

Supporting Information

for

Revision of the oxygen reduction reaction on N-doped graphenes by grand-canonical DFT

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Section S1. Gibbs free energy calculation.

To calculate the Gibbs free energy, we used the following form of the equation where zero-point energy (ZPE) contribution is decoupled from the vibrational one:

$$G = E_e + ZPE + k_B T \left(-\ln(Z) + V \left(\frac{\partial \ln(Z)}{\partial V} \right)_T \right)$$

where E_e is the electronic energy obtained from DFT calculations, ZPE is the zero-point energy, and the last term is the contributions of the vibrational and translational/rotational (in the case of molecules in gas/liquid phase) motion of atoms to the Gibbs free energy derived from the partition function Z^1 .

The total partition function of an individual molecule or graphene surface with chemisorbed intermediate Z can be written as

$$Z = \begin{cases} Z_{vib} & \text{for graphene + adsorbed/chemisorbed molecule} \\ Z_{vib} \cdot Z_{trans} \cdot Z_{rot} & \text{for an individual molecule in a gas/liquid phase} \end{cases}$$

where Z_{vib} , Z_{trans} , Z_{rot} are the vibrational, translational, and rotational partition functions, respectively.

Vibrational partition function for graphene with adsorbed/chemisorbed molecule and for an individual molecule (excluding zero-point vibrations):

$$Z_{vib} = \prod_{i=1}^{N_{modes}} \frac{1}{1 - \exp\left(-\frac{\hbar\omega_i}{k_B T}\right)}$$

The eigenfrequencies were calculated using the finite difference method. The amplitude of perturbations for calculating the force matrix was equal to 0.02 Bohr. The vibrational spectrum was calculated at the Γ point only.

According to the ideal gas and rigid-body approximations² translational and rotational partition function for an individual molecule:

$$Z_{trans} = V \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2} = \frac{k_B T}{P} \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}$$

$$Z_{rot} = \begin{cases} \frac{2Ik_B T}{\sigma \hbar^2} & , \text{if linear molecule} \\ \frac{(2k_B T)^{3/2} (\pi I_1 I_2 I_3)^{1/2}}{\sigma \hbar^3} & , \text{if non-linear molecule} \end{cases}$$

where I_1, I_2, I_3, I are the (principal) moments of inertia, σ is a symmetry number ($\sigma = 1$ for OOH; $\sigma = 2$ for H₂, O₂, H₂O, and H₂O₂).

To access the free volume V for the solvated molecules we apply the technique, suggested by De-Cai Fang³:

$$V = (\sqrt[3]{V_{cav}} - \sqrt[3]{V_{mol}})^3$$

where the cavity volume V_{cav} and molecule volume V_{mol} can be estimated from the overlapping spheres⁴ with IDSCFR⁵ and Bader's⁶ radii, respectively. For the reference H₂ molecule the $P = 1$ atm were taken to calculate the translational entropy and enthalpic correction.

Section S2. Additional Figures.

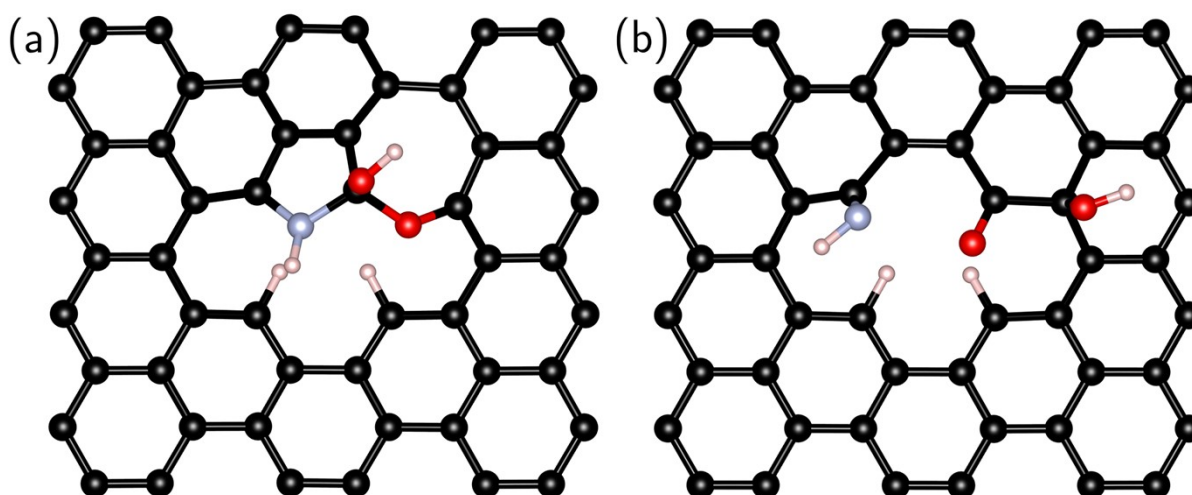


Fig. S1. The configurations of pyrrole defect reconstruction after ^{*}OOH dissociation.

