Electronic Supplementary Information:

Microscopic effects of the bonding configuration of nitrogen-doped graphene on its reactivity toward hydrogen peroxide reduction reaction

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Table S1 Adsorption energy of oxidants and reductants in each reaction step of H_2O_2 reduction on graphene

		$G\cdots H_2O_2 + H^+ + e^- \rightarrow G{-}OH + H_2O$	$G{-}OH + H^+ + e^- \rightarrow G + H_2O$
pristine graphene	E_{ad} (oxidants) (kJ / mol)	–9.645	–18.523
	E_{ad} (reductants) (kJ / mol)	–18.523	–16.787
	ΔE (kJ / mol)	8.878	–1.736
pyridinic N-graphene	E_{ad} (oxidants) (kJ / mol)	–45.344	–61.363
	E_{ad} (reductants) (kJ / mol)	–61.363	–51.810
	ΔE (kJ / mol)	16.019	–9.553
pyrrolic N-graphene	E_{ad} (oxidants) (kJ / mol)	–44.369	–57.493
	E_{ad} (reductants) (kJ / mol)	–57.493	–51.896
	ΔE (kJ / mol)	13.124	–5.597
graphitic N-graphene	E_{ad} (oxidants) (kJ / mol)	–14.958	–24.748
	E_{ad} (reductants) (kJ / mol)	–24.748	–20.888
	ΔE (kJ / mol)	9.790	–3.860

