Dimer-hydrogen adsorption process on borophene β_{12} surfaces for hydrogen storage application

Anwar Husen Sadili, Silvia Aprilia Qotrunnada, Artoto Arkundato, et al.

View Online

Export Citation

Dimer-Hydrogen Adsorption Process on Borophene β_{12} Surfaces for Hydrogen Storage Application

Anwar Husen Sadili[1], Silvia Aprilia Qotrunnada[1], Artoto Arkundato[1], Agung Tjahjo Nugroho[1], Yudi Aris Sulistiyo[1], Muhammad Yusrul Hanna[2], Gagus Ketut Sunnardiarto[2, a)]

[1]*Faculty of Mathematics and Natural Sciences, University of Jember, Jl. Kalimantan Tegalboto No.37, Sumbersari, Jember, Jawa Timur, 68121, Indonesia*
[2]*Research Center for Physics, National Research and Innovation Agency (BRIN), South Tangerang, 15314, Indonesia*

a)   Corresponding author: gagu001@brin.go.id

Abstract.   Based on density functional theory, we investigate the interaction of a hydrogen molecule in a borophene surface. The hydrogen molecule is shown to dissociate producing the most stable dimer configuration of hydrogenated borophene. The minimum energy pathway shows that the most stable configuration of dimer-hydrogenated borophene is para configuration, which hydrogen molecule dissociation to be exothermic with energy barrier of 0.97 eV, exists along the reaction pathways and hydrogen molecule desorption from borophene surface, to be endothermic. The study reveals the mechanism of dimer-hydrogenation process for hydrogen storage application.

INTRODUCTION

Energy is a very important component for human's daily life activities. Energy sources in the world that used by humans are still dominated by fossil energy such as oil, gas, and coal and only a small fraction comes from renewable energy sources [1]. The rapid development of technology causes humans to use conventional energy sources (fossil fuels) excessively without paying attention to the environmental impacts they may cause. Air pollution and global warming are the negative impact of exploited fossil fuels [2]. The combustion of fossil fuel causes global warming and air pollution due to the increased in CO_2 emissions [3]. The depletion of fossil energy sources [4] and the climate change led to the use of alternative energy.

Hydrogen (H_2) is one of the promising alternative energy to be used as an clean energy sources. The characteristics of hydrogen energy are green, low carbon, and sustainable [5]. Hydrogen can be produced easily from water by several methods, including water thermolysis, water electrolysis, thermochemical water splitting, and photocatalytic water splitting, furthermore there are several hydrogen production technologies based on biomass [6]. Although hydrogen technology has promising prospects, there are several challenges that need to be faced to realize a large-scale use of hydrogen technology such as production cost, infrastructure investments, and transport & distribution (safety consideration) [7]. Building an efficient hydrogen storage becoming a big deal challenge. The material for storing hydrogen has several requirements such as low cost production, low weight, and being easy to synthesize [8], and should act as reversible hydrogen storage that may undergo rapid adsorption and desorption [9].

Recently, a new two-dimensional (2D) nanomaterials called borophene that consist a single layer of boron atom has been synthesized on a silver substrate (Ag (111)) under ultrahigh-vacuum [10]. Two-dimensional (2D) nanomaterials have a potential for gas sensing applications because of physical and chemical gas adsorption capabilities and high surface ratio [11]. The differences among methods and substrate that used for synthesize a borophene, make it has several phases. The four phases of borophene are β_{12}, 2-Pmmn, honeycomb phases, and χ_3 [12]. Recent study due to the stability of borophene for β_{12}, χ_3 and stripped borophene phases shows that χ_3 and β_{12} are dynamically, mechanically and thermodynamically stable [13]. A first principles study of borophene as hydrogen storage shows a weak hydrogen molecule adsorption over pristine borophene and several methods that

