Supporting information

Heteroatom-Doped Carbon Nanomaterials as Potential Heterogeneous Fenton Reaction Catalysts

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Computational methods

Spin-unrestricted DFT calculations were performed based on the DMol^3 code.[1,2] The exchange-correlation effect was described by the Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional.[3] All-Electron Relativistic (AER) approach was implemented for core electrons treatment and Double Numerical Plus Polarization (DNP) was employed as the basis set.[4] The dispersion correction within the Grimme scheme was employed to describe the van der Waals (vdW) interaction.[5] The convergence tolerances of energy, maximum force, and displacement during the geometry optimization were 1.0×10^{-5} Ha, 2.0×10^{-3} Ha/Å, and 5.0×10^{-3} Å, respectively. The smearing value was set as 0.005 Ha to accelerate the energy convergence. The conductor-like screening model (COSMO) was used to describe the water solvent environment, and the dielectric constant was set as 78.54 for the H_2O solvent.[6] The activation energies for the elemental step were determined by the LST/QST method. The adsorption energy (E_{ads}) was calculated as $E_{ads} = E_{sys} - E_{cat} - E_{mol}$, where E_{sys}, E_{cat}, and E_{mol} represent the total energies of the adsorption system, the catalyst, and the adsorbate molecule, respectively. In order to eliminate interaction between neighboring periodic cells, the single-layer graphene was modeled by periodically repeated p(4×4) unit cells with a 15 Å vacuum layer. For the same purpose, the CNT was built in an orthorhombic lattice with axis lengths of 22 Å in the *a* and *b* directions, while the nanoribbons were constructed with lattice parameters of 25 Å and 15 Å along the a and c directions, respectively.

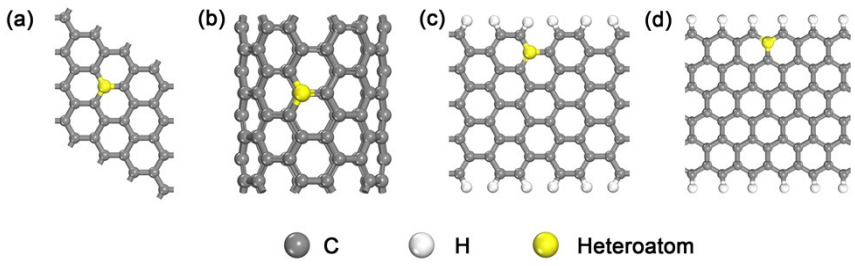

Fig. S1. The atomic structures of heteroatom doped carbon nanomaterials, including graphene (a), CNTs (b), armchair (c) and zigzag (d) carbon nanoribbon.

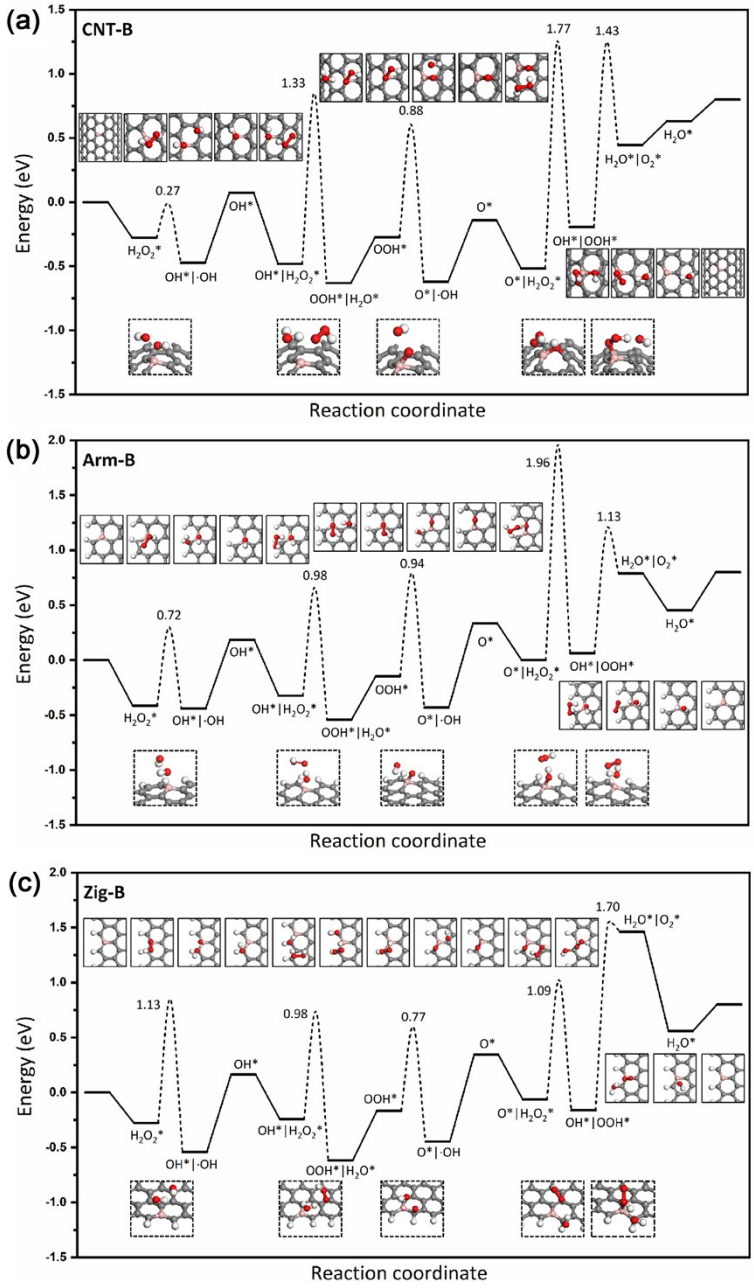

Fig. S2. The reaction energy diagrams of H_2O_2 dissociation on CNT-B (a), Arm-B (b) and Zig-B (c).

