Electronic Supplementary Information

First Principles Study of Oxygen Molecule Interaction with Graphitic Active Sites of Boron-doped Pyrolyzed Fe-N-C Catalyst

Apresio Kefin Fajrial[1,2], Adhitya Gandaryus Saputro[1,2]*, Mohammad Kemal Agusta[1,2], Nugraha[1,2], Febdian Rusydi[3], and Hermawan K. Dipojono[1,2]

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

*email address: ganda@tf.itb.ac.id

1 Relative energy of N/B atom location

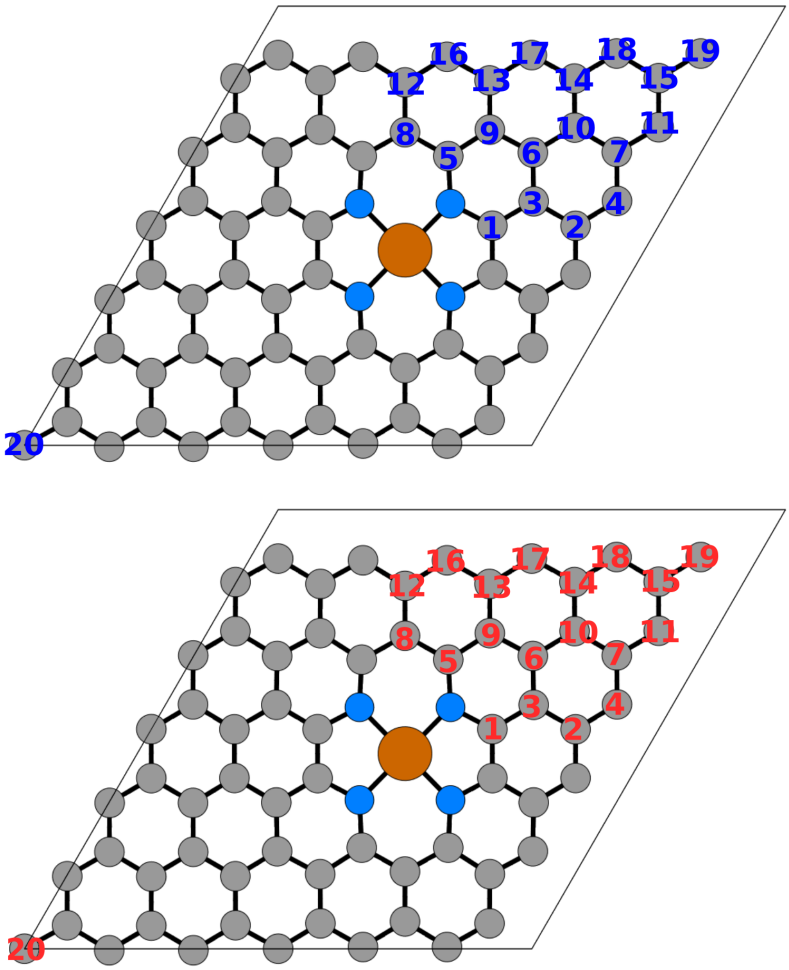


Figure S1: Possible location of N (top) or B (bottom) atom location on the FeN_4-embedded graphene

Table S1: Relative energies of substitutional N/B configurations and distances from N/B to the center of FeN_4 active site. The index of N/B atom refers to Fig. S1

Index of N	N–Fe(Å)	$E_{relative}$(eV)	Index of B	B–Fe(Å)	$E_{relative}$(eV)
1	2.6	0.50	1	2.6	0.38
2	5.0	0.02	2	5.0	2.07
3	4.0	0.10	3	4.0	1.95
4	6.3	0.06	4	6.3	2.07
5	3.0	0.94	5	3.0	0.00
6	4.7	0.02	6	4.7	1.15
7	6.8	0.03	7	6.8	2.04
8	3.4	0.16	8	3.4	0.84
9	4.3	0.22	9	4.3	1.03
10	6.1	0.10	10	6.1	2.03
11	8.2	0.04	11	8.2	1.36
12	4.9	0.28	12	4.9	0.92
13	5.6	0.17	13	5.6	1.83
14	7.0	0.10	14	7.0	1.95
15	8.9	0.00	15	8.9	1.30
16	5.8	0.14	16	5.8	1.77
17	6.8	0.10	17	6.8	1.93
18	8.4	0.09	18	8.4	1.94
19	8.2	0.09	19	8.2	1.29
20	12.4	0.09	20	12.4	1.21

