First-principles study of hydrogen adsorption on two-dimensional C$_2$N sheet

Pongdet Netrattana$^1$ and Pakpoom Reunchan$^{1,2}$

$^1$Department of Physics, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

$^2$Thailand Center of Excellence in Physics (ThEP Center), Commission on Higher Education, Bangkok 10400, Thailand

E-mail: pakpoom.r@ku.ac.th

First-principles calculations based on density functional theory (DFT) are carried out to study the adsorption behaviours of molecular H$_2$ on the graphene-like material C$_2$N. The plausible adsorption sites on top of bonds, on carbon atom and nitrogen atom and the center of C-C hexagon and the C-N hexagon are considered. The calculated adsorption energies are found to be in the physisorption regime. We find that the most favourable site of H$_2$ is above the center of C-N hexagon. In addition, we demonstrate the inclusion of the Van der Waals interactions through the DFT-D2 method via the generalized gradient approximation (GGA) functional gives the consistent trend of H$_2$ adsorption with that obtained via the local-density approximation (LDA) functional. The effects of Van der Waals interactions on the adsorption energies and equilibrium distance between H$_2$ and C$_2$N are discussed.

1. Introduction

Search for renewable and sustainable energy resources has become an urgent issue because of the decreasing fossil fuel supplies and their unpleasant effects on the environment [1]. The use of hydrogen as an energy carrier has been of great interest because of its advantages [2,3], such as zero production of greenhouse gases from the combustion. However, the big challenge to successfully make hydrogen as an ideal alternative energy is the storage technique [4]. The reversibly storage materials with large gravimetric density that function at ambient temperature and pressure are required [5].

Recently, nitrogenated holey two-dimension structures (C$_2$N), a graphene-like with evenly distributed holes has been successfully synthesized [6]. The results of optical band-gap measurement and first-principles calculations showed that C$_2$N is direct band-gap semiconductor with the band gap value of 1.96 eV [6,7]. Because of its unique chemical composition and atomic structure, C$_2$N is also proposed for many applications including hydrogen storage material. Understanding how molecular hydrogen (H$_2$) interact with the pristine C$_2$N sheet is a necessary basis for the development of storage application.

In this work, we present an investigation of the hydrogen adsorption behavior of C$_2$N layer using first-principles calculations based on density functional theory (DFT). The interaction between C$_2$N layer and molecular hydrogen (H$_2$) are studied through the generalized gradient approximation (GGA)
of Perdew Burke and Ernzerhof (PBE) and the local density approximation (LDA). The effects of Van der Waals interactions are also included within GGA-PBE functional. We report the adsorption energies and the equilibrium distance of H\textsubscript{2} on C\textsubscript{2}N layer for all plausible adsorption sites. The most favorable adsorption site is also determined.

2. Computational details

Our first-principles calculations were based on the density functional theory (DFT) as implemented in the Vienna \textit{ab initio} simulation package (VASP) [8]. The generalized gradient approximation of Perdew Burke and Ernzerhof (GGA-PBE) [9] and projector augmented wave potentials were used. Effect of van der Waals (vdW) interaction was included via the method of Grimme (DFT-D2) [10-12]. The energy cutoff of 400 eV was used for the plane-wave expansion. Our calculations used a 5×5×1 mesh of Monk horst-Pack k-point for the Brillouin zone integration. All calculations were repeated using the local density approximation (LDA) for the comparison with the GGA. The total energy calculations were performed using the 18-atom C\textsubscript{2}N unit cell with an interlayer distance of 15.0 Å. Static calculations were performed to examine the interactions between H\textsubscript{2} and C\textsubscript{2}N.