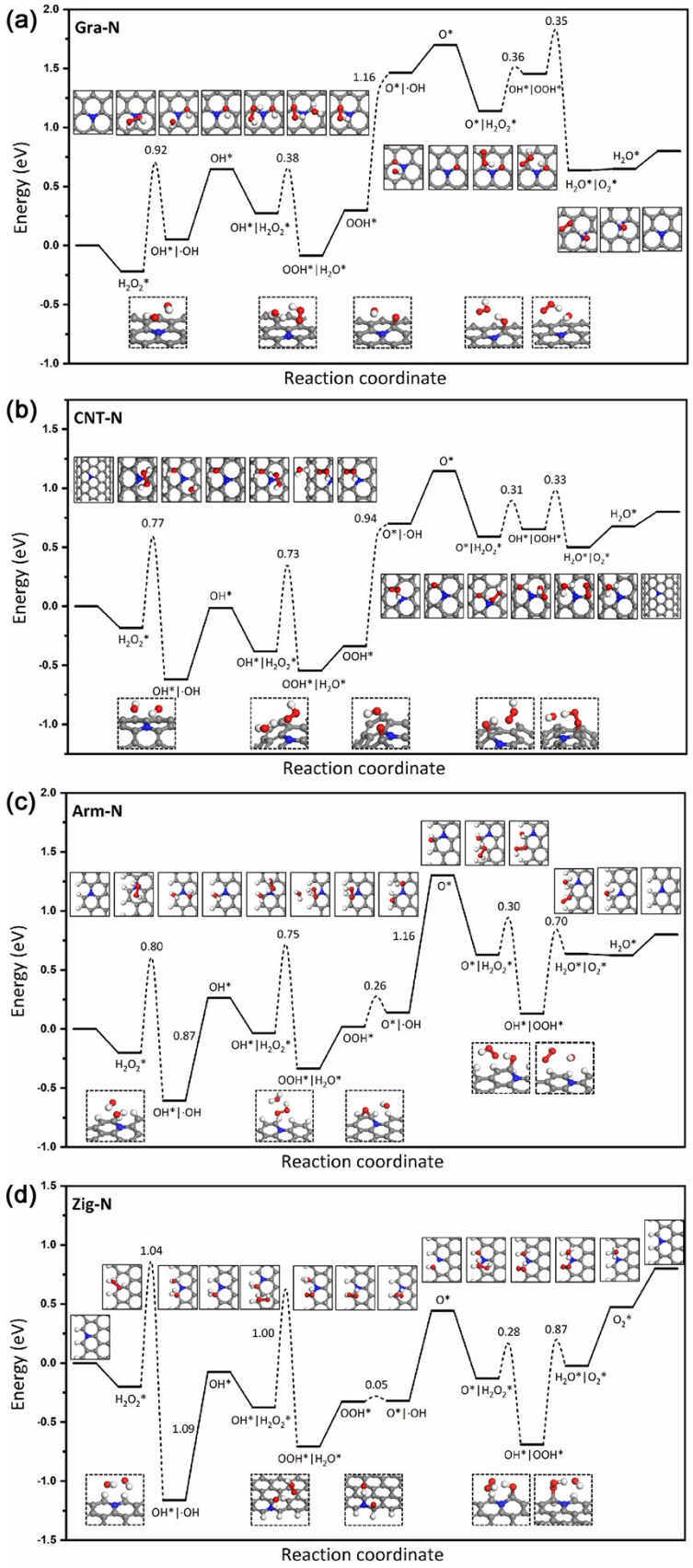

Fig. S3. The reaction energy diagrams of H_2O_2 dissociation on Gra-N (a), CNT-N (b), Arm-N (c) and Zig-N (d).