may be used to enhance the hydrogen molecule adsorption over pristine borophene are a metal decoration such as Li, Na, and Ca and variation of borophene point defects [14]. An investigation of borophene with Pmmn phase for the hydrogen storage capability that perform by standard and van der Waals-corrected density functional theory (DFT) calculations shows that a pristine Pmmn8 sheet is not suited for hydrogen storage applications [15]. Ti-decorated borophene χ_3 shows a high capacity of hydrogen storage with a gravimetric density of 15.065 wt% and may perform a reversible adsorption-desorption reaction [16]. The adsorption process of hydrogen molecules on borophene β_{12} shows that hydrogen molecules is dissociated into 2 hydrogen atoms then chemisorbed on borophene β_{12} [17].

The aim in this study is to know the mechanism of dissociative-chemisorption of dimer-hydrogenated borophene By investigating three dimer hydrogen configurations (ortho, meta and para) on borophene surfaces using DFT calculations. The method in this study might similar to the previous research by Liu, *et al* [17], However, we only focus on the process of dissociative-chemisorption of dimer hydrogenated borophene to observe the reaction pathway, its energy barrier and whether the reaction occurs endothermically or exothermically.

METHOD

The optimization process was performed using Quantum espresso (QE) [18] software that implemented a density functional theory [19]. The projector-augmented-wave method and the ultra-soft pseudo potential were used in the simulation [20]. The convergence criterion for the structural optimization was met when the total energy became less than 10^{-5} Ry and the total absolute value of the interatomic force vector became less than 10^{-4} Ry/a.u. The structure models for simulation were borophene consists of 14 boron atoms with β_{12} phases. We used nudged elastic band (NEB) [21] method to investigate the reaction pathways of hydrogen molecule adsorption-desorption process on the borophene β_{12} surfaces and to calculate the activation energy barrier.

In this study, before considering dimer-hydrogen adsorption, monomer hydrogen was also investigated to determine the active site (hollow, top and bridge site) as shown in Figure 1. Once the most stable active site is reached, the dimer- hydrogen structures (ortho, meta and para) were constructed. The configuration with the lowest energy was the most stable one. The reaction pathways of the hydrogen molecule adsorption-desorption process on the borophene β_{12} surfaces were performed by optimizing the initial state configuration as the condition before hydrogen atoms adsorbed on the borophene β_{12} surfaces and 3 different configurations (ortho, meta, and para) as condition after hydrogen atoms adsorbed on the borophene β_{12} surfaces. The activation energy barrier was obtained through the energy difference between initial state and transition state, which described the minimum energy reaction pathway of the hydrogen molecules adsorption-desorption process on the borophene β_{12} surfaces.
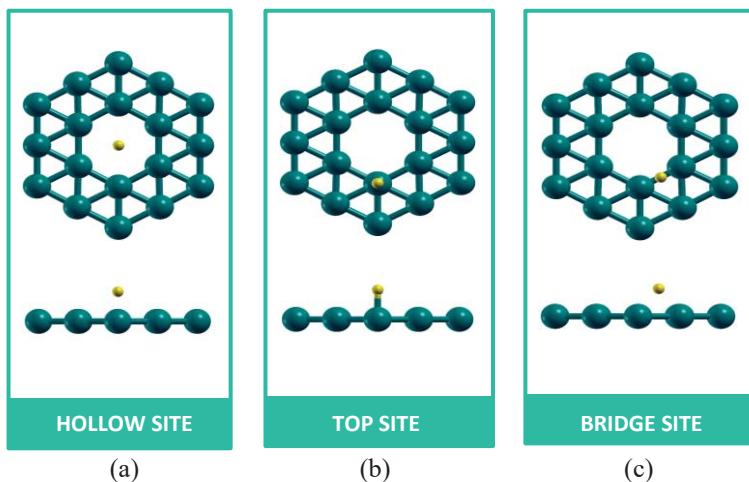

HOLLOW SITE	TOP SITE	BRIDGE SITE
(a)	(b)	(c)