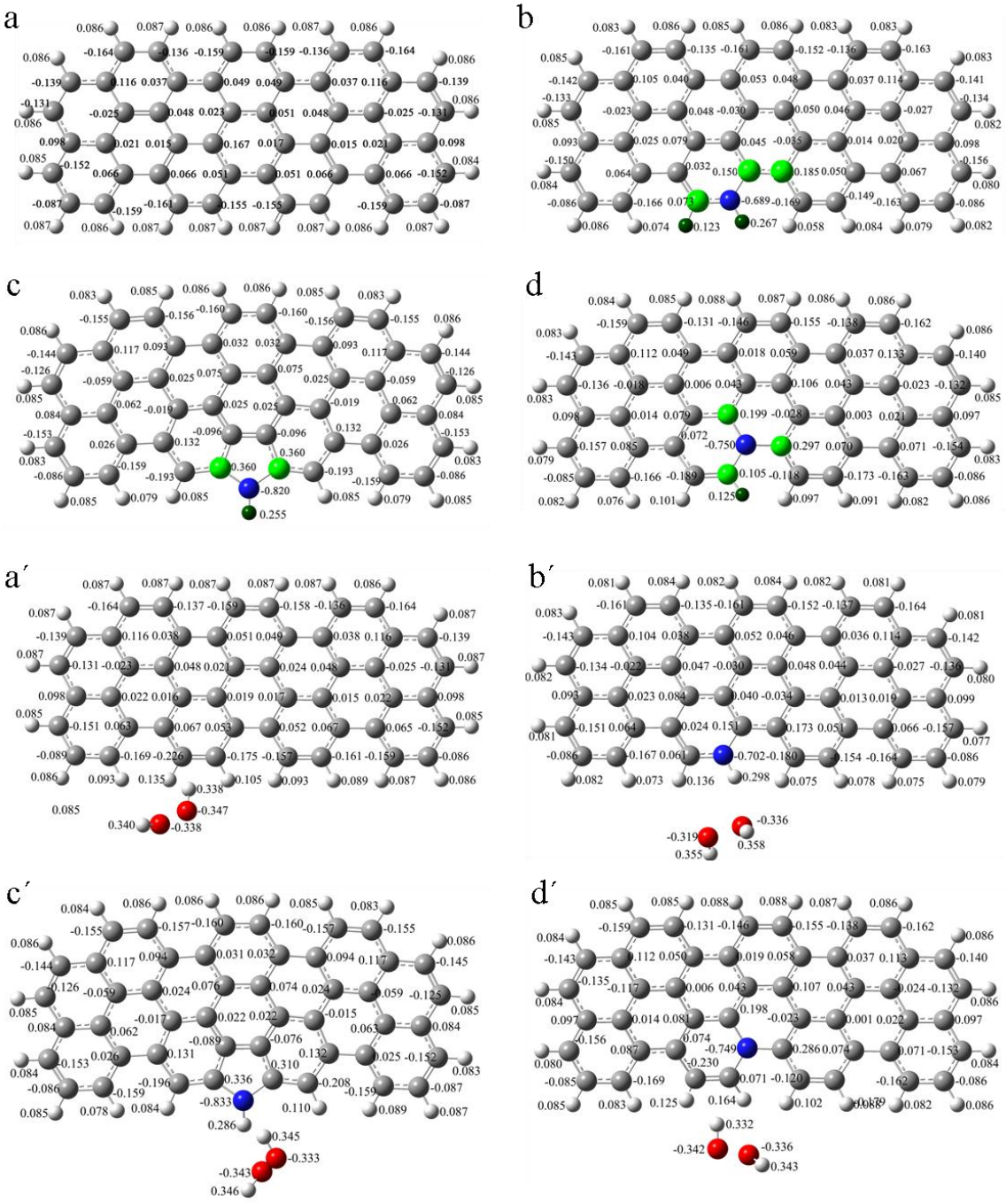


Fig. S1 Charge densities on each atom in pristine (a, a′) and N-graphene with pyridinic (b, b′), pyrrolic (c, c′), and graphitic N-doped structure (d, d′), respectively, in their optimized forms before (a–d) and after (a′–d′) H_2O_2 adsorption. Atomic color code: gray, carbon; red, oxygen; white, hydrogen; and blue, nitrogen. The green and dark green balls are those carbon and hydrogen atoms, respectively, having significant enhancement in charge density after N doping.

