Electronic Supplementary Information

Oxygen Reduction Reaction Mechanism on Phosporus-doped Pyrolyzed Graphitic Fe/N/C Catalyst

Hermawan K. Dipojono[1,2], Adhitya Gandaryus Saputro[1,2], Apresio K. Fajrial[3], Mohammad Kemal Agusta[1,2], Fiki T. Akbar[4], Febdian Rusydi[5,6], and Dedy H.B. Wicaksono[7]

[1] *Advanced Functional Materials Research Group, Institut Teknologi Bandung, Jl.Ganesha 10, Bandung 40132, Indonesia*

[2] *Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia*

[3] *Department of Mechanical Engineering, University of Colorado, Boulder, CO 80309, USA*

[4] *Theoretical High Energy Physics and Instrumentations Research Group, Institut Teknologi Bandung, Jl.Ganesha 10, Bandung 40132, Indonesia*

[5] *Theoretical Physics Research Group, Department of Physics, Faculty of Science and Technology, Airlangga University, Surabaya 60115, Indonesia*

[6] *Research Center for Quantum Engineering Design, Airlangga University, Surabaya 60115, Indonesia*

[7] *Department of Biomedical Engineering, Faculty of Life Sciences and Technology, Swiss German University, Tangerang 15143, Indonesia*

1 Relative energy of several possible FeN_4G-PN structures

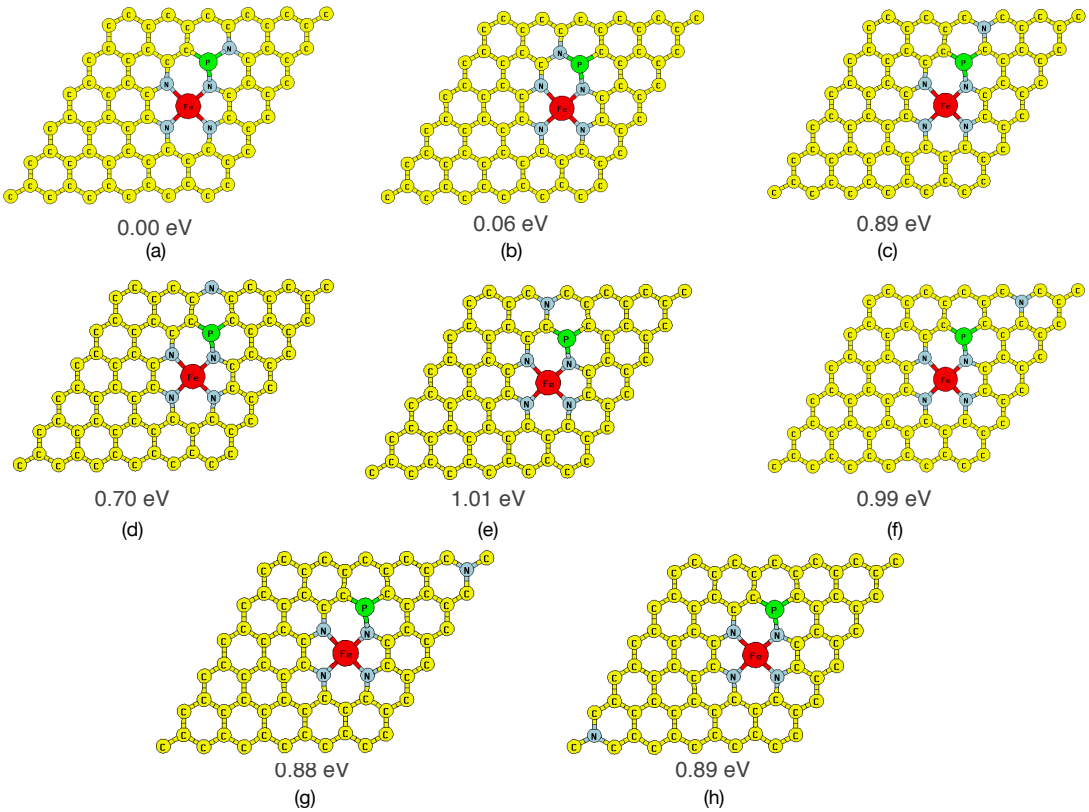

Figure S1: Several FeN_4G-PN configurations. Value below the figure is energy of the structure relative to (a)