FIGURE 1. The monomer hydrogenation configurations on the borophene β_{12} surfaces were (a) hollow site, (b) top site, and (c) bridge (top=top view, bottom=side view, green atoms were boron atoms and yellow atoms were hydrogen atoms)
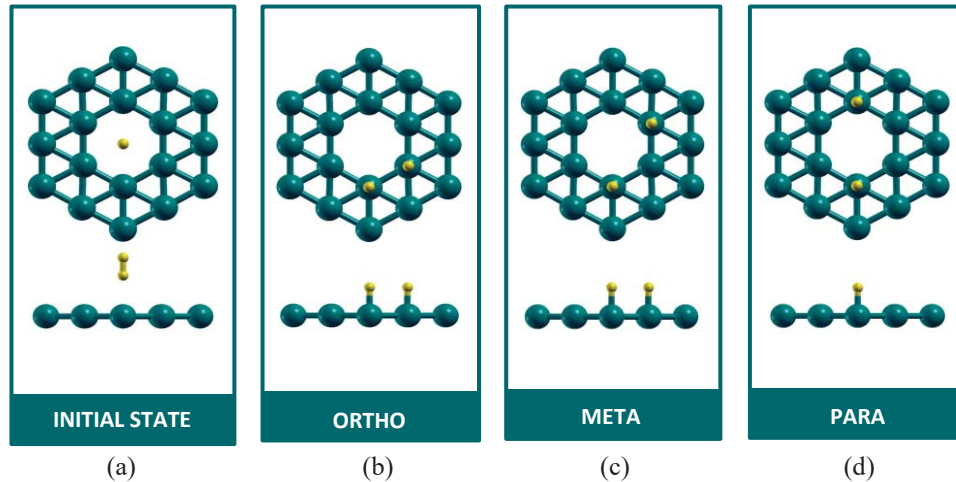
FIGURE 2. The hydrogen dimer configurations on the borophene β_{12} surfaces were (a) initial state, where hydrogen molecule above the borophene surface, (b) ortho, (c) meta, and (d) para (top=top view, bottom=side view, green atoms were boron atoms and yellow atoms were hydrogen atoms)

RESULT

Optimization of the Hydrogen Monomer Configuration on Borophene β_{12} Surfaces

Optimization of the adsorption process (chemisorption) of monomer hydrogen on the borophene β_{12} surfaces has been studied by observing three different locations of monomer hydrogen. The monomer hydrogen configuration was related to the possible position of the hydrogen atom adsorbed on the borophene β_{12} surfaces. This study used three different locations that is hollow site, top site, and bridge site. The hollow site configuration is a configuration where the hydrogen is located above the hollow site of the borophene β_{12}'s vacancy atom (defect) as shown in Figure 1.a. The top site configuration is a configuration where the position of the hydrogen atom is located on one of the borophene β_{12}'s boron atoms as shown in Figure 1.b. The bridge configuration is a configuration where the hydrogen atom is located on the bridge site (covalent bonds of the borophene β_{12}'s boron atoms) as shown in Figure 1.c. The optimization structure would be identified through calculating the total energy.

