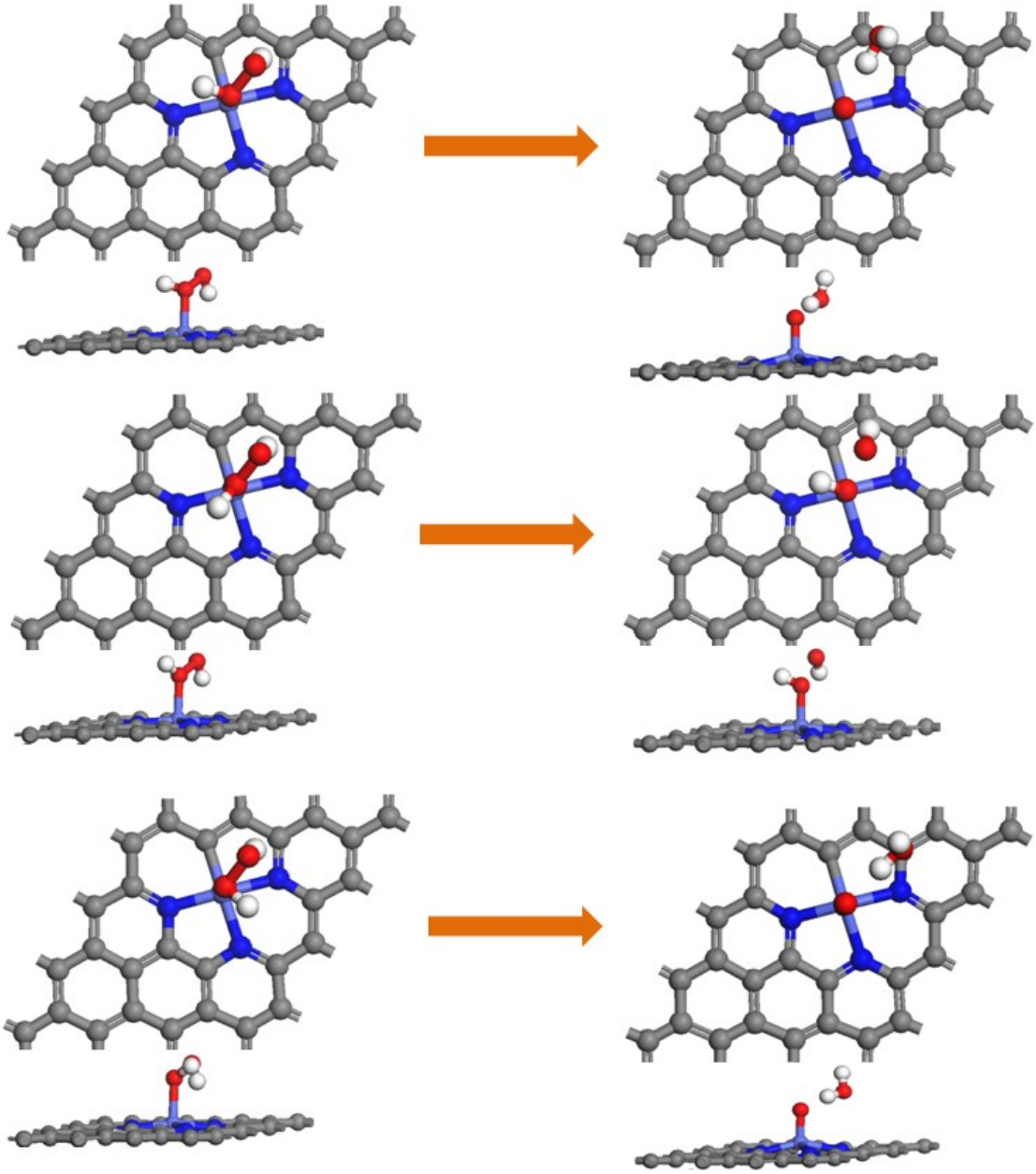


Fig. S2. Atomic structures of the designed initial state (left panel) and optimized final state (right panel) for HOOH species on CoN_3 embedded graphene.