2 O_2 adsorption configurations on several active sites

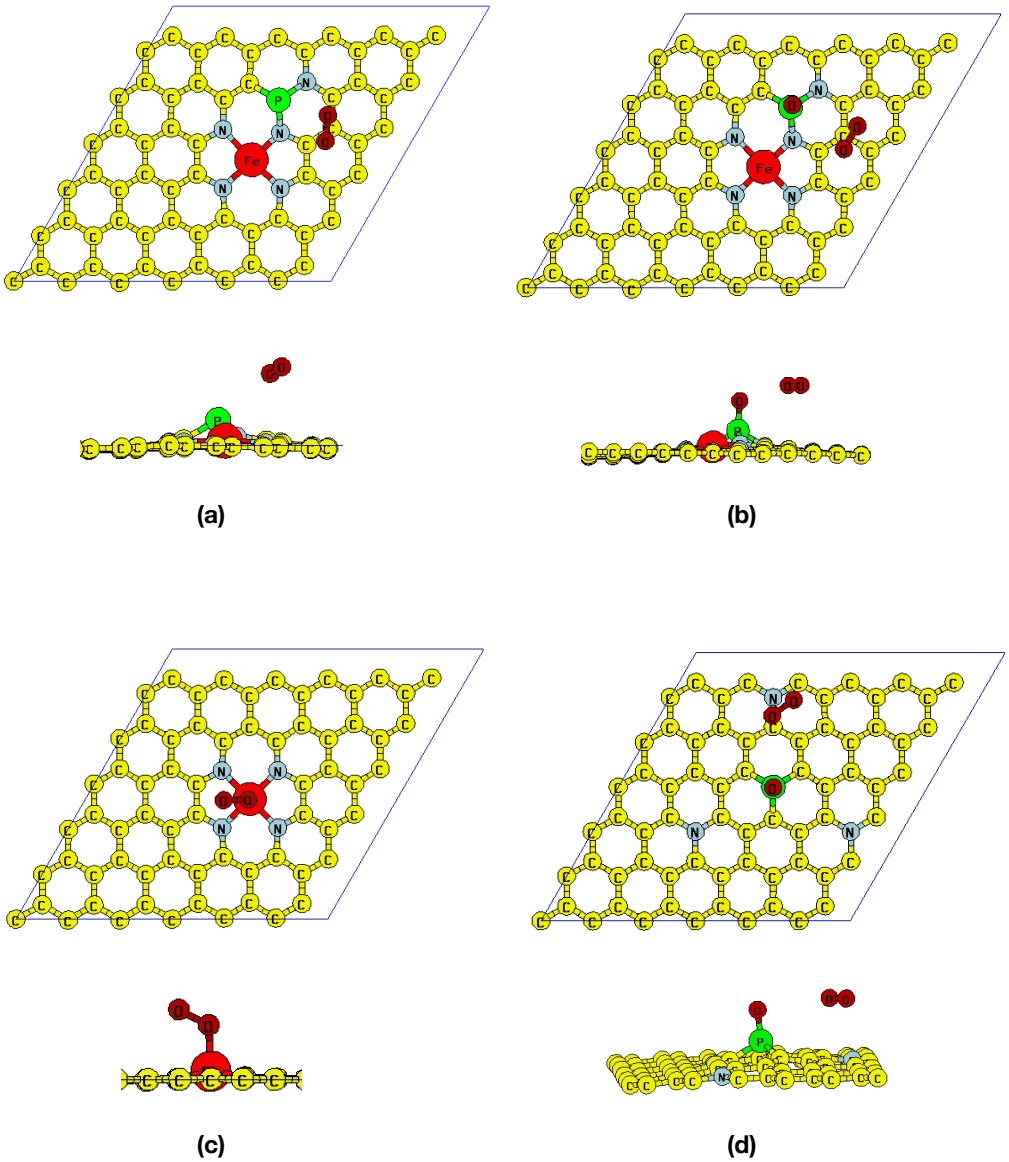

Figure S2: O_2 adsorption configurations on C-N site of FeN_4G-NP (a), C-N site of FeN_4G-NP=O (b), FeN_4 site of undoped FeN_4G (c) and C-N site of GN_3PO (d).

3 Electronic properties of O_2 interaction with FeN_4G-PN systems

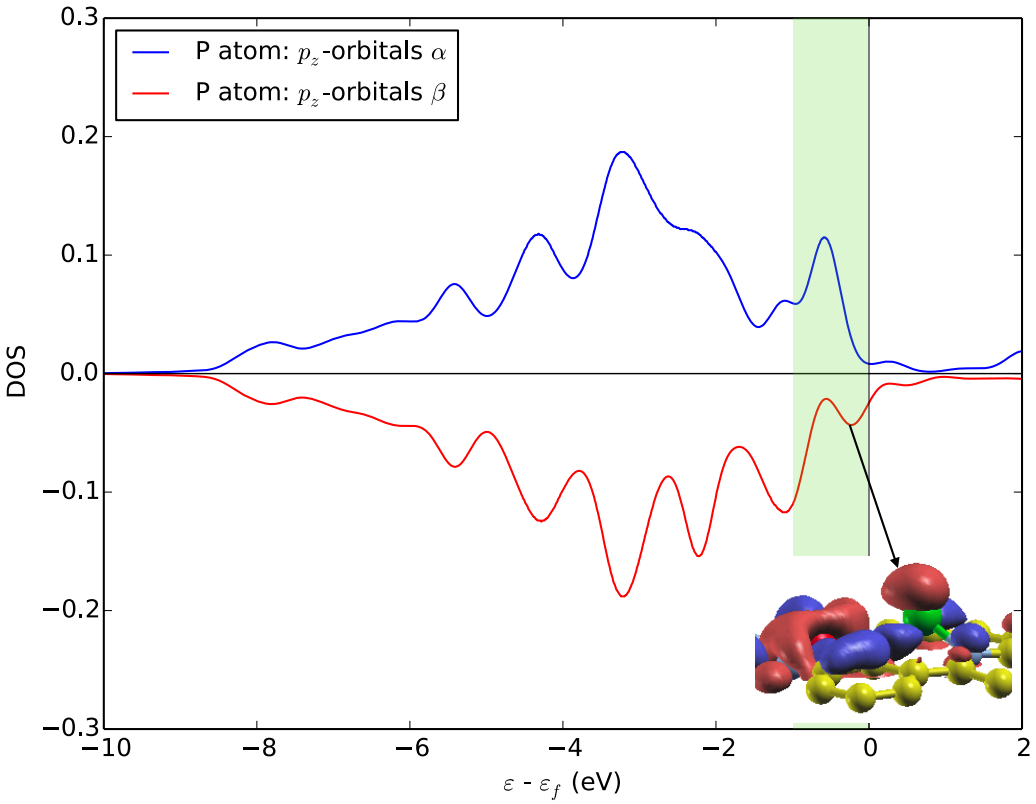

Figure S3: The localized p_z state on the P_{subs} site located right below the fermi level.

