Energy adsorption of carbon-based material doping boron with Ti and Ni metal ion decoration for hydrogen storage application using density functional theory

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Abstract. The adsorption of hydrogen and the gravimetric capacity of boron-doped graphene decorated with transition metals, titanium and nickel as candidates for hydrogen storage material have been investigated earlier by using Density Functional Theory. Our calculations based on Perdew-Burke-Ernzerhof function of the Generalized Gradient Approximation method and the van der Waals interaction calculations correction using Grimme DFT + D2 method were implemented in Quantum ESPRESSO. Our result showed that from 6 of the 27 proposed material designs were tested and had adsorption energy in accordance with the criteria range of hydrogen storage material to obtain storage that can react at room temperature and achieve hydrogen gravimetric capacity of 8.927% to 9.568% which was corresponding to the target of the US Department of Energy for Light Fuel Cell Vehicles by 2020 which is only 4.5%. The six materials had average hydrogen adsorption energy of -0.397 eV to -0.223 eV per hydrogen molecule.

1. Introduction
There are at least three main reasons why hydrogen has the potential to be the ideal energy carrier to replace fossil fuels [1, 2]. First, the availability of hydrogen in nature is abundant because hydrogen is a forming element of water molecule. The next reason is that hydrogen has high efficiency for energy conversion with its energy density of 142 MJ / kg which is four times as big as its energy density contained in liquid hydrocarbon products. The last reason is that hydrogen fuel is one of the environmentally friendly energy because the emission of hydrogen energy is water vapor.

In hydrogen economy, there are two crucial aspects of its implementation namely the activity to produce hydrogen and the hydrogen storage activity. However, in this study, we focused solely on the problem of hydrogen storage to propose the design of hydrogen storage material that meets the requirement which is 4.5% of hydrogen weight for storage purposes of Light-Duty Vehicle which becomes the target of the US Department of Energy by 2020 [3]. From many methods in hydrogen storage, we have chosen hydrogen storing method with solid-state material which is safer and potentially containing more hydrogen mass with less storage space than other storage methods [4].
There are many materials that have been studied as hydrogen storage material candidates. One of the many materials that interest us is carbon-based hydrogen storage material. This is because the availability of carbon in nature is as much as the availability of hydrogen. The reason why we conducted a preliminary study of hydrogen storage using carbon-based materials is that carbon-based nanomaterials have been extensively studied for its lightweight characteristics and high surface-volume ratio [5, 6]. Unfortunately, pure carbon-based hydrogen storage material, in its use according to the adsorption, has a very small adsorption energy and cannot achieve a corresponding adsorption energy level of about -0.7 to -0.2 eV to produce an alternating process in hydrogen storage [7, 8].

In this study, we conducted a preliminary study to observe the adsorption of hydrogen molecules on carbon-based materials by comparing pure carbon materials in graphene form, boron-substituted graphene carbon material, and boron-substituted graphene carbon material with additional decoration of titanium and nickel transition-metal materials. According to the substitution of carbon atoms with boron atoms, it was found that boron opened the band gap on graphene carbon material that made the material suitable to perform atomic switches and device formation which made the material better in its use [9]. In those substitution, there was also chemical optimization of electron transmutation that obtained extra electrons from metal atoms, and boron had a property similar to carbon [10-12]. Furthermore, decorating using transition metals had been successful on improving and meeting the criteria of the gravimetric efficiency of hydrogen storage material in computation study [13]. The purposes of this research is to conduct a study on the effects of transition-metal atoms on both substituted and unsubstituted graphene carbon materials and to design the material meets the criteria that have been required.

2. Experimental method
The Density Functional Theory calculations which were implemented in the Quantum ESPRESSO software package [14] and used XCrysDen [15] were conducted to visualize the material designs. In these calculations, the Ultrasoft potential with Generalized Gradient Approximation (GGA) in Perdew-Burke-Ernzerhof (PBE) [16] format for the potential of correlations was used to ensure the accuracy of calculation for electron exchange and Grimme DFT + D2 empirical correction scheme to calculate van der Walls interaction effects [17-19]. The Plane-wave cutoff energy has been set to 25 Ry and the convergence of the force of each atom was less than 0.05 eV / Å.

The modeling of the carbon material as the material base of the surface taken from the graphene form by taking eight atoms which were expected to represent the whole graphene (bulk graphene) is shown in Figure 1. The modeling of the surface material with the parameter of a and c lattice length of 4.926 Å, based on the results of the experiment which was conducted [20, 21], used a vacuum space of 20 Å to avoid interaction. The Monkhorst-Pack matrix [22] with k-mesh was used to perform Brillouin zone sampling.

Figure 1. Simplifikasi permodelan material karbon grafena.
The relaxation simulation which was performed on all models was conducted by calculating the application of the self-consistent field to find the most stable condition of the system geometrically, and in order that energy obtained from the system represents the amount of system energy in a stable state. The energy was obtained from the relaxation calculations of each model to be used to calculate the energy of the transition-metal bond and the adsorption energy of the hydrogen molecule to obtain hydrogen storage material candidate.