2 Procedure to determine the most stable BN-FeN_4G configuration

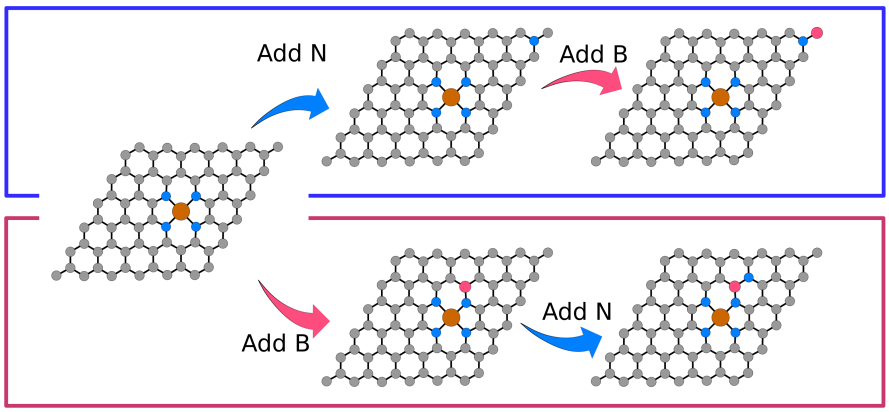
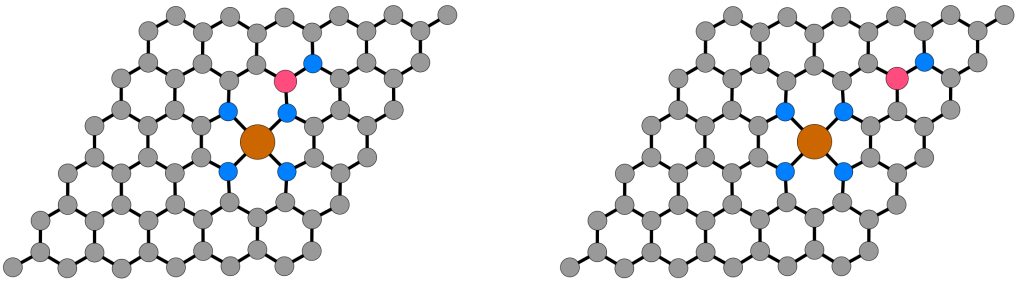


Figure S2: Steps to find the most stable BN-FeN_4G structure

In order to determine the most stable configuration of BN-FeN_4G structure, we follow the procedures in Fig. S2. We used two steps of substitutional atom addition. There are two possible procedures to determine the most stable configuration of B and N atom on the FeN_4G structure i.e locating the N atom first followed by B atom, and locating the B atom first followed by N atom which owns the lowest total energy. In the first procedure, we seek the location of N atom which possess the lowest energy compared to other location. Subsequently, we find the location of B atom in the FeN_4G with the presence of N atom resulting on the lowest total energy. While, in the second procedure, the order of substitutional atom addition is reversed that B atom first and then N atom. Then, we compare the structure of BN-FeN_4G from both procedures and determine the configuration with the lowest total energy.