Figure 3 shows a graph of the total energy value for each configuration during the structural optimization simulation process. The total energy graph shows a downward curve trend that indicated the energy of the system was decreased, then along with the increasing of optimization step number, the graph shows that the energy of the system is convergent that was indicated by a horizontal curve.
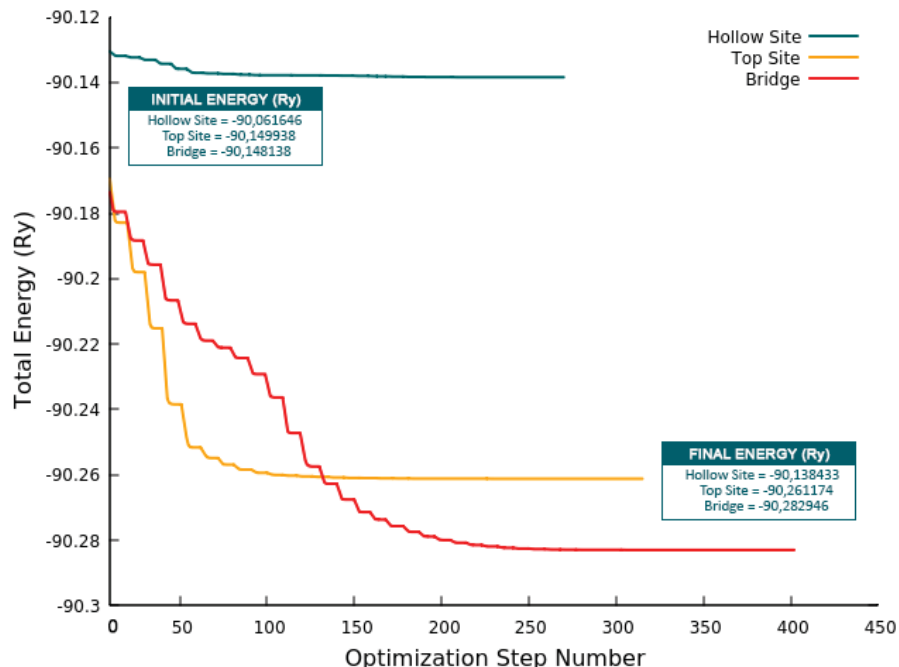
FIGURE 3. Total energy of monomer hydrogenation

The most stable configuration of monomer hydrogen on the borophene β_{12} surfaces was obtained by comparing the total energy value of each configuration. The configuration with the lowest total energy is the most stable configuration. The comparison of total energy of monomer hydrogen configurations on the borophene β_{12} surfaces is shown in table 1.

TABLE 1. Total energy of monomer hydrogen configurations with different locations (hollow, top and bridge)

No	Configuration	Final Total Energy (Ry)
1	Hollow Site	-90,138433
2	Top Site	-90,261174
3	Bridge	-90,282946

Table 1 shows that the bridge configuration has the lowest total final energy value of -90.282946 Ry, followed by the top site configuration (-90.261174 Ry), and the hollow site configuration (-90.138433 Ry). This result shows that the hollow site configuration was less stable compared to other configurations according to the total energy. The result indicated that the monomer adsorption process on the borophene β_{12} surfaces with a stable condition has possibility in the form of bridge and top site configurations at the initial state. Although, the initial state is in the bridge site, the borophene will move to the top site of boron after optimization. Therefore, we consider top site of dimer hydrogen adsorption on the borophene surface.

Optimization of the Hydrogen Dimer Configuration on Borophene β_{12} Surfaces

The borophene β_{12} surfaces might adsorb hydrogen molecules in atomic form instead of molecular form (dissociative chemisorption). The adsorption process of dimer hydrogenationon borophene β_{12} surfaces has been studied by observing of three different position of dimer hydrogen. The configuration before the hydrogen atom adsorbed was initial state configuration that would be use for initial state of PES calculation as shown in Figure 2.a. The configuration after the hydrogen atoms adsorbed were ortho, meta, and para configurations which are shown in Figure 2b, 2c and 2d, respectively.

Figure 4 shows a graph of the total energy value for each configuration during the structure optimization simulation process. The graph shows a similar pattern in which at the beginning of the simulation there was a

