Supporting Information

Oxygen Reduction Reaction Mechanism on P, N Co-doped Graphene: A Density Functional Theory Study

Zhao Liang[a], Chao Liu*[a,b], Mingwei Chen[a], Xiaopeng Qi[a], U. Pramod Kumar[a], S. Gouse Peera[c], Juan Liu[d], Julong He[b], Tongxiang Liang*[a]

[a] School of Materials Science and Engineering, Jiangxi University of Science and Technology, Ganzhou 341000, China

[b] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China

[c] Department of Environmental Science and Engineering, Keimyung University, Daegu 42601, Republic of South Korea

[d] Key Laboratory of Advanced Packaging Materials and Technology of Hunan Province, School of Packaging and Materials Engineering, Hunan University of Technology, Zhuzhou 412007, China

* Corresponding Author.

E-mail address: liuchao198967@126.com (Chao Liu) and liang_tx@126.com (Tongxiang Liang).

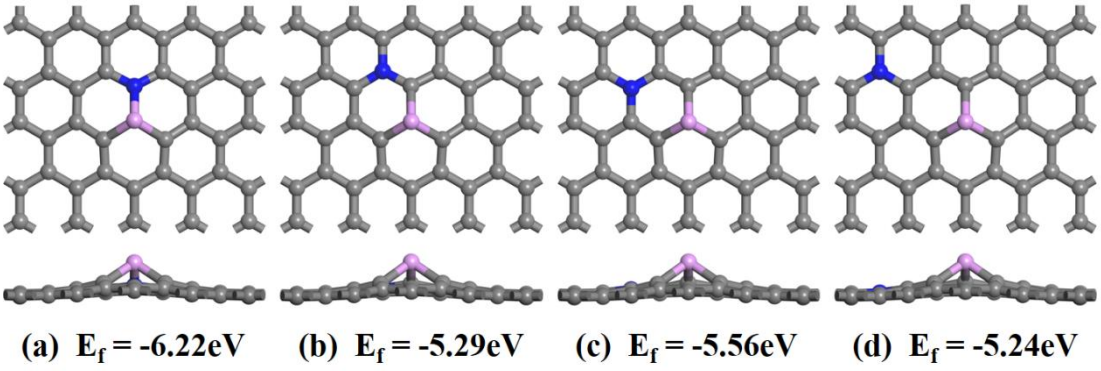

Figure S1 Several possible P, N co-doped configurations and corresponding formation energies.

