Supporting Information

Direct four-electron process on Fe-N_3 doped graphene for oxygen reduction reaction: a theoretical perspective

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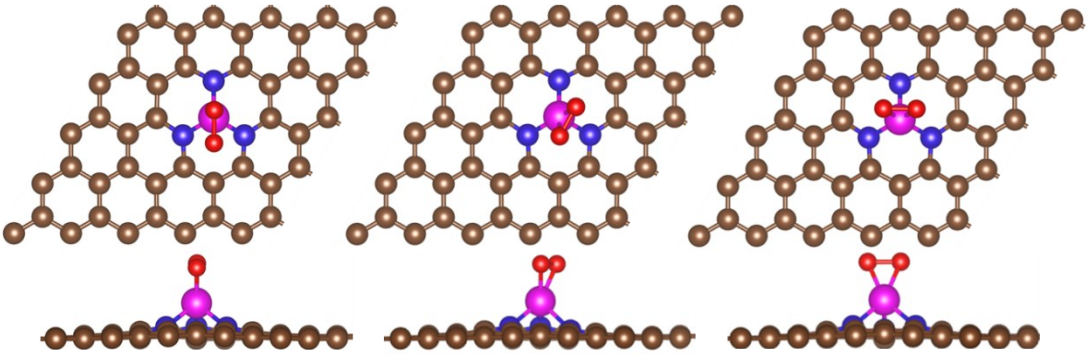
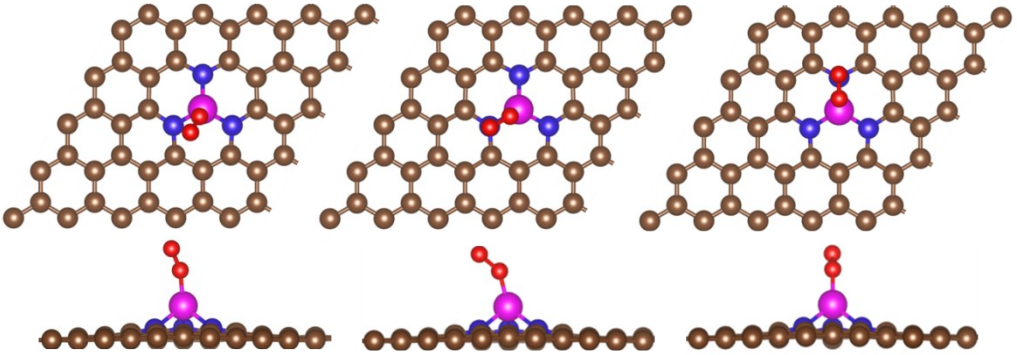
Optimized adsorption structure --- side-on O_2



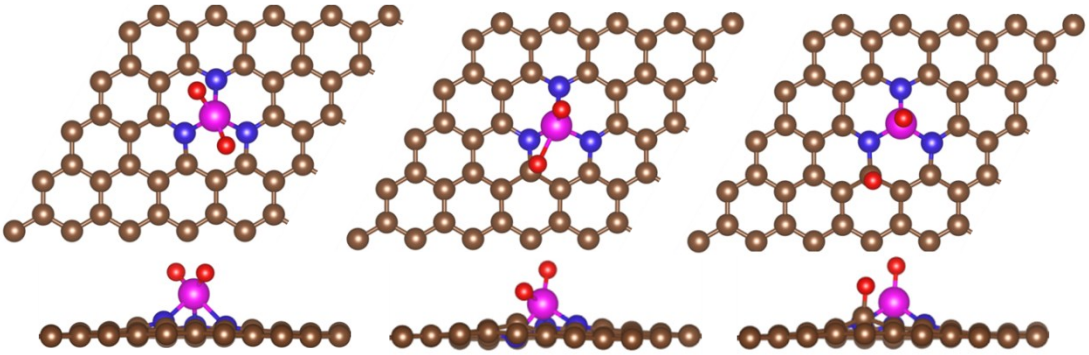
ΔE_{ads}=-3.17 eV ΔE_{ads}=-3.15 eV ΔE_{ads}=-3.15 eV