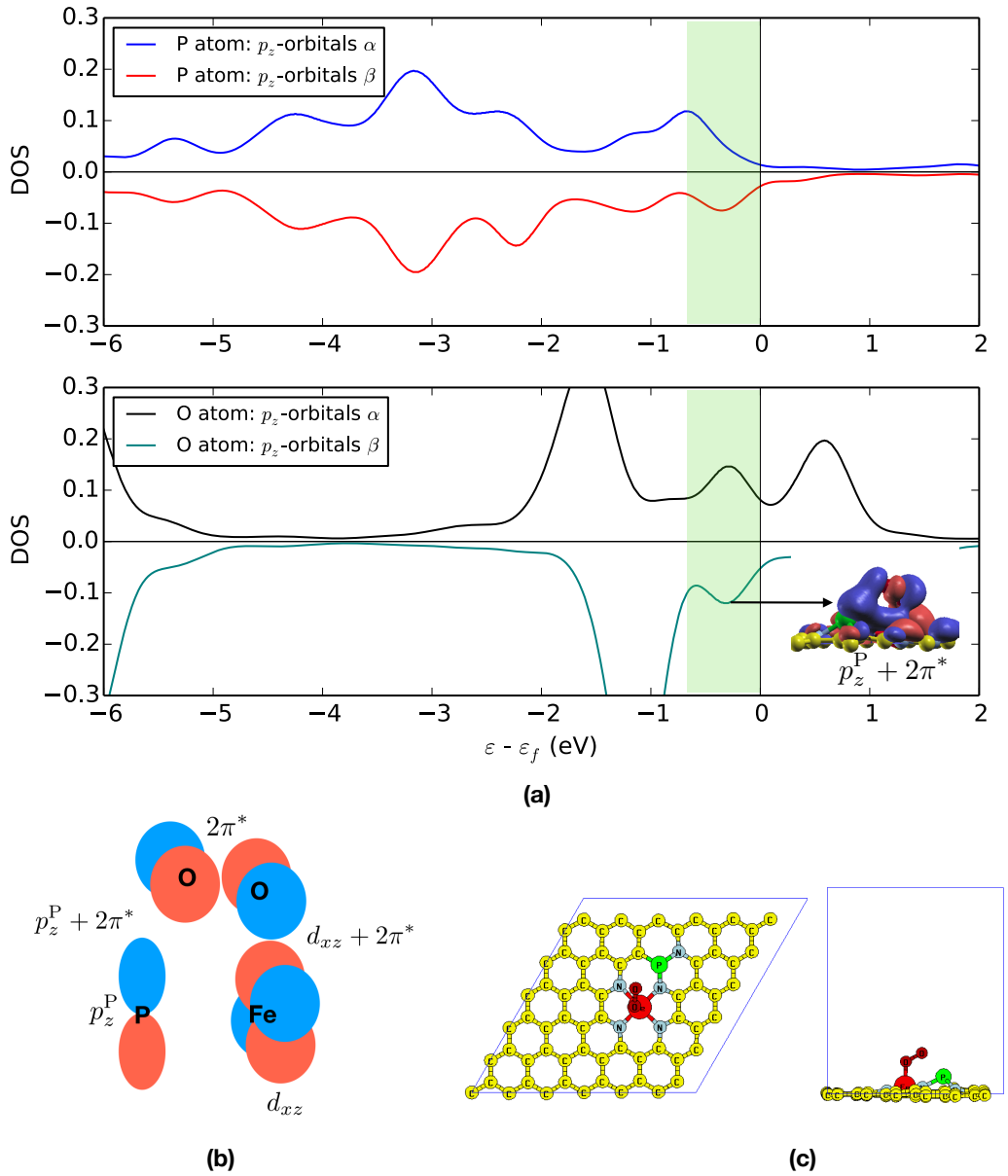

Figure S4: Local density of states (LDOS) of the interaction between localized p_z state of the P_{subs} site and $2\pi^*$ orbital of O_2 molecule in the O_2 end-on adsorption on the Fe_4 site of FeN_4G-NP system (a). The schematic of this interaction is shown in (b). This bonding is formed in addition to the usual interaction between d_{xz} state of the Fe atom and $2\pi^*$ orbital of O_2 molecule. The O_2 adsorption configuration is shown in (c).