downward curve trend that indicated the energy of the system was decreased, then the graph shows that the energy of system is getting convergent (indicated by a horizontal curve) along with the increasing of optimization step number. The para configuration has the fastest optimization times and the lowest total energy among other after the hydrogen atoms adsorbed on the borophene β_{12} surfaces, followed by meta, and ortho configurations.
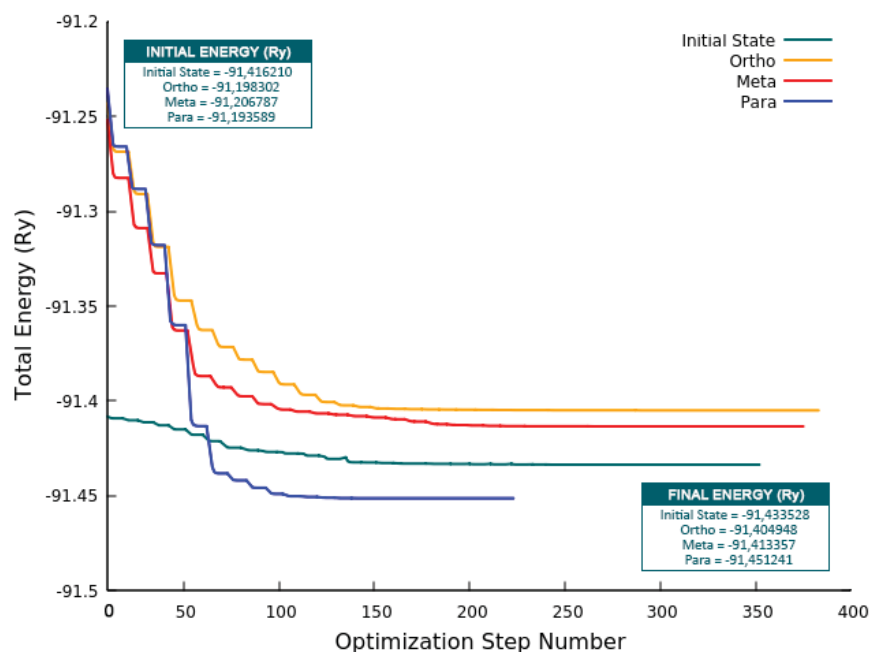

INITIAL ENERGY (Ry)
Initial State = -91,416210
Ortho = -91,198302
Meta = -91,206787
Para = -91,193589

FINAL ENERGY (Ry)
Initial State = -91,433528
Ortho = -91,404948
Meta = -91,413357
Para = -91,451241

FIGURE 4. Total energy of dimer hydrogenation

The most stable configuration of dimer hydrogen on the borophene β_{12} surfaces was obtained by comparing the total energy value. The most stable configuration has the lowest total energy among other configurations. The total energy of dimer hydrogenation on the borophene β_{12} surfaces is shown in table 2.

TABLE 2. Total energy of dimer hydrogenation with different configuration

No	Configuration	Total Energy (Ry)
1	Initial State	-91,433528
2	Ortho	-91,404948
3	Meta	-91,413357
4	Para	-91,451242

Table 2 shows that the para configuration has the lowest energy value (-91.451242 Ry), and then followed by the meta configuration (-91.413357 Ry), and the ortho configuration (- 91.404948 Ry). This result indicates that the ortho configuration was less stable compared to other after the hydrogen atoms adsorbed on the borophene β_{12} surfaces. The adsorption of dimer hydrogen on the borophene β_{12} surfaces with a stable condition has possibility in the form of para configuration. Thus, we consider the minimum energy pathways of para configuration as a priority mechanism of dissociative-chemisorption of hydrogen molecule on the borophene surface and showing that the para configuration would be easily exist.

Potential Energy Surface (PES) for Para Scheme

PES is a graph that can describe the energy of a system during a chemical reaction process from a reactant to produce a product. The dissociation process of hydrogen molecules and adsorption process of hydrogen atoms on the borophene β_{12} surfaces was observed with dimer-para configurations on the borophene β_{12} surfaces. PES required an initial condition (reactant) and final condition (product), therefore the hydrogen adsorption process on the borophene β_{12} surfaces will be carried out by optimizing the initial state configuration as the condition before

