

BORON AND NITROGEN DOPANT ATOMS PRECISE TUNING (INCREMENT AND REDUCTION) OF CHARGE-TRANSFER RATES IN HYDROGENATED GRAPHENE

G.K. Sunnardianto^{1,2*}, F. Triawan², A.M. Aamer², S. Hastuty³, A.B.D. Nandiyanto⁴,
A.G. Abdullah⁵

¹Research Center for Chemistry, Indonesian Institute of Sciences (LIPI), Kawasan Puspitek Serpong, Tangerang Selatan, 15314, Indonesia

²Faculty of Engineering and Technology, Sampoerna University, Jl. Raya Pasar Minggu, Kav 16, Jakarta, Indonesia

³Department of Mechanical Engineering, Universitas Pertamina, Jl. Teuku Nyak Arief, Kebayoran Lama, Jakarta, Indonesia

⁴Departemen Kimia, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudi no 229, Bandung 40154, Indonesia

⁵Departemen Teknik Elektro, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudi no 229, Bandung 40154, Indonesia

*e-mail: gagus.ketut.sunnardianto@lipi.go.id

Abstract. Graphene is a new remarkable material for diverse applications, especially when grapheme is interacted with hydrogen. The charge-transfer rates (CTR) from hydrogen to graphene is substantial to determine the electronic properties. A new approach to increase and decreases the charge-transfer from hydrogen to graphene is proposed. By using density functional theory calculation method, the effect of B and N doping on the CTR of hydrogenated graphene is investigated. The results found that both of dopants (B and N) had opposite effect on the CTR of hydrogenated graphene. B doping increased CTR, while N doping decreased CTR from hydrogen to graphene. The research finding may provide a promising rule for quantitatively tuning and or controlling of CTR in hydrogenation graphene by atom dopant, which is potential importance for their use in electrochemical and energy-related application.

Keywords: charge-transfer rates (CTR), graphene, hydrogenation, coverage, dopant

1. Introduction

The Chemical functionalization is an attractive way to modify physical and chemical properties of graphene. The chemical inertness of graphene surface and the absence of band gap motivates researcher in modifying graphene by substituting dopant atom in order to improve the integration of graphene in electronic and chemical device application.

The most common dopant atom for carbon materials is Boron (B) and Nitrogen (N) [1]. It has been reported that B or N substitution in CNT has been widely studied experimentally and theoretically [2,3]. Not only in CNT, B and N doping in graphitic carbon materials also has been widely studied experimentally and theoretically [4,5]. Also, B and N doped graphene have been successful realized [6,7]. Experimental works show that the electrochemical

performance of B and N doped graphene is better than pristine graphene [8]. B and N can form the most stable defect and can be readily incorporated in graphene lattice [1,9]. Additionally, B and N doped graphene materials are highly promising materials for electronic, electrochemical applications, and transport properties [10, 11], such as energy storage [12], sensing [13] and capacitors [14].

Doping of graphene with N was realized experimentally [15,16] and has promising properties towards application in the field of electrochemical sensing [15], lithium-ion batteries [17], p-n junction [18] and fuel cells [19].

Hydrogen is a widely available element, an ideal partner for carbon atoms to make strong covalent [20] and the most broadly used as adsorbate to functionalize graphene [21]. Furthermore, hydrogen on graphene surface has been the subject of intense studies for hydrogen storage [22,23]. Hydrogenations of these doped graphene appear to be feasible route to have hydrogenated of doped graphene. The charge-transfer rate from hydrogen to graphene is substantial to determine the electronic properties of graphene for diverse applications. Therefore, how to tune the CTR from hydrogen to graphene is important to be revealed.

Recently, Sunnardianto et al. [24] succeeded to derive the rule to determine the charge-transfer rates (CTR) from hydrogen to graphene in wide range of coverage. The finding reveals that the CTR roughly shows a linear behavior from 0.22e for the dilute limit to 0.15e for the half-coverage limit [24]. The next step is how to control the CTR (increase and decrease of CTR) by dopant atom.

To the best of our knowledge, the impact of dopant (B and/or N atoms) on CTR of hydrogenated graphene has not been explored yet. In order to fundamentally understand how to tune and or control of CTR value in optimizing graphene for device application, a simple strategy to control and conveniently tune of CTR from hydrogen to graphene was proposed in this study. This study would give a tremendous impact on the design of doped graphene system from the electrochemical device application point of view. On the other hand, it would also open new ways on how to design and control CTR of hydrogenated doped graphene.