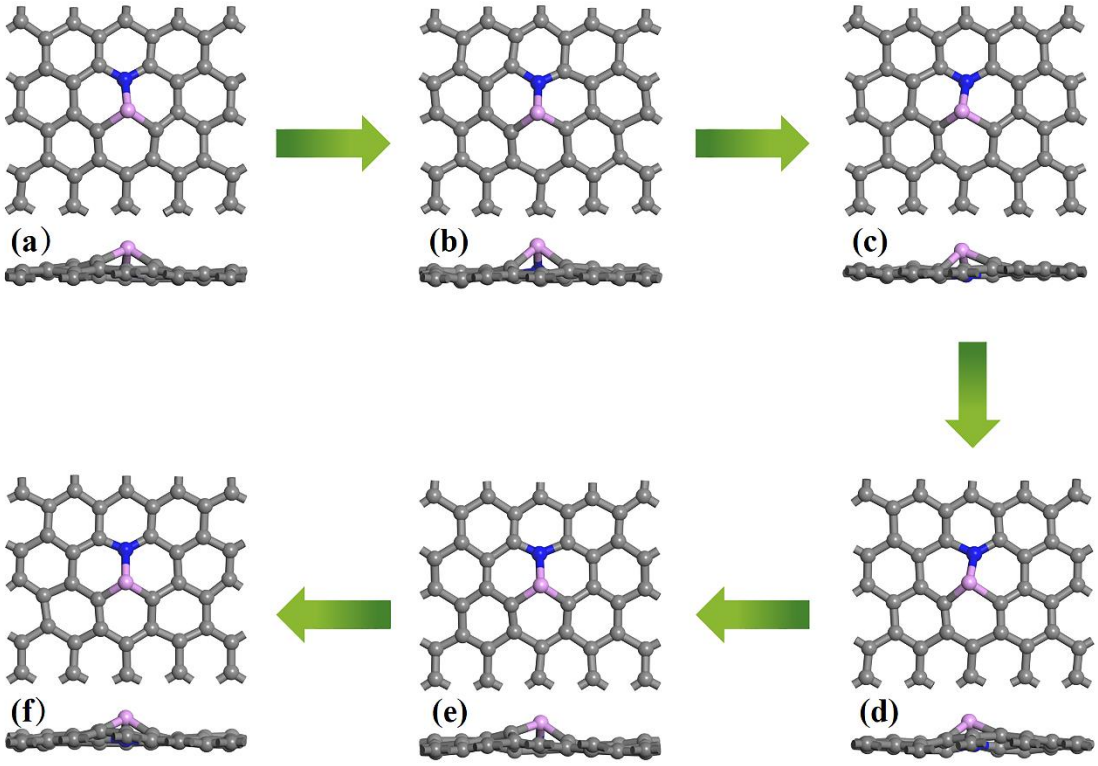

Figure S2 PN-Gra structure from the molecular dynamics simulation (1000 K, NVT) at (a) 500 fs, (b) 1000 fs, (c) 1500 fs, (d) 2000 fs, (e) 2500 fs and (f) 3000 fs. All bond distances are in Å.

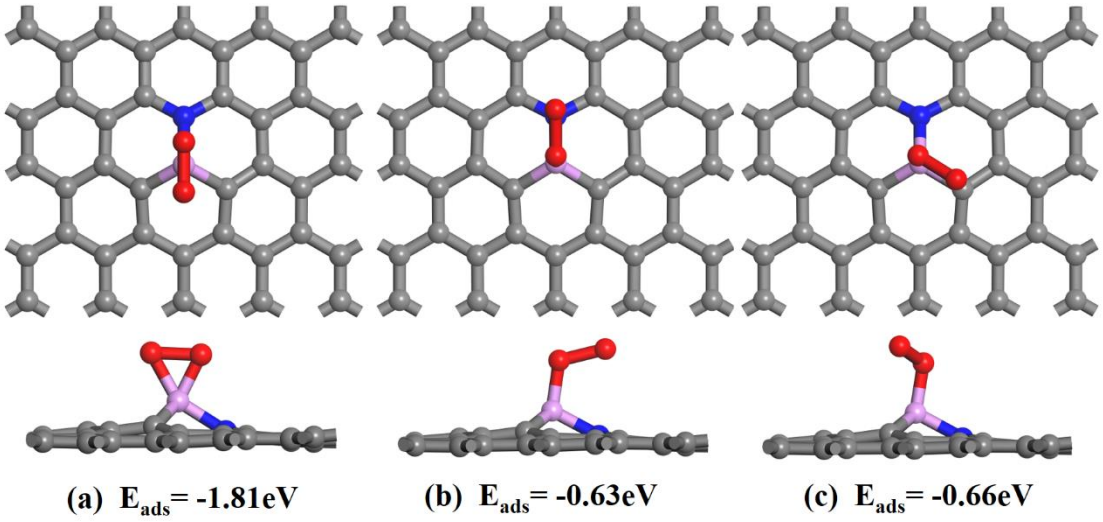

Figure S3 Several possible adsorption configurations of O_2 on PN-Gra and corresponding adsorption energies.

