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Theoretical research on oxidation mechanism of doped carbon based catalysts for oxygen reduction reaction

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Table S1. Relevant thermodynamic data of gas-phase species and adsorbents, at T=298 K and P=1 bar. DFT total energies, zero-point energy and entropy, the entropy of H_2O is calculated at 0.035 atm, which corresponds to the vapor pressure of liquid water. [S1] All values are given in eV.

	$\Delta g_{H_2O}^{exp}$	E^{DFT}	ZPE	$T\Delta S$
H_2O(l)	-2.46 (l)	-14.22	0.57	0.22 0.67 (0.035bar)
H_2(g)		-6.76	0.27	040
CO(g)	-	-14.80	0.13	0.61
CO_2(g)	-	-22.98	0.31	0.66
***OH**	-	-	0.39	0.07
***O**	-	-	0.09	0.05
***OOH**	-	-	0.46	0.16
***C**	-	-	0.14	-
***COH**	-	-	0.57	-
***CO**	-	-	0.25	-
***COOH**	-	-	0.65	-
***CO_2**	-	-	0.34	-

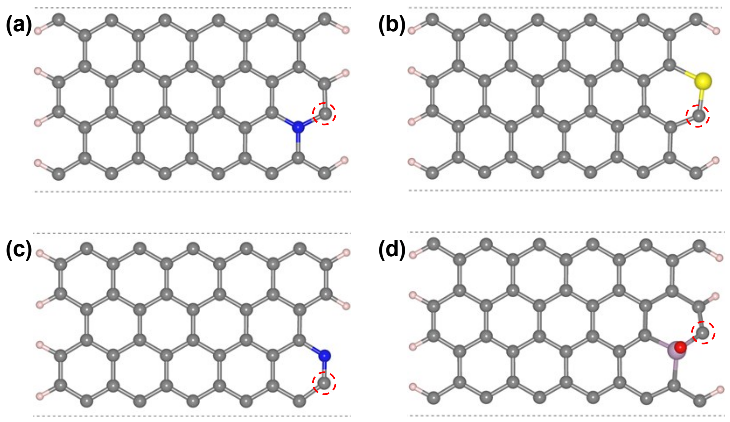

Figure S1. Four kinds of doped-graphene models: (a) graphitic-N doped graphene (Ng-G), (b) S doped graphene (S-G), (c) pyridinic-N doped graphene (Np-G) and (d) P doped graphene (P-G). The grey, white, blue, yellow, red and pink spheres represent the C, H, N, S, O and P atoms, respectively.

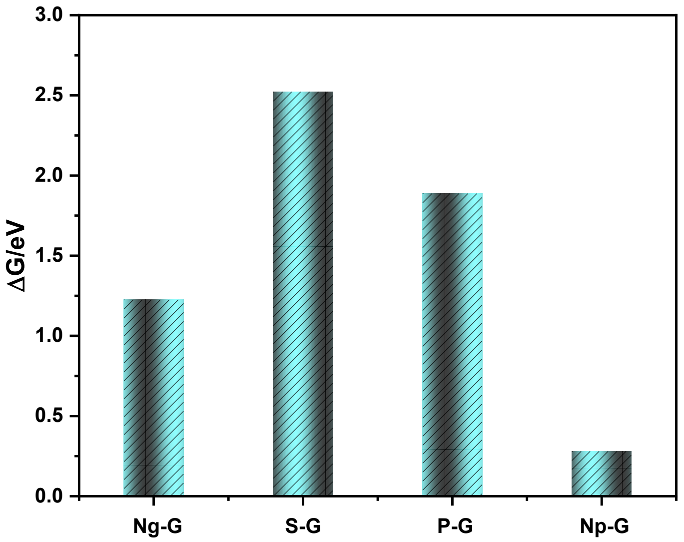

Figure S2. The different energy level of *C of the four doped-graphene relative to pure graphene ($\Delta G = \Delta G_{*C}^{doped-graphene} - \Delta G_{*C}^{pure-graphene}$, pure graphene with $\Delta G = 0$). And the more negative the values are, the more stability of doped-graphene structure.

Table S2. The adsorption energies (ΔE_{ads}), adsorption free energies (ΔG_{ads}) and bond lengths (d_{O-O}) of O_2 molecular on the investigated models.