2. Materials and method

In this study, the arrangement of hydrogen atom randomly on B and N doped graphene were considered. At each coverage (H/C: 0.125, 0.25, 0.375), ten possible configurations of hydrogen arrangement were used. In this case, the effect of single dopant on the CTR of hydrogenated graphene was proposed. As for N doped graphene, three common C-N bonding configurations are normally obtained when doping nitrogen into the graphene lattice; pyridinic N, pyrrolic N, and graphitic N. Graphitic N is the substitution of carbon atom by nitrogen, pyridinic N is the substitution of carbon atom by nitrogen at the edge of vacancy. Experimentally observed pyridinic N type is energetically favorable for high concentration of N, but thermally unstable, while graphitic N type is the most energetically favorable than other N types doping for low concentration of N [25]. Since a single doping was used, so N-graphene in the form of graphitic N was considered.

The structure models used for simulation are graphene sheets consisting 47 carbon atoms in rectangular super cells (see Fig. 1). For low coverage of H adsorption, the most favorable H adsorption site is the nearest-neighbor position of the dopant site for B and N doped graphene and for larger H coverage the formation of dimers close to the dopant site is energetically favorable over hydrogenation [20]. In these simulations, we keep at least two or three of hydrogen atoms lie on the carbon atoms neighboring the substitution boron sites to know the effect of dopant to the CTR.

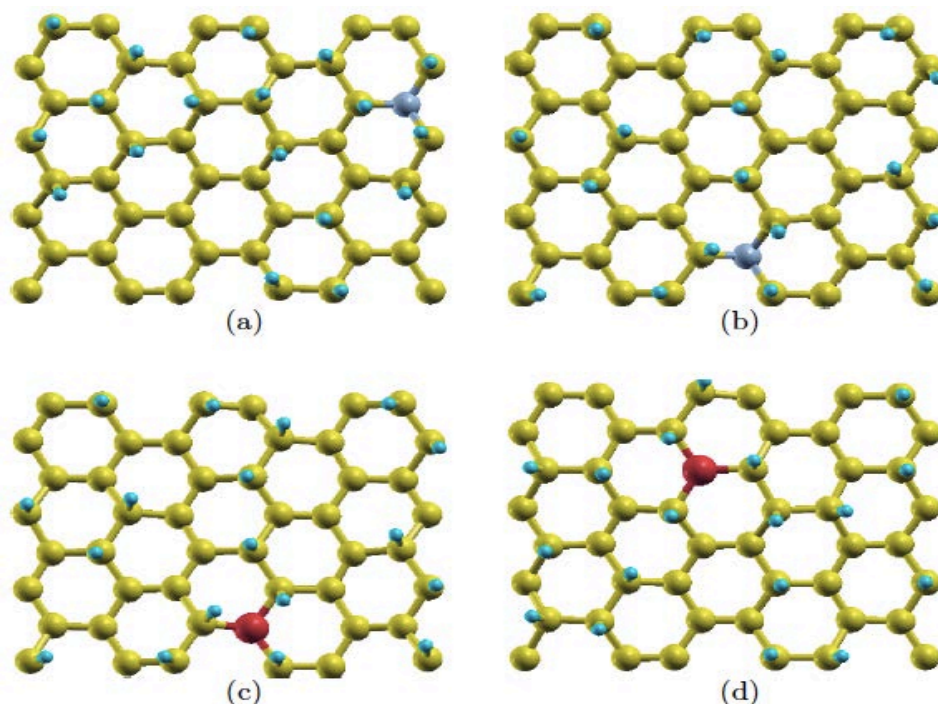


Fig. 1. The structures of N and B doped graphene in certain hydrogen coverage (H/C: 0.375). The upper is N doped graphene and the lower panel is B doped graphene. The yellow, blue, purple and red atoms denote carbon, hydrogen, nitrogen and boron, respectively

Calculations were done using density functional theory [25] implemented in the quantum espresso (QE) code [26, 27]. The local density approximation by the Perdew-Zunger parametrization was adopted [28]. The projector-augmented wave method and ultra-soft pseudo potential were used [29, 30]. The parameters for hydrogenated of doped graphene in a super cell were the energy cut off of 40 Ry for the plane wave expansion of the wave function and 400 Ry for the expansion of the augmented charge. The convergence criterion for the structural optimization was that the total absolute value of the inter-atomic force vector became less than 10^{-4} Ry/a.u. The distance between graphene planes was separated by 10 Å in order to avoid interaction between layers. Distribution of k-points on a mesh of 12x12x1 was selected via Monkhorst Pack scheme [31]. The distribution of the transferred charge was estimated by determining charge difference from the neutral value on each atom site of graphene. The local charge assigned at each atomic site was obtained by the Löwdin charge analysis [32].

