Synthesis of a half metallic material on a substrate is highly desirable for diverse applications. Herein, we have investigated structural, adsorptive, and magnetic properties of metal free graphitic carbon nitride (g-C\(_4\)N\(_3\)) layer on hexagonal BN layer (h-BN) using the optB88-vdW van der Waals density functional theory. It is found that g-C\(_4\)N\(_3\) layer can be adsorbed on BN layer due to the change of lattice constant of the hybridized system. The newly found lattice constant of g-C\(_4\)N\(_3\) was 9.89 Å, which is approximately 2% lower and larger than to those of free standing BN and g-C\(_4\)N\(_3\), respectively. Also, \(2\times3\) surface reconstruction geometry predicted in free standing g-C\(_4\)N\(_3\) layer disappears on the BN layer. Interestingly, we have found that metal free half metallic behavior in g-C\(_4\)N\(_3\) can be preserved even on BN layer and the characters of spin polarized planar orbitals suggest that our theoretical prediction can be verified using normal incidence of K-edge X-ray magnetic circular dichroism (XMCD) measurement.

3d transition metal elements are believed to be essential to introduce magnetism. However, many studies showed that magnetism could occur in the absence of the 3d transition metal elements and it is referred to as \(d^0\) magnetism. Examples of \(d^0\) magnetism from various types of oxide materials\(^{12}\) and semiconductors\(^{14}\) have been reported and in most of discussions the \(d^0\) magnetism is attributed to the effect of vacancy defects or lattice distortion. Half metallic magnetism also received great research interest because half metallic materials have various potential applications in spintronics. In most of previous studies on half metallic systems, the combination of various types of materials with 3d transition metal elements has been investigated\(^{5,6}\). Besides the magnetism of conventional 3d systems, 2p electron systems also yield another interesting property. Usually, 2p electron systems are known to display non-magnetic behavior in bulk state. Nonetheless, further studies in two dimensional structures have indicated that magnetic state is likely to be achieved in low dimensional geometry. For instance, many reports have shown the development of magnetic state in graphene or BN; the influence of vacancy defect or adatom defect has been discussed\(^{7,8}\). Here, the local magnetic moment has been discussed in most cases.

For spintronics, it is of interest to examine ferromagnetism in pure 2p electron systems in the absence of transition metal elements because large spin relaxation time is expected owing to the relatively weak spin-orbit coupling. Hence, the investigation of biocompatible material with half metallic properties of particular interest. Among various candidates, C-N based materials show great potential. In this respect, considerable efforts have been devoted to polymeric graphitic carbon nitride (g-C\(_3\)N\(_4\))\(^{9-11}\). This structure features intrinsic vacancies that are expected to produce spin polarized state. However, g-C\(_3\)N\(_4\) displays non-magnetic properties. Recently, a similar material g-C\(_4\)N\(_3\) in the framework of g-C\(_3\)N\(_4\) has been synthesized\(^{12}\). This metal free material showed half metallic properties in the free standing state, as reported by Du et al\(^{13-16}\). Additionally, the authors claimed that the g-C\(_4\)N\(_3\) has a \((2 \times 2)\) surface reconstructed geometry due to a buckling feature in the free standing layer.

It is highly desirable to synthesize a half metallic material on a substrate for diverse applications because one can avoid various difficulties of manipulating free standing layer. It is therefore necessary to choose a supporting material that does not disturb the intrinsic half metallic properties of g-C\(_4\)N\(_3\). However, investigation of half metallic properties of metal-free g-C\(_4\)N\(_3\) on a supporting material has yet to be reported. Herein, we for the first time investigate structural, adsorption, and magnetic properties of g-C\(_4\)N\(_3\)/BN.