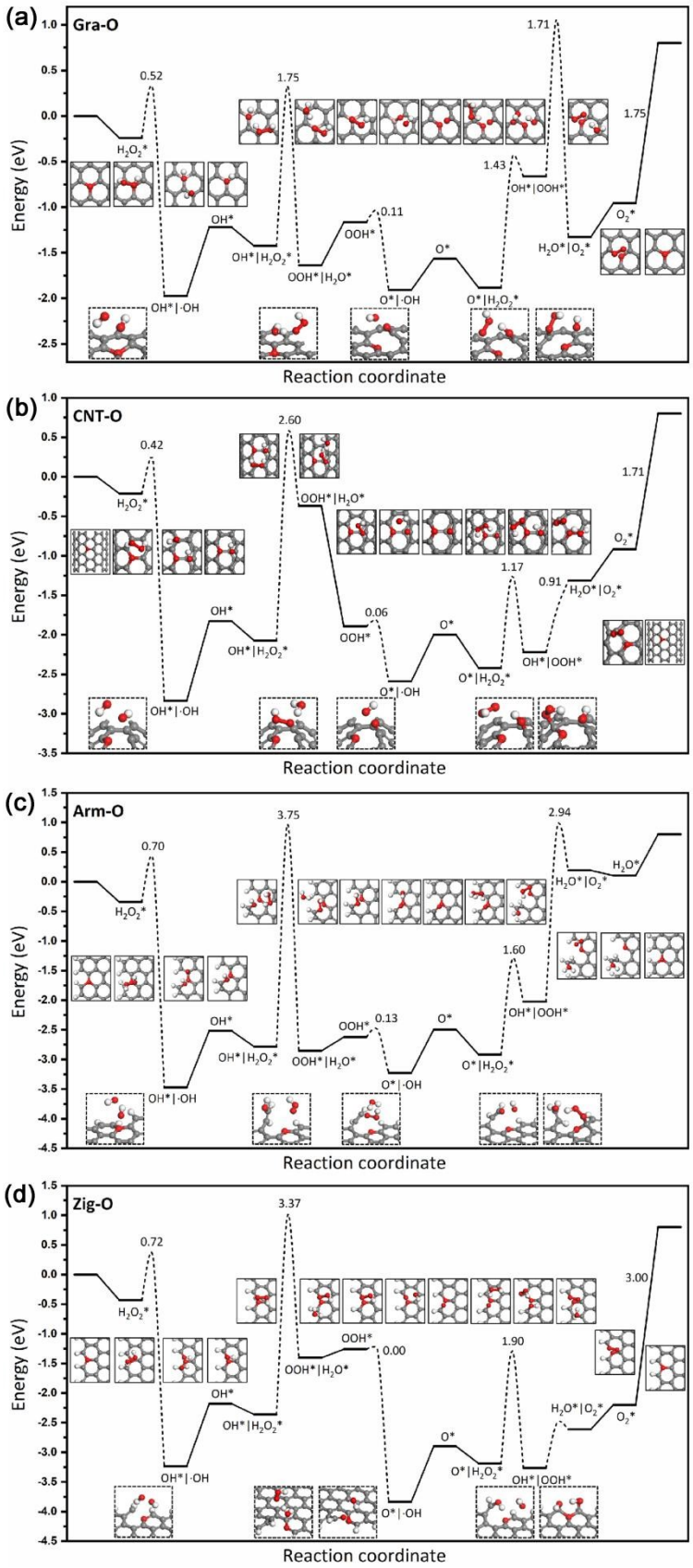

Fig. S4. The reaction energy diagrams of H_2O_2 dissociation on Gra-O (a), CNT-O (b), Arm-O (c) and Zig-O (d).

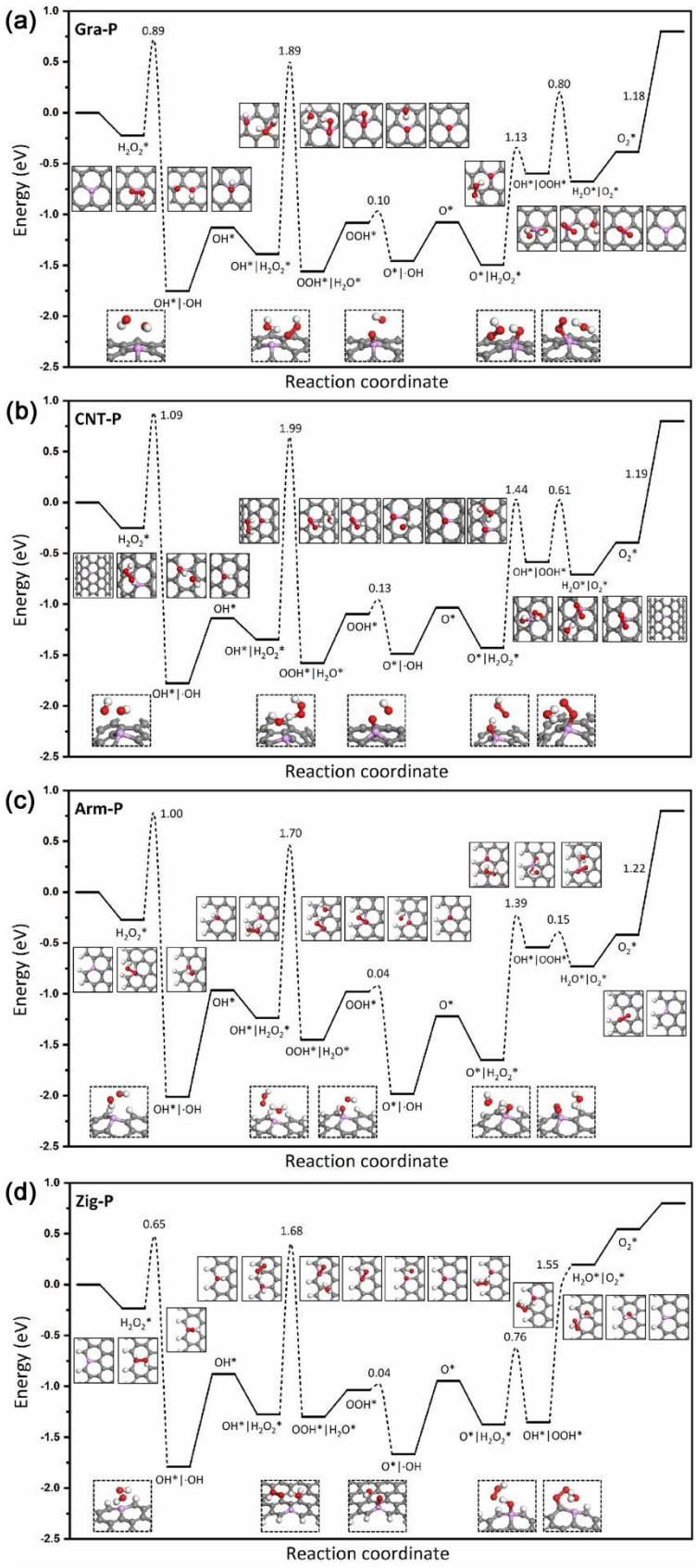

Fig. S5. The reaction energy diagrams of H_2O_2 dissociation on Gra-P (a), CNT-P (b), Arm-P (c) and Zig-P (d).

