# Effects of iron atom, substrate on two-dimensional $C_2N$ crystals

*Min Jong Noh*[1], *Yong Hoon Kim*[2]

[1]*Graduate School of EEWS, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Korea*

E-mail: y.h.kim@kaist.ac.kr

Recently, there has been a lot of researches related to two-dimensional (2D) materials due to their new properties and applications emerging upon 2D confinement. A new type of graphene like two-dimensional layer material, nitrogenated holey two-dimensional structure C2N-h2D, that is possession of evenly distributed holes and nitrogen atoms with proper bandgap has been synthesized. Previous calculation studies already have shown that the variance of the orbital interaction, band structure of few-layer C2N-h2D suggests that interlayer coupling does play an important role in its electronic properties. In this point, using first-principles density functional theory calculation, we here explore the effect of porous embedded iron atom and iron substrate on encapsulated few layer C2N-h2D. We show the atomic structures and the corresponding electronic structures of Fe@C2N to elucidate the effect of iron. Finally, this study demonstrates that embedded iron C2N has AA-stacking as most favorable stacked structure in contrast to pure C2N. In addition, iron substrate modifies its encapsulated C2N from semi-metallic states to metallic state.

## INTRODUCTION

From the discovery of graphene, many types of two-dimensional crystalline materials have been explored due to the unique properties of 2D materials. There are many examples; Graphene, Graphane, h-BN, $NbSe_2$, $MoS_2$ etc. Recently, a new type of two-dimensional structure, Nitrogenated holey two-dimensional structure ($C_2N$-*h*2D), is synthesized via a simple chemical reaction. $C_2N$ has special properties because of its structure; periodical holes and nitrogen atom facing hole. It gives not only proper bandgap (1.70eV) but also potential for various application. [1]

Previous calculation studies suggest $C_2N$ electronic properties sensitively depend on stacking order, layer number and external electric field. [2] And another experimental paper report that cobalt oxide encapsulated in $C_2N$ show good catalytic performance for hydrogen evolution. [3]

To summary of those points, here we perform first-principles calculations to investigate trilayer $C_2N$ for finding stable stacking order and effect of embedded iron in $C_2N$ hole and substrate iron on $C_2N$, respectively.

## CALCULATION METHODS

All the results reported in this work were obtained based on first-principles density-functional theory (DFT) calculation. DFT calculations were carried out using the Linear Combination of Atomic Orbitals software (LCAODFTLab) within the Perdew-Burke-Ernzerhof (PBE) parameterization of generalized gradient approximation. (GGA) We applied the Grimme D2 dispersion correction method and used spin-polariation for Fe atoms. Core electrons were replaced by Troullier-Martins-type norm-conserving pseudopotentials, and the Kohn-Sham wavefunctions were expended in terms of double-ζ-plus-polarization-level numerical atomic basis sets defined by the confinement energy of 100 meV. Real-space mesh defined with the cut-off energy of 200 Ry was employed for the grid operations, and a $5\times5\times1\,\vec{k}$ -points in the Monkhorst-Pack scheme were sampled. A finer $15\times15\times1\,\vec{k}$ -points mesh was sampled for the calculation of density of states. (DOS)

Due to many iron atoms in substrate, Self-consistent field (SCF) failed to converge. By using plane wave basis set implemented VASP package, we only have performed optimization in Fe substrate system. It also performed by PBE- GGA. An energy cutoff 450 eV for the wavefunctions and a force convergence criterion of 0.01 eV $Å^{-1}$. The pairwise dispersions were corrected by the DFT-D3 method by Grimme et al. The $1\times1\times1\,\vec{k}$ -points (Γ point) was sampled for optimization.

To obtain optimized geometries of $C_2N$, we used a hexagonal unit cell having initial $C_2N$ interlayer distance 3.27 Å with a size of 8.36× 8.36×25 $Å^3$ for $C_2N$, 8.36×8.36×45 $Å^3$ for $C_2N$ with Iron substrate to avoid the unphysical interactions.