3. Results and discussion

Reduction of CTR by nitrogen doping. We found that N doped graphene is energetically favorable than B doped graphene, this is in agreement with the previously calculation [1]. In this case, the N atom form covalent bonds with the C atom with bond length of C-N of 1.41 Å. If we compare it with bond length of C-C in pristine graphene which is around 1.42 Å, we could conclude that the N doped only a little bit distort the graphene lattice and N atom a little bit moves downward but still keeping the planar graphene structure. Once hydrogenation is introduced, the nitrogen atom moves more downward of 0.13 Å and hydrogenated carbon atom move upward of 0.37 Å with C-H bond length 1.15 Å. Since the C-H bond length a bit longer/weaker, the CTR from hydrogen atom to carbon atom in graphene decrease.

As seen in Fig. 2 and Table 1, we found CTR is around 0.1852e for low H coverage (represented by H/C = 0.125), when the more hydrogen are sequentially introduced into

N-graphene up to $H/C = 0.25$ (middle coverage), CTR decrease to be around $0.1727e$, after continuously H adsorbs on the N-graphene up to $H/C = 0.375$ (high coverage), CTR decrease to be around $0.1584e$. There are two conclusions based on the result. Firstly, substitution of N doping modulates CTR from hydrogen to grapheme. In this case, CTR per hydrogen decrease is about by $0.01e$ for low coverage and middle coverage and by $0.002 e/H$ for high coverage of adsorbed H. Secondly at the whole, in accordance with hydrogenation on pristine graphene, hydrogenated on N doped graphene also show CTR from hydrogen to N doped graphene decrease linearly with respect to increasing of hydrogen coverage.

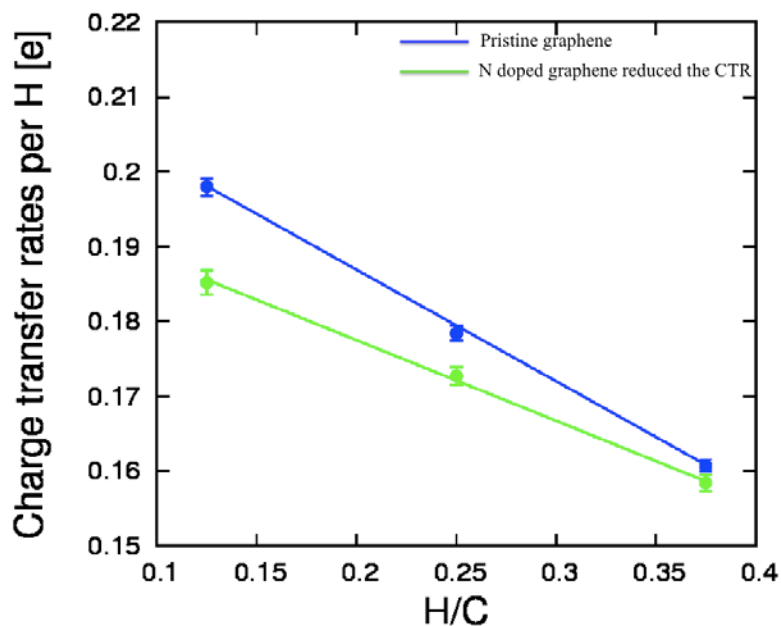


Fig. 2. The CTR of hydrogen on N doped graphene. For comparison, the data CTR for hydrogenation on pristine graphene is shown. A solid blue circle and solid green circle denote CTR of hydrogen on pristine graphene and N doped graphene, respectively

Table 1. The averaged CTR value (Av-CTR) of hydrogenation of N doped graphene in different coverage of H. The standard deviation of CTR (SD) coming from random arrangement is also shown

Materials	H/C	Av-CTR [e]	SD [e]
Graphene (47C+6H+N)	0.125	0.1852 ± 0.0016	0.0051
Graphene+(47C+12H+N)	0.25	0.1727 ± 0.0012	0.0038
Graphene+(47C+18H+N)	0.375	0.1584 ± 0.0011	0.0034

Enhancement of CTR by boron doping. As for B doped graphene, we found a B-C bond length before hydrogenation is around 1.49 \AA in consistent with previously calculation [20], while the nearest-neighbor of C-C bond length are slightly shortened of 1.40 \AA . After hydrogenation the B-C bond length weaker to be 1.52 \AA , Boron move upward of 0.42 \AA and hydrogenated carbon atom move upward of 0.52 \AA with the nearest C-H bond length B doping is around 1.14 \AA .