Optimized adsorption structure --- end-on O_2

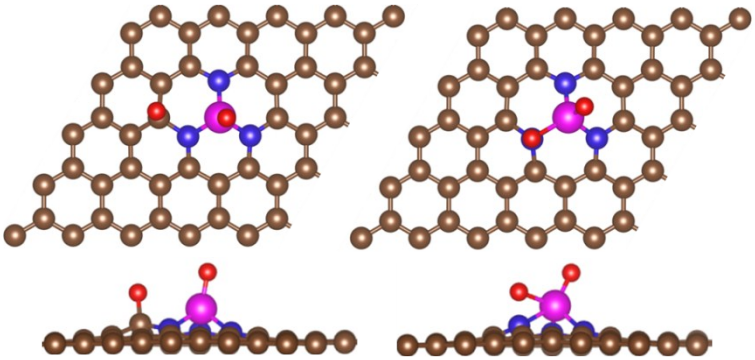


ΔE_{ads}=-2.30 eV ΔE_{ads}=-2.29 eV ΔE_{ads}=-2.29 eV

Optimized adsorption structure --- O+O

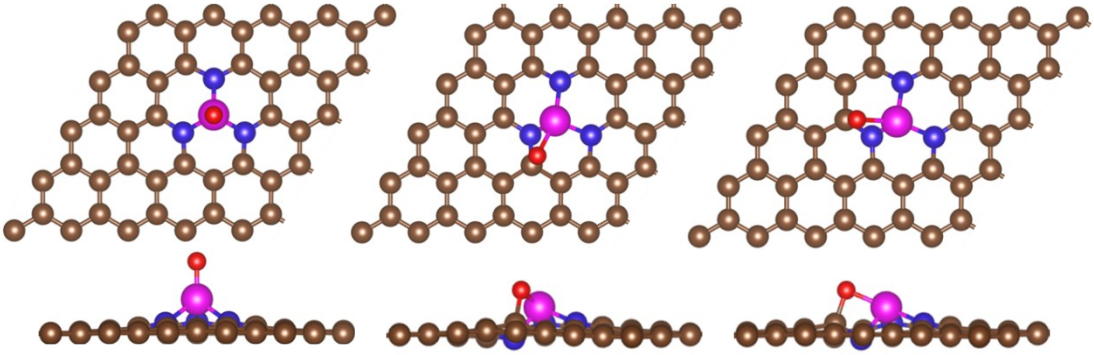


ΔE_{ads}=-10.10 eV ΔE_{ads}=-9.52 eV ΔE_{ads}=-9.12 eV



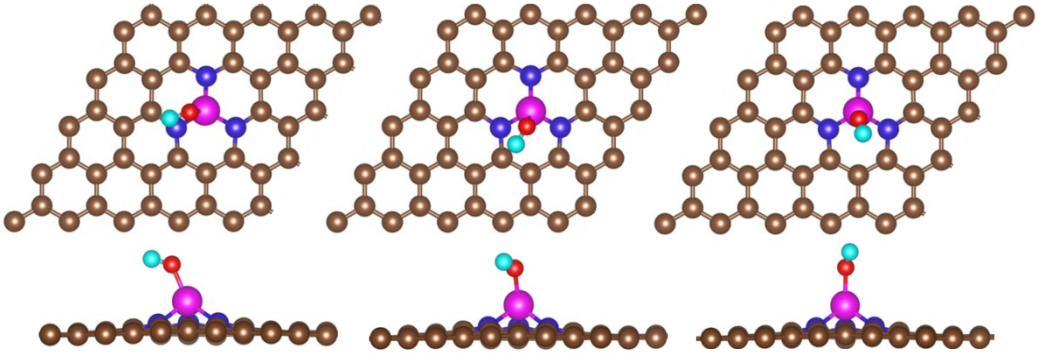
ΔE_{ads}=-9.12 eV ΔE_{ads}=-8.76 eV

Optimized adsorption structure --- O



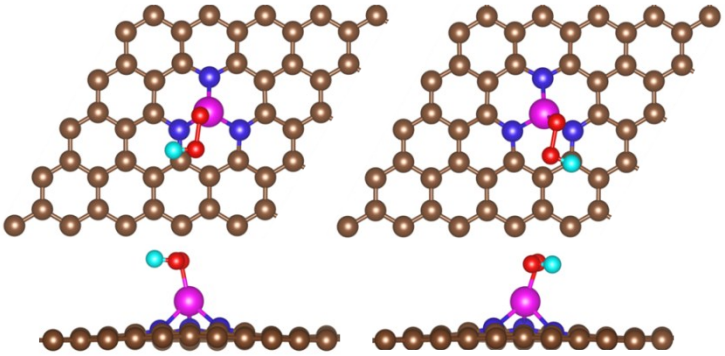
ΔE_{ads}=-6.45 eV ΔE_{ads}=-4.65 eV ΔE_{ads}=-4.65 eV