	Ng-G	Np-G	S-G	P-G
ΔE_{ads} /eV	-1.84	-1.72	-1.54	-2.11
ΔG_{ads} /eV	-1.14	-1.03	-0.85	-1.42
d_{O-O} /Å	1.40	1.36	1.38	1.37

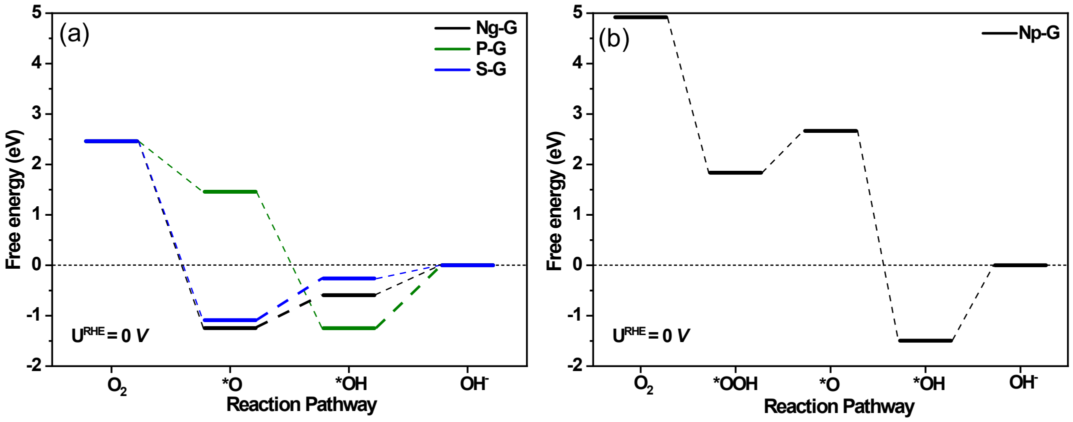

Figure S3. The calculated free energy diagram of carbon sites at zero potential (U^{RHE} = 0 V *vs.* RHE). (a) dissociative mechanism and (b) associative mechanism of ORR.

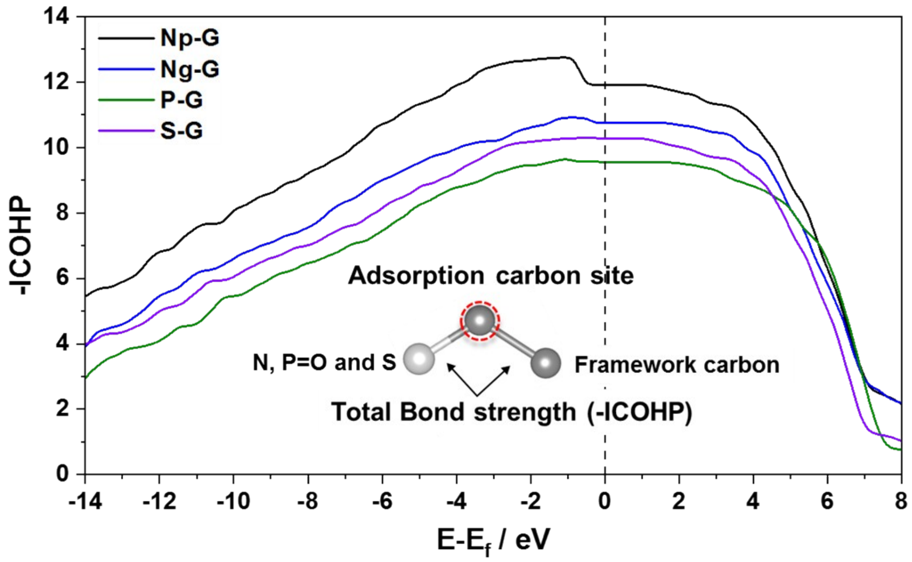

Figure S4. The -ICOHP curve of the four doped-graphene configuration.