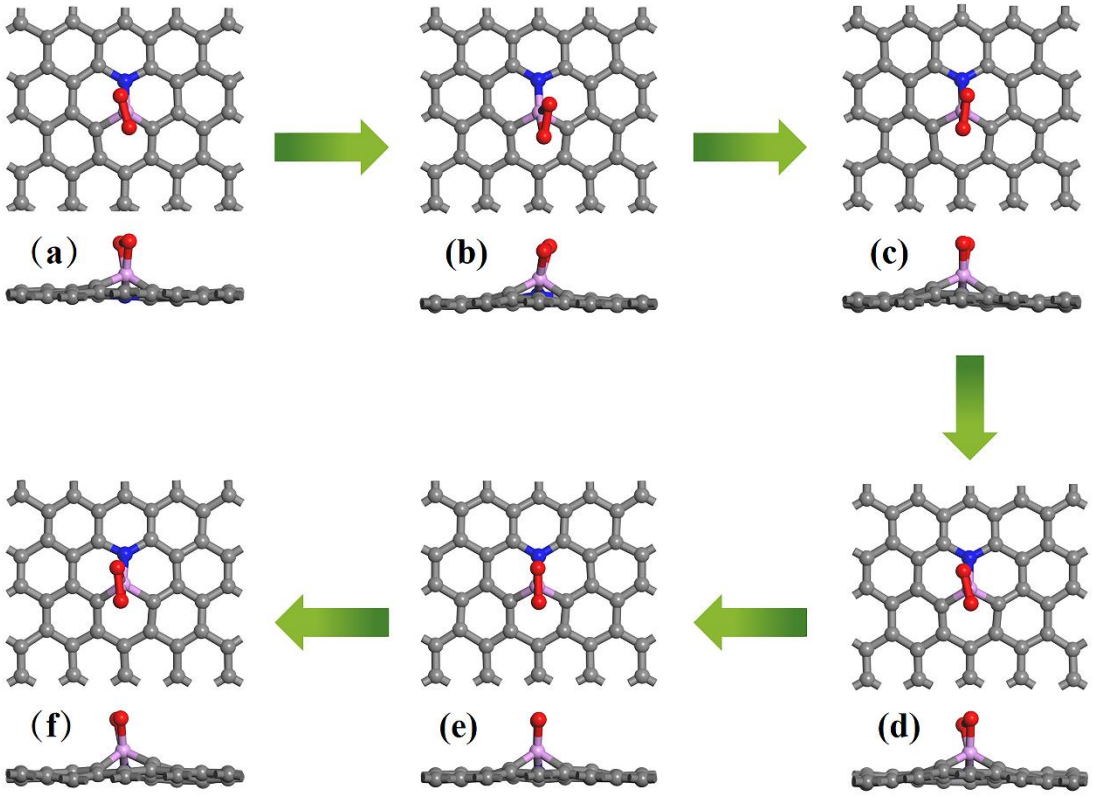

Figure S4 Structure of O_2 adsorbed on PN-Gra (side-on) from the molecular dynamics simulation (353 K, NVT) at (a) 500 fs, (b) 1000 fs, (c) 1500 fs, (d) 2000 fs, (e) 2500 fs and (f) 3000 fs.