2. Quantum Chemical Molecular Dynamics Simulations

To further confirm that whether the HOOH species could stably exist on the surface of CoN_3-Gra catalyst, we performed the Quantum Chemical Molecular Dynamics (QM/MD) simulations on the decomposition of non-optimized HOOH species. The QM/MD was implemented based on the self-consistent charge density functional tight-binding (SCC-DFTB) method [1]. This method consists of the integration of classical equations of motion, in conjunction with a quantum chemical potential. The equations of motion were integrated by employing the Velociy−Verlet algorithm [2] with a time step of 0.5 fs for the time propagation. The decomposition reaction temperature (T_n) was held constant at 300 K in the NVT ensemble via a Nosé−Hoover chain thermostat [3].

The standard trans3d-0-1 [4] and mio-0-1 [1] parameter sets were employed in the simulation process. The orbital occupation in Fermi−Dirac distribution was employed with an electronic temperature (T_e) [5] of 2000 K.

We chose six different initial configurations. In a, b and c configurations, the OOH configurations are the same but the orientation of H atoms are left-facing, down-facing and right-facing, respectively. This also applys to d, e and f configurations. During the simulations, we performed three decomposed trails for each configuration at different initial velocities. (For instance, a-1, a-2 and a-3 represent three decomposed trails for a configuration). As illustrated in Fig. S3, the O-O bond of non-optimized HOOH configuration cleavages immediately, forming either OH+OH or O+H_2O species. As a result, the HOOH species could not exist on the surface of CoN_3-Gra catalyst. As a consequence, the ORR on CoN_3-Gra catalyst is a direct four-electron process.

[1] Elstner M, Porezag D, Jungnickel G, Elsner J, Haugk M, Frauenheim T, et al. Self-consistent-charge density-functional tight-binding method for simulations of complex materials properties. Phys. Rev. B 1998;58:7260-8.

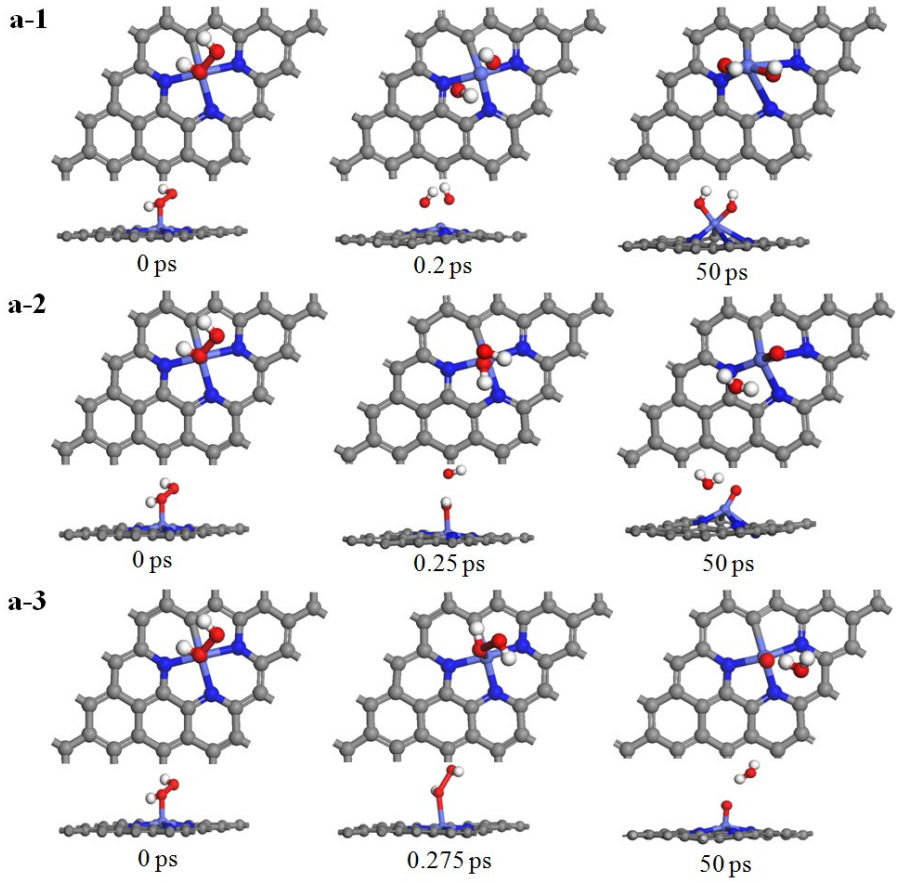
[2] Swope WC, Andersen HC, Berens PH, Wilson KR. A computer simulation