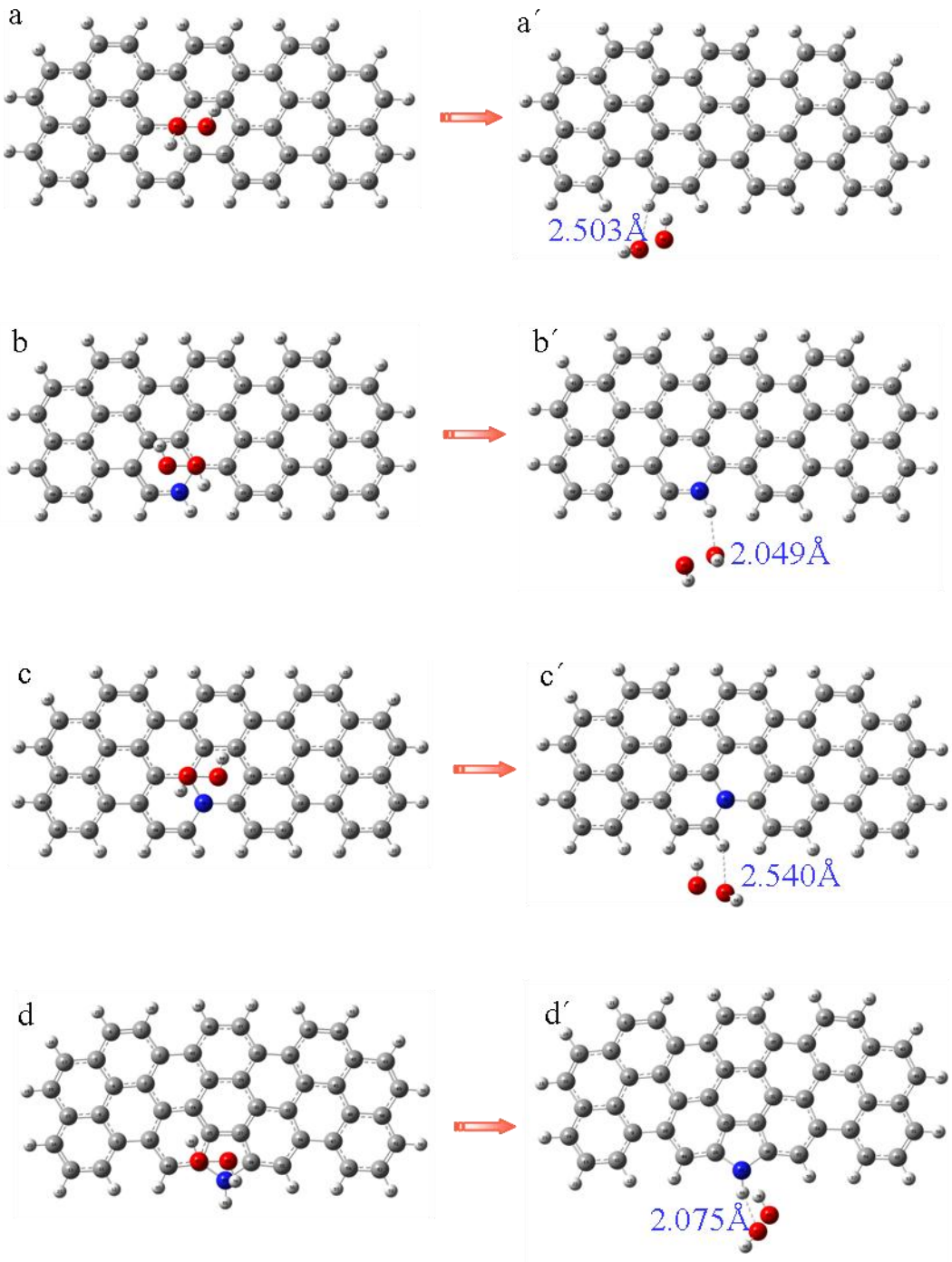


Fig. S2 Optimized structure for the adsorption of H_2O_2 molecules onto the pristine (a, a′), pyridinic (b, b′), pyrrolic (c, c′), and graphitic N-doped graphene sheet. (a–d) and (a′–d′) illustrate the initial position and final optimization structure for the adsorption of the H_2O_2 molecule, respectively. Atomic color code: gray, carbon; red, oxygen; white, hydrogen; and blue, nitrogen.

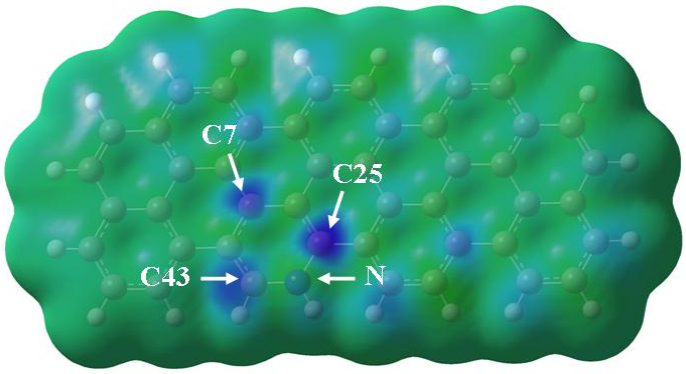


Fig. S3 The spin density distribution on the pyridinic N-doped graphene. The C7, C25, and C43 atoms have higher spin densities than other carbon atoms. The high spin density is favor to the formation of chemical bond of C–O.