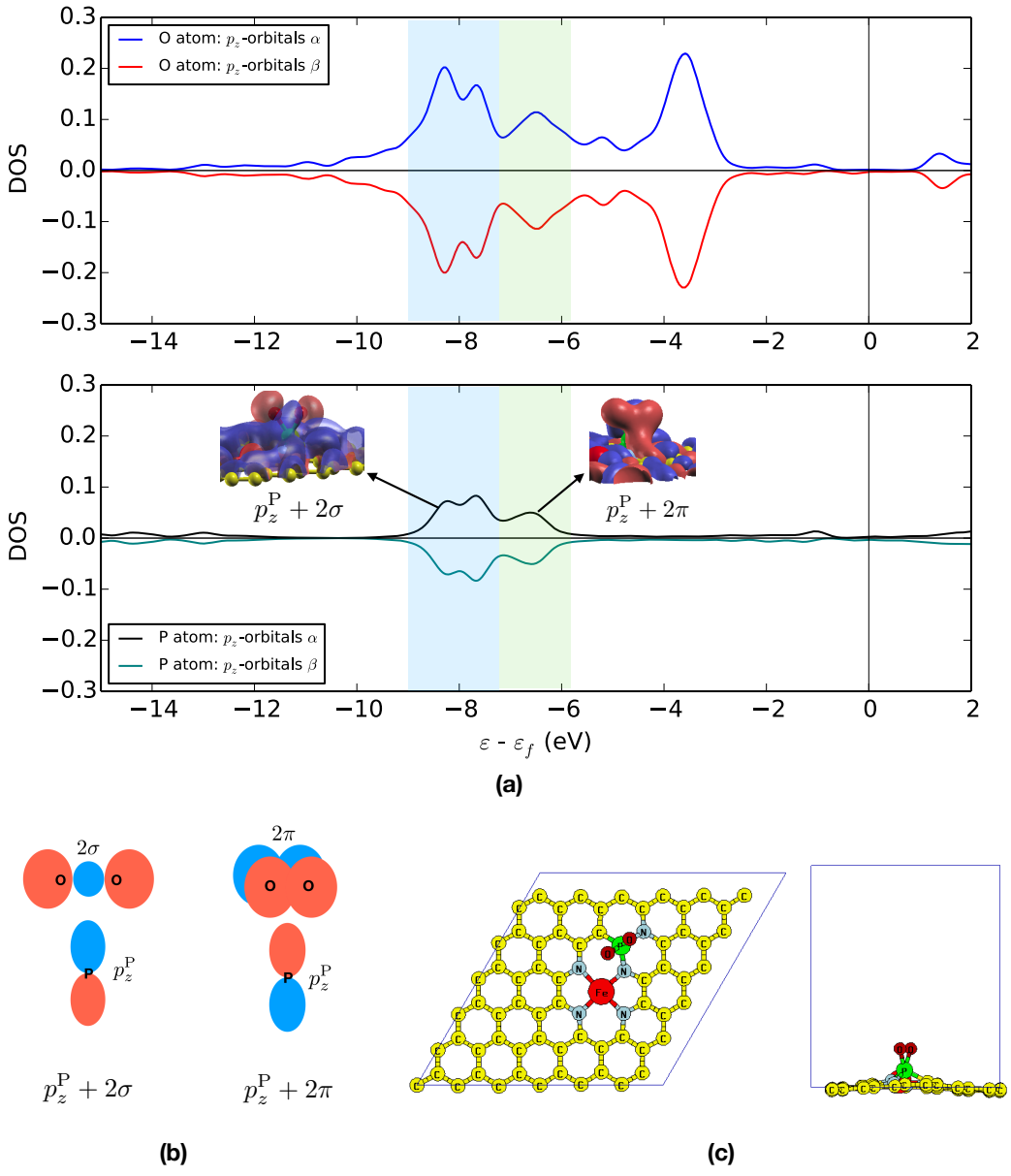

Figure S5: Local density of states (LDOS) of the interaction between localized p_z state of the P_{subs} site with 2σ and 2π orbitals of O_2 molecule in the O_2 side-on adsorption on the P_{subs} site of FeN_4G-NP system (a). The schematic of this interaction is shown in (b). The O_2 adsorption configuration is shown in (c).