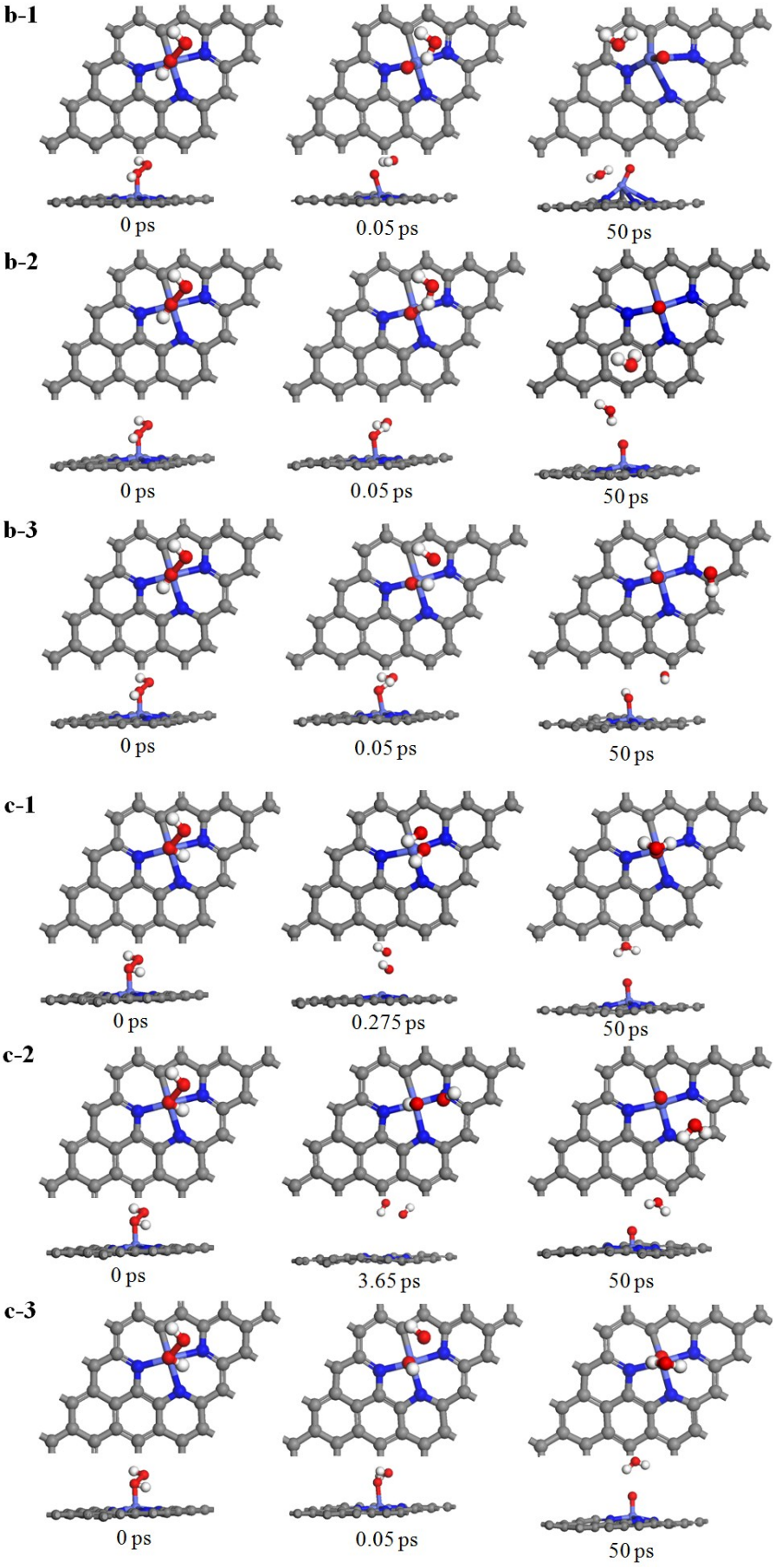
method for the calculation of equilibrium constants for the formation of physical clusters of molecules: Application to small water clusters. J. Chem. Phys. 1982;76:64-49.

[3] Martyna GJ, Klein ML, Tuckerman M. Nosé–Hoover chains: The canonical ensemble via continuous dynamics. J. Chem. Phys. 1992;97:262-43.