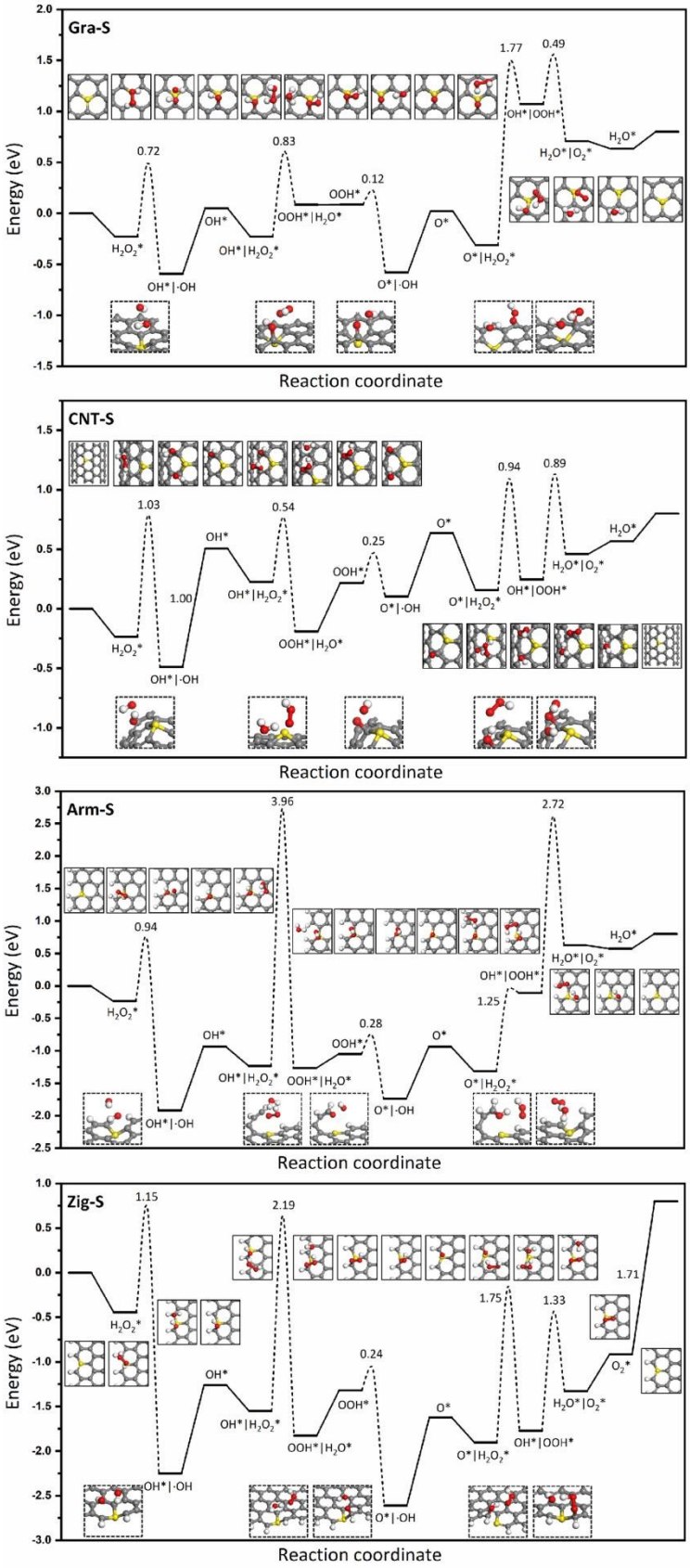

Fig. S6. The reaction energy diagrams of H_2O_2 dissociation on Gra-S (a), CNT-S (b), Arm-S (c) and Zig-S (d).

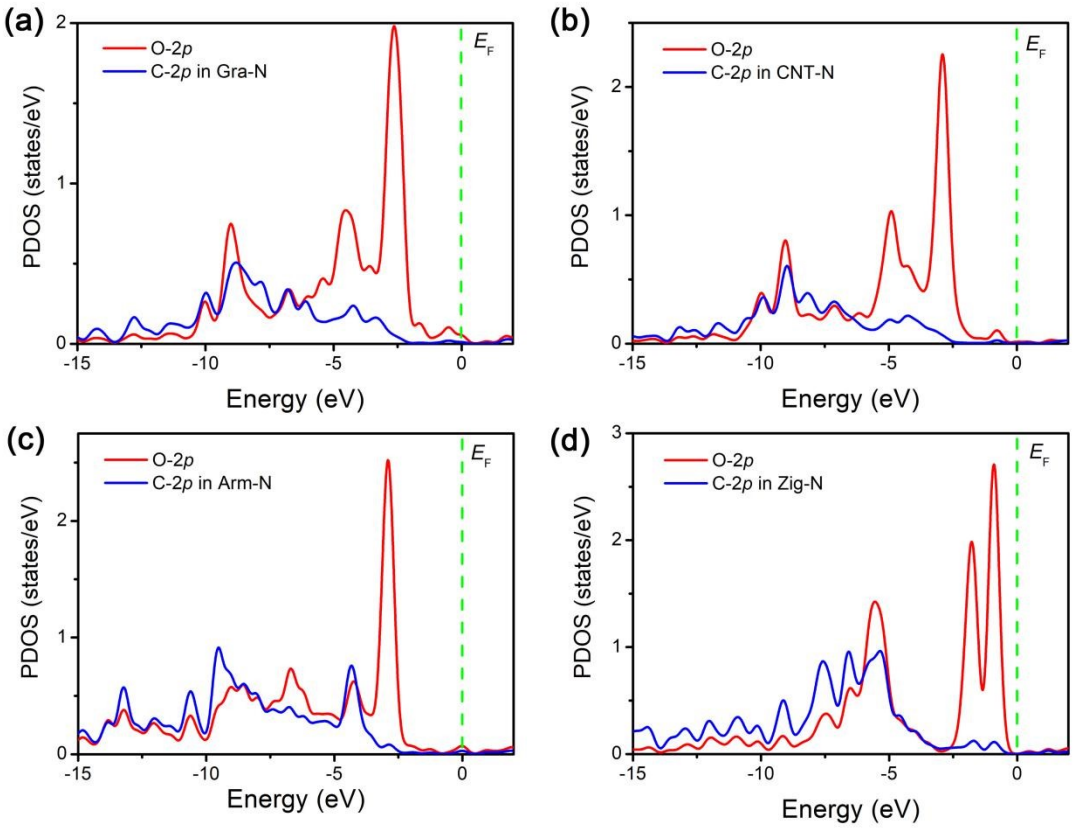

Fig. S7. Partial density of states (PDOS) of O adsorbed on N-doped carbon nanomaterials: (a) Gra-N, (b) CNT-N, (c) Arm-N, and (d) Zig-N.

