The effect of nitrogen dopant on hydrogenated graphene for hydrogen storage application

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Abstract. We investigated the effect of nitrogen dopant on the charge transfer rate (CTR) and reaction pathways of hydrogen molecule dissociation on graphene and nitrogen-doped graphene based upon first principle calculation. We found that the nitrogen atom form covalent bonds with the carbon atoms with bond length of C-N of 1.41 Å. The geometry optimization results in nitrogen doped pristine graphene revealed that nitrogen pulled downward the nearest neighbor of carbon atom, thus the structure is a bit downward. We found the charge transfer rates from hydrogen to carbon atom is decrease with respect to pristine graphene and nitrogen doping also can decrease the activation barrier of hydrogen molecule dissociation on graphene surfaces.

1. Introduction

As promising material, graphene provides unique properties among other potential materials. Harder than some material, but flexible and give very thin area as graphene is 2D symmetry material. Refinement of graphene properties and performance becoming promising scheme in order to face world’s globalization which still remain challenging duty. Controlling properties by electron addition to the pristine graphene could be a solution.

By modifying electron bands of graphene, tailoring the properties become realizable idea. Doping is an efficient way to significantly change graphene’s electronic properties and chemical reactivity with different atoms like Nitrogen, Boron, Silicon and etc [1]. Those material substitutes carbon in pristine graphene and could significantly shift graphene properties. N-doping classified into the most common doping configuration and gives interesting prospect for various application. N-doped could induce additional charge and n-type carriers to the carbon system, it is crucial for semiconductor devices, energy conversion and storage system [1].

It was revealed that N-doped graphene exhibits superior electrocatalytic than most other electrocatalyst [2]. N-doping not only contributes to the additional charge and shifting the electronic properties but also carbon system was enhanced by N-doping. It would increase the performance of molecular sensing application. Nitrogen doped graphene could efficiently identify organic molecules and provide highly sensitive surface for controlled modifications. Nitrogen atom as doping would help
stabilize structural defects like vacancies. Finally, synthesizing this Nitrogen doped graphene is via a simple and efficient way AP-CVD method (Atmospheric-pressure chemical vapor deposition) [1]. Density functional theory was used to inquire stability, adsorption and desorption process in nitrogen-doped graphene as hydrogen storage system. Nitrogen position related to properties of graphene, effect of nitrogen substitution observed by density function theory. In addition, Gao et al. revealed a simple model of stability for hybrid carbon-conjugated material and computational was verified [3].

Importantly, various N-doped graphene including single vacancy in graphene have been previously synthesized [4]. For further investigation of Nitrogen-doped graphene, STM/STS experiment combined with ARPES and XPS was conducted and proves the effect of charge distribution and electron from nitrogen substitution into nitrogen-doped graphene [5]. Those experiment added with theoretical argument allows us to observed the effect of nitrogen doping. Electron and charge distribution classified into two major state based on the concentration which are localized state (high nitrogen oxidized) and delocalized state.

Many researchers have modified the pristine graphene in order to meet the need of hydrogen storage applications by creation of single vacancy on the graphene surfaces[6-8]. Here, we would like to modify the pristine graphene by inserting nitrogen doping into graphene surface to reduce the activation barrier of hydrogen molecule dissociation and to know the adsorption-desorption characteristic under nitrogen doping. As a part of the adsorption process, we also investigated the charge transfer rate (CTR) from hydrogen to graphene with and without nitrogen doping.

2. Method
We performed the optimization using density functional theory [9]. The simulations have been done using the quantum espresso (QE) code [10]. We used the projector-augmented- wave method and the ultra-soft pseudo potential [11]. The local density approximation by the Perdew-Zunger parameterization [12] was adopted. The parameters for hydrogenated graphene with and without nitrogen doping 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 orders to avoid interaction between layers. Distribution of k-points on a mesh of 12x12x1 was selected via Monkhorst-Pack scheme [13]. The structure models used for simulation are graphene sheets consisting of 48 carbon atoms in rectangular super cells. We used lowdin charge analysis to calculate the charge transfer rates from hydrogen to graphene and n-doped graphene [14]. In order to predict the reaction pathways and calculate the energy barrier, we used NEB method to investigate the reaction pathways of adsorption-desorption process of hydrogenated graphene and nitrogen-doped graphene [15].

3. Results

3.1 Charge transfer rates
When hydrogen interacts with N-doped graphene, there is a charge transfer from hydrogen to graphene. Thus, it is important to calculate the charge transfer rate from hydrogen to graphene. We investigated the charge transfer from hydrogen to N-doped graphene and compared the result of CTR from hydrogen to graphene surface without doping. The optimized structure is showed in Figure 1.

Table 1 shows the CTR from hydrogen to pristine graphene is about 0.20e, while the CTR from hydrogen to N-doped graphene is decrease to be 0.14e. The results indicated that N doped decreasing the CTR from hydrogen to graphene due to the presence of N doping. It can be analyzed from the optimized structure of hydrogenated graphene and hydrogenated N-doped graphene.
### Table 1. Value of CTR from hydrogen to graphene with and without N doping.

| Pristine graphene | CTR [e] | N-doped graphene | CTR [e] |
|-------------------|---------|------------------|---------|
| 48+3H             | 0.2035  | 47+N+3H          | 0.1428  |
| 72+3H             | 0.2041  | 71+N+3H          | 0.1430  |
| 96+3H             | 0.2041  | 95+N+3H          | 0.1433  |

3.2 Deformed structure

It is necessary to understand the reason why the CTR is decreasing in hydrogenated N-doped graphene. Figure 1 shows the optimum structure of hydrogenated graphene with and without nitrogen doping. We found that the location of nitrogen atom is a bit shifted downward around -0.13 Å and hydrogenated carbon atom around nitrogen a bit shifted upward around 0.37 Å.

![Figure 1](image)

3.3. Potential Energy Surfaces

We investigated the reaction pathways and energy barrier of hydrogen molecule dissociation on the pristine graphene, nitrogen doped graphene and boron doped graphene. We added the result of reaction pathways of H₂ dissociation on boron doped graphene to compare the activation barrier of the most stable of doped graphene (boron and nitrogen doping).

Firstly, we have the same of the initial state of hydrogen molecule on pristine graphene and doped graphene, the hydrogen molecule is located on the vacuum. Along the reaction, we can see the energy of the system is increase followed by dissociation of hydrogen molecule into hydrogen atoms with an energy barrier of 1.3 eV (pristine graphene). Here, we reported that due to the presence of nitrogen doping, the activation barrier of hydrogen dissociation is decrease, which is a new finding that we could decrease the activation barrier only by nitrogen doping.

We also added another doping (boron doping) for the comparison since either nitrogen doping or boron doping of graphene have been observed experimentally. Thus, single nitrogen doping into graphene surface can be regarded as a “doped-catalytic” reaction center, which has a role to reduce the...
energy barrier. We observed that the reaction of hydrogen molecule dissociation to form two hydrogen atoms and adsorbed to the graphene surface with or without doping is exothermic reaction with difference energy between initial state and final state is < 1.5 eV.

![Figure 2](image)

**Figure 2.** Minimum energy pathway of dissociation of hydrogen molecule on pristine graphene, nitrogen-doped graphene and boron-doped graphene.

4. Conclusion

The effect of nitrogen dopant on the interaction between hydrogen molecules on the graphene surface was investigated by using density functional theory calculation. We found a new finding on how to reduce the activation barrier of hydrogen molecule dissociation on graphene surface by single nitrogen doping.

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