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First principles investigation on the nitrogen-doped planar aluminene for hydrogen storage application

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Abstract. With the rise of carbon emission daily, a pursuit for cleaner energy such as hydrogen fuel is necessary. Obtaining a good hydrogen storage is one of the main bottleneck to achieve a working hydrogen economy. Materials including two-dimensional systems have been widely investigated for potential hydrogen storage. In this work, the effects of nitrogen on the hydrogen adsorption on planar hexagonal aluminene was studied using density functional theory. Aluminene was decorated with nitrogen at different sites: top, hollow and bridge. Results showed that nitrogen was adsorbed at the top, bridge and hollow sites at a distance of 0.00Å to 1.80 Å with binding energies of 2.71 eV, 4.88 eV, and 3.44 eV, respectively. Comparing to the pristine aluminene, there was no major difference with its electronic and magnetic properties based on the density of states of the nitrogen-doped aluminene while the nitrogen atom gained some charges from the aluminium atoms based on the charge difference. On the other hand, a hydrogen molecule was adsorbed with binding energies ranging from 13.4meV to 26.3 meV close enough to the adatom on the decorated system. Minimal broadening of energy level was found from the density of states. This work shows that aluminene with nitrogen impurity can adsorb hydrogen molecules. However, high concentration of nitrogen will lower the hydrogen capacity of aluminene.

Keywords: Density Functional Theory, Hydrogen Storage, Aluminene, Nitrogen, Impurity

1. Introduction

World energy demands have been steadily rising. According to the World Energy Outlook 2018, global energy consumption has risen 31.8% since 2000 [1]. Fossil fuels have played an important role in meeting world energy demands and in turn progressing modern society to where it is today, but it is non-renewable, and it has drastically increased atmospheric CO₂ levels. As climate change becomes a growing concern, the need for a cleaner renewable alternative fuel grows with it [2, 3].

Hydrogen has shown much potential in being that cleaner renewable alternative fuel. It is one of the most abundant elements on the planet, making it readily available [4, 5]. Fuel cell technology also allows it to be used alongside oxygen to produce electricity with no carbon emissions. The only byproduct of a hydrogen fuel cell being water vapor. But many obstacles still hinder the practicality of a hydrogen economy. With Hydrogen storage being one of the largest [6].



Currently, the most common methods of storing hydrogen are through cryo-compression and liquefaction. Both of which being very energy intensive. This is due to hydrogen being very sparse and in turn having a low energy density values by volume. To counteract this cryo-compression cools hydrogen to low temperatures which allows it to be stored in high pressure tanks at six times the normal atmospheric pressure. Similarly, liquefaction turns hydrogen into a liquid by cooling it down to temperatures below 20.25K [7-9]. Material-based storage brings with it the possibility of a more efficient method of storing hydrogen. Studies in 2D materials such as graphene, germanene and silicene have shown it to have hydrogen storage capabilities. These 2D materials present a larger surface area where hydrogen can bind to it, allowing hydrogen to be packed closer together. Studies have also shown that introducing dopants to these materials can cause it to adsorb hydrogen much more efficiently [10-13]. These materials have also been shown to be capable of attaining the optimal binding energies of hydrogen, 0.2eV-0.6eV, for use as a hydrogen storage device [14].

Recent studies have found that a planar honeycomb monolayer of aluminum, also called aluminene, can possibly be used for hydrogen storage [15,16]. These studies have also shown it to be stable and have similar properties to other 2D materials [17,18]. As such, the introduction of dopants or impurities to aluminene may enhance its hydrogen storage capabilities. Many studies have shown nitrogen used as a dopant in 2D materials to have this very effect [19-24]. As of this moment, no study has been found investigating the effects of nitrogen on the hydrogen storage capacity on pristine aluminene. In this study, hydrogen adsorption on nitrogen-doped aluminene was determined using first principles calculations.

2. Methodology

Density functional theory (DFT) via Vienna Ab-Initio Simulation package (VASP) [25-28] was used for geometry optimization and ground state property calculations. The approximation for the exchange-correlational energy was calculated using Perdew-Burke-Ernzerhof (PBE) [29].