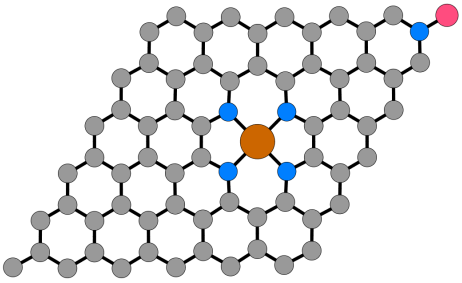
3 Relative energy of several possible BN-FeN_4G structures

Here we show some possible configurations of B an N atom around the FeN_4 active site. The relative energies among configurations are provided on Fig. S3. The configuration with 0.00 eV relative energy is the reference structure. Positive value of relative energy convey that the particular configuration posses higher energy compared to the reference structure. We also checked some BN-FeN_4G configurations which did not follow the rule in the scheme Fig. S2 i.e. the Fig. S3b and Fig. S3d and they still possess significantly higher total energies compared to the lowest BN-FeN_4G configuration.

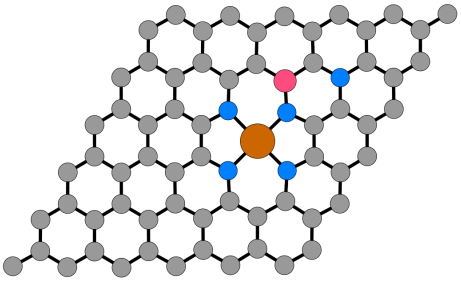


(a) 0.00 eV

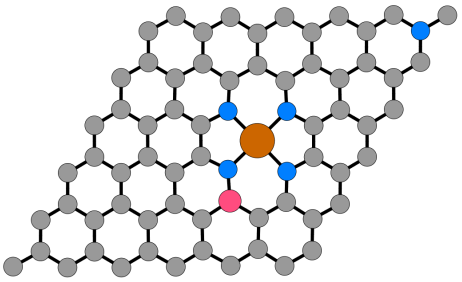
(b) 0.86 eV



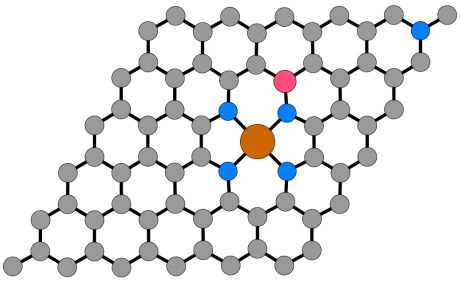
(c) 0.96 eV



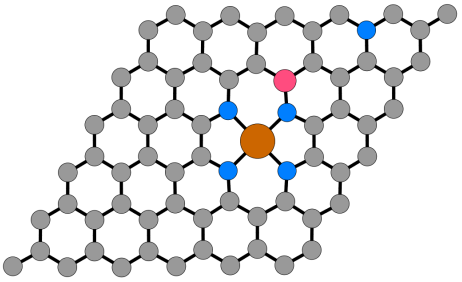
(d) 1.13 eV



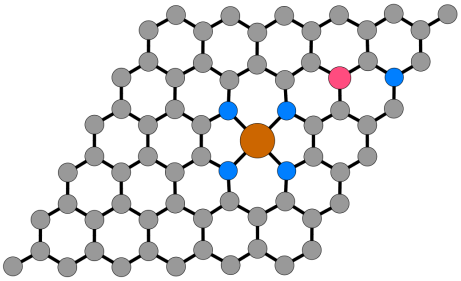
(e) 1.31 eV



(f) 1.39 eV



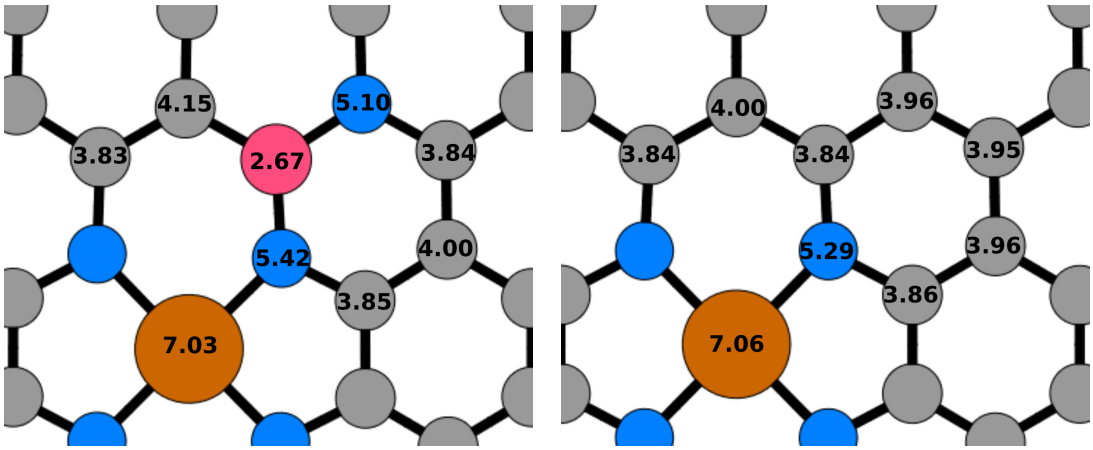
(g) 1.40 eV



(h) 2.08 eV

Figure S3: Several BN-FeN4G configurations. Value below the figure is energy of the structure relative to (a)

4 Löwdin charge distribution around B, N and FeN_4 active sites



