Density functional theory investigation on hydrogen adsorption on buckled aluminene

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Abstract. Hydrogen storage is one of the challenging components in hydrogen economy towards a cleaner energy. Two-dimensional materials are being explored as a potential hydrogen storage material. Adsorption of hydrogen on buckled aluminene was investigated using first principles with the incorporation of van der Waals correction via Tkatchenko-Scheffler method. Four possible adsorption sites were identified: top of the first layer, bridge, hollow, and top of the lowest layer. Critical results of energy calculations showed that hydrogen molecule can be physisorbed on any sites of buckled aluminene with a binding energy of 0.77 eV without additional energy needed to store it. This physisorption is demonstrated in the density of states showing a slight broadening of energies. Hydrogen would prefer to be adsorbed as a molecule due to a dissociation barrier of 3.23 eV to recover the hydrogen. Another critical finding is that buckled aluminene has more possible hydrogen adsorption sites and higher binding energy than that of planar aluminene indicating a better candidate as a potential hydrogen storage material at a higher ambient temperature.

Keywords: hydrogen storage, density functional theory, aluminene, aluminum

1. Introduction

Coal, petroleum and natural gas are the main energy source consumed by our society. With the increasing world population, clean energy is much more needed [1]. The industry and scientific community are now more propelled to seek for alternative ways of producing electricity without carbon dioxide emission and obtain independence from the major source of energy: coal [2]. Among the viable supply of green energy, hydrogen fuel cell is identified as the best source of energy with water as its sole excess output of the chemical reaction. It has the greatest energy density of all known fuels by weight (143.0 MJ/kg) which can be produced from no carbon emission. With the use of hydrogen fuel cell, the gasoline consumption can be reduced up to 24% in 2035 and 69% in 2050 based on the study of the US National Research Council [3].

Hydrogen economy can be achieved through numerous scientific, technical and institutional development. Three issues in manufacturing research and development for hydrogen economy were identified by the United States Department of Energy (DOE) namely: efficient hydrogen fuel cells,
hydrogen production techniques, and hydrogen storage systems [4]. Among these three issues, the hydrogen storage material remains the greatest bottleneck to achieve hydrogen economy for transportation [4]. Low temperature freezing and compression, liquefaction, or chemically hydrogen-bonded on metals or chemical compounds are the common methods to store hydrogen [5-8]. The first three methods are expensive requiring large amount of energy to store, while preprocessing reactions are required to recover the material. Compressing hydrogen would also require equivalently to 15% to 30% of the stored energy. Some studies focused on chemically stored hydrogen gas from metal hydrides via exothermic reaction [9-10]. Solid-state materials for hydrogen storage have advantages over compressed and cryogenic storage namely: (1) superior volumetric density, (2) safer method for hydrogen delivery since the process is endothermic, and (3) storage process is reversible. Two dimensional materials such as graphene became one of the most promising candidates due to their large surface area and low weight. Recent computational studies have shown that a two-dimensional aluminum is dynamically and thermodynamically stable in two forms: planar and buckled. [11-13]. Previous studies have shown that aluminum can produce hydrogen from the hydroxide from through the splitting of water. Aluminium hydroxide can be used again back to aluminum by a process called Hall-Heroult [14-16]. This material would be promising if aluminum can be used for hydrogen production, and hydrogen storage. First principles are commonly to calculate energetics and electronic properties of nanomaterials of potential hydrogen storage [17-24]. This method has been widely used in search for a good hydrogen storage material and other systems, and there are no previous literature found on buckled aluminene as a hydrogen storage. Adsorption energies of hydrogen molecule at different adsorption sites of buckled aluminene were calculated to determine its possibility as hydrogen storage material.

2. Methodology
Structure relaxations and ground state electronic properties were calculated using density functional theory [25]. From the fully relaxed two aluminum atoms unit cell, a 3 by 3 supercell was created to avoid any H₂ interactions with the neighboring image. A separation distance of twenty angstoms along the z-axis was added to simulate the planar and buckled aluminene as shown in Figure 1.

![Figure 1](image-url) Buckled aluminene (a) Unit cell (b) Supercell (c) H₂ adsorption sites and H₂ orientation

There are two initial orientations (parallel and perpendicular to the x-axis) of H₂ were used for adsorption on aluminene surfaces. For buckled aluminene, there are 4 possible adsorption sites (hollow, bridge, top1, top2) as seen in Figure 1. Top1 refers to the top of the aluminum atom of upper layer while top2 refers to the top of the aluminum atom of the lowest layer. The total energy of the system at different distances of hydrogen molecule from the top surface of aluminene shown in Figure 1c were calculated. This scheme provided the possible adsorption locations without a need to add an external energy. After identifying the lowest energy positions, relaxed calculations with dispersion correction were performed. The relaxed structures resulted to non-dissociated H₂ molecule or dissociated H₂ molecule on the aluminene surface which corresponds to their preferred state with the lowest ground state energy. For system(s) with dissociated H₂ having a negative adsorption energy (energy difference based on equation...
a nudge elastic band (NEB) calculation was performed to determine any energy barriers. The relaxed H$_2$ on aluminene with the lowest energy was used as the initial image, while the relaxed structure with dissociated H$_2$ was used as the final image.