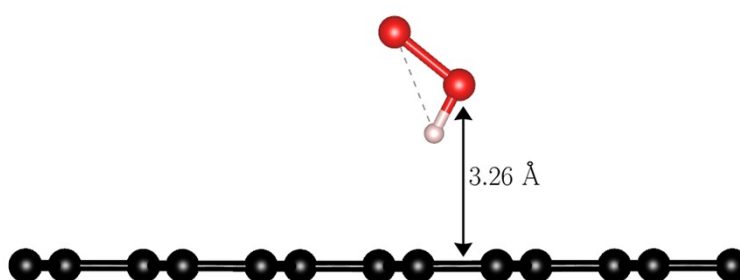


Fig. S2. The configuration of a physically adsorbed ion OOH_{phys}^- on the pristine graphene.

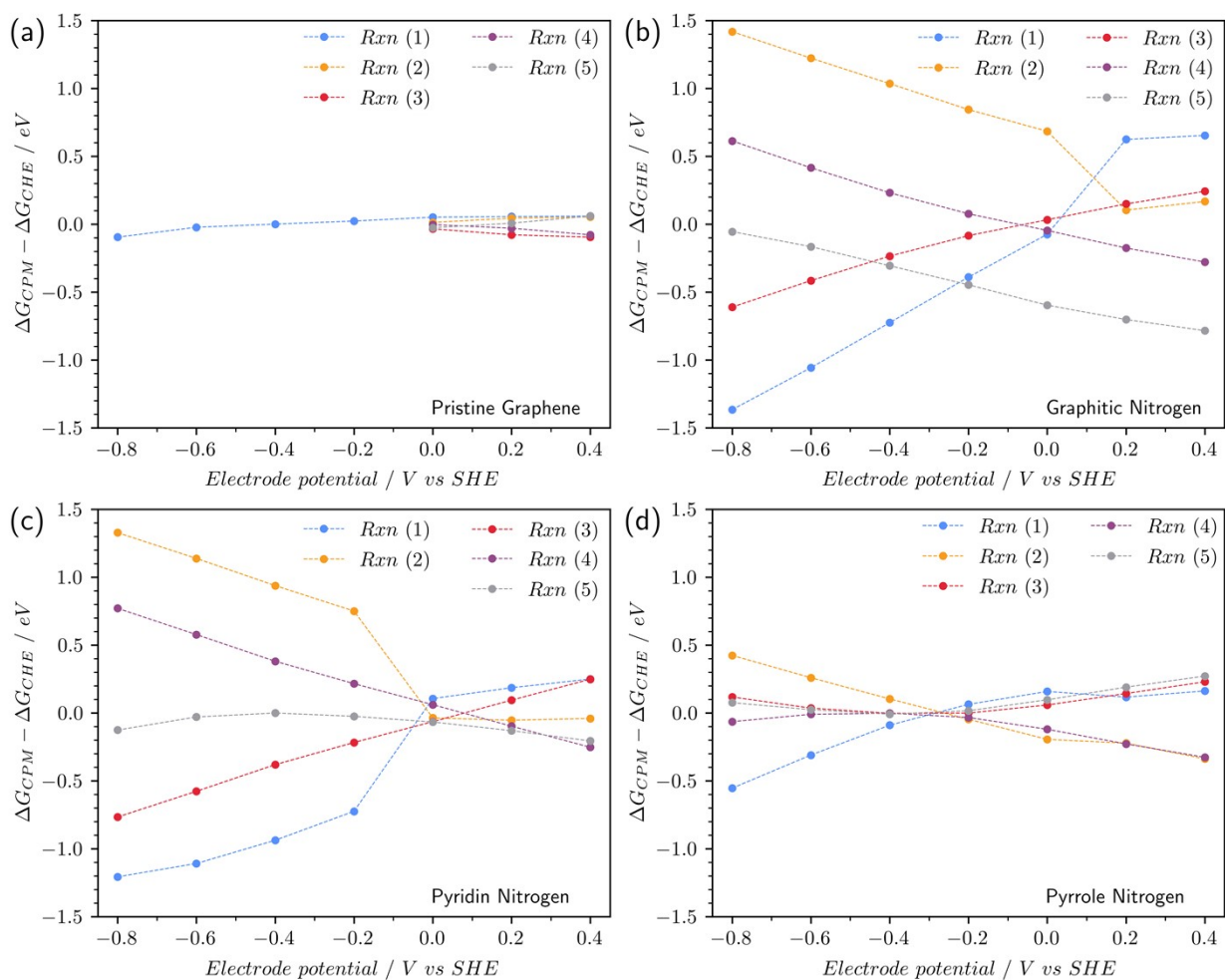


Fig. S3. The difference in reaction free energy calculated according to constant potential ΔG_{CPM} and computational hydrogen electrode (CHE) ΔG_{CHE} methods for 4e-mechanism.