Optimized adsorption structure --- OH



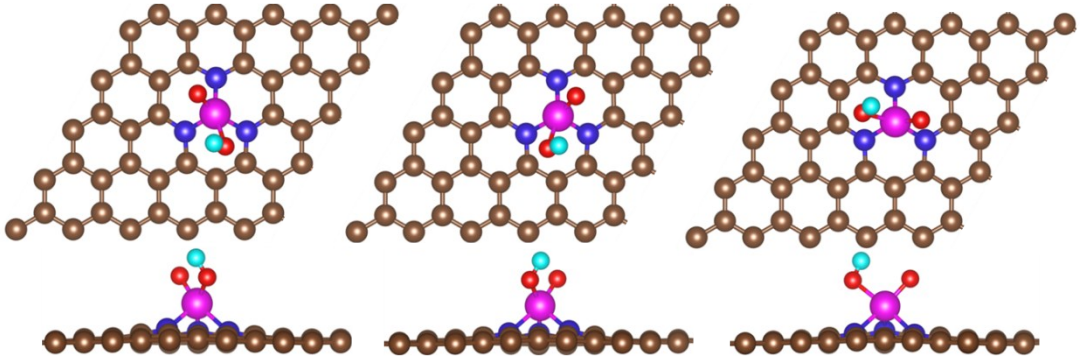
ΔE_{ads}=-4.2 eV ΔE_{ads}=-4.33 eV ΔE_{ads}=-4.30 eV