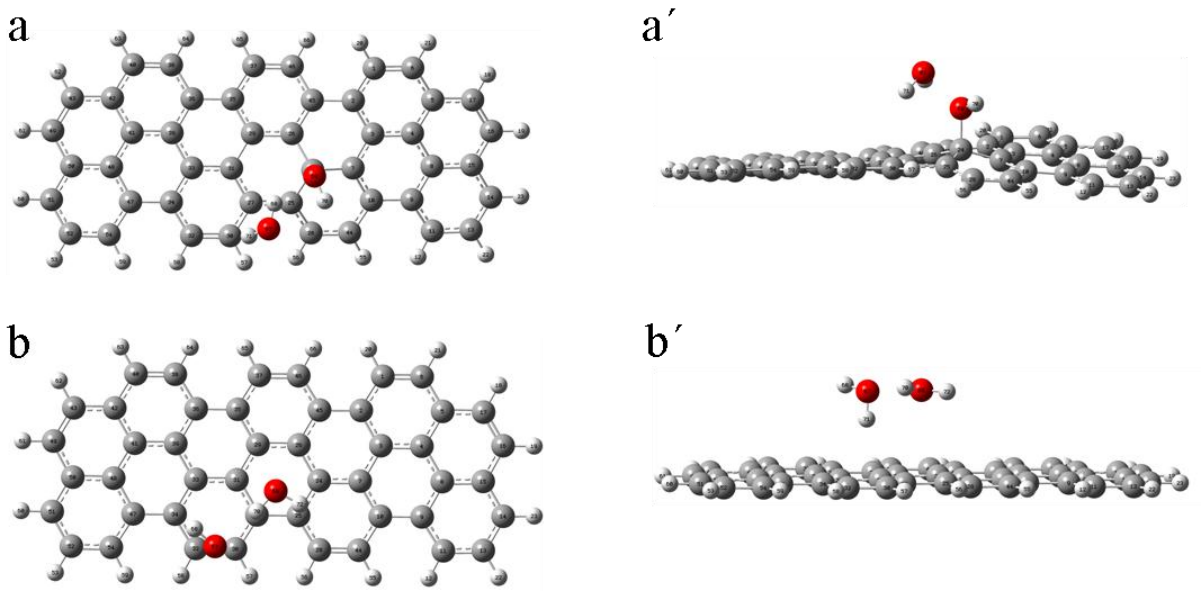


Fig. S4 Top (a, b) and side (a′, b′) views of the optimized configurations of steps 2a and 3a of H_2O_2 reduction processes at the surface of pristine graphene for reaction path I. (a, a′) Cleavage of the O−O bond in the adsorbed H_2O_2 molecule and formation of one adsorbed OH group and the first H_2O molecule; (b, b′) cleavage of the C−O bond and the formation of the second H_2O molecule. Atomic color code: gray, carbon; red, oxygen; and white, hydrogen.

