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Effects of non-metals doping on oxygen reduction reaction of Fe-C_2N electrodes

Dan Shu, [a] Dan Wang, *[b] and Yan Wang *[c]

[a] *School of Physics and Electronic Science, Hunan University of Science and Technology, Xiangtan 411201, China.*

[b] *College of Science, Central South University of Forestry and Technology, Changsha 410004, China. E-mail: wangdan@hnu.edu.cn*

[c] *School of Information and Electrical Engineering, Hunan University of Science and Technology, Xiangtan 411201, China. E-mail: ywang8@hnust.edu.cn*

In electrochemistry, the basic reaction steps of four electrons under acidic conditions can be expressed as follows:

$$* + O_2 + H^+ + e^- \rightarrow *OOH\#(1)$$

$$*OOH + H^+ + e^- \rightarrow *O + H_2O\#(2)$$

$$*O + H^+ + e^- \rightarrow *OH\#(3)$$

$$*OH + H^+ + e^- \rightarrow H_2O\#(4)$$

Where * represents the active site of O containing intermediates (* O, * OH and * OOH) on the material surface. The Gibbs free energy of O-containing intermediates involved in ORR is calculated as follows:

$$\Delta G_{*O_xH_y} = G_{*O_xH_y-M} - G_M - \left[xG_{H_2O} - (2x-y)G_{H_2}/2\right]\#(5)$$

Where $G_{*O_xH_y-M}$, G_M, G_{H_2O} and G_{H_2} represent the total Gibbs free energy, the Gibbs free energy of the substrate, the Gibbs free energy of H_2O and the Gibbs free energy of H_2. The change in Gibbs free energy of the ORR step can be calculated as:

$$\Delta G_1 = \Delta G_{*OOH} - 4.92\#(6)$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OOH}\#(7)$$

$$\Delta G_3 = \Delta G_{*OH} - \Delta G_{*O}\#(8)$$

$$\Delta G_4 = -\Delta G_{*OH}\#(9)$$

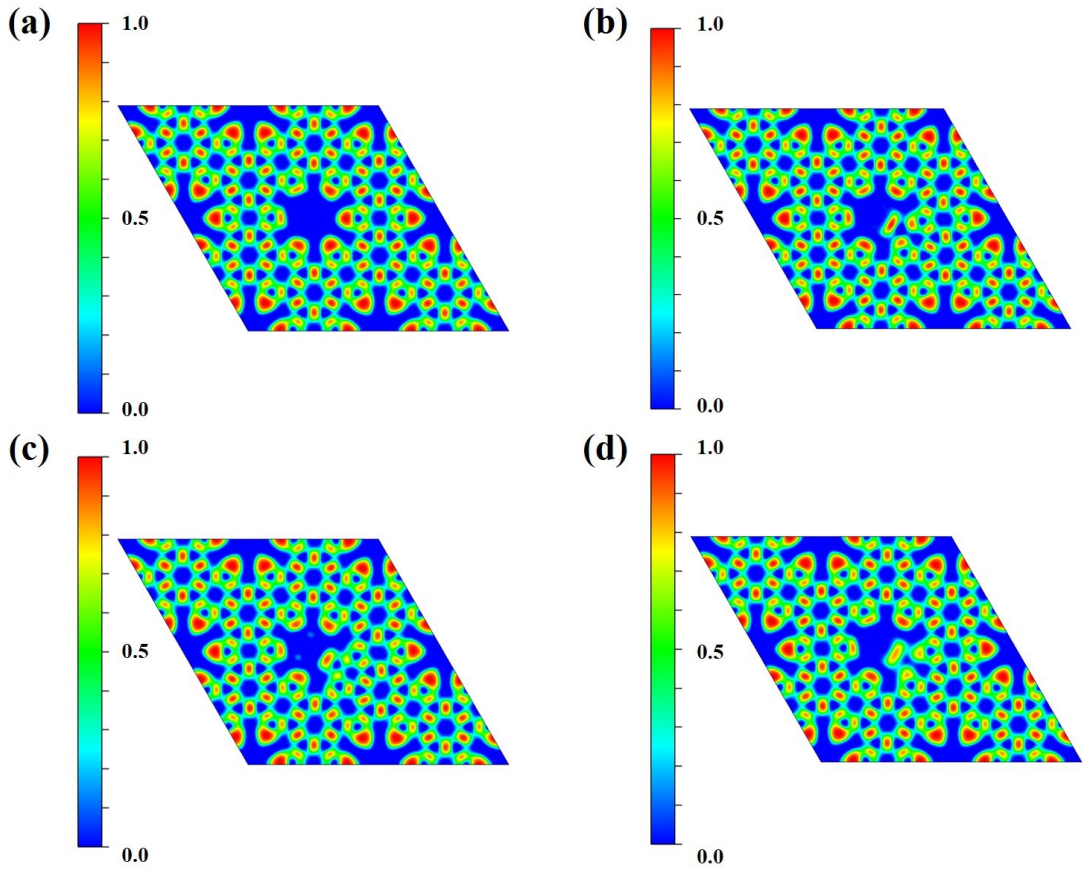

Figure S1. The ELF plot of Fe-C_2N (a); FeB-C_2N (b); FeN-C_2N (c) and FeP-C_2N (d).

