First-principles study of hydrogen adsorption on two-dimensional C_2N sheet

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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_2N. 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_2N 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 gaseous 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_2N), 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_2N 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_2N is also proposed for many applications including hydrogen storage material. Understanding how molecular hydrogen (H_2) interact with the pristine C_2N 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_2N layer using first-principles calculations based on density functional theory (DFT). The interaction between C_2N 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_2 on C_2N 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 *ab initio* simulation package (VASP) [8]. The generalized gradient approximation of Perdew Burke and Ernzerhof (GGA-PBE) [9] and projector augmented wave pseudopotentials 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 $5\times5\times1$ 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_2N unit cell with an interlayer distance of 15.0 Å. Static calculations were performed to examine the interactions between H_2 and C_2N.

3. Results and discussion

The hexagonal primitive cell of two-dimensional C_2N is composed of twelve carbon atoms and six nitrogen atoms, which those carbon and nitrogen atoms are bonded with sp^2 hybridization. Based on GGA-PBE functional, the calculated lattice constant of C_2N monolayer is 8.33Å, which is in good agreement with the experimental value of 8.30Å [6]. The calculated hole diameter is 5.51 Å, two inequivalent C-C bonds length are 1.47Å and 1.43Å, respectively, and C-N bond length is 1.34Å [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_2 approach to C_2N layer as shown in Fig.2. The potential energy curves were obtained by varying the distance between H_2 and C_2N layer and then the total energy of corresponding configuration was calculated. We selected the perpendicular orientation of the molecular axis to the C_2N 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_2N layer are following to the equation (1), where $E_{ad}, E_{C_2N}, E_{H_2}, E_{system}$ are the adsorption energy of H_2, total energy of C_2N, total energy of H_2 and total energy of C_2N-H_2 system.

$$E_{ad} = E_{C_2N} + E_{H_2} - E_{system} \tag{1}$$

We found that the most favorable adsorption site of H_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_2 and C_2N of HN is also the most nearest with distance is 2.98 Å.

Table 1. Structural parameters of C_2N obtained by GGA-PBE and LDA functionals.

	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	

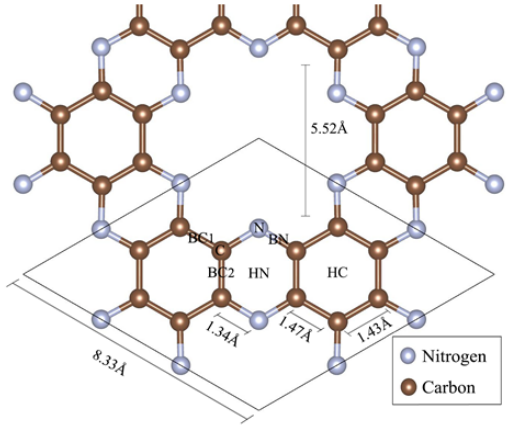

Figure 1. The structure of C_2N that combined with carbon atom (brown ball) and nitrogen atom (blue ball), the lattice parameter are shown additionally as same as the possible adsorption sites of H_2 of HN, HC, C, N, BC1,BC2 and BN.

Furthermore, the parallel approach of H_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_2 approach to the C_2N 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.

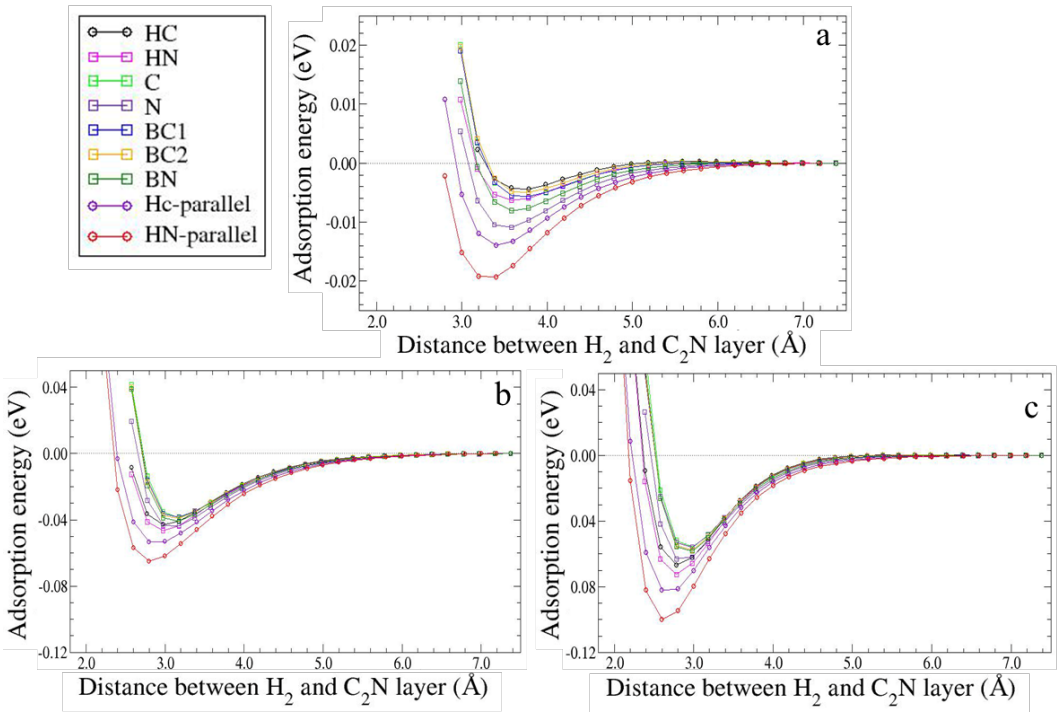

Figure 2. The potential energy curves of H_2 approach to the C_2N layer obtained by (a) GGA-PBE included vdW interactions (b) LDA (c) GGA-PBE functionals.

Table 2. Adsorption energies (eV) and equilibrium distance (Å) of H_2 in C_2N 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 H_2 adsorption on C_2N layer. Our results show that H_2 adsorption is physisorption with slightly different adsorption energies for all plausible configurations. The HN hexagonal channel is the most favorable adsorption site for H_2. 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

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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] Schlapbach 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