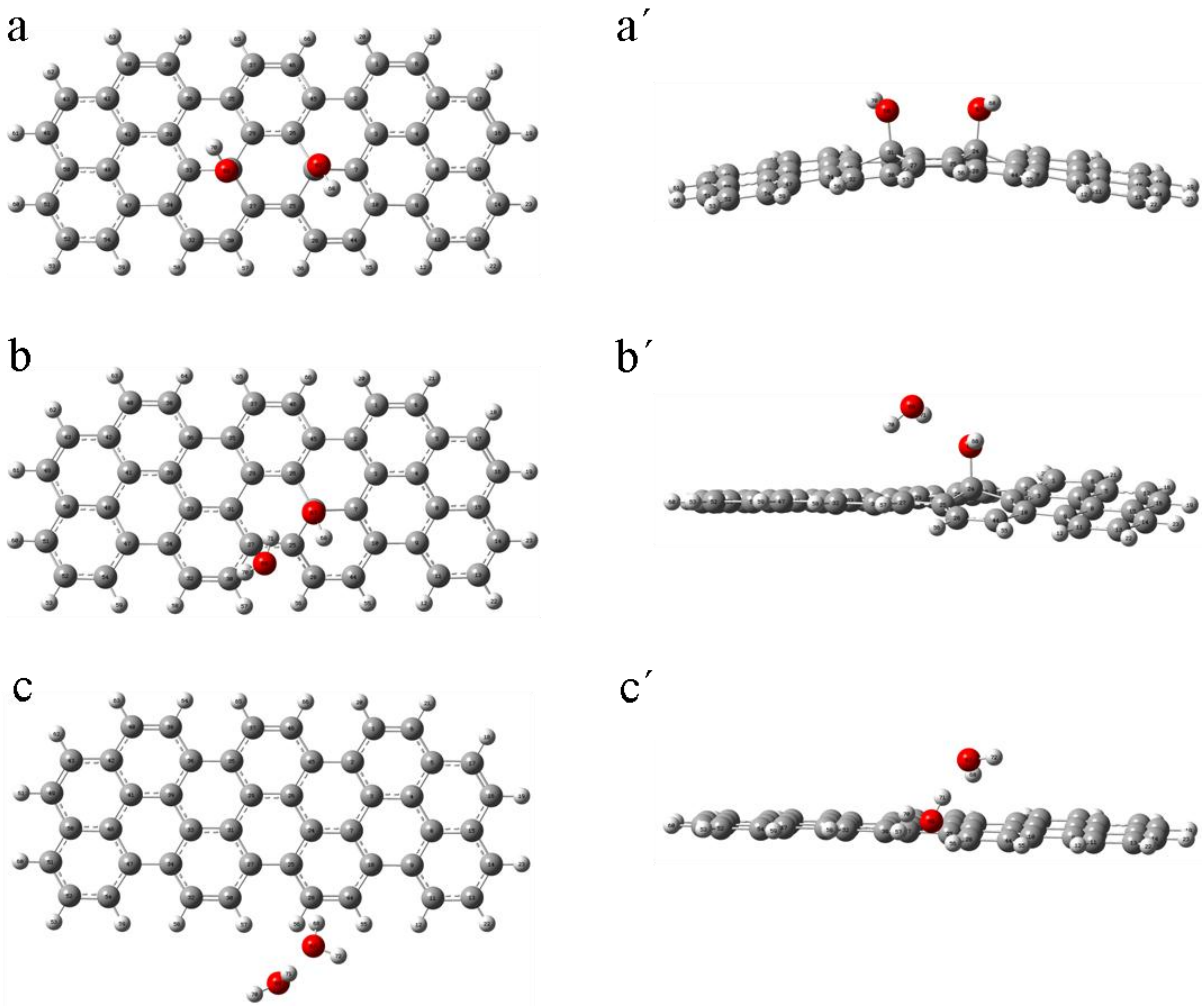


Fig. S5 Top (a, b, and c) and side (a′, b′, and c′) views of the optimized configurations of steps 2b, 3b, 4 for H_2O_2 reduction processes at the surface of pristine graphene for reaction path II. (a, a′) Cleavage of the O−O bond in the adsorbed H_2O_2 molecule and formation of two adsorbed OHs; (b, b′) formation of the first H_2O molecule; (c, c′) formation of the second H_2O molecule. Atomic color code: gray, carbon; red, oxygen; and white, hydrogen.