Optimized adsorption structure --- OOH



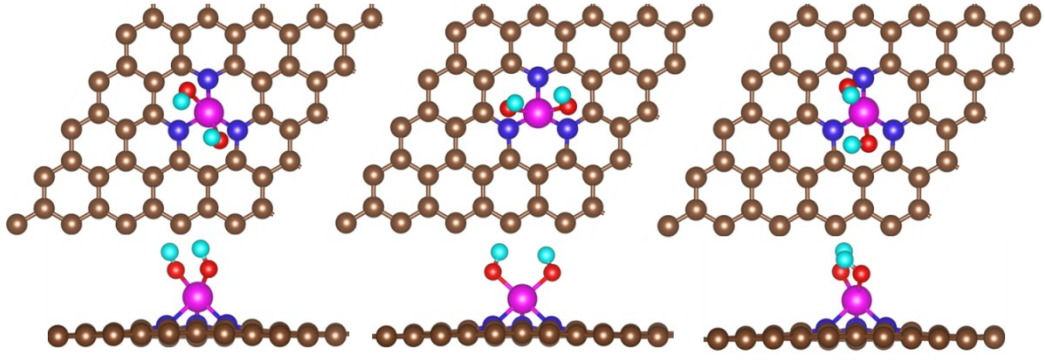
ΔE_{ads}=-3.00 eV ΔE_{ads}=-3.00 eV

Optimized adsorption structure --- O+OH

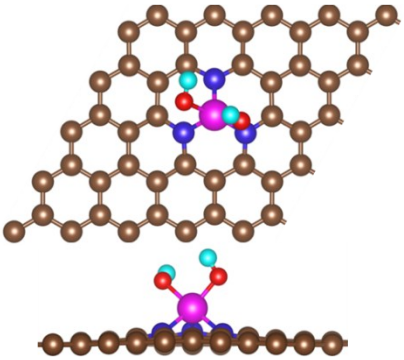


ΔE_{ads}=-8.82 eV ΔE_{ads}=-8.82eV ΔE_{ads}=-8.81 eV

Optimized adsorption structure --- OH+OH

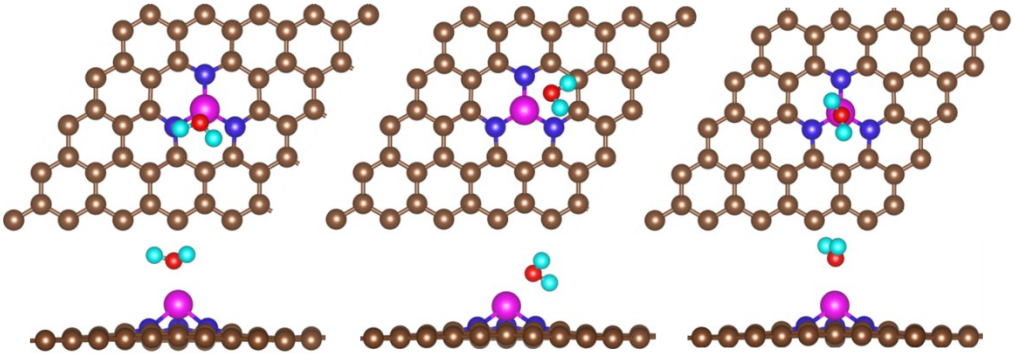


ΔE_{ads}=-8.82 eV ΔE_{ads}=-8.82eV ΔE_{ads}=-8.81 eV



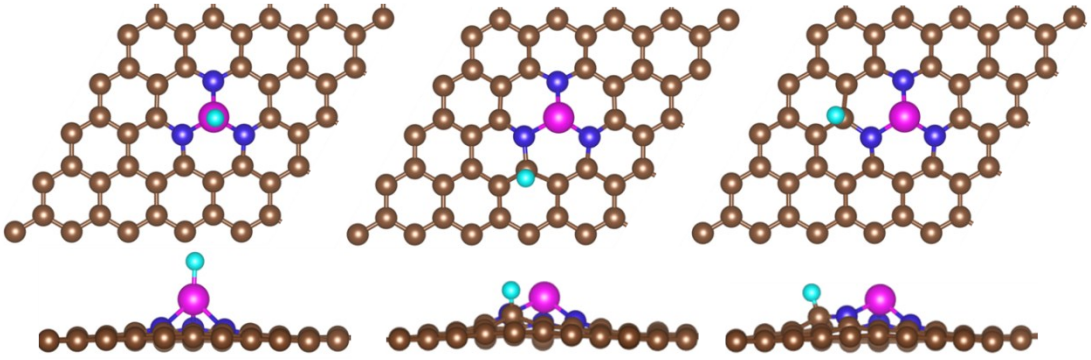
ΔE_{ads}=-7.70 eV

Optimized adsorption structure --- H_2O



ΔE_{ads}=-0.80 eV ΔE_{ads}=-0.58 eV ΔE_{ads}=-0.11 eV

Optimized adsorption structure --- H



ΔE_{ads}=-2.79 eV ΔE_{ads}=-1.50 eV ΔE_{ads}=-1.50 eV

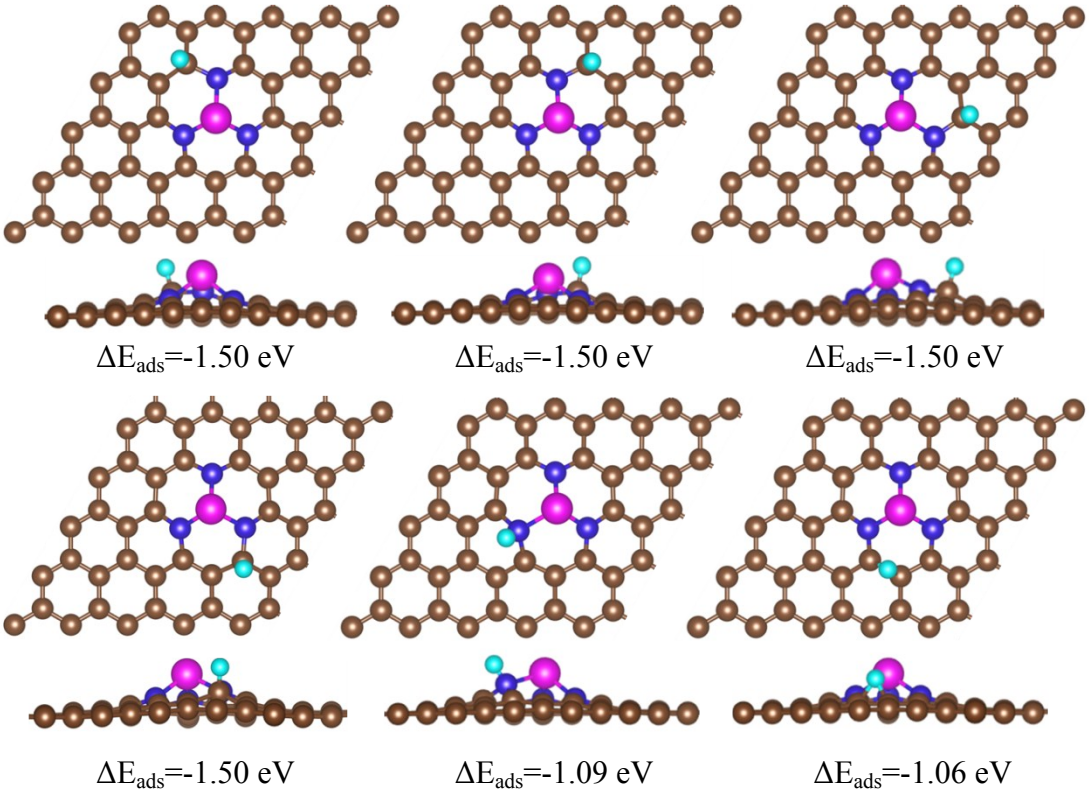


Fig. S1 Possible configurations for each adsorbed species (side-on O_2, end-on O_2, O+O, O, OH, OOH, O+OH, OH+OH, H_2O and H) involved in the ORR on Fe-N_3-Gra. ΔE_{ads} is the adsorption energy (eV). In the figure, the brown, pink, blue, red, and cyan balls represent C, Fe, N, O and H atoms, respectively.

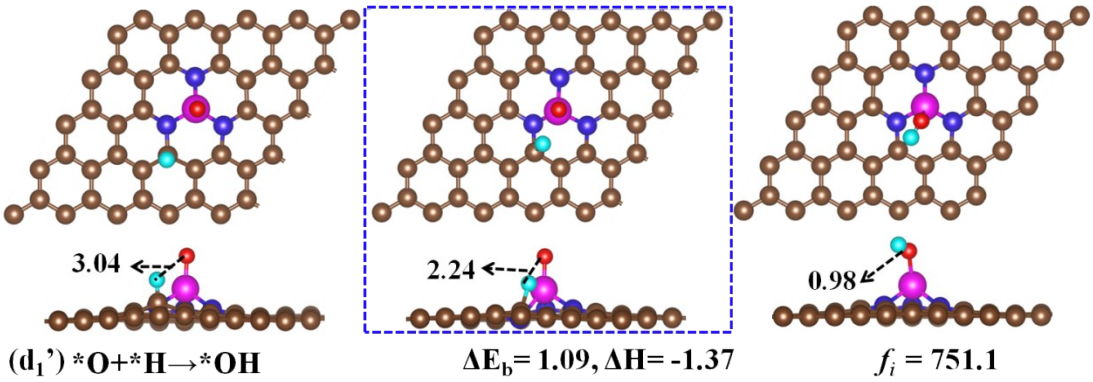


Fig. S2 The O hydrogenation into OH (d_1'). ΔE_b is the energy barrier (eV) and ΔH is the reaction energy (eV).

Quantum Chemical Molecular Dynamics Simulations

The Quantum Chemical Molecular dynamics (QM/MD) simulations of HOOH species decomposition for the ORR on the Fe-N_3-Gra catalyst were performed based on the self-consistent charge density functional tight-binding (SCC-DFTB) method [1]. The standard trans3d-0-1 [2] and