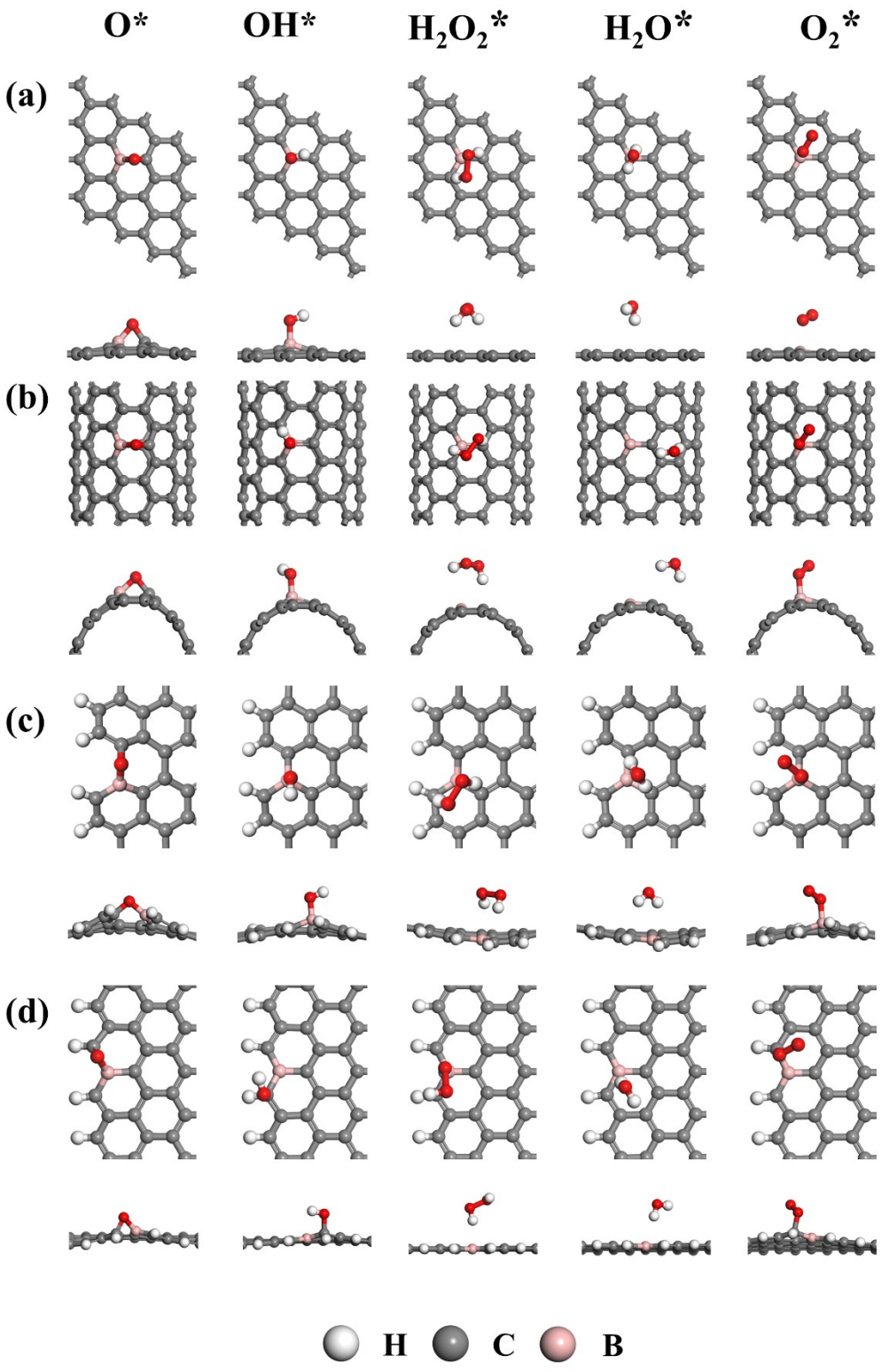

Fig. S8. Top and side views of reaction intermediates adsorbed on B-doped graphene (a), CNTs (b), armchair (c) and zigzag (d) carbon nanoribbons.