hydrogen atoms adsorbed on the borophene β_{12} surfaces and dimer- para as condition after hydrogen atoms adsorbed on the borophene β_{12} surfaces (final state).
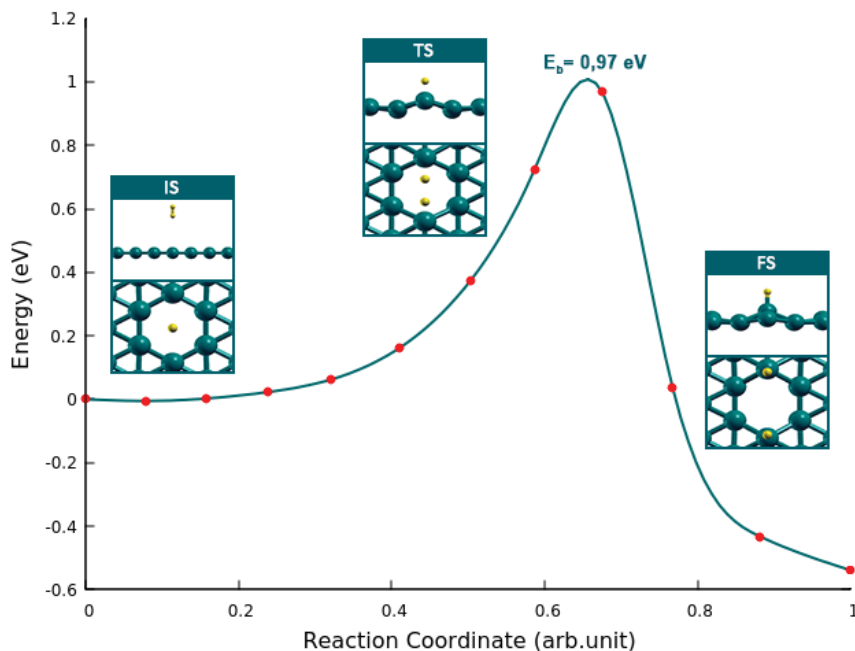

FIGURE 5. Potential energy surface of para scheme (IS=Initial State, TS=Transition State, FS=Final State, green atoms were boron atoms and yellow atoms were hydrogen atoms, respectively)

Figure 5 is a graph of the minimum energy pathway with para configuration. The hydrogen molecule located above the borophene β_{12} surfaces slowly rotates downwards due to the Van der Waals force because of the interaction of hydrogen atoms with the borophene β_{12} surfaces. After the hydrogen molecules close enough to borophene β_{12} surfaces, it was dissociated into hydrogen atoms and adsorbed on top of the borophene β_{12}'s boron atoms in para configuration. Initial State (IS) was the initial condition that the hydrogen molecule was located above on the borophene β_{12} surfaces. The system energy increased because of the interaction of hydrogen molecules with the borophene β_{12} surfaces until it reached the activation energy barrier level, then the hydrogen molecules were dissociated into hydrogen atoms and adsorbed on the borophene β_{12} surfaces in the form of para configuration. Transition state (TS) is the state of the system with the highest energy when the hydrogen molecules dissociated into hydrogen atoms. This shows that the energy required for the hydrogen molecule to completely dissociated and form a covalent bond with the borophene β_{12}'s boron atoms was 0.97 eV. Final state (FS) is a condition when hydrogen atoms were fully bonded to the borophene β_{12}'s boron atoms. As can be seen that the dissociative-chemisorption would be occurred exothermically with activation barrier of 0.97 eV indicating the dissociative-chemisorption on the borophene β_{12} surfaces might be occurred spontaneously without a catalyst or increasing system temperature. As shown in the graph, the hydrogen desorption process on the borophene β_{12} surfaces occur endothermically. Desorption of hydrogen will cause the system energy changes to break the covalent bonds between boron and hydrogen atoms. The covalent bonds of boron and hydrogen atoms break slowly then the adsorbed hydrogen atoms were slowly separated from the boron atoms and move upward. The desorbed hydrogen atoms attracted to each other and began to form a hydrogen molecule. This is a sub-process for considering the borophene for hydrogen storage application due to its good reversibility.