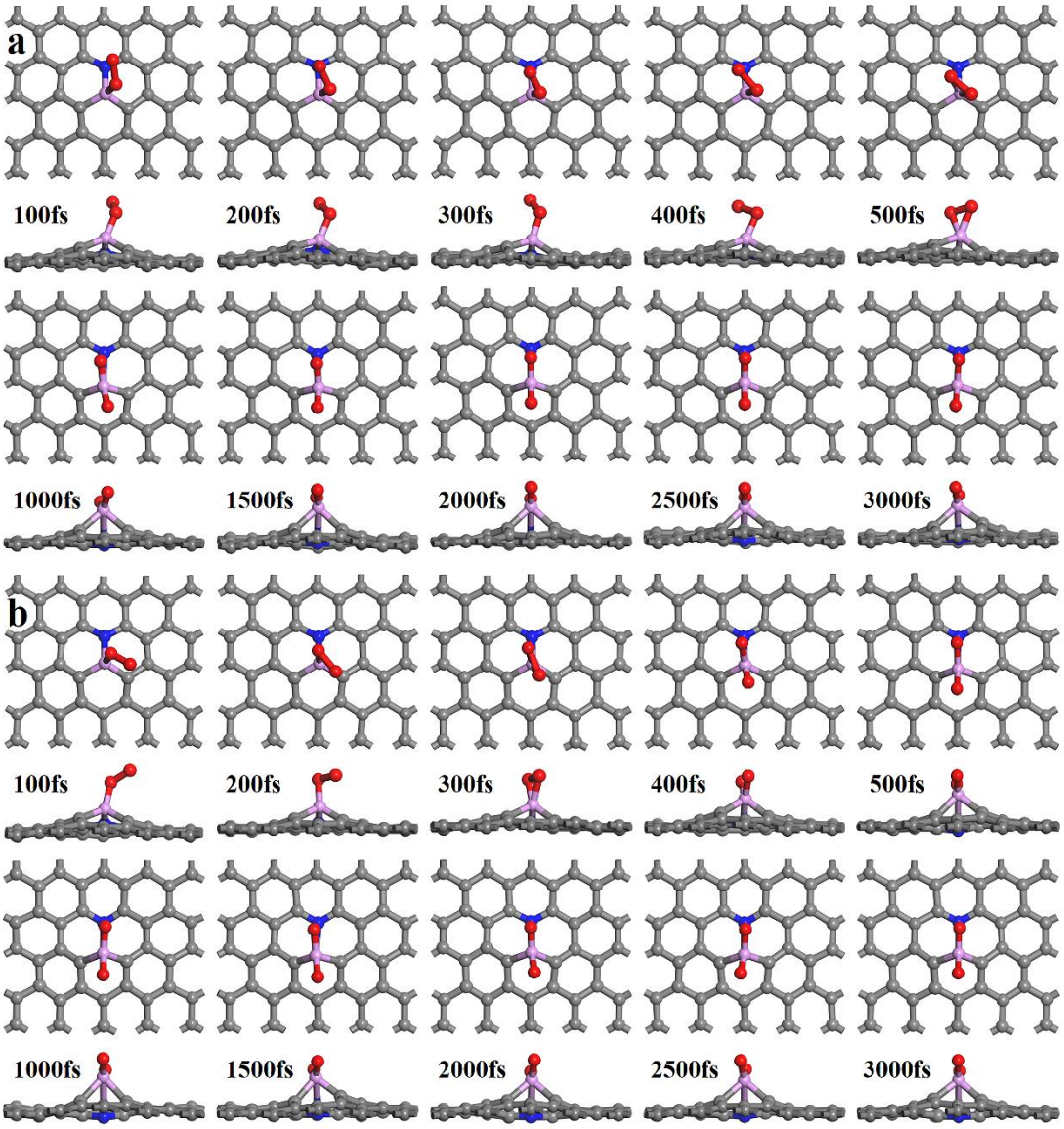

Figure S5 Structures of O_2 adsorbed on PN-Gra (end-on) from the molecular dynamics simulation (353 K, NVT).

Table S1 Free energy change (ΔG) of ORR elemental steps on PN-Gra at T=298.15 K, PH=0 and U= 0 V.

Elementary reactions	ΔG(eV)	Elementary reactions	ΔG(eV)
$O_2 \rightarrow OH^* + O^*$	-3.83	$2OH^* \rightarrow OH^* + H_2O$	-0.27
$O_2 \rightarrow O^* + OH^*$	-3.50	$O^* \rightarrow OH^*$	0.73

$OH^*+ O^* \rightarrow 2OH^*$	-0.40	$OH^* \rightarrow H_2O$	-0.42
$O^* + OH^* \rightarrow O^* + H_2O$	-1.73		

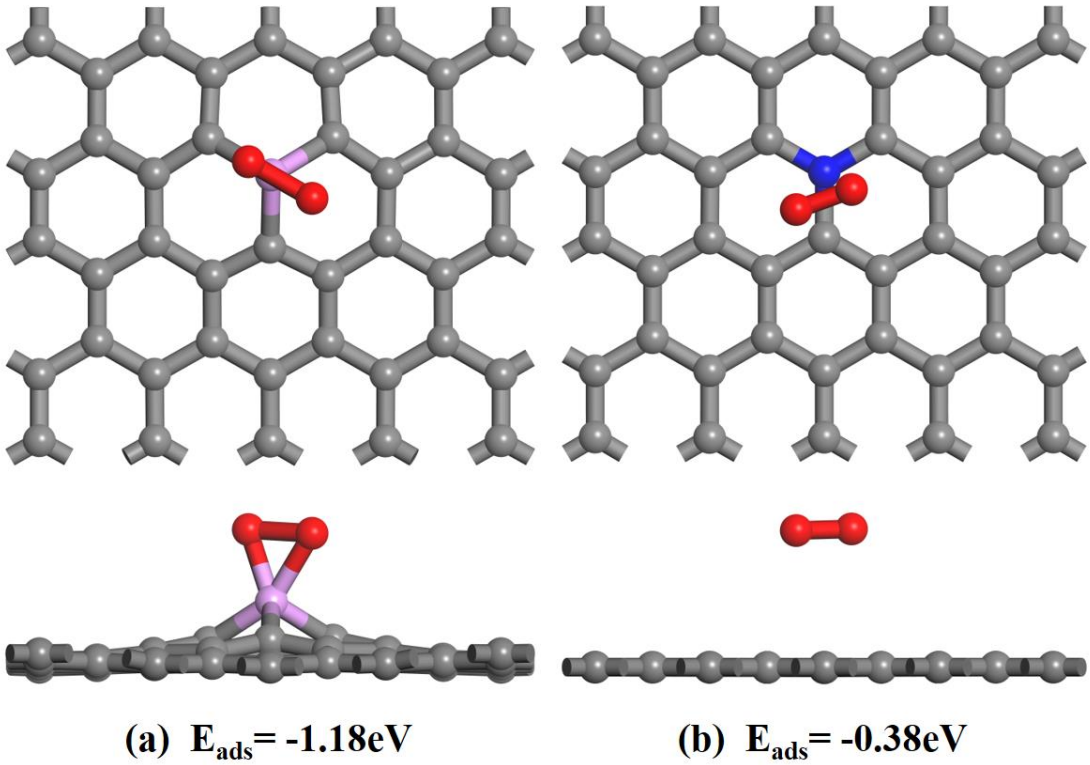

Figure S6 O_2 adsorption configuration and corresponding adsorption energy of (a) P-Gra and (b) N-Gra.