[4] Zheng GS, Witek HA, Bobadova-Parvanova P, Irle S, Musaev DG, Prabhakar R, et al. Parameter calibration of transition-metal elements for the spin-polarized self-consistent-charge density-functional tight-binding (DFTB) method: Sc, Ti, Fe, Co, and Ni. J. Chem. Theory. Comput. 2007;3:119-67.

[5] Weinert M, Davenport JW. Fractional occupations and density-functional energies and forces. Phys. Rev. B 1992;45:1409-12.

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0.05 ps
50 ps
b-2
0 ps
0.05 ps
50 ps
b-3
0 ps
0.05 ps
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c-1
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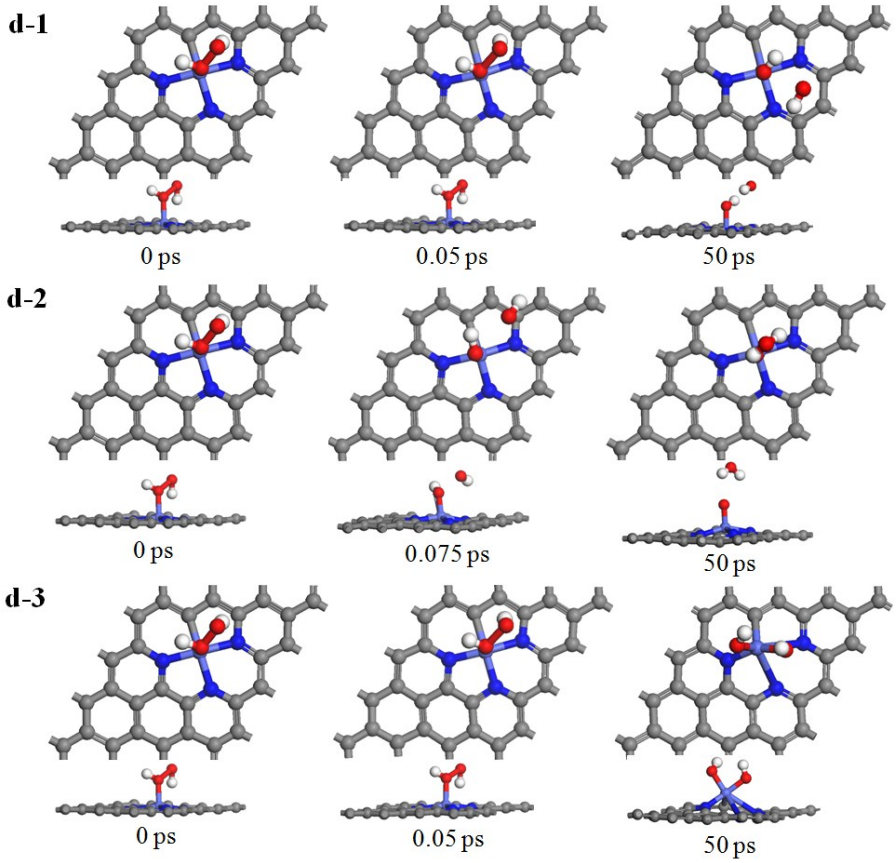
c-2
0 ps
3.65 ps
50 ps
c-3
0 ps
0.05 ps
50 ps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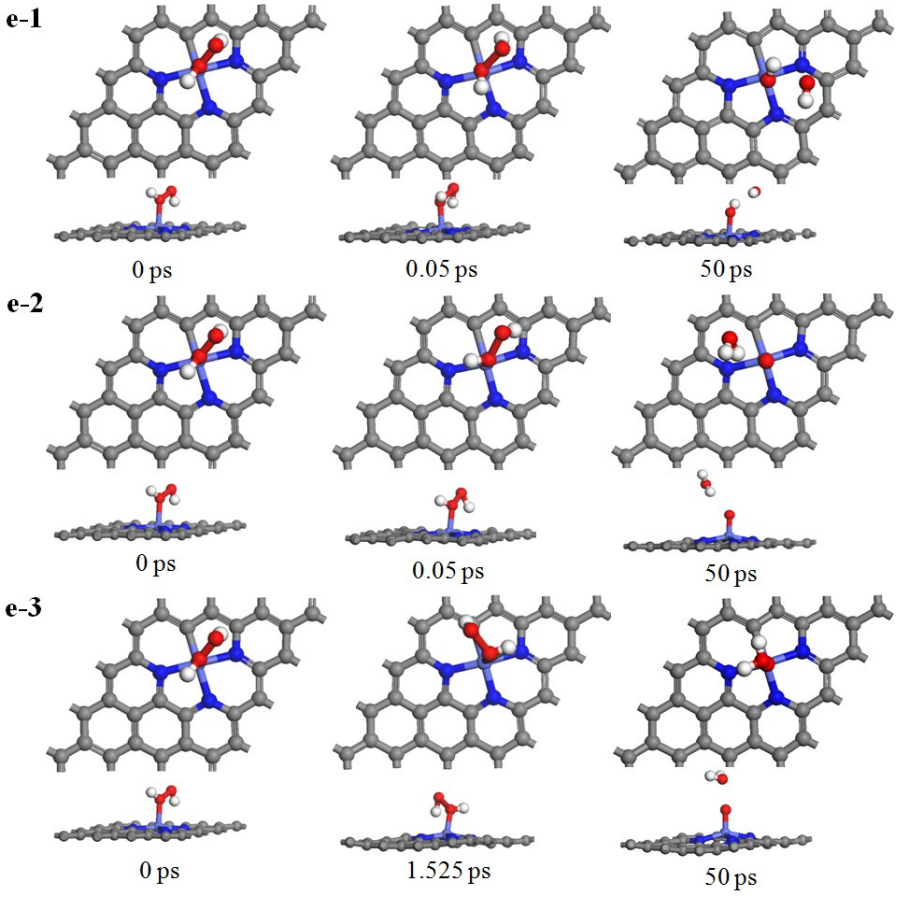
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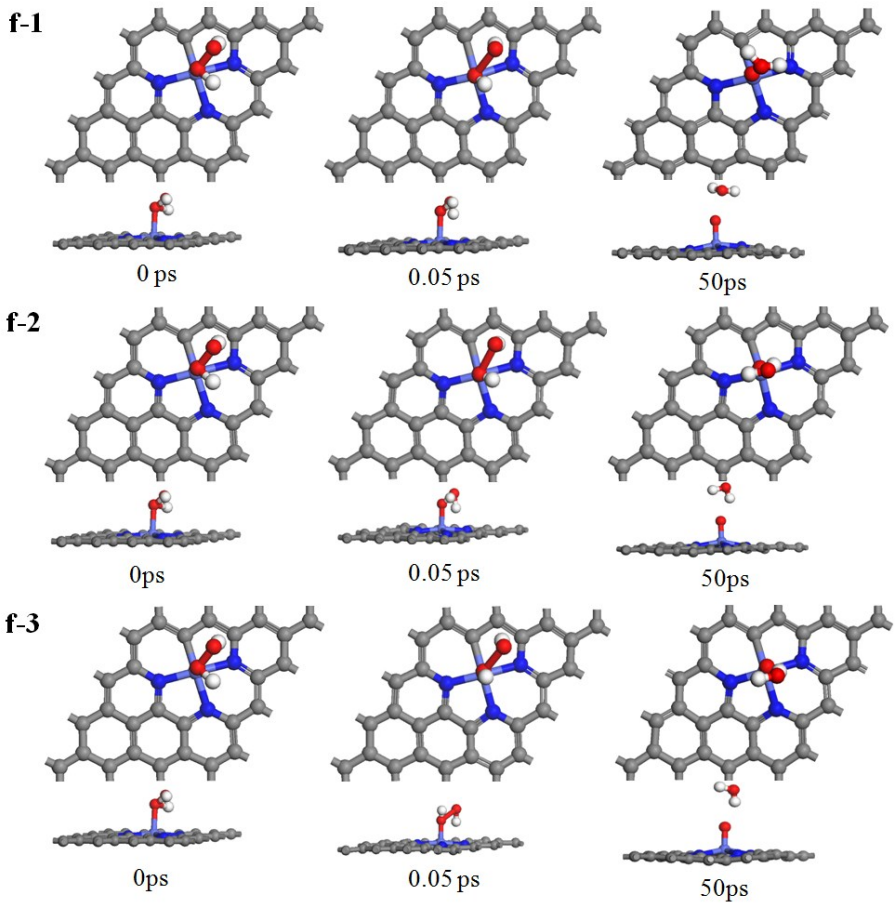

Fig. S3. Molecular dynamic simulations of HOOH species adsorbed on CoN_3 embedded graphene at 300 K.