To implement the first principle calculations, Quantum Espresso was used [26]. The exchange-correlation with ultrasoft pseudopotential Perdew–Burke–Ernzerhof - Rappe–Rabe–Kaxiras–Joannopoulos (PBE-RRJKUS) [27-28] were used in this study. The energy of isolated H$_2$ molecule, 3 by 3 of aluminene unit cell. The energy difference of the H$_2$-adsorbed systems and the total energy of the individual H$_2$ molecule and clean aluminene were computed as indicated by equation one:

\[ E_{\text{diff}} = E_{\text{combined}} - (E_{\text{H}_2} + E_{3\times3\text{ Al}}) \]  

where \( E_{\text{diff}} \) is the energy difference, \( E_{\text{combined}} \) is the energy of H$_2$ on aluminene surface, \( E_{\text{H}_2} \) is the energy of the hydrogen molecule, \( E_{3\times3\text{ Al}} \) is the energy of the 3 by 3 aluminene. If the energy difference is negative, it means that the hydrogen molecule can be adsorbed without additional energy.

3. Discussion of Calculation Results

To verify the structure reliability, the band structures and geometric structures were compared to the previous literature. Table 1 shows the structural parameters of the unit cell of our systems which are comparable to the previous literature [11-13].

| Position/Orientation | Unit Cell Lattice Parameter a (Å) | Buckling height (Å) |
|----------------------|----------------------------------|---------------------|
| Planar*              | 2.7089                           | 2.4459              |
| Buckled*             | 2.7480                           | 2.4530              |
| Planar a             | 4.4860                           | 0.0000              |
| Planar b             | 4.4860                           | 0.0000              |
| Planar c             | 4.4891                           | 0.0000              |
| Buckled a            | 2.7480                           | 2.4530              |
| Buckled*             | 2.7089                           | 2.4459              |

* This work  

**Table 1. Geometric Structure of Aluminene**

3.1 Energy Calculations.

Figure 2 show the potential energy calculations as H$_2$ approaches the buckled aluminene surface. The figure shows that all sites are potential binding sites with a distance ranging 3.0 Å to 3.6 Å from the surface. At these distances, the adsorption corresponds only to physisorption. Only the Top2 parallel to the y-axis has the weakest binding energy at this stage. The distance from the surface with the minimum energy without relaxation can be found between 3.0 Å to 3.5 Å corresponding to
Physorption. In comparison to planar aluminene, the bridge site perpendicular to the x-axis has the lowest binding energy. Take note that these energy differences correspond to systems without relaxation. This means that hydrogen molecule without additional energy would simply approach the surface until it reaches the distance from the surface with the minimum energy. Each system was relaxed at the position with the minimum energy. Table 2 shows the adsorption energies of hydrogen on the relaxed systems for buckled aluminum.

| Position/Orientation | Dissociated | Distance of H\textsubscript{2} atoms (Å) | Adsorption Energy (eV) with Dispersion Correction (eV) |
|----------------------|-------------|-----------------------------------------|--------------------------------------------------|
| Top1/Parallel to X   | Yes         | 0.994                                   | 0.146                                           |
| Top1/Parallel to X   | No          | 3.338                                   | -0.773                                          |
| Top1/Parallel to Y   | No          | 3.353                                   | -0.776                                          |
| Top2/Parallel to X   | No          | 3.410                                   | -0.779                                          |
| Top2/Parallel to Y   | No          | 3.403                                   | -0.780                                          |
| Bridge/Parallel to X | No          | 3.353                                   | -0.086                                          |
| Bridge/Parallel to Y | No          | 3.359                                   | -0.780                                          |
| Hollow/Parallel to X | No          | 3.417                                   | -0.780                                          |
| Hollow/Parallel to Y | No          | 3.432                                   | -0.770                                          |

The hydrogen molecule dissociates on Top1 parallel to the x-axis of buckled aluminene when an additional energy of 3.23 eV is placed on the system as shown in Figure 2b from the results of nudge elastic band calculation. However, the H\textsubscript{2} molecule on the surface is more favorable compared to the dissociated H\textsubscript{2} on the buckled surface. In comparison to hydrogen dissociation on the planar aluminene, the activation barrier is about 3.3 eV and the adsorption energy is -0.78 eV without dispersion correction. On the other hand, the binding energy is -0.79 eV with energy dispersion correction [24]. The dissociated H\textsubscript{2} on the surface was further investigated using density of states and Mulliken population analysis as shown in Figure 3. These properties provided a deeper understanding on the interaction of H\textsubscript{2} on with the aluminum atoms. It can be seen in Figure 3a that the hydrogen s-orbital deviates out. Moreover, the Al-s and Al-p orbitals of around the hydrogen atoms slightly moved, and it aligned with the hydrogen s-orbital.

\[ \text{Figure 3} \] (a) Projected Density of States; (b) Electron density difference slice with charges
Using charge Mulliken population analysis, the substrate was found to be more positively charged, while the hydrogen atoms are negatively charged. There was about a transfer of charge of 0.40e\textsuperscript{−} compared to 0.60e\textsuperscript{−} in planar aluminene [24]. This leads to an attractive force between the H ions and the surface leading to the chemisorption of hydrogen atoms.

4. Conclusion
The capability of buckled aluminene as adsorbing hydrogen molecule was investigated using first principles calculation. Molecular hydrogen can be adsorbed on the buckled surface without any energy barrier. Without addition of energy, hydrogen molecule can be adsorbed easily by physisorption. Dissociated hydrogen molecule has an energy barrier of 3.3 eV on top of the aluminum atom. Recovering the hydrogen atoms will need about 2.8 eV. Thus, hydrogen prefer to be adsorbed as a molecule having a lower energy state due. The transfer of electrons from the aluminene surface to the hydrogen led to its attraction and alignment of s-orbital of hydrogen with the p-orbitals of aluminum. Buckled aluminene is found to be a better hydrogen storage due to better binding energies and numerous binding sites. However, its storage capacity would be lower compared to planar aluminene due to a smaller lattice constant. This study can be further extended by calculating the gravimetric capacity of the planar and buckled systems through the use of monte-carlo simulations.

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