mio-0-1 [1] parameter sets were used the in simulations. The occupancy of each molecular orbital was described by a Fermi-Dirac distribution function with an electronic temperature (T_e) [3, 4] of 2000 K. The Newtonian equations were integrated by using the Velociy-Verlet algorithm [5] with a time step of 0.5 fs. The decomposition reaction temperature (T_n) was held constant at 300 K in the NVT ensemble throughout the simulations via a Nosé−Hoover chain thermostat [6].

Two initial configurations are selected, that is, the HOOH species without adsorbing ($d_{Fe\text{-}O}$ = 5 Å) and with adsorbing ($d_{Fe\text{-}O}$ = 2 Å) on the Fe-N_3-Gra surface. We performed three decomposed trails for each configuration at different initial velocities during the 50 ps simulations. A time step of 0.5 fs is used for these simulations. The calculated results show that the HOOH first adsorbs on T_{Fe} site and then breaks immediately to form OH+OH or O+H_2O structures for the HOOH without adsorbing ($d_{Fe\text{-}O}$ = 5 Å) configuration, as shown in Fig. 3. The O-O bond cleavages occur at 0.075 ps, 0.15 ps, and 0.05 ps for three decomposed trails, respectively. The result suggests that the O-O bond can immediately be broken. Similarly, the phenomena

could also be observed for the HOOH species with adsorbing ($d_{Fe\text{-}O}$ = 2 Å) on Fe-N_3-Gra surface, as shown in Fig. S3. Therefore, our calculations demonstrated that ORR is a direct four-electron process for Fe-N_3-Gra.