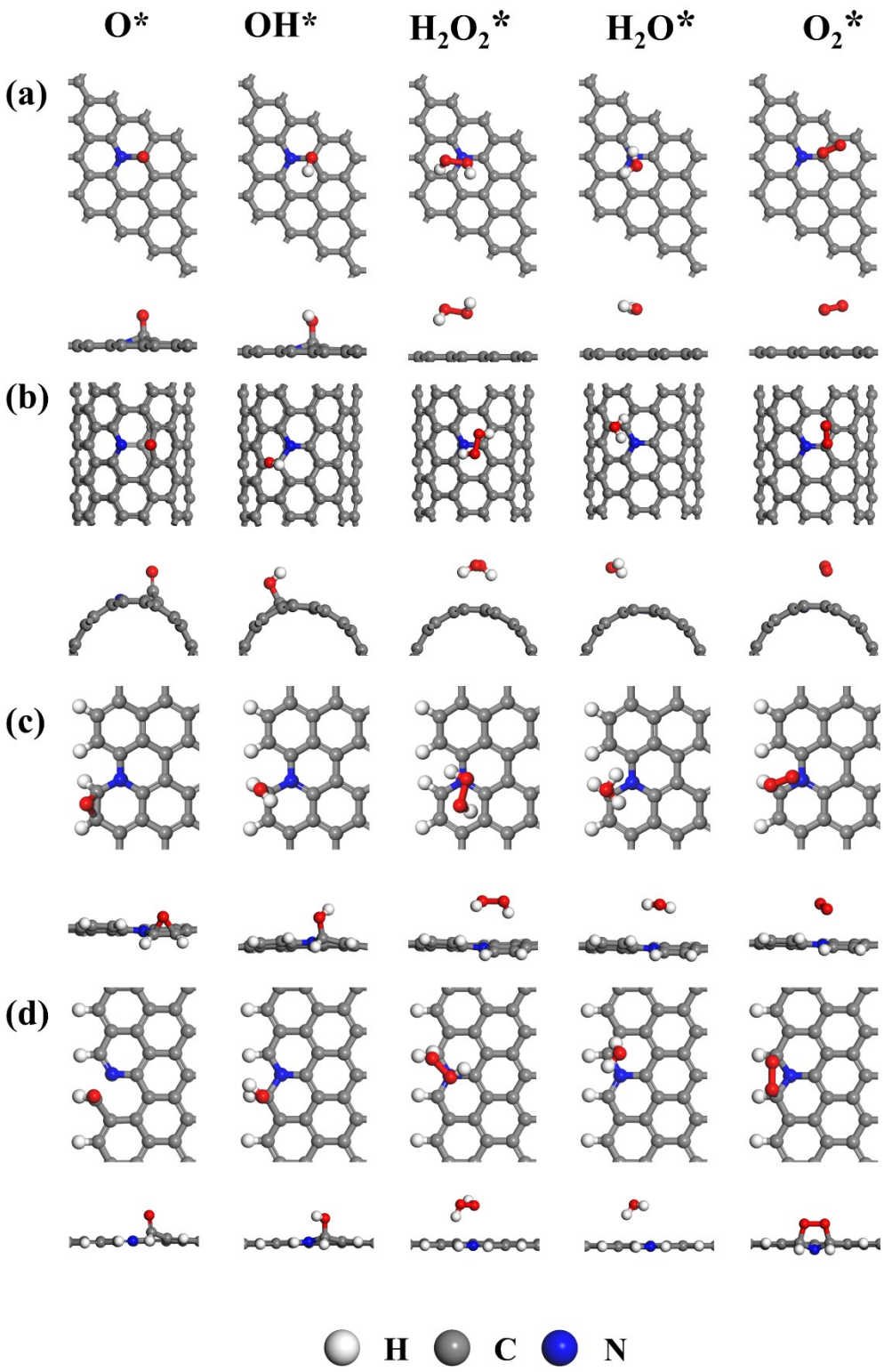

Fig. S9. Top and side views of reaction intermediates adsorbed on N-doped graphene (a), CNTs (b), armchair (c) and zigzag (d) carbon nanoribbons.

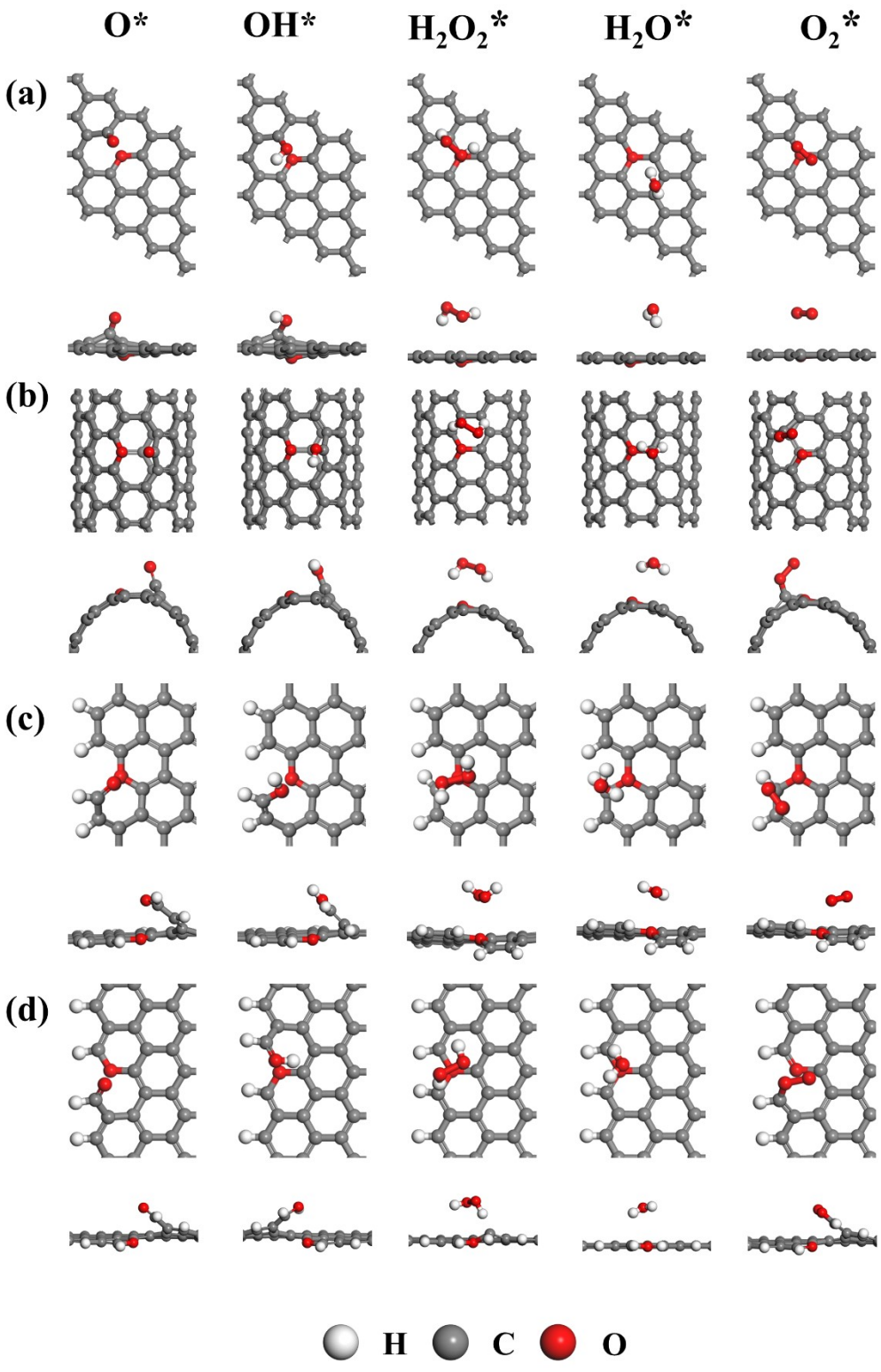

Fig. S10. Top and side views of reaction intermediates adsorbed on O-doped graphene (a), CNTs (b), armchair (c) and zigzag (d) carbon nanoribbons.