In our study, there were three equations involved. Firstly, it was to calculate the transition-metal bonding energy at the surface. Secondly, it was to calculate the average adsorption energy of hydrogen. And the last was the equation to calculate the hydrogen gravimetric of the overall material designs.

The first equation is $E_b$, Energy bond of the transition metal on the surface material was calculated by using the equation:

$$E_b = E_d - (E_s + E_{TM}) \quad (1)$$

where $E_d$ is the energy when the surface has transition-metal decoration or the total energy of the material surface, $E_s$ is the energy of the surface or the energy of the material surface, and $E_{TM}$ is the total energy of the free transition-metal atoms. Furthermore, our study focused on hydrogen storage capacity. There were two natural calculations in this section, the calculation of hydrogen adsorption energy and gravimetric or the weight of hydrogen contained in the cell unit.

For the calculation of hydrogen adsorption energy, it can be calculated by using equation (2).

$$E_a = (E_T - (E_d + nE_{H_2}))/n \quad (2)$$

where $E_T$ is the total energy of hydrogen adsorption in the surface material with or without transition metals, $E_d$ has the same terminology with equation (1). $E_{H_2}$ is the total energy of free hydrogen molecules, and $n$ represents the sum of the adsorbed hydrogen molecules.

Next, we used equation (3) to calculate the weight percentage or gravimetric of the hydrogen molecule.

$$\text{H}_2(\text{wt}\%) = \left[ \frac{m_{H_2}}{m_{H_2} + m_{\text{host}}} \right] \times 100 \quad (3)$$

where $m_{H_2}$ is the mass of a total number of the adsorbed $\text{H}_2$ molecule and $m_{\text{host}}$ is the mass of the surface.

3. Result and discussion

This study focused on the calculations which involve those three equations above divided into three parts of the research. The first calculation was to calculate the bond energy of nickel and titanium transition metals of the surface material either substituted by boron atoms or not. The next calculation was the calculation of the adsorption energy of hydrogen molecules on the overall surface designs, either with or without transition-metal decoration. The last calculation applied if in the previous stage, the surface design obtained the adsorption energy of the corresponding hydrogen molecule or about -0.7 eV, then the surface will be recalculated by the amount of hydrogen that meets the needs of the United States Department of Energy.

3.1 Bond energy of transition-metal decoration

The bond energy of transition-metal decoration can be obtained by using equation (1). It was the
calculation of the bond energy of surface material which was substituted by boron or not towards nickel and titanium transition metals. There were three surfaces to be tested, namely the surface of eight carbon atoms (C8), one boron-substituted atom on carbon (BC7), and two boron-substituted atoms on carbon (B2C6), as shown in Figure 2. Then there were three possible locations for placing the transition metals such as the bridge site that was on the carbon-carbon or boron-carbon bond center, the hollow site which was located on the hollow or the hexagon ring of the surface, and the top site where the position of decorating atoms located directly above carbon or boron atoms.

![Figure 2](image)

Figure 2. The model surface of, (a) C8, (b) BC7, and (c) B2C6, where the carbon show as the yellow atom and the boron show as the grey atom.

Table 1 is the summary of the bond energy calculations of nickel transition-metal decoration of the surface material. Based on the results of the calculations, it can be seen that the increase in the number of boron atoms in the substitution of carbon results in the increase of bond energy (more negative).

| Location | \( E_b \) on C8 (eV) | \( E_b \) on BC7 (eV) | \( E_b \) on B2C6 (eV) |
|----------|---------------------|---------------------|---------------------|
| Bridge   | -1.736              | -2.593              | -2.863              |
| Hollow   | -1.877              | -2.921              | -3.260              |
| Top      | -1.685              | -2.594              | -2.554              |

Like nickel decoration, titanium transition-metal decoration of the surface also applied the same thing, the increase of bond energy occurred was in direct proportion to the increase of the amount of boron atoms substitution of the surface material at each bonding site. In the case of the best sites of each material type was not like nickel decoration, on C8 and BC7 surface materials, they had the best site at hollow sites and for B2C6 surface material, titanium decoration had a preference at the bridge site. A summary of the calculation of the bond energy of the titanium transition-metal decoration can be seen in Table 2.