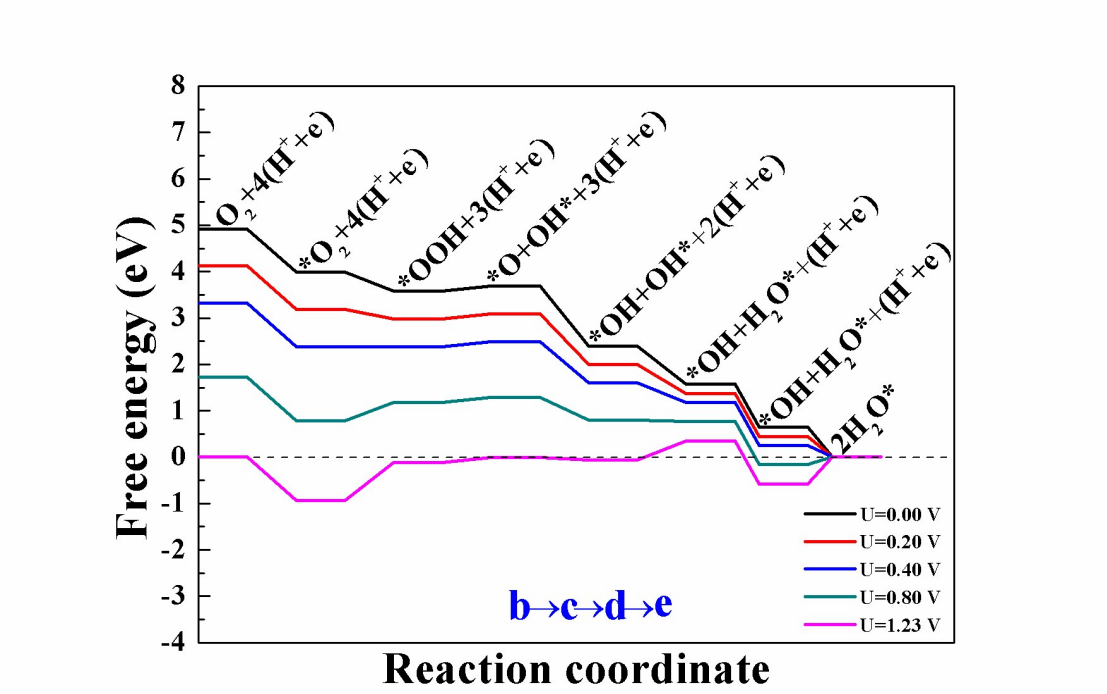

Fig. S4. Free energy diagrams for the reaction pathway b→c→d→e on CoN_3 embedded graphene at different electrode potentials.

4. Microkinetic Modeling [1] **of ORR mechanism on CoN_3 embedded graphene in acid environment**

On the basis of the calculated optimum reaction mechanism, i.e., b→f→e in Fig. 3, we deduced the ORR Tafel kinetics by using microkinetics.

We obtain the following reaction equations with rate constant k_x and k_{-x} for the corresponding reverse reaction step:

$O_2 + H^+ + e^- \xrightarrow{k_1} OOH$

$OOH \xrightarrow{k_{-1}} O_2 + H^+ + e^-$

$OOH + H^+ + e^- \xrightarrow{k_2} O + H_2O$

$O + H_2O \xrightarrow{k_{-2}} OOH + H^+ + e^-$

$O + H^+ + e^- \xrightarrow{k_3} OH$

$OH \xrightarrow{k_{-3}} O + H^+ + e^-$

$OH + H^+ + e^- \xrightarrow{k_4} H_2O$

$H_2O \xrightarrow{k_{-4}} OH + H^+ + e^-$

The reaction rate r for product formation is obtained by the equation:

$$r_1 = \frac{da(O_2)}{dt} = k_1 \cdot a(H^+) \cdot a(e^-) \cdot \theta_{O2} - k_1^{-1} \cdot \theta_{OOH}$$

$$r_2 = \frac{da(OOH)}{dt} = k_2 \cdot a(H^+) \cdot a(e^-) \cdot \theta_{OOH} - k_2^{-1} \cdot \theta_O \cdot a(H_2O)$$

$$r_3 = \frac{da(O)}{dt} = k_3 \cdot a(H^+) \cdot a(e^-) \cdot \theta_O - k_3^{-1} \cdot \theta_{OH}$$

$$r_4 = \frac{da(OH)}{dt} = k_4 \cdot a(H^+) \cdot a(e^-) \cdot \theta_{OH} - k_4^{-1} \cdot a(H_2O)$$