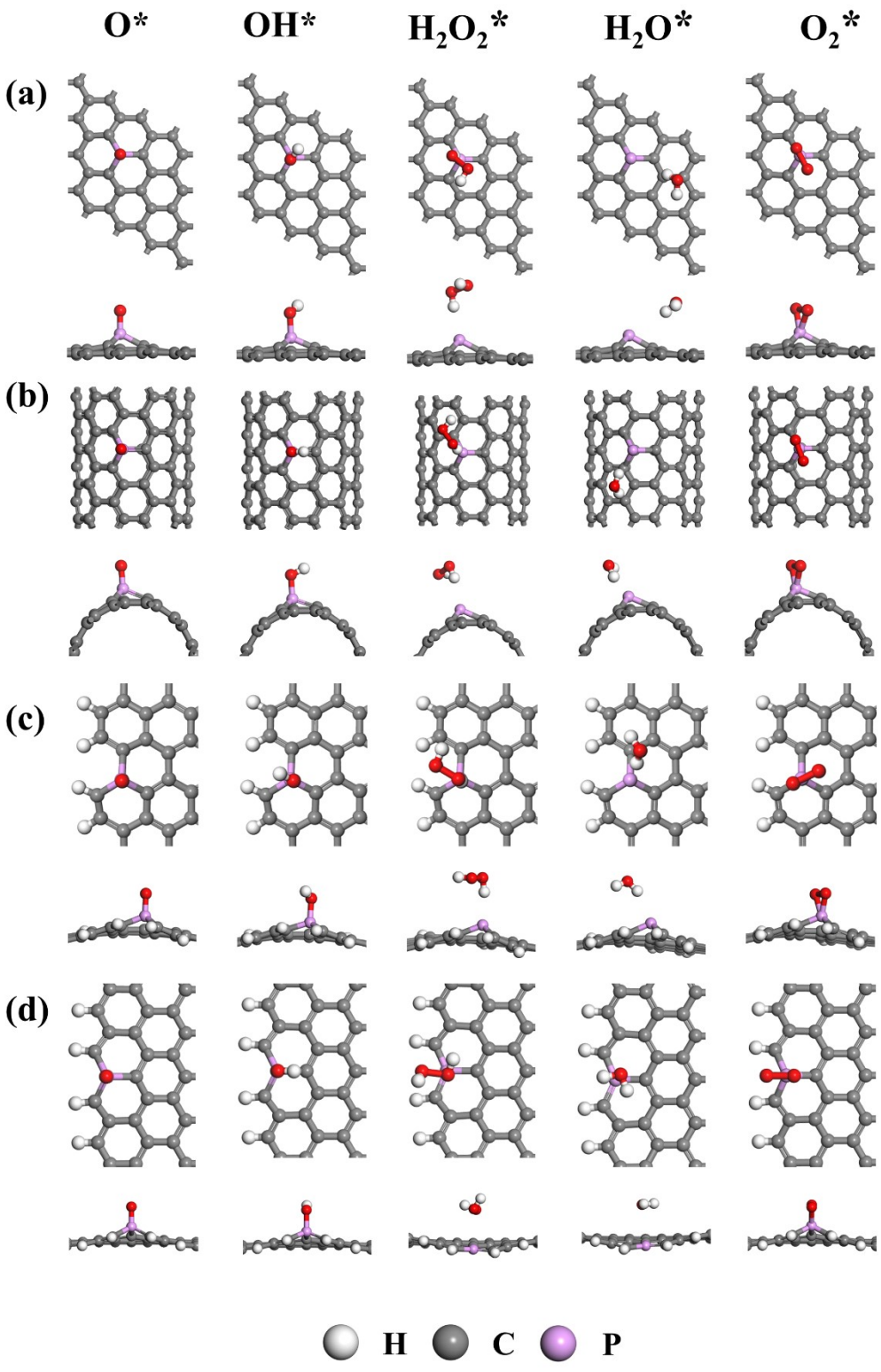

Fig. S11. Top and side views of reaction intermediates adsorbed on P-doped graphene (a), CNTs (b), armchair (c) and zigzag (d) carbon nanoribbons.