CONCLUSION

We investigated the interaction of molecular hydrogen on the borophene surfaces using DFT calculation. We calculated the potential energy surface (PES) for the dissociative chemisorption of molecular hydrogen on the borophene surface to reach the known stable of dimer-para hydrogened borophene. We found the pathways for H_2

dissociative chemisorption on the borophene surface and measured the energy barriers of dissociative chemisorption dimer hydrogenated borophene to be around 0.97 eV. This study provides a basic understanding in the mechanism of hydrogenation processes for hydrogen storage application, especially on the dissociative paths of H_2 molecule on the borophene surface.

ACKNOWLEDGMENTS

REFERENCES

1.   C. Zou, Q. Zhao, G. Zhang, and B. Xiong, *Natural Gas Industry B*. **3**, 1-11 (2016).
2.   F. Martins, C. Felgueiras, M. Smitkova, and N. Caetano, *Energies*. **12**, 964 (2019).
3.   M. Hoel and S. Kvemdokk, *Resource and Energy Economics*.**18**, 115-136 (1996).
4.   M. Hook and X. Tang, *Energy Policy*. **53**, 797-809 (2013).
5.   Z. Li, W. Zhang, R. Zhang and H. Sun, *Energy Exploration & Exploitation*. **38**, 2099-2127 (2020).
6.   M. Wang, G. Wang, Z. Sun, Y. Zhang, and D. Xu, *Global Energy Interconnection.* **2**, 436-443 (2019).
7.   F. Eljack and M.K. Kazi*, Frontiers in Sustainability*. **1**, 14(2021).
8.   Y. Sun and H.C. Zhou, *Sci Technol Adv Mater*. **16**, 054202 (2015).
9.   G. K. Sunnardianto, G. Bokas, A. Hussein, C. Walters, O. A. Moultos, P. Dey, *International Journal of Hydrogen Energy*. **46**, 5485-5494 (2021).
10. A.J. Mannix, X.F. Zhou, B. Kiraly, J.D. Wood, D. Alducin, B.D. Myers, X. Liu, B.L. Fisher, U. Santiago, J.R. Guest, M.J. Yacaman, A. Ponce, A.R. Oganov, M.C. Hersam, and N.P. Guisinger, *Science*. **350**, 1513-1516 (2015).
11. Y. Zeng, S. Lin, D. Gu, and X. Li, *Nanomaterials*. **8**, 851 (2018).
12. Z.Q. Wang, T.Y. Lu, H.Q. Wang,Y.P Feng, and J.C. Zheng, *Front.Phys.* **14**, 23404 (2019).
13. B. Peng, H. Zhang, H. Shao, Z. Ning, Y. Xu, G. Ni, H. Lu, D.W. Zhang and H. Zhu, *Mater. Res. Lett*. **5**, 399-407 (2017).
14. S. Haldar, S. Mukherjeea, and C.V. Singh, *RSC Advances*. **8**, 20748 (2018).
15. A. Lebon, R.H. Aguilera del Toro, L.J. Gallego, and A.Vega. *International Journal of Hydrogen Energy*. **44**, 1021-1033 (2019).
16. T.Z. Wen, A.Z. Xie, J.L. Li, and Y.H. Yang, *International Journal of Hydrogen Energy*.**45**, 29059-29069 (2020).
17. T. Liu, Y. Chen, H. Wang, M. Zhang, L.Yuan, and C. Zhang, *Materials*. **10**, 1399 (2017).
18. G.Kresse and J. Hafner, *Phys. Rev. B*. **47**, 558-561 (1993)
19. R.M. Martin, *Electronic Structure, Basic Theory, and Practical Method* (Cambridge University Press, Cambridge, 2004)
20. P.E. Blochel, *Phys. Rev. B*. **50**, 17953-17979 (1994).
21. G. Henkelman and H. Jonsson, *J. Chem. Phys*. **113**, 9978–9985 (2000).