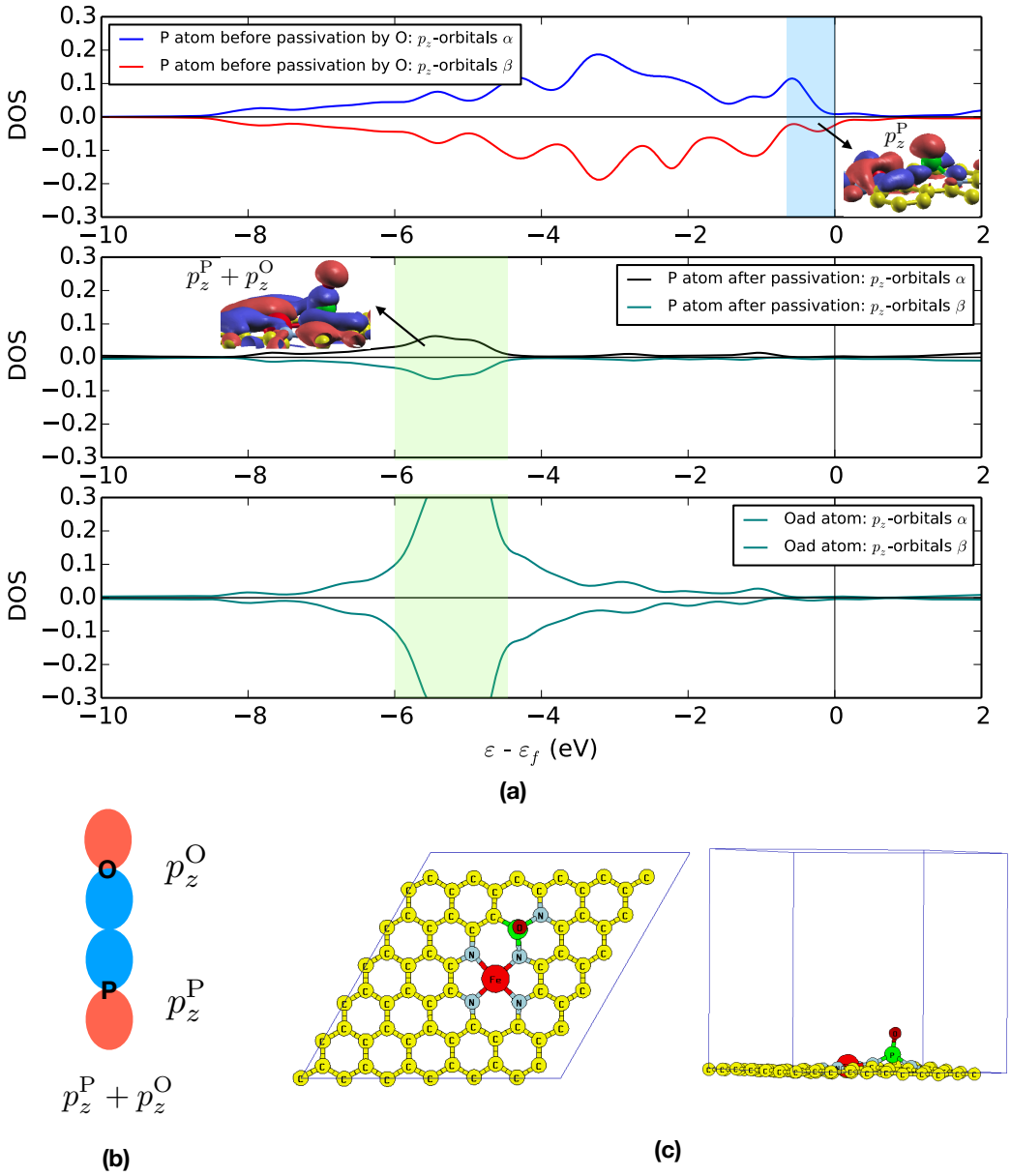

Figure S6: Local density of states (LDOS) of the interaction between localized p_z state of the P_{subs} site with p_z orbital of O atom in the FeN_4G-NP=O system (a). The schematic of this interaction is shown in (b). The FeN_4G-NP=O configuration is shown in (c).

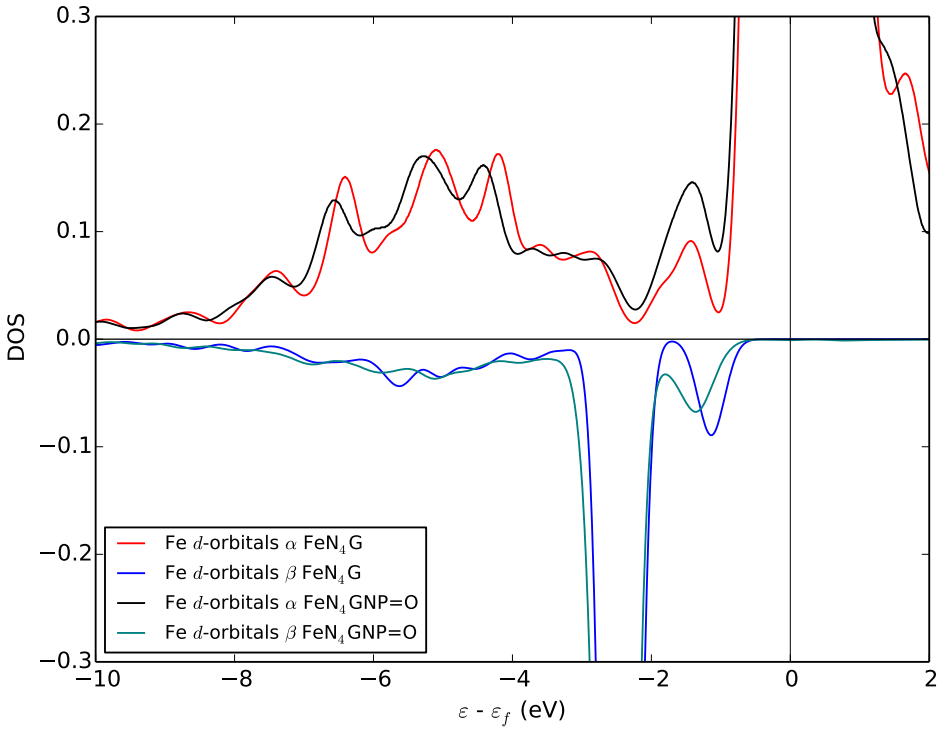

Figure S7: Local density of states (LDOS) of the d-states of FeN_4G-NP=O and undoped FeN_4G.