3. Results and discussion

The hexagonal primitive cell of two-dimensional C\textsubscript{2}N is composed of twelve carbon atoms and six nitrogen atoms, which those carbon and nitrogen atoms are bonded with sp\textsuperscript{2} hybridization. Based on GGA-PBE functional, the calculated lattice constant of C\textsubscript{2}N monolayer is 8.33 Å, which is in good agreement with the experimental value of 8.30 Å [6]. The calculated hole diameter is 5.51 Å, two inequivalent C-C bonds length are 1.47 Å and 1.43 Å, respectively, and C-N bond length is 1.34 Å [7,13]. The structural parameters obtained by GGA-PBE and LDA functional are shown in Table 1.

We considered seven plausible adsorption sites as shown in Fig. 1., which are above of carbon-nitrogen hexagonal center (HN), above of carbon hexagonal center (HC), on top of carbon atom (C), on top of nitrogen atom (N), center above of outer C-N ring carbon bond (BC1), center above of inner C-N ring carbon bond (BC2), center above carbon-nitrogen bond (BN). To determine the adsorption energy we constructed the potential energy curves of H\textsubscript{2} approach to C\textsubscript{2}N layer as shown in Fig.2. The potential energy curves were obtained by varying the distance between H\textsubscript{2} and C\textsubscript{2}N layer and then the total energy of corresponding configuration was calculated. We selected the perpendicular orientation of the molecular axis to the C\textsubscript{2}N sheet for all adsorption sites. In addition, the parallel orientation of the molecular axis was included for the adsorption on HN (HN-parallel) and HC (HC-parallel).

The adsorption energy of hydrogen molecule on C\textsubscript{2}N layer are following to the equation (1), where \(E_{\text{ad}}, E_{C_{2}N}, E_{H_{2}}, E_{\text{system}}\) are the adsorption energy of H\textsubscript{2}, total energy of C\textsubscript{2}N, total energy of H\textsubscript{2} and total energy of C\textsubscript{2}N-H\textsubscript{2} system.

\[
E_{\text{ad}} = E_{C_{2}N} + E_{H_{2}} - E_{\text{system}}
\]  

(1)

We found that the most favorable adsorption site of H\textsubscript{2} is HN configuration with the adsorption energy of 0.049 eV as shown in Table 2. The adsorption energies of HC, C, N BC1, BC2 and BN are 0.045 eV, 0.042 eV, 0.048 eV, 0.041 eV, 0.042 eV and 0.044 eV. The adsorption length between H\textsubscript{2} and C\textsubscript{2}N of HN is also the most nearest with distance is 2.98 Å.

**Table 1.** Structural parameters of C\textsubscript{2}N obtained by GGA-PBE and LDA functionals.

| Parameter                  | GGA-PBE | LDA   | Experiment |
|----------------------------|---------|-------|------------|
| Lattice constant (Å)       | 8.33    | 8.20  | 8.30       |
| C-C bond length (Å)        | 1.43 1.47 | 1.41 1.44 |           |
| C-N bond length (Å)        | 1.34    | 1.32  |            |
| Hole diameter (Å)          | 5.51    | 5.41  |            |
Figure 1. The structure of C\textsubscript{2}N that combined with carbon atom (brown ball) and nitrogen atom (blue ball), the lattice parameter are shown additionally as same as the possible adsorption sites of H\textsubscript{2} of HN, HC, C, N, BC1,BC2 and BN.

Furthermore, the parallel approach of H\textsubscript{2} molecule gives larger adsorption energy and nearer adsorption length. The adsorption energy and length of HN-parallel are 0.069 eV and 2.86, respectively. Figure 2 show the potential energy curves of H\textsubscript{2} approach to the C\textsubscript{2}N layer for all configurations. LDA and GGA-PBE are also shown to compare the results.

Our calculations show that the adsorption energies obtained by GGA-PBE functional are relatively small compared to that obtained by other functionals. Conversely, the adsorption length is the longest. The adsorption energy and adsorption length of HN, HC, HN-parallel and HC-parallel for all functionals are shown in Table 3. Moreover, the trend of some potential energy curves within GGA-PBE functional is different to that obtained by LDA functional. However, the inclusion of Van der Waals interaction leads to higher adsorption energies and results agree well with that obtained by LDA.