If we compare the C-H bond length on N doped graphene, the C-H bond length on B doped graphene is strengthened. It is indicated that CTR increase. Also compared with N doped, B atom induces a bigger lattice distortion in graphene system because the size of boron atom is larger than carbon so the presence of boron modifies the structure of graphene, while the size of N atom is close to the carbon.

As seen in Fig. 3 and Table 2, we found CTR is around $0.2133e$ for low H coverage

(represented by $H/C = 0.125$), when the more hydrogen are sequentially introduced into B-graphene up to $H/C = 0.25$ (middle coverage), CTR decrease to be around $0.1870e$, after continuously H adsorbs on the B-graphene up to $H/C = 0.375$ (high coverage), CTR decrease to be around $0.1703e$. As a result, we could conclude that first, substitution of B doping modulates CTR from hydrogen to graphene, in this case, CTR per hydrogen increase is about by $0.02e/H$ for low coverage and by $0.01e/H$ for middle coverage and high coverage of adsorbed H. Secondly at the whole, in accordance with hydrogenation on pristine graphene, hydrogenated on B doped graphene also show CTR from hydrogen to B doped graphene decrease linearly with respect to increasing of hydrogen coverage.

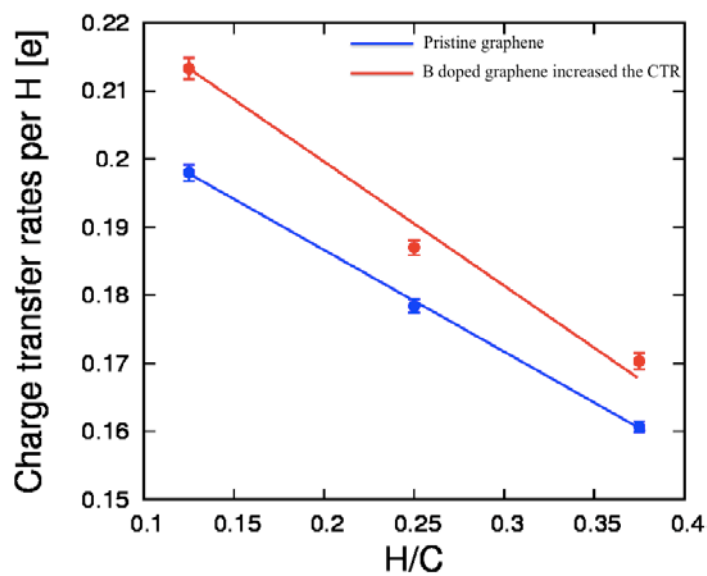


Fig. 3. The CTR of hydrogen on B- doped graphene. For comparison, CTR for hydrogenation on pristine graphene is shown. A solid blue circle and solid red circle denote CTR of hydrogen on pristine graphene and B- doped graphene, respectively

Table 2. The averaged CTR value (av-CTR) of hydrogenation of B doped graphene in different coverage of H. The standard deviation of CTR (SD) coming from random arrangement is also shown

Materials	H/C	Av-CTR [e]	SD [e]
Graphene (47C+6H+B)	0.125	0.2133 ± 0.0016	0.0049
Graphene+(47C+12H+B)	0.25	0.1870 ± 0.0011	0.0032
Graphene+(47C+18H+B)	0.375	0.1703 ± 0.0012	0.0038

The reduced and increased CTR by nitrogen and boron doping, which caused the different of electronic properties, would be important to meet the requirement of diverse engineering applications, such as in hydrogen storage application [22-24,33] and hydrogen molecule conversion system to NH_3 [34] effectively.