## RESULTS AND DISCUSSION

### $C_2N$ trilayer stacking

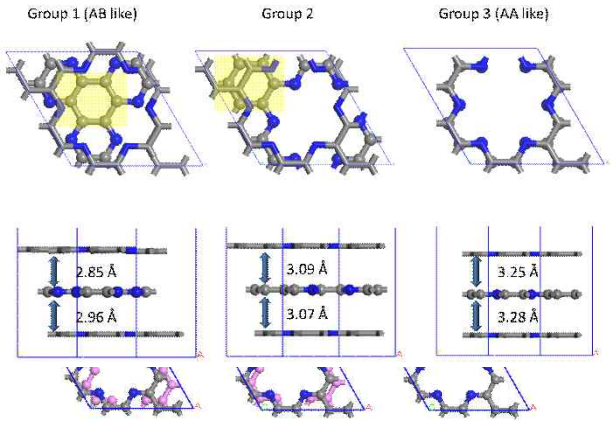



Fig. 1. The atomic structures of trilayer $C_2N$-*h*2D. The pink balls represents second layer $C_2N$.

To investigate stacking order in trilayer $C_2N$, we made 9 different models those second $C_2N$ (Fig.1. pink balls) slightly sliding from ABA stacking to AAA stacking. The sliding scale is a 1/9 unit cell vector which is divided 9 step from ABA to AAA.

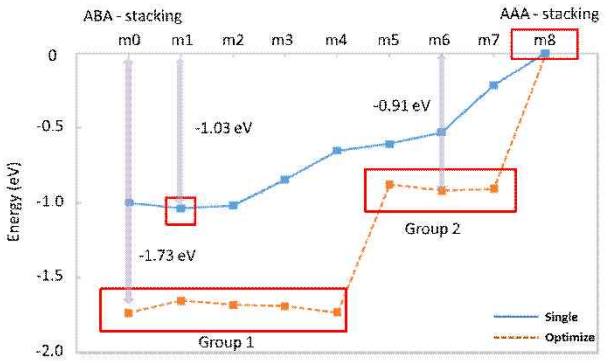



Fig. 2. Relative total energy (blue line) single point calculation (orange dot) geometry optimization.

In the single point calculation, the points show linear relationship between energy and models(from AAA stackingn to ABA stacking). ABA like stacking is more energetic favorable than AAA like stacking. Another important point is m1 model has slightly more stable than totally ABA-stacking.

To confirm whether trilayer $C_2N$ has different stacking order, we perform to optimize those models respectivey. It shows another interesting result. Trilayer $C_2N$ has three different optimized group.

Fig. 3. The three different optimized $C_2N$ trilayer sturcture with top view and side view.

From m0 to m4 models are similarly optimized like Group 1 model. (Fig.3) Group 1 model is most energetically stable among the groups. From m5 to m7 models become Group 2 model. Only m8, AAA like model does not change after optimizing

Comparing those Group models, Group 1 show its second $C_2N$ $C_6$ ring in a nitrogen hole. In the same way, Group 2 show only half of $C_6$ ring in the hole. Group 3 totally match first and third $C_2N$ layer. On other hand, it shows more stable structure, more shorter interlayer distance.

We can find ABA-stacking is not most stable structure in trilayer $C_2N$, Trilayer $C_2N$ has different optimized group and when the AAA stacking are slightly broken, it does not remain AAA stacking.

We now move on to consider the electronic band structure along different stacking order.

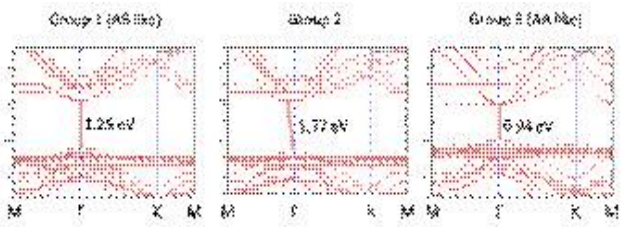


Fig. 4. Band structures of Group 1,2,3. Γ (0.0, 0.0, 0.0), M (0.5, 0.5, 0.0), and K (1/3, 1/3, 0.0) refer to special points in the first Brillouin zone.

25
ce
ns

same trend and difference size of bandgap. In addition to, Group 2 has indirect band gap 1.37 eV.