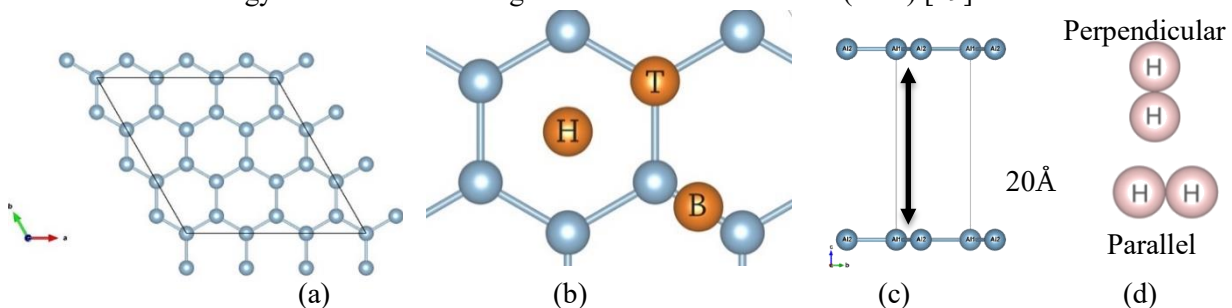


Figure 1. (a) Unit Cell of Planar Aluminene (b) H₂ Adsorption Sites (c) Super Cell (d) H₂

2.1. Unit Cell of Planar Aluminene and Nitrogen Adsorption

The unit cell contains 18 atoms of aluminum with a hexagonal lattice as seen in figure 1a. The repeated aluminum sheet is separated by a vacuum of 20Å along the z-axis to avoid self-interaction, as shown in figure 1c. After geometry optimization it was found to have a lattice constant of 13.458 Å, where alpha and beta are 90°, and gamma is 120°.

Nitrogen was placed on three possible adsorption sites: top, bridge and hollow, as shown in figure 1b. A static calculation for the total energy was done from 0.20 Å to 6.00Å with an increment of 0.20 Å. Ionic relaxation was done on the lowest energy position and the binding energy of the nitrogen atom on aluminene was calculated on the system with the minimum energy. From there, the material's electronic properties were calculated. The adsorption energy is defined by equation 1.

$$E_{ads-H} = E_{H+Al+N} - (E_{Al+N} + E_H) \quad (1)$$

where $E_{H/surface}$ is the energy of adsorbed hydrogen molecule on the surface, $E_{surface}$ is the energy of the nitrogen doped surface without the adsorbed hydrogen, and E_H is the energy of the hydrogen molecule. The binding energy is defined by equation 2.

$$E_b = E_{Al} + E_N - E_{N+Al} \quad (2)$$

where E_b , E_{Al} , and E_{N+Al} are the energies of aluminene, nitrogen and the nitrogen-doped aluminene, respectively. The hydrogen molecule was placed on top of the decoration with its center of mass acting as reference for its initial positions. Static calculations for the total energy were done from 0.20 Å to 6.00 Å. The system with the minimum energy had ionic relaxation performed and binding energy calculated. The resulting structure then yielded a non-dissociated hydrogen molecule. Followed by the electronic property calculations.

3. Results and Discussion

3.1 Nitrogen Adsorption

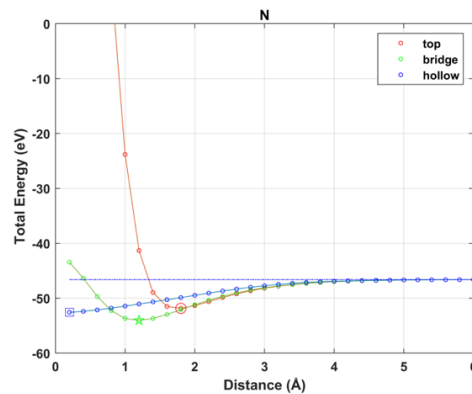


Figure 2. Total Energy of Nitrogen on Aluminene

The total energy of nitrogen on the different adsorption sites on the surface of aluminene are shown in Figure 2. The distance which gives the lowest sum of the individual energies of nitrogen on the surface of aluminene are given by the red circle, green star and blue square for the top, bridge and hollow sites respectively. While the sum of the individual energies of nitrogen and aluminene are represented by the blue dashed line. Adsorption in the hollow site gave the shortest adsorption distance at 0.08 Å followed by the bridge site at 1.18 Å, while the top site gave the farthest distance at 1.75 Å. All three sites gave good binding energies with the bridge site having the strongest at 4.88 eV followed by the hollow site at 3.44 eV and the top site having the weakest binding energy at 2.71 eV.