[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] 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.

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

[4] Wentzcovitch RM, Martins JL, Allen PB. Energy versus free-energy conservation in first-principles molecular dynamics. Phys Rev B 1992;45:1142-4.

[5] 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.

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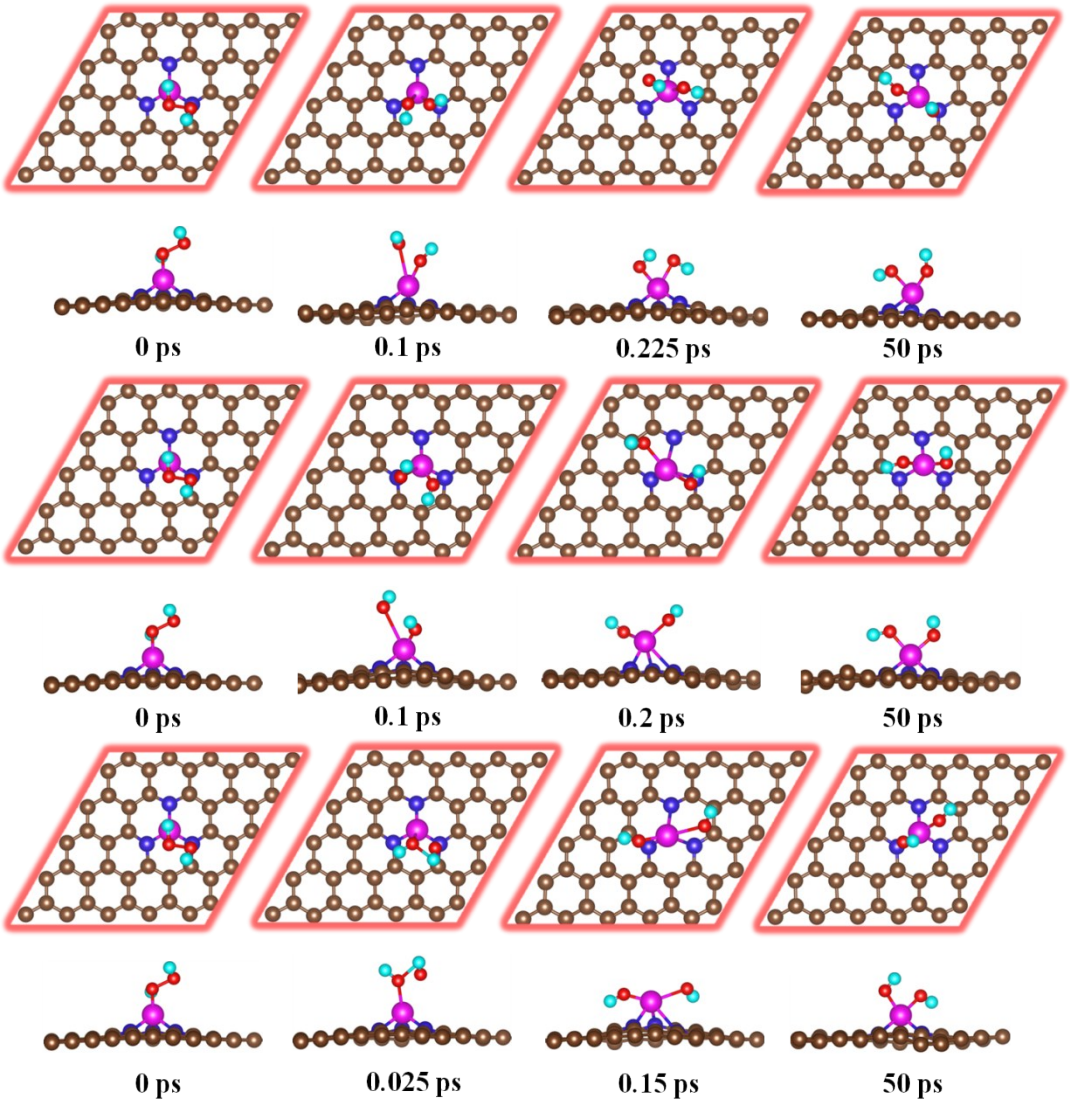

Fig. S3 Evolution of molecular dynamic simulations of the HOOH species with adsorbing ($d_{Fe\text{-}O}$ = 2 Å) on the Fe-N_3-Gra surface at 300 K.