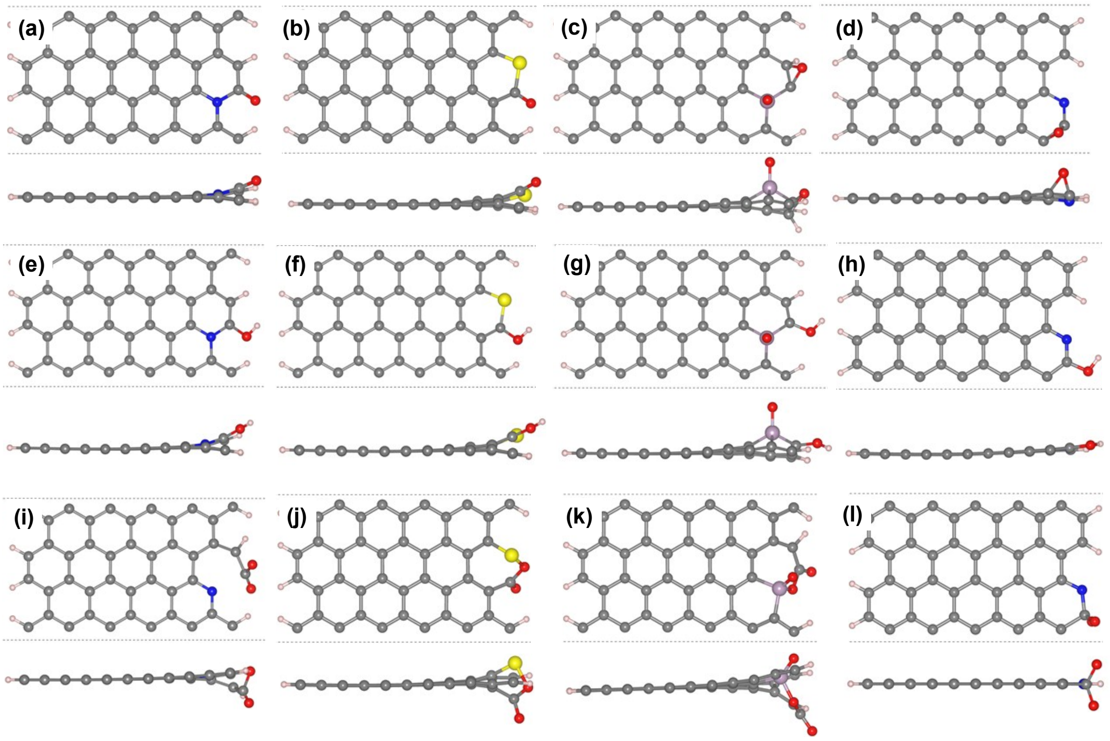

Figure S5. The *CO (a-d), *COH (e-h) and *CO_2 (i-l) adsorption configurations on the four doped-graphene surface.

For a given electrocatalytic process, the exchange current density (j_0) can be theoretically computed as follows equation:

$$j_0 = nFk^0C^{1-\alpha}_{O}C^{\alpha}_{R}$$

Here, for the reaction $O_2(oxidant, O) + H_2O + 4e^- \rightarrow 4OH^-(reductant, R)$, the *n, F* and k^0 are the electron transfer number, the Faraday constant and the standard rate constant, respectively. The α is transfer coefficient, and which as a measure the symmetry of the potential energy surface could range from 0 to 1. C_O *and* C_R is the reacting surface concentration of O and R, respectively. Simultaneously, the bulk concentrations (adjacent to the reacting surface) of C^*_O and C^*_R can be related to K at the equilibrium:

$$K = \frac{C_R}{C_O} = \frac{C^*_R}{C^*_O} = exp\left[-\frac{1}{k_BT}\left(\Delta G_{PDS}(U^0)\right)\right]$$

Here, $\Delta G_{PDS}(U^0)$ is the maximal free energy change value among all the element reaction steps at the ORR equilibrium potential ($U^0 = 1.23\ V$ vs RHE).

And the coverage ϑ of reductant R can be expressed by:

$$\theta = \frac{C_R}{C_{total}} = \frac{K}{1+K}$$

Here, $C_{total} = C_R + C_O$ is total number of surface active sites. Therefore, the exchange current density can be theoretically computed as follows equation:

$$j_0 = nFk^0 C_{total}[(1-\theta)^{1-\alpha}\theta^{\alpha}]$$

Where the α value and pre-factor $A = nFk^0 C_{total}$ could be obtained by fitting the experimental data of the exchange current densities. [S2]

Table S3. ORR exchange current density of experimental [S2] and theory of the four doped-graphene before and after carbon oxidation.

	Catalyst	ΔG_{PDS} (eV)	j_0^{theory}(A/cm^2)	j_0^{exp}(A/cm^2) [1]
Initial	Pt	0.45 [2]	3×10^{-7}	4.8×10^{-7}
	Ng-G	0.54	6.3×10^{-8}	3.0×10^{-9}
	S-G	0.56	3.8×10^{-8}	3.5×10^{-12}
	P-G	0.52	7.8×10^{-8}	7.7×10^{-11}
	Np-G	1.47	7.1×10^{-16}	--
Partial oxidation	Ng-G	1.02	4.5×10^{-12}	--
	S-G	1.64	2.6×10^{-17}	--
	P-G	0.47	2.0×10^{-7}	--
	Np-G	1.52	2.7×10^{-16}	--
Complete oxidation	Ng-G	0.90	4.7×10^{-11}	--
	S-G	1.53	2.2×10^{-16}	--
	P-G	0.87	8.4×10^{-11}	--
	Np-G	0.94	2.1×10^{-11}	--

Reference

S1. Norskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. Origin of the overpotential for oxygen reduction at a fuel-cell cathode. *J Phys Chem B* **2004,** *108* (46), 17886-17892.

S2. Jiao, Y.; Zheng, Y.; Jaroniec, M.; Qiao, S. Z. Origin of the electrocatalytic oxygen reduction activity of graphene-based catalysts: a roadmap to achieve the best performance. *Journal of the American Chemical Society* **2014,** *136* (11), 4394-403