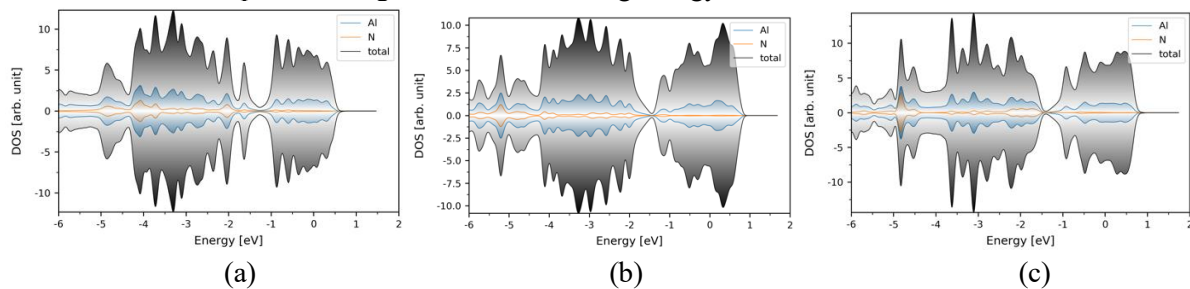


Figure 3. Density of States at the (a) Top (b) Bridge and (c) Hollow Sites

The partial density of states in figure 3 show alignment of the peaks of the density of states of the nitrogen atom and those of the aluminum atoms nearest to it. This indicates chemical bonding between the two, which is consistent with the calculated binding energies mentioned earlier. This is also supported by the charge density difference found in figure 4. This shows the transfer of electrons between the nitrogen and aluminum atoms. The charge density difference is defined by equation 3.

$$\Delta\rho = \rho_{N/Al} - (\rho_N + \rho_{Al}) \quad (3)$$

where the charge density of the nitrogen-doped aluminene, $\rho_{N/Al}$, is subtracted by the sum of the charge densities of nitrogen, ρ_N , and aluminene, ρ_{Al} . It is also notable to point out the symmetry shown in figure 3 which implies that the material is non-magnetic.

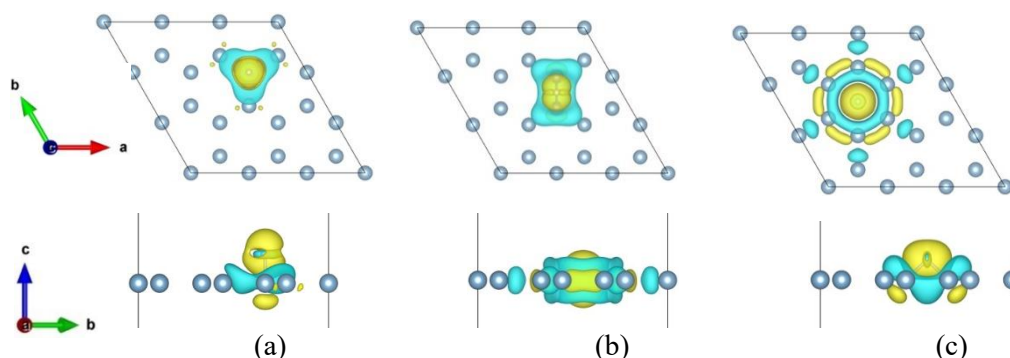


Figure 4. Charge Density Difference at the (a) Top, (b) Bridge, and (c) Hollow Sites