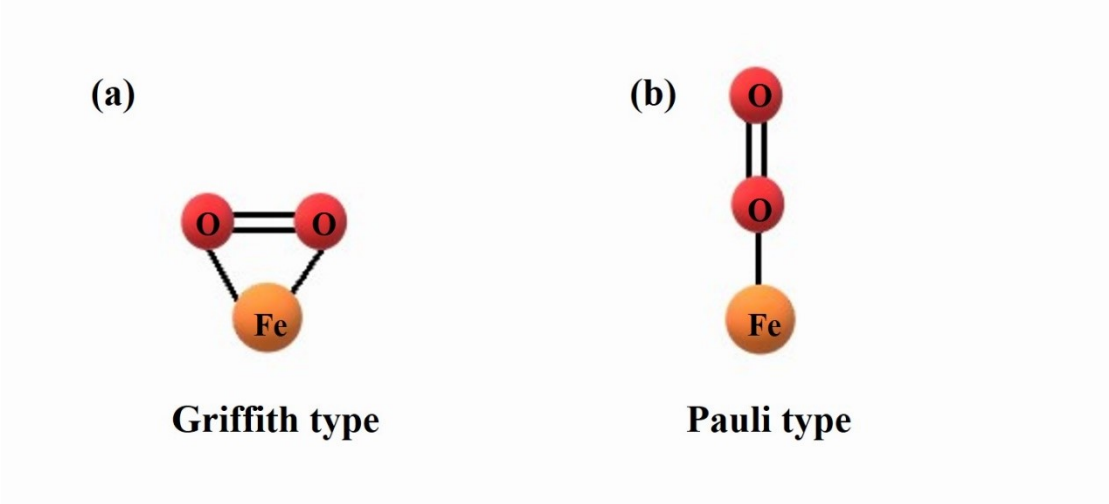

Figure S2. Griffith and Pauli adsorption configurations of O_2.

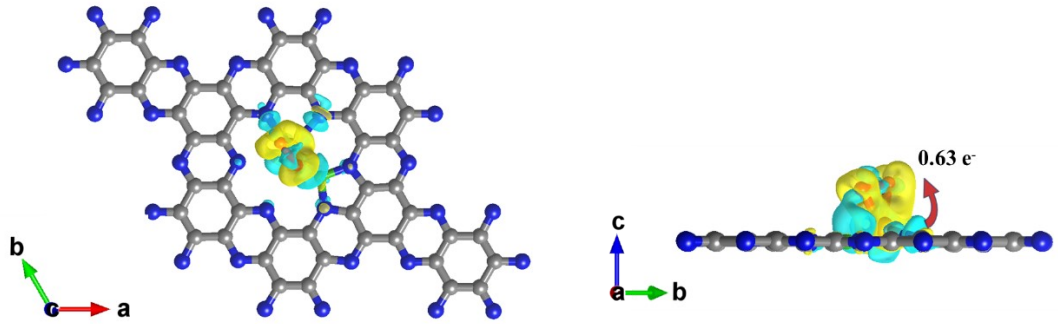

Figure S3. Charge density difference for O_2 adsorption states and corresponding Bader charge transfer number on FeB-C_2N. Color code: yellow stands for electron accumulation and cyan stands for electron depletion.

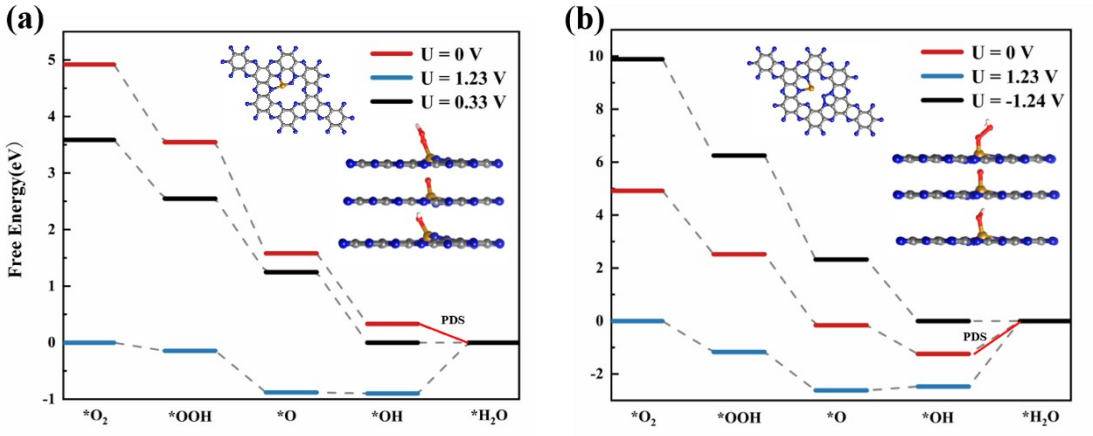

Figure S4. The free energy diagram of the ORR of the adjacent (a) and symmetric (b) sites of Fe-C_2N under different potentials in vacuum. Red solid line represents the PDS.

Table S1. Overpotential of materials with different doping.

	Fe-C_2N	FeB-C_2N	FeC-C_2N	FeN-C_2N	FeP-C_2N
η_{ORR} (V)	1.38	3.05	0.87	2.47	1.24

Table S2. The adsorption energy of different materials for * OH.

	Fe-C_2N	FeB-C_2N	FeC-C_2N	FeN-C_2N	FeP-C_2N
E_{ads} (eV)	-11.26	-10.77	-10.74	-12.33	-11.09