**$C_2N$ with embedded Fe atom in hole**

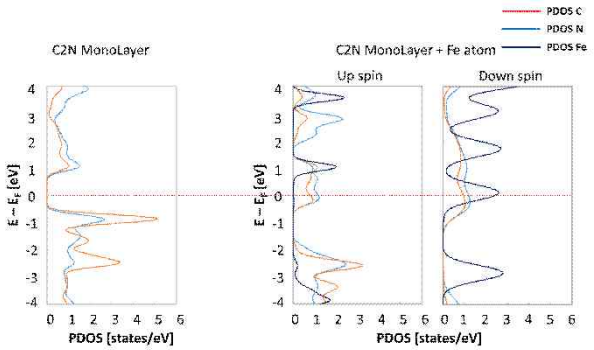



Fig. 5. Projected density of states (PDOS) plot (left) $C_2N$ mononlayer (Right) with embedded Fe atom in hole. Because of spin-polarization, it has two state, up and down. (red line) PDOS C, (blue line) PDOS N, (dark blue line) PDOS Fe, (red dot) Fermi energy fixed 0.

As shown above, only $C_2N$ monolayer show band gap and its fermi energy exists between conduction band minimum (CBM) and valence band maximum (VBM). Embedded Fe atom change $C_2N$ monolayer from semi metallic to metallic by shifting fermi energy.

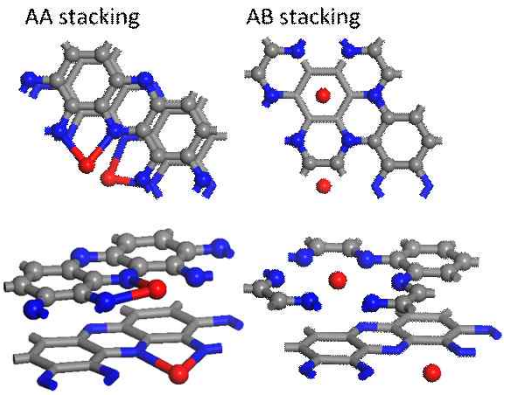



Fig. 6. $C_2N$ bilayer stacking AA (left), AB (right) with embedded Fe atom in a hole

From the Fig. 6. we test two different stacking $C_2N$ structure with embedded Fe atom in a hole. At AB stacking, the Fe atom is in a middle of hole. In contrast, Fe atom in AA stacking move to nitrogen atoms and make bonding. We also know that the AA stacking total energy is smaller than AB stacking in 0.28 eV. It shows embedded Fe atom effect on $C_2N$ not only electronic structure but also atomic structure.

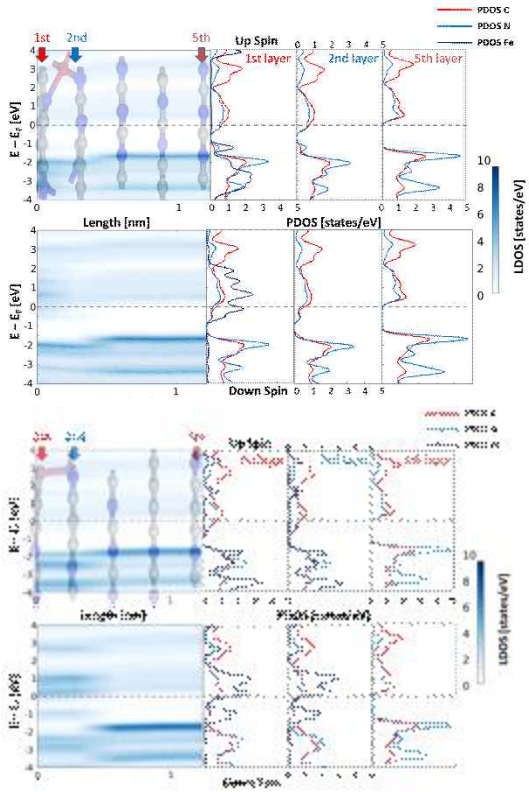


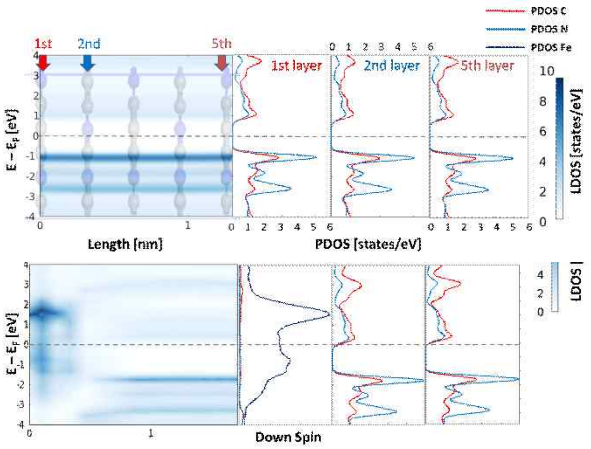

Fig. 7. Local density of state and Projected density of state for the model that three AB like stacking $C_2N$ on (left side) one-Fe atom AA stacking (up) two-Fe atom AA stacking.