4 ORR profiles for associative and dissociate mechanism at $U = 1.23$ V

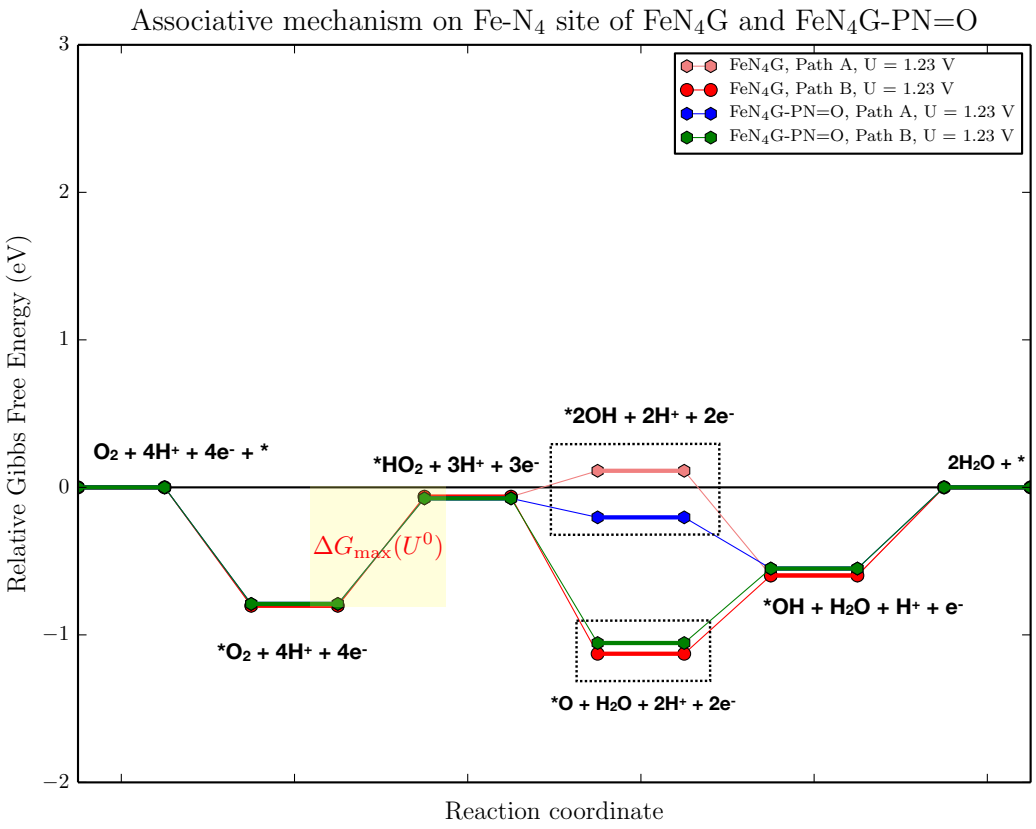

Figure S8: ORR energy profiles at $U = 1.23$ V for associative mechanism on the FeN_4 site of FeN_4G-NP=O system compared to that of undoped FeN_4G system.

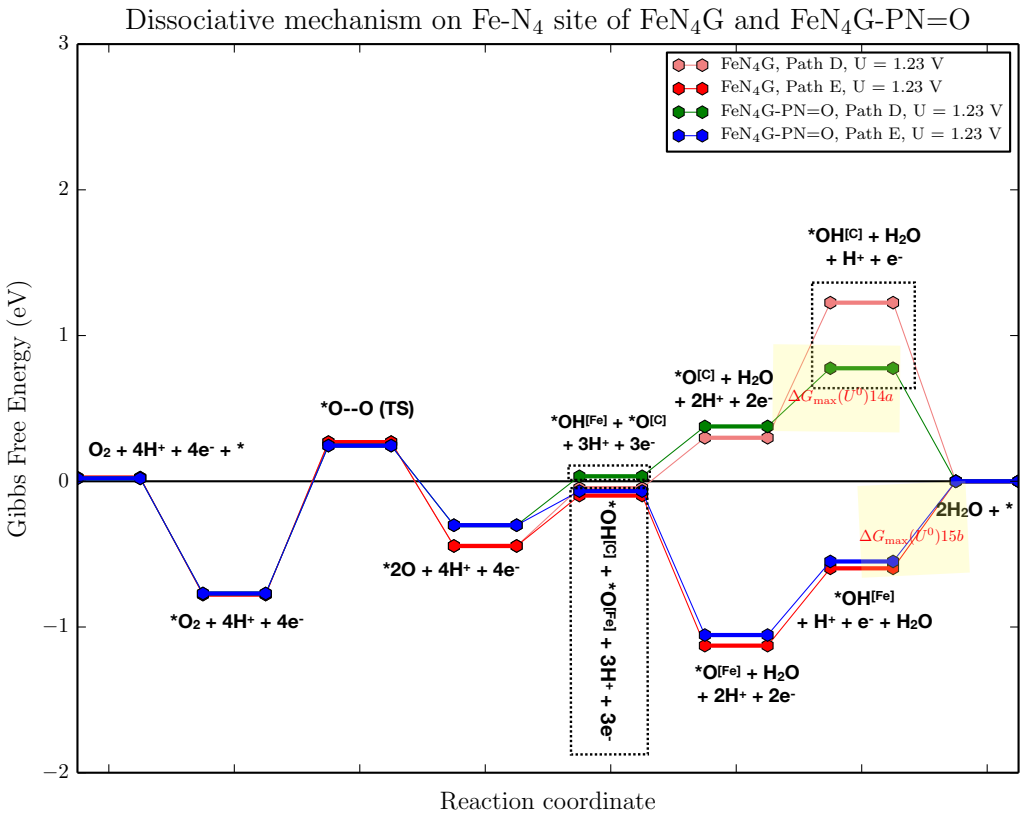

Figure S9: ORR energy profiles at $U = 1.23$ V for dissociative mechanism on the FeN_4 site of FeN_4G-NP=O system compared to that of undoped FeN_4G system.