The activities of hydrion, electrons and H_2O are assumed to be constant, i.e., $a(H^+) = a(e^-) = a(H_2O) = 1$. The coverage of surface species (θ_{O2}, θ_{OOH}, θ_O and θ_{OH}) are obtained from steady state approximation [2]. For CoN_3-Gra, the coverageθ_{O2}, θ_{OOH}, θ_O and θ_{OH} of the precursors can be obtained as solutions of the following differential equation:

$$\frac{d\theta_{OOH}}{dt} = k_1 \cdot a(H^+) \cdot a(e^-) \cdot \theta_{O_2} - k_1^{-1} \cdot \theta_{OOH} - k_2 \cdot a(H^+) \cdot a(e^-) \cdot \theta_{OOH} + k_2^{-1} \cdot a(H_2O) \cdot \theta_O = 0 \quad (1)$$

$$\frac{d\theta_O}{dt} = k_2 \cdot a(H^+) \cdot a(e^-) \cdot \theta_{OOH} - k_2^{-1} \cdot a(H_2O) \cdot \theta_O - k_3 \cdot a(H^+) \cdot a(e^-) \cdot \theta_O + k_3^{-1}\theta_{OH} = 0 \quad (2)$$

$$\frac{d\theta_{OH}}{dt} = k_3 \cdot a(H^+) \cdot a(e^-) \cdot \theta_O - k_3^{-1} \cdot \theta_{OH} - k_4 \cdot a(H^+) \cdot a(e^-) \cdot \theta_{OH} + k_4^{-1} \cdot a(H_2O) = 0 \quad (3)$$

Taking into account the relation:

$$\theta_{O_2} + \theta_{OOH} + \theta_O + \theta_{OH} = 1 \quad (4)$$

The rate constant k_1 and k_1^{-1} were calculated employing transition state theory summarized in eqns. (5) to (6):

$$k_1 = \frac{k_B \cdot T}{h} \cdot e^{-\frac{\Delta G_1^a}{k_B \cdot T}} \cdot e^{\frac{a_1 \cdot F \cdot \eta}{R \cdot T}} \quad (5)$$

$$k_1^{-1} = \frac{k_B \cdot T}{h} \cdot e^{-\frac{\Delta G_{-1}^a}{k_B \cdot T}} \cdot e^{-\frac{(1-a_1) \cdot F \cdot \eta}{R \cdot T}} \quad (6)$$

where ΔG_1^a and ΔG_{-1}^a represent the calculated free energy barriers of elementary reactions in the ORR process. a_1 is the assuming symmetry factor which is set to be 1/2. k_B, h, F and R represent Boltzmann constant, Planck constant, Faraday constant and the universal gas constant, respectively. The temperature (T) is fixed to be 298.15 K. The same situation applies to k_2, k_2^{-1}, k_3, k_3^{-1}, k_4 and k_4^{-1}.

By Faraday's law, the reaction rate r is transformed into the current density j:

$$j = e \cdot z \cdot r \cdot N_{cat}$$

where e denotes the elementary charge, z is the number of transferred electrons, which equals 1 for the elementary reaction of ORR and N_{cat} is the number of active places per cm^2 area on the catalyst's surface.

The j_{tot} can be calculated according to:

$$j_{tot} = j_{O_2} \cdot \theta_O + j_{OOH} \cdot \theta_{OOH} + j_O \cdot \theta_O + j_{OH} \cdot \theta_{OH} \quad (7)$$

The overpotential η=1.23 eV-U (U denotes the external potential) as a function of the calculated decade logarithm of the total current density log (j_{tot}) establishes a so-called Tafel plot [η vs. log (j_{tot}) relation], which is depicted in Fig. 6 of the manuscript.

[1] Exner KS, Anton J, Jacob T, Over H. Full Kinetics from First Principles of the Chlorine Evolution Reaction over a RuO_2(110) Model Electrode. Angew. Chem. Int. Ed. 2016;55(26):7501-04.

[2] Bukoski A, Abbott HL, Harrison I. Microcanonical unimolecular rate theory at surfaces. III. Thermal dissociative chemisorption of methane on Pt(111) and detailed balance. J. Chem. Phys. 2005;123:1-18.