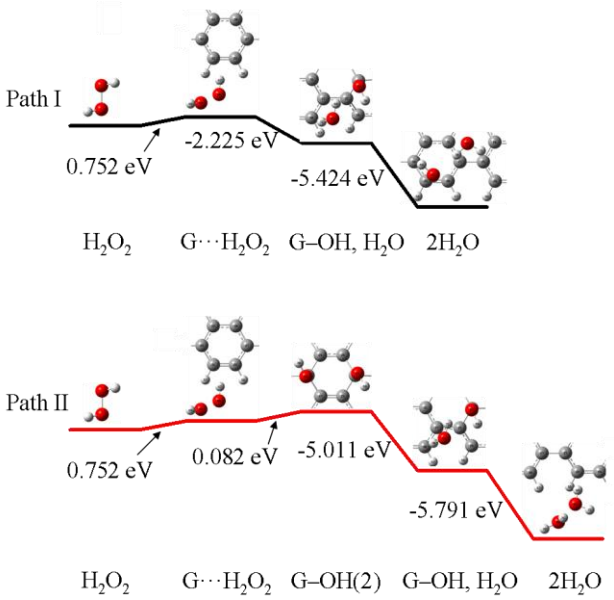


Fig. S6 Illustration of the relative energy and configurations for the reaction intermediates (showing only part of the graphene) in reaction paths I and II of the H_2O_2 reduction process on pristine graphene surface. The values are the relative energies for each step of the reaction system. For the first step, the reference energy state is the free energy of the optimized pristine graphene and isolated H_2O_2 molecule. For the other reaction steps, the reference energy states are the free energy of the product of the previous reaction and $H^+ + e^-$. Atomic color code: gray, carbon; red, oxygen; white, hydrogen; and blue, nitrogen.

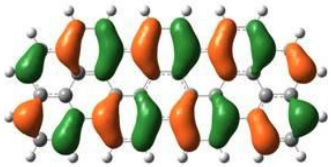
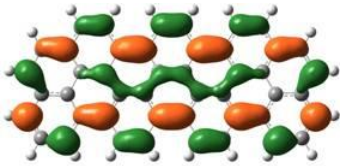
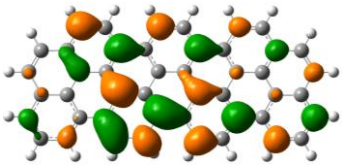
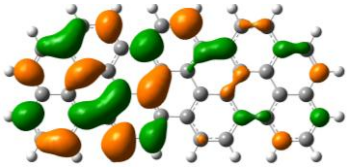
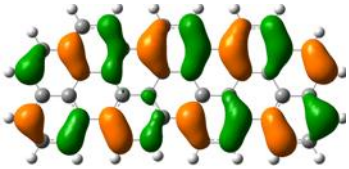
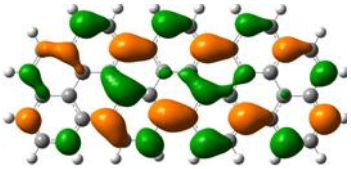
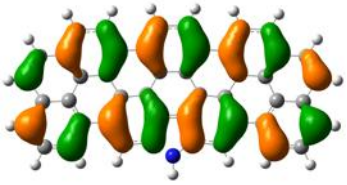
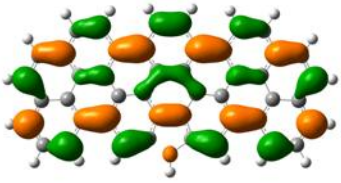
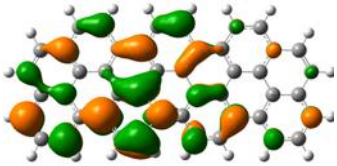
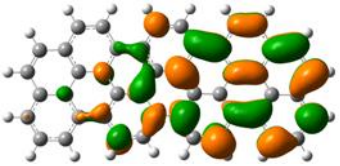
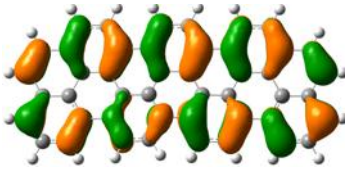
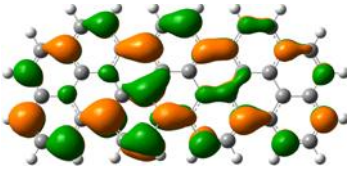
		HOMO	LUMO
pristine graphene	α, β electrons		
pyridinic N-graphene	α electron		
	β electron		
pyrrolic N-graphene	α, β electrons		
graphitic N-graphene	α electron		
	β electron		

Fig. S7 HOMO and LUMO spatial distributions of α electron and β electron for pure graphene and N-graphene with pyridinic, pyrrolic, and graphitic N-doped structure, respectively.