(a) With BN (b) Without BN

Figure S4: Löwdin charge population of atoms around the neigbouring active sites with the presence of B and N (a), and the absence of B and N (b)

5 Adsorption of H_2O on the active sites of BN-FeN_4G

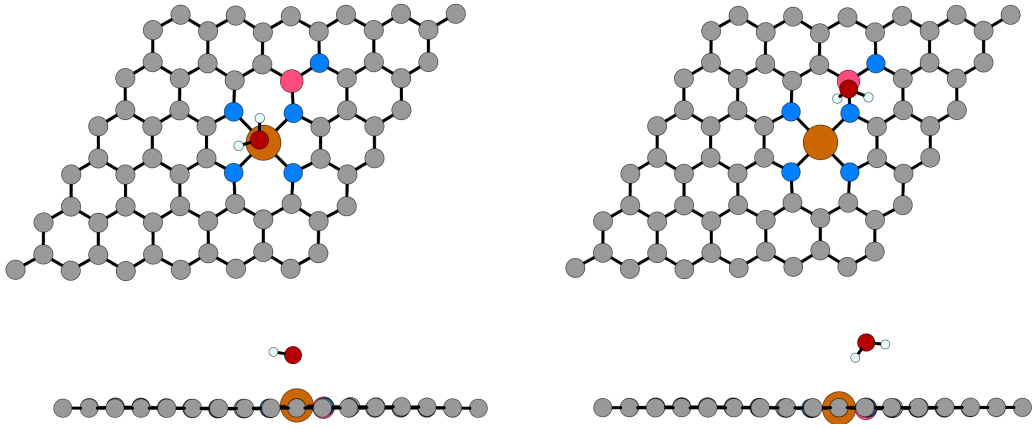


Figure S5: H_2O adsorption on Fe atom and B atom of BN-FeN_4G

Since FeN4 and B site can bind O_2 molecule quite strong, we have to check the possibility whether these sites might also bind the formed H_2O molecule (the final product of ORR) strongly which will result in active sites poisoning. Therefore, we checked the adsorption of H_2O molecule on the FeN_4 and B sites. This adsorption energy corresponds to the amount of energy needed to desorp the H_2O. The adsorption energy on top of Fe atom and top of B atom, which geometry can be seen in Fig. S5, are -0.37 eV and -0.17 eV, respectively. This value is much weaker than that of O_2 adsorption case. The adsorption distance of H_2O molecule is also quite large (O–Fe 2.360 Å; O–B 3.110 Å). This indicates that the interaction of BN-FeN_4G active site and H_2O molecule is quite weak. Therefore, the active site poisoning due to H_2O adsorption might not present on this system.