Table 2. Summary calculation energy binding (\( E_b \)) of titanium atom on the surface.

| Location | \( E_b \) on C8 (eV) | \( E_b \) on BC7 (eV) | \( E_b \) on B2C6 (eV) |
|----------|---------------------|---------------------|---------------------|
| Bridge   | -1.761              | -3.431              | -4.053              |
| Hollow   | -2.489              | -3.775              | -4.047              |
| Top      | -1.525              | -3.141              | -3.813              |

3.2 Adsorption energy of the hydrogen molecule

The purpose of this preliminary study is to observe the adsorption of hydrogen on carbon-based material either with boron atoms substitution or not and the presence of nickel or titanium decoration atoms at three points of symmetry on the surface (bridge, hollow, and top site). We tested all three types of material surfaces at all points of symmetry. Firstly, the test was performed on the surface materials
without transition-metal decoration. The second test was performed on surface materials with nickel decoration. And the last was on the surface materials with titanium decoration. The test involved equation (2) to obtain the energy adsorption of the hydrogen molecule.

Based on the calculation of the adsorption energy of hydrogen molecules on surfaces which were not decorated with transition metals, we found that nothing can reach the range of adsorption energy in accordance with the literature [6, 7]. On the surface of C8, it could achieve adsorption energy of -0.066 eV at the hollow site, -0.062 eV at hollow sites of the surface of BC7, and -0.066 eV at the top site of the B2C6 surface. The summary of the calculations is shown in Figure 3.

![Figure 3. Summary adsorption energy calculation on surface without decoration.](image)

The presence of nickel transition-metal material decoration improved the material's ability to adsorb hydrogen molecules. In our calculations, a material design, nickel which was decorated at the bridge site on the surface of the BC7 material, reached the recommendation range for adsorption energy of hydrogen storage with an adsorption energy of -0.352 eV. The other two designs gained the adsorption energy value which was under the recommendation range or below -0.7 eV namely nickel-decorated...
BC7 material at the hollow site and the nickel transition-metal decorated B2C6 surface material at the top site which had bond energy with one hydrogen molecule of -0.732 eV. Both designs were indeed more negative than the recommended value as hydrogen storage material because the hydrogen molecules will be bonded more strongly with greater energy that greater energy to break the bond was also needed. However, we believed in adding the number of hydrogen molecules to our material designs. A summary of these overall calculations was depicted in the gradient in Figure 4, where the calculations below the recommendation line will be further calculated by adding the number of hydrogen molecules.

The titanium decoration at the top sites was successful in improving the ability of surface materials to achieve the range of adsorption energy of hydrogen molecule for the recommended hydrogen storage application. We obtained three design materials that meet the needs. Firstly, C8 material surface which had an adsorption energy of -0.362 eV. Secondly, BC7 material surface with an energy of -.0337 eV. The last was B2C6 material surface which had adsorption energy of -0.308 eV. The summary of the calculations we performed is presented in the graph shown in Figure 5.

3.3 Further calculation with more hydrogen molecule
Those six materials that had met the requirements for further calculations will be recalculated by adding the number of hydrogen molecules. For surfaces with nickel transition-metal atomic decoration, we added seven more hydrogen molecules to all candidate material designs, and added six hydrogen molecules to the surface with titanium decoration.

Table 3. Hydrogen adsorption energy calculation result with gravimetric above US Department of Energy target.

| Material Combination | nH₂ | Total adsorption energy (eV) | Average adsorption energy (eV) | Gravimetric (%) |
|----------------------|-----|-----------------------------|-------------------------------|-----------------|
| bridge-Ni@BC7        | 8   | -1.938                      | -0.242                        | 9.502           |
| hollow-Ni@BC7        | 8   | -1.783                      | -0.223                        | 9.502           |
| top-Ni@B2C6          | 8   | -2.737                      | -0.342                        | 9.568           |
| top-Ti@C8            | 7   | -2.779                      | -0.397                        | 8.927           |
| top-Ti@BC7           | 7   | -2.926                      | -0.366                        | 8.995           |
| top-Ti@B2C6          | 7   | -2.429                      | -0.347                        | 9.064           |

Figure 5. Summary adsorption energy calculation on surface with Titanium decoration.
The summary of the results can be seen in Table 3, all material designs have reached the recommendation range of hydrogen adsorption energy for hydrogen storage to obtain back and forth storage in the temperature room and to obtain gravimetric value over the target of US Department of Energy for light-duty fuel cell vehicle for 2020. From the results of this adsorption energy, the material designs we proposed could be good candidates for the hydrogen storage.

4. Conclusion
In this research, the Density Functional Theory calculations for our pilot study has been performed concerning on hydrogen adsorption of our material designs combined with transition-metal decoration on carbon-based material both with and without boron substitution. It is found that the addition of transition metals can increase the adsorption energy of carbon-based materials so that the addition of hydrogen molecules can produce the average adsorption energy that reaches the range of adsorption energy which is suitable for hydrogen storage. Our results showed that the adsorption energy has fulfilled the needs of the United States Department of Energy on carbon-based material with boron doping and transition-metal decoration. The average hydrogen adsorption energy of -0.397 eV to -0.223 eV with gravimetric of 8.927% to 9.568% is close to the energy required to obtain back and forth storage at room temperature. Therefore it would be a good candidate for hydrogen storage.

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