Figure 2. The potential energy curves of H\textsubscript{2} approach to the C\textsubscript{2}N layer obtained by (a) GGA-PBE included vdW interactions (b) LDA (c) GGA-PBE functionals.
Table 2. Adsorption energies (eV) and equilibrium distance (Å) of H₂ in C₂N layer calculated using GGA-PBE included effects of Van der Waals interactions via method of Grimme (DFT-D2).

| Configuration | C   | N   | BC1  | BC2  | BN  | HN  | HN-parallel | HC   | HC-parallel |
|---------------|-----|-----|------|------|-----|-----|-------------|------|-------------|
| Adsorption energy (eV) | 0.042 | 0.048 | 0.041 | 0.042 | 0.044 | 0.049 | 0.069 | 0.045 | 0.058 |
| Adsorption length (Å) | 3.17 | 3.07 | 3.12 | 3.11 | 3.10 | 2.98 | 2.86 | 2.98 | 2.86 |

Table 3. The adsorption energy and adsorption length of HC, HC-parallel, HN and HN-parallel for GGA-PBE, GGA-PBE included vdW interaction and LDA compared with result of Graphene system.

| Configuration | Adsorption energy (eV) | Adsorption length (Å) |
|---------------|------------------------|-----------------------|
|               | GGA-PBE | GGA-PBE+vdW | LDA | GGA-PBE | GGA-PBE+vdW | LDA |
| HC            | 0.004     | 0.045      | 0.066 | 3.81 | 2.98 | 2.81 |
| HC-parallel   | 0.015     | 0.058      | 0.083 | 3.49 | 2.86 | 2.69 |
| HN            | 0.006     | 0.049      | 0.072 | 3.56 | 2.98 | 2.78 |
| HN-parallel   | 0.021     | 0.069      | 0.100 | 3.36 | 2.86 | 2.67 |
| Graphene18 atoms | 0.011   | 0.061      | 0.088 | 3.49 | 2.86 | 2.69 |

4. Conclusion
We perform density-functional calculations based on GGA-PBE with and without Van der Waals interactions and LDA functional to investigate H₂ adsorption on C₂N layer. Our results show that H₂ adsorption is physisorption with slightly different adsorption energies for all plausible configurations. The HN hexagonal channel is the most favorable adsorption site for H₂. Nevertheless, the differences between the adsorption energies corresponding to different configurations are small. Furthermore, we find that the results obtained by LDA are in good agreement with that from GGA-PBE included Van der Waals interactions.

5. Acknowledgments
This work is supported by Kasetsart University Research and Development Institute (KURDI).

References
[1] Cook TR, Dogutan DK, Reece SY, Surendranath Y, Teets TS and Nocera DG 2010 Chemical Reviews 110 6474-502
[2] Ströbel R, Garche J, Moseley PT, Jörissen L and Wolf G 2006 Journal of Power Sources 159 781-801
[3] Schlappbach L and Zuttel A 2001 Nature 414 353-8
[4] Zhou L 2005 Renewable and Sustainable Energy Reviews 9 395-408
[5] Shevlin SA and Guo ZX 2009 Chemical Society Reviews 38 211-25
[6] Mahmood J, Lee EK, Jung M, Shin D, Jeon I-Y, Jung S-M, et al. 2015 Nat Commun 6
[7] Ma DW, Wang Q, Yan X, Zhang X, He C, Zhou D, et al. 2016 Carbon 105 463-73
[8] Kresse G and Furthmüller J 1996 Computational Materials Science 6 15-50
[9] Perdew JP, Burke K and Ernzerhof M 1996 Physical Review Letters 77 3865-8
[10] Grimme S 2004 Journal of Computational Chemistry 25 1463-73
[11] Grimme S 2006 Journal of Computational Chemistry 27 1787-99
[12] Bučko T, Hafner J, Lebègue S and Ángyán JG 2010 The Journal of Physical Chemistry A 114 11814-24
[13] Sahin H 2015 Physical Review B 92 085421