4. Conclusion

The CTR of H atoms on B and N doped graphene has been investigated and discussed based on the DFT calculations. We provided a feasible way on how to increase and decrease CTR from hydrogen to doped graphene by introducing dopant such as boron and nitrogen. B doping enhances CTR, while N doping reduces CTR. The presence of a single substitution boron atom increases the CTR from hydrogen to graphene by $0.02e/H$ for low coverage and by $0.01e/H$ for middle coverage and high coverage of adsorbed H. While the presence of a

single substitution nitrogen atom decreases the CTR from hydrogen to graphene by 0.01e for low and middle coverage and by 0.002 e/H for high coverage of adsorbed H. Those results indicated that the increment and reduction of CTR from hydrogen to graphene could be tuned by B and N substitutional dopant and its concentrations.

Acknowledgements. *The calculations were done in the computer centers of Faculty of Engineering and Technology, Sampoerna University and supported by supercomputer facilities of Graduate school of Engineering Science, Osaka University. GKS gratefully acknowledges to Prof. Koichi Kusakabe at Osaka University, Japan for his continuous support.*

References

- [1] Leenaerts O, Sahin H, Partoens B, Peeters FM. First-principles investigation of B- and N-doped fluorographene. *Phys. Rev. B*. 2013;88: 035434.
- [2] Han W, Bando Y, Kurashima K, Sato T. Boron-doped carbon nanotubes prepared through a substitution reaction. *Chemical Physics Letters*. 1999;299(5): 368-373.
- [3] Zhou YG, Zu XT, Gao F, Nie JL, Xiao HY. Adsorption of hydrogen on boron-doped graphene: A first-principles prediction. *Journal of Applied Physics*. 2009;105(1): 014309.
- [4] Kurita N. Molecular orbital calculations on lithium absorption in boron- or nitrogen-substituted disordered carbon. *Carbon*. 2000;38(1): 65-75.
- [5] Endo M, Hayashi T, Hong SH, Enoki T, Dresselhaus MS. Scanning tunneling microscope study of boron-doped highly oriented pyrolytic graphite. *Journal of Applied Physics*. 2001;90(11): 5670-5674.
- [6] Panchakarla LS, Subrahmanyam KS, Saha SK, Govindaraj A, Krishnamurthy HR, Waghmare UV, Rao CNR. Synthesis, structure, and properties of boron and nitrogen doped graphene. *Advanced Materials*. 2009;21(46): 4726-4730.
- [7] Liu H, Liu Y, Zhu D. Chemical doping of graphene. *J. Mater. Chem*. 2011;21: 3335-3345.
- [8] Wu ZS, Ren W, Xu L, Li F, Cheng HM. Doped graphene sheets as anode materials with superhigh rate and large capacity for lithium ion batteries, *ACS Nano*. 2011;5(7): 5463-5471.
- [9] Panchakarla LS, Subrahmanyam KS, Saha SK, Govindaraj A, Krishnamurthy HR, Waghmare UV, Rao CNR. Synthesis, structure, and properties of boron- and nitrogen-doped graphene. *Advanced Materials* 2009;21(46): 4726-4730.
- [10] Carroll DL, Redlich P, Blase X, Charlier JC, Curran S, Ajayan PM, Roth S, Rühle M. Effects of nanodomain formation on the electronic structure of doped carbon nanotubes. *Phys. Rev. Lett*. 1998;81: 2332-2335.
- [11] Endo M, Hayashi T, Hong SH, Enoki T, Dresselhaus MS. Scanning tunneling microscope study of boron-doped highly oriented pyrolytic graphite. *Journal of Applied Physics*. 2001;90(11): 5670-5674.
- [12] Firlej L, Roszak S, Kuchta B, Pfeifer P, Wexler C. Enhanced hydrogen adsorption in boron substituted carbon nanopores. *The Journal of Chemical Physics*. 2009;131(16): 164702.
- [13] Lazar P, Zboril R, Pumera M, Otyepka M. Chemical nature of boron and nitrogen dopant atoms in graphene strongly influences its electronic properties. *Phys. Chem. Chem. Phys*. 2014;16: 14231-14235.
- [14] Endo M, Kim C, Karaki T, Tamaki T, Nishimura Y, Matthews M, Brown SDM, Dresselhaus MS. Structural analysis of the b-doped mesophase pitch-based graphite fibers by raman spectroscopy. *Phys. Rev. B*. 1998;58: 8991-8996.
- [15] Wang X, Li X, Zhang L, Yoon Y, Weber PK, Wang H, Guo J, Dai H. N-doping of graphene through electrothermal reactions with ammonia. *Science*. 2009;324(5928): 768-771.