5 Additional figures

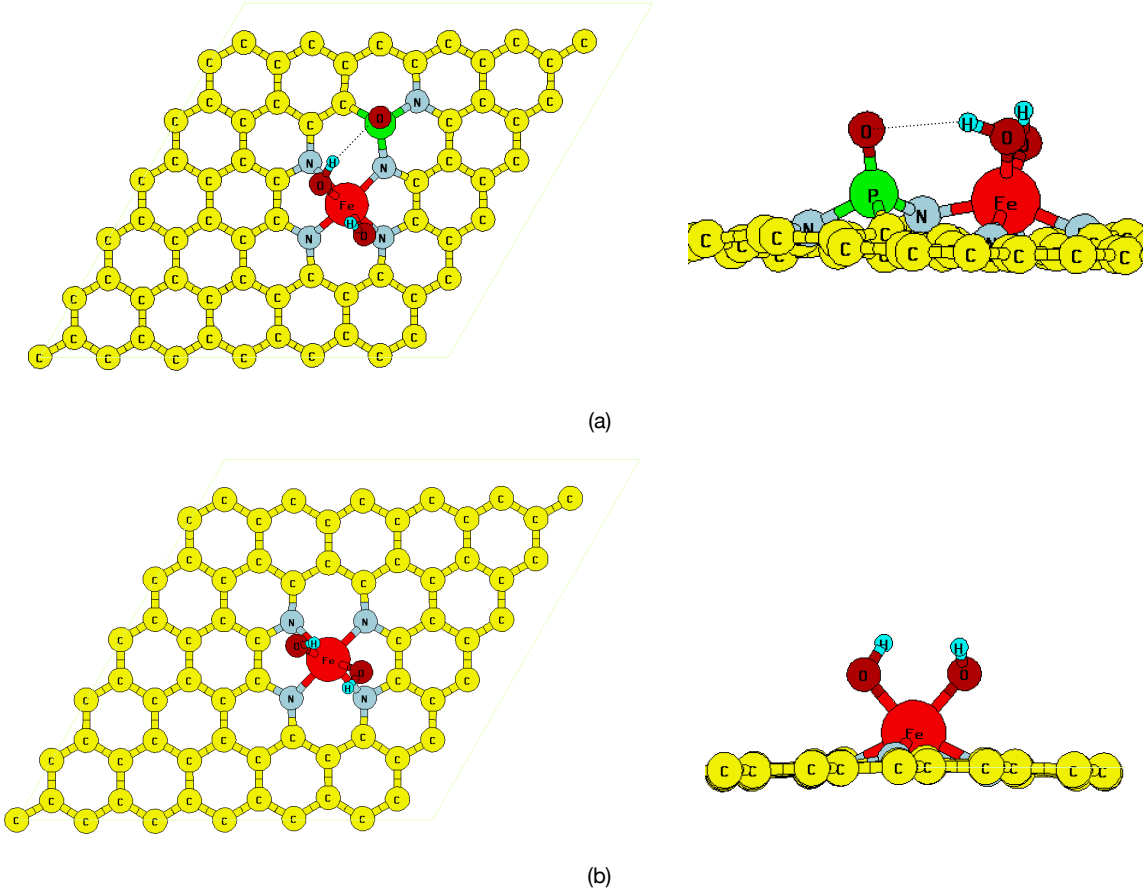

Figure S10: 2OH adsorption configurations on the FeN_4 site of FeN_4G-NP=O system (a) and undoped FeN_4G system (b).