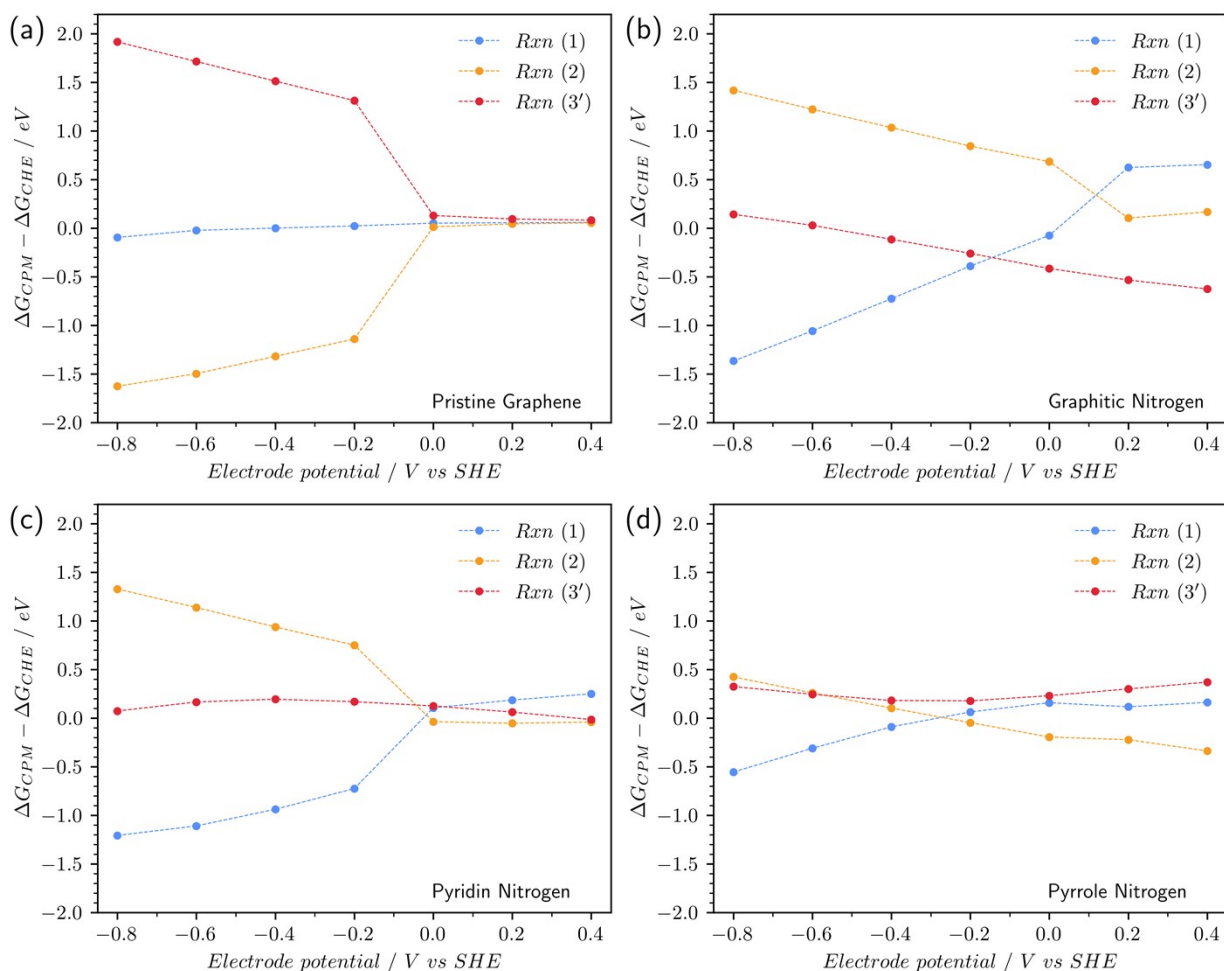


Fig. S4. The difference in reaction free energy calculated according to constant potential ΔG_{CPM} and computational hydrogen electrode (CHE) ΔG_{CHE} methods for 2e-mechanism.

References:

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