3.2 Hydrogen Adsorption

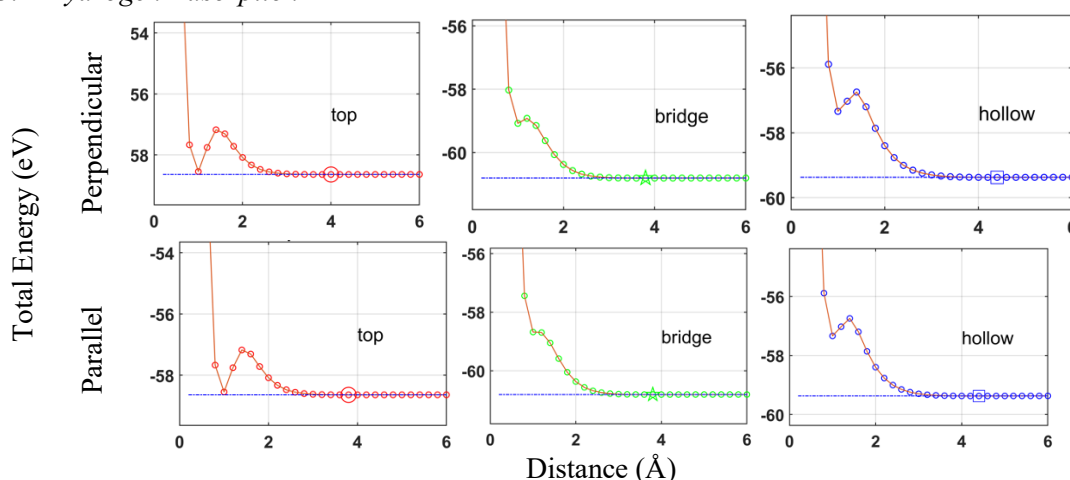


Figure 5. Total Energy of Hydrogen on the Nitrogen-doped planar Aluminene System

Figure 5 shows the energy of the system (hydrogen molecule on the surface) as H_2 approaches the nitrogen-doped aluminene surface at the top, bridge and hollow adsorption sites. The parallel and perpendicular positions refer to the hydrogen molecule's position relative to the nitrogen-doped aluminene surface. Similar to that of Figure 2 the sum of the individual energies of nitrogen and aluminene are also represented by the blue dashed line. Results show that there are two minima in the energy curves for each site and configuration. The systems at the energy minima were geometrically relaxed.

Table 1. Energetics of the relaxed hydrogen molecule on the nitrogen-doped aluminene surface

Site of H_2	H_2 Orientation	Distance (\AA)	Adsorption	Distance (\AA)	Adsorption
		Near	Energy (eV)	Far	Energy (meV)
Top	Parallel	0.61	3.47	4.00	9.73
	Perpendicular	0.60	3.47	3.80	9.66
Bridge	Parallel	0.61	1.52	3.80	10.83
	Perpendicular	0.71	0.03	3.80	13.01
Hollow	Parallel	0.74	0.17	4.40	13.01
	Perpendicular	0.76	0.13	4.40	13.02

Table 1 shows the calculated binding energies of the hydrogen molecule on the different positions and orientations. The results show a broad range of binding energies for the hydrogen molecule on the nitrogen-doped aluminene surface along with a varying distance between the parallel and perpendicular orientation. Results showed that the hydrogen molecule dissociated at the top and bridge sites with

dissociation barrier of more than 3 eV as shown in Figure 5. The top site shows to be the most stable for hydrogen molecule adsorption with the binding energies indicating it to be done through chemisorption with the nitrogen atom. Figure 5 also shows an energy barrier for the hydrogen molecule to be adsorbed at a closer distance for all three adsorption sites. It is important to note that binding energies were also calculated from 4.00 Å to 4.40 Å with results showing them to be low, ranging from 9.66 meV to 13.02 meV as shown in table 1.

4. Conclusion

Hydrogen adsorption on nitrogen-doped planar aluminene was investigated using density functional theory. Results showed nitrogen adsorption onto the aluminene surface to be most stable at the hollow site with a binding energy of 4.88 eV at a distance of 1.18 Å. The binding energies, density of states, and charge density difference all indicate nitrogen to be chemically bonded to the aluminum atoms at all three adsorption sites. With the partial density of states also showing nitrogen-decorated aluminene to be non-magnetic. The binding energies of hydrogen molecule on the nitrogen-decorated aluminene show adsorption to be most stable at the top site. They also show a broad range of binding energies which allows hydrogen to be adsorbed through both chemisorption and physisorption. None of the binding energies are within the optimal range of 0.20 eV - 0.60 eV for hydrogen storage applications. These results suggest that nitrogen atoms can easily become impurities on aluminene during synthesis or exposure to nitrogen atmosphere. These nitrogen atoms will decrease the hydrogen capacity of aluminene. However, it is important to note that calculations were done without van der Waals correction which may bring binding energies at the hollow sites within that range.

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