Table S2 Free energy ΔG (eV) of ORR elemental steps on P-Gra and N-Gra at T=298.15 K, PH=0 and U=0 V.

	ΔG1	ΔG2	ΔG3	ΔG4
P-Gra	-1.43	-3.53	-0.21	0.25
N-Gra	-0.08	-2.18	-1.19	-1.46

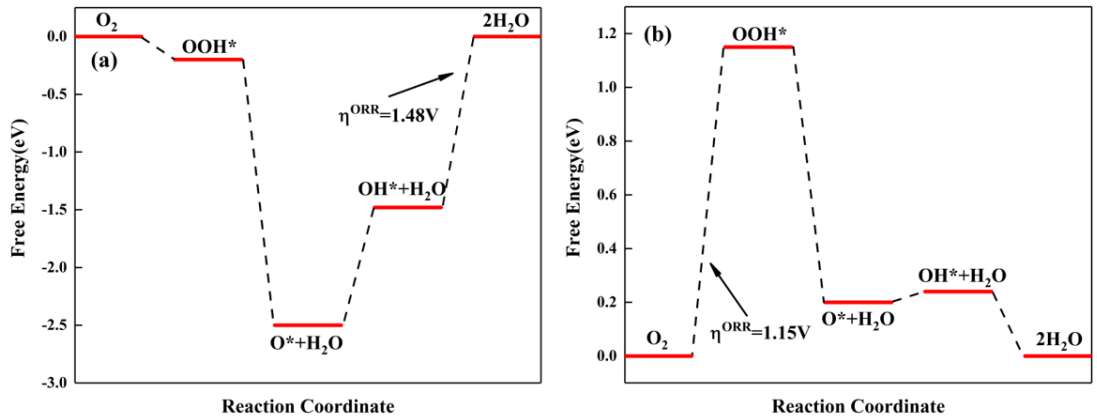

Figure S7 Free energy diagram for ORR on (a) P-Gra and (c) N-Gra at the equilibrium potential (U=1.23 V).

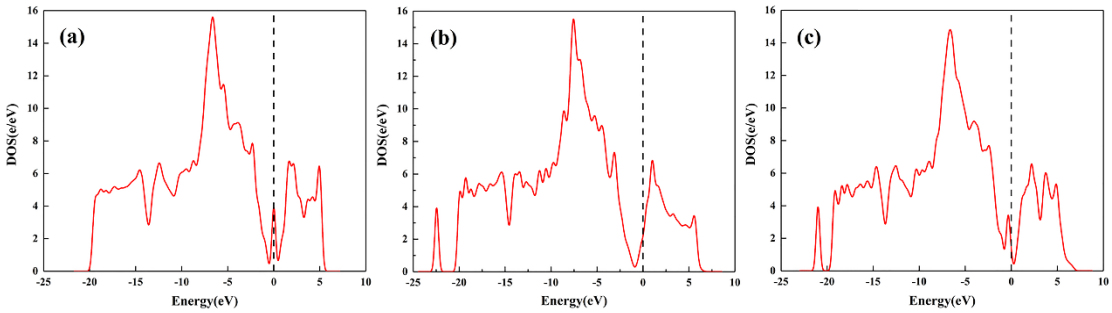

Figure S8 Electronic density of states (DOS) of (a) P-Gra, (b) N-Gra and PN-Gra, the dashed line at zero energy represents the Fermi level.

Table S3 Values of DOS abundance near Fermi level (D_F) in different intervals.

	P-Gra	N-Gra	PN-Gra
$D_F=\int_{-0.5}^{E_f} D(E)dE$	1.05	0.80	1.43
$D_F=\int_{-1.0}^{E_f} D(E)dE$	1.63	1.02	2.26
$D_F=\int_{-1.5}^{E_f} D(E)dE$	2.89	1.41	3.47
$D_F=\int_{-2.0}^{E_f} D(E)dE$	5.12	2.28	5.72

$D_F=\int_{-2.5}^{E_f} D(E)dE$	8.77	3.85	9.24