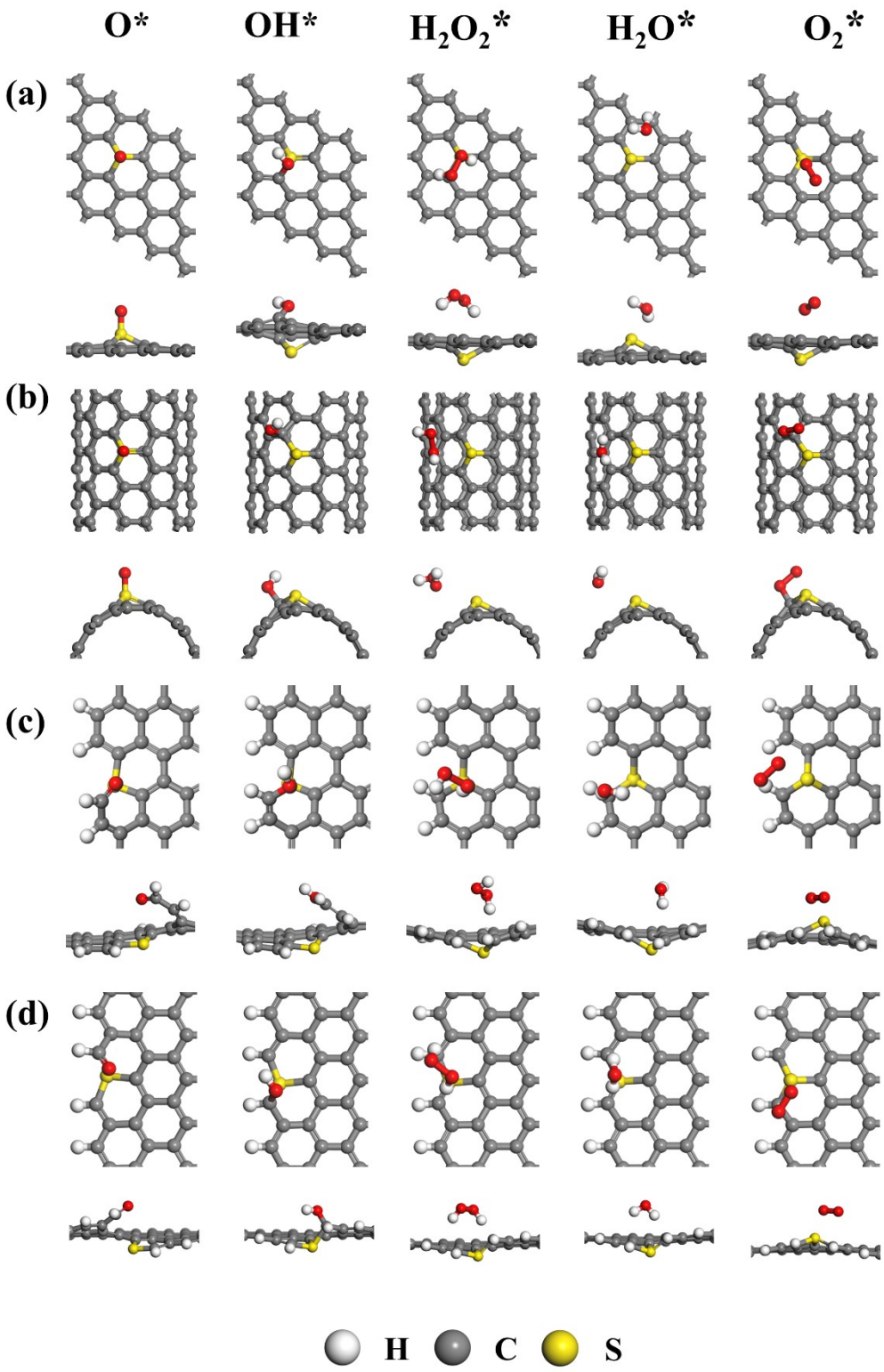

Fig. S12. Top and side views of reaction intermediates adsorbed on S-doped graphene (a), CNTs (b), armchair (c) and zigzag (d) carbon nanoribbons.

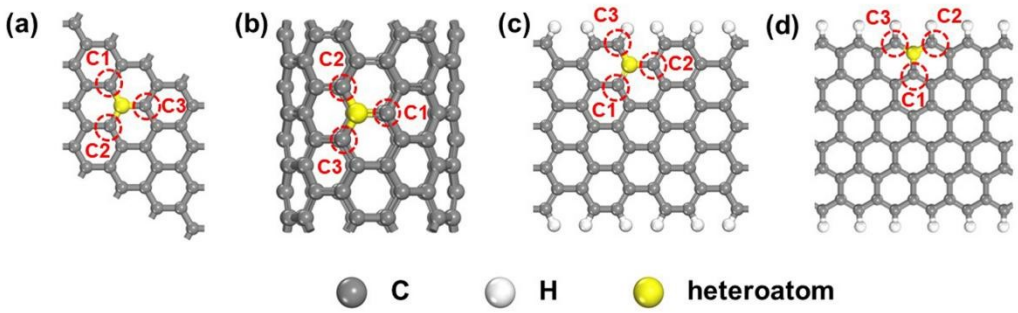

Fig. S13. The atomic index of heteroatom doped carbon nanomaterials.

Table S1. Adsorption energies of different species on heteroatom doped carbon nanomaterials. All results were in unit of eV. The corresponding adsorption structures were shown in Figs. S8-S12.

		O	OH	H_2O_2	H_2O	O_2
B	graphene	-3.761	-2.194	-0.255	-0.199	0.337
	CNT	-5.074	-2.646	-0.278	-0.171	-0.048
	Armchair	-4.599	-2.534	-0.415	-0.358	0.184
	Zigzag	-4.590	-2.554	-0.277	-0.241	0.055
N	graphene	-3.234	-2.072	-0.218	-0.151	0.116
	CNT	-4.021	-2.770	-0.182	-0.137	-0.010
	Armchair	-3.886	-2.456	-0.202	-0.160	0.072
	Zigzag	-4.489	-2.795	-0.201	-0.155	-1.116
O	graphene	-6.499	-3.940	-0.240	-0.148	0.102
	CNT	-6.931	-4.548	-0.211	-0.134	-1.714
	Armchair	-7.429	-5.237	-0.342	-0.285	-0.110
	Zigzag	-7.832	-4.901	-0.431	-0.198	-2.996
P	graphene	-6.013	-3.849	-0.223	-0.165	-1.186
	CNT	-5.967	-3.858	-0.250	-0.188	-1.195
	Armchair	-6.155	-3.684	-0.271	-0.205	-1.220
	Zigzag	-5.880	-3.598	-0.233	-0.228	-1.129
S	graphene	-5.093	-2.671	-0.228	-0.235	0.149
	CNT	-4.911	-2.213	-0.236	-0.233	-0.082
	Armchair	-5.874	-3.658	-0.236	-0.188	-0.040
	Zigzag	-6.559	-3.981	-0.445	-0.320	-0.115

Table S2. The Mulliken charges of the heteroatoms and their adjacent C atoms. The corresponding atomic index was shown in Fig. S13.

		heteroatoms	C1	C2	C3
graphene	O	-0.583	0.238	0.238	0.228
	N	-0.452	0.186	0.185	0.177
	S	-0.054	-0.06	-0.061	-0.068
	P	0.618	-0.331	-0.333	-0.334
	B	0.087	-0.075	-0.079	-0.079
Armchair	O	-0.527	0.278	0.241	0.106
	N	-0.389	0.201	0.181	0.064
	S	-0.024	-0.117	-0.077	-0.024
	P	0.589	-0.305	-0.338	-0.381
	B	0.085	-0.069	-0.108	-0.21
Zigzag	O	-0.454	0.275	0.061	0.061
	N	-0.295	0.178	0.005	0.005
	S	-0.056	-0.051	-0.159	-0.159
	P	0.980	-0.411	-0.485	-0.485
	B	0.016	-0.116	-0.157	-0.157
CNTs	O	-0.517	0.207	0.160	0.160
	N	-0.434	0.203	0.181	0.181
	S	-0.019	-0.041	-0.075	-0.075
	P	0.619	-0.325	-0.331	-0.331
	B	0.140	-0.123	-0.095	-0.095

Reference

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