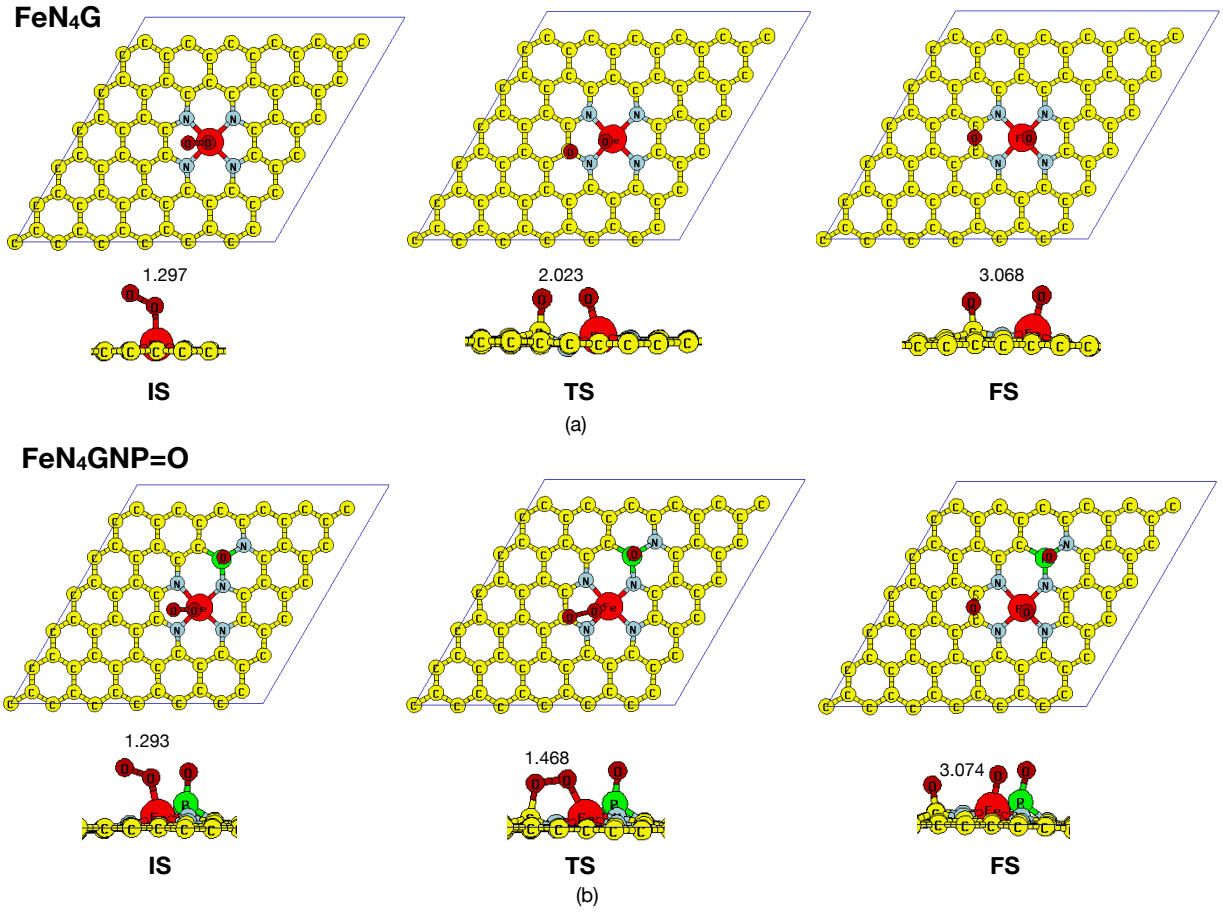

Figure S11: Initial state (IS), transition state (TS) and final state (FS) configurations of O_2 dissociation on the FeN_4 site of FeN_4G-NP=O (a) and undoped FeN_4G systems (b).

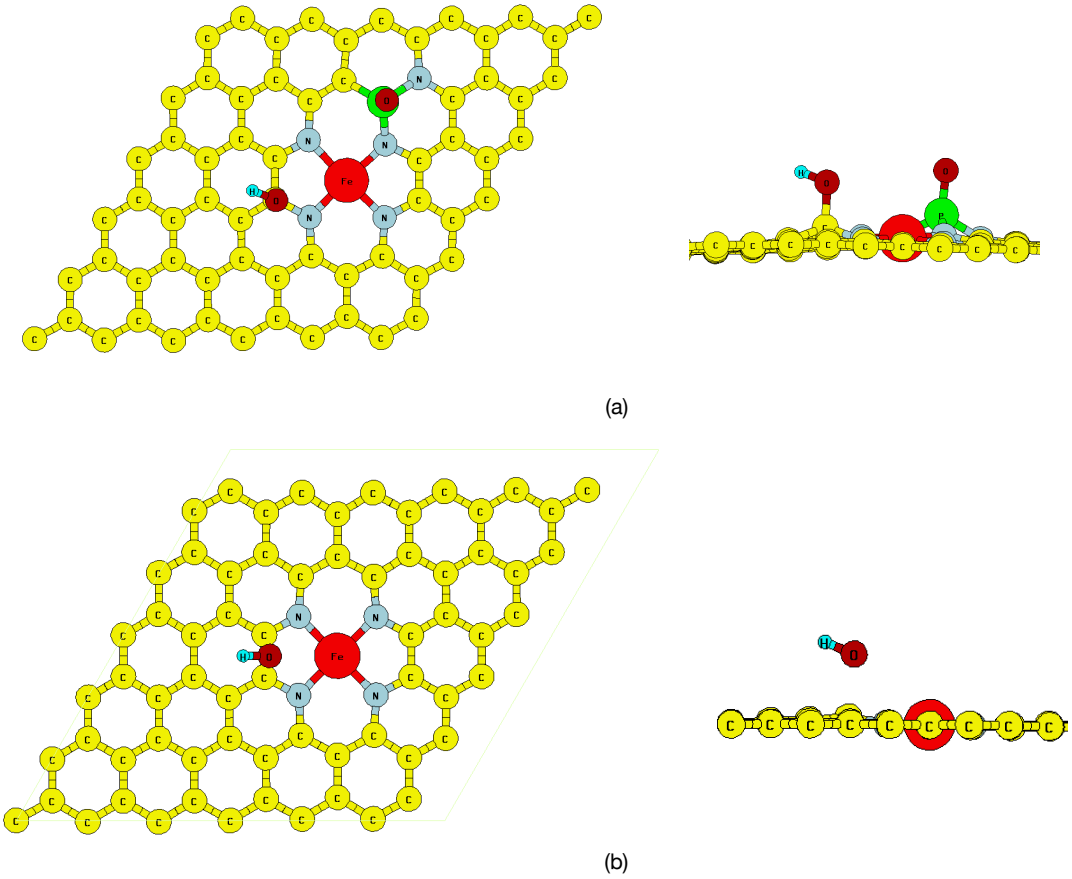

Figure S12: OH adsorption configurations on the C site of FeN_4G-NP=O system (a) and undoped FeN_4G system (b).

6 Adsorption energies of ORR related molecules

Table S1: Adsorption energies of HO_2, OH and H_2O on various active sites configurations.

Configuration	Active site	E_{ads} HO_2 (eV)	E_{ads} OH (eV)	E_{ads} H_2O (eV)
FeN_4G-NP=O	FeN_4	-2.33	-1.45	-0.77
	C-N	-	-0.18	-0.76
FeN_4G	FeN_4	-2.32	-1.50	-0.37
G-N_3PO	C-N	-1.44	-1.14	-0.49