One experimental paper [3] show the average $C_2N$ layer encapsulating is 5 layer. Now, we focus on the effect of Fe atom on 5 layer $C_2N$. 5 Layer made by two part; 1-2 layer from the AA $C_2N$ structure with Fe atom, 3-5 Layer from the AB like $C_2N$ trilayer stacking because of its energetic favourable.

Fig. 7. we find that one or two Fe atom influence all the $C_2N$ electronic structure. Especially, 5 Layer $C_2N$ which is no Fe atoms in the hole is changed from semi-metallic to metallic. It is important phenomenon for using any kind of catalyst system. On the other hand, comparing one-Fe and two-Fe atom in a hole, one-Fe atom move to centre of 1-2 layer but two-Fe atom remain well. It implies some interaction between each Fe atom exists and it make total system more stable.

**$C_2N$ on the iron substrate**

Finally, we check effect of iron substrate on $C_2N$ layer. we made only AB stacking $C_2N$ because the models do not include Fe atom itself. (because of stability as discussed above) It shows similar result in the case of Fe atom embedded. Only $C_2N$ case, it maintains bandgap from 1 layer to 5 layer. In contrasts, $C_2N$ with Fe substrate shows the fermi energy change




resulting to metallic $C_2N$.

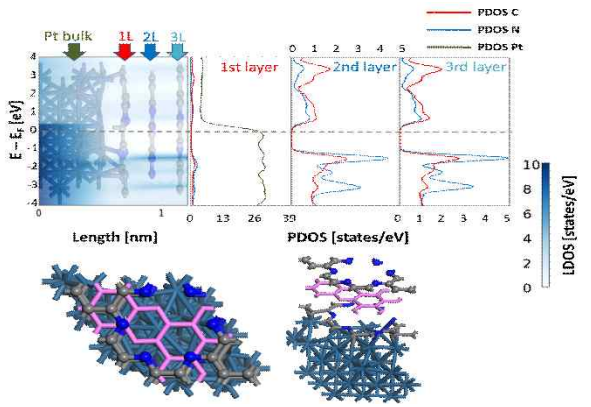



Fig. 9. (up) Local density of state and Projected density of state for trilayer $C_2N$ on Pt substrate. (bottom) the calculation model top view and side view

To confirm our result, we build $C_2N$ trilayer on platinum substrate which is known for superior catalytic material and make electronic structure. It shows Pt substrate do not change $C_2N$ layer metallic. In other words, we cannot expect higher catalytic performance by encapsulating $C_2N$ on platinum.

## CONCLUSION

In conclusion, on the basis of DFT calculations, we have investigated more stable than AB stacking exists in trilayer $C_2N$ and the effect of iron on $C_2N$. Embedded Fe atom or substrate Fe change $C_2N$ electronic structure from semi-metallic to metallic. It shows an evidence that encapsulating $C_2N$ has higher performance. Comparing Pt substrate case, our theoretical predictions suggest that ferromagnetism character of Fe make the results be.

## ACKNOWLEDGEMENT

This research was supported by the EDISON Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Science, ICT & Future Planning (2012M3C1A6035302)

## REFERENCES

[1] J. Mahmood, E. K. Lee, M. Jung, D. Shin, I. Jeon, S. Jung, H. Choi, J. Seo, S. Bae, S. Sohn, N. Park, J. H. Oh, H. Shin and J. Baek, Nat. Commun., 2015, 6, 6486.

[2] R. Zhang, B. Li, and J. Yang, Nanoscale, 2015 7, 14062

[3] J. Mahmood, S. M. Jung, S. J. Kim, J. M. Park, J. W Yoo and J. Baek Chem. Mater. 2015, 27, 4860