- [16] Zhao L, He R, Rim KT, Schiros T, Kim KS, Zhou H, Gutiérrez C, Chockalingam SP, Arguello CJ, Pálová L, Nordlund D, Hybertsen MS, Reichman DR, Heinz TF, Kim P, Pinczuk A, Flynn GW, Pasupathy AN. Visualizing individual nitrogen dopants in monolayer graphene. *Science*. 2011;333(6045): 999-1003.
- [17] Reddy ALM, Srivastava A, Gowda SR, Gullapalli H, Dubey M, Ajayan PM. Synthesis of nitrogen-doped graphene films for lithium battery application. *ACS Nano*. 2010;4(11): 6337-6342.
- [18] Cheianov VV, Fal'ko V, Altshuler BL. The focusing of electron flow and a veselago lens in graphene p-n junctions. *Science*. 2007;315(5816): 1252-1255.
- [19] Qu L, Liu Y, Baek JB, Dai L. Nitrogen-doped graphene as efficient metal-free electrocatalyst for oxygen reduction in fuel cells. *ACS Nano*. 2010;4(3): 1321-1326.
- [20] Pizzochero M, Leenaerts O, Partoens B, Martinazzo R, Peeters FM. Hydrogen adsorption on nitrogen and boron doped graphene. *Journal of Physics: Condensed Matter*. 2015;27(42): 425502.
- [21] Elias C, Nair RR, Mohiuddin TMG, Morozov SV, Blake P, Halsall MP, Ferrari AC, Boukhvalov DW, Katsnelson MI, Geim AK, Novoselov KS. Control of graphene's properties by reversible hydrogenation: Evidence for graphene. *Science*. 2009;323(5914): 610-613.
- [22] Sunnardianto GK, Maruyama I, Kusakabe K. Storing-hydrogen processes on graphene activated by atomic-vacancies. *Int. J. Hydrogen Energy* 2017;42(37): 23691-23697
- [23] Sunnardianto GK, Maruyama I, Kusakabe K. Dissociation chemisorption pathways of H₂ molecule on graphene activated by a hydrogenated mono-vacancy V₁₁. *Adv. Sci. Eng. Med*. 2016;8(6): 421-426.
- [24] Sunnardianto GK, Maruyama I, Kusakabe K. Systematic study of the effect of H adsorption on the electron transfer rate in graphene. *J. Comput. Theor. Nanosci*. 2016;13(8): 4883-4887
- [25] Martin RM. *Electronic Structure, Basic Theory, and Practical Methods*. Cambridge; 2004.
- [26] Kresse G, Hafner J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B*. 1993;47: 558-561.
- [27] Giannozzi P, Baroni S, Bonini N, Calandra M, Car R, Cavazzoni C, Ceresoli D, Chiarotti GL, Cococcioni M, Dabo I, Corso AD, de Gironcoli S, Fabris S, Fratesi G, Gebauer R, Gerstmann U, Gougoussis C, Kokalj A, Lazzeri M, Martin-Samos L, Marzari N, Mauri F, Mazzarello R, Paolini S, Pasquarello A, Paulatto L, Sbraccia C, Scandolo S, Sclauzero G, Seitsonen AP, Smogunov A, Umari P, Wentzcovitch RM. Quantum espresso: a modular and open-source software project for quantum simulations of materials. *Journal of Physics: Condensed Matter*. 2009;21(39): 395502.
- [28] Perdew JP, Zunger A. Self-interaction correction to density-functional approximations for many-electron systems. *Phys. Rev. B*. 1981;23: 5048-5079.
- [29] Blöchl PE. Projector augmented-wave method. *Phys. Rev. B*. 1994;50: 17953-17979.
- [30] Vanderbilt D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Phys. Rev. B*. 1990;41: 7892-7895.
- [31] Monkhorst HJ, Pack JD. Special points for brillouin-zone integrations. *Phys. Rev. B*. 1977;16: 1748.
- [32] Sanchez-Portal D, Artacho E, Soler JM. Projection of plane-wave calculations into atomic orbitals. *Solid State Communications*. 1995;95(10): 685-690.
- [33] Sunnardianto GK, Larasati IA, Triawan F, Aamer MA. Effect of charge on graphene vacancy for hydrogen storage application. *MATEC Web Conf*. 2018;197: 04001.
- [34] Aziz M, Juangsa FB, Triawan F, Nandiyanto ABD, Abdullah AG. Integrated Nitrogen Production and Conversion of Hydrogen to Ammonia. *Chemical Engineering Transactions* 2018;70: 571-576.