Vienna ab initio simulation package (VASP) was used. Herein, the van der Waals interaction of optB88-vdW method\(^{17-19}\) was employed to investigate the physical properties of g-C\(_4\)N\(_3\)/BN. A vacuum distance of 15 Å was applied along the perpendicular direction to the film surface. All calculations were performed based on using \(9 \times 9 \times 1\) k-points and a kinetic energy of 700 eV cutoff.
Figure 1 | Schematic illustrations of top and side views for adsorption structure. (a)–(b) C1 on top of BN hollow and N1 and C2 on top of B (c)–(d) C1 on top of B and N1 and C2 on top of BN hollow (e)–(f) C1 on top of N belonged to BN layer and N1 and C2 on top of BN hollow (g) $(1 \times 1)$ structure of g-C$_4$N$_3$.

Figure 2 | Schematic illustrations of top and side views for adsorption structure. (a)–(b) C1 on top of N belonged to BN layer and N1 and C2 on top of B (c)–(d) C1 on top of hollow and N1 and C2 on top of N (e)–(f) C1 on top of B and N1 and C2 on top of N.
The most stable lattice constant of $g$-C$_4$N$_3$/BN was investigated by calculating the total energy as a function of lattice parameter. For the adsorptive and magnetic properties of hybridized $g$-C$_4$N$_3$/BN system, we have considered a $(2 \times 2)$ $g$-C$_4$N$_3$ layer onto a $(4 \times 4)$ BN layer. Structure optimization was performed via force and energy minimization process. In addition, ferromagnetic (FM), antiferromagnetic (AFM) and non-magnetic spin configurations were considered for the magnetic ground state. It is worth noting that the lattice constant of $(1 \times 1) g$-C$_3$N$_4$ unit cell is 4.74 Å, but that of $(1 \times 1) g$-C$_4$N$_3$ is 4.84 Å. Moreover, the $g$-C$_4$N$_3$ is known to have a $(2 \times 2)$ reconstructed surface geometry, thus the ground state lattice constant becomes 9.68 Å. This suggests that the lattice constant of $g$-C$_4$N$_3$ is likely to be modified in the presence of external effect. Consequently, we will explore the most stable lattice structure of $g$-C$_4$N$_3$/BN hybridized system by changing its lattice constant.

Fig. 1 and Fig. 2 show the schematic configurations of $g$-C$_4$N$_3$/BN systems featuring 6 different adsorption sites. The green and pink spheres represent the N, B atom in BN layer, respectively, while the gray and blue spheres represent the C and N atoms in $g$-C$_4$N$_3$ layer, respectively. The $(1 \times 1)$ unit cell of $g$-C$_4$N$_3$ is depicted in Fig. 1(g); the C and N atoms that are located on the hexagonal ring are referred as C$_1$ and N$_1$, respectively, whereas C atom located outside the ring is denoted as C$_2$. It should be noted that the bridge adsorption site is not observed because the atoms orient themselves into the configuration shown in Fig. 1(b), regardless of the initial calculations. Table I presents the calculated total energy differences among ferromagnetic (FM) and antiferromagnetic (AFM) spin arrangements, and the distances between BN and $g$-C$_4$N$_3$ layers. The results were based on the most stable lattice constant. The total energy for configuration depicted in Fig. 1(a) was set to zero as a reference energy that produced the most stable system. The interlayer distance for this configuration was 3.18 Å. Interestingly, the FM ground state was still preserved even in the BN underlayer, and was independent of the adsorption sites. It is worth noting that the energy difference for configuration 1(a) between FM and non-magnetic states was 278 meV. Fig. 3 shows the total energy curve as a function of the

| Structure          | (a) | (b) | (c) | (d) | (e) | (f) |
|--------------------|-----|-----|-----|-----|-----|-----|
| FM                 | 0   | 65  | 139 | 161 | 282 | 324 |
| AFM                | 177 | 258 | 352 | 351 | 570 | 551 |
| Interlayer distance | 3.18| 3.25| 3.28| 3.31| 3.39| 3.44|

Figure 3 | Calculated total energy Difference (in meV) and interlayer distances (in Å) in each configuration

Figure 4 | Electronic band structure along high symmetry directions. The blue and red lines represent majority and minority spin bands respectively. The black horizontal line denotes the Fermi level.

Figure 3 | Calculated total energy as a function of lattice constant.
lattice constant for the configuration Fig. 1(a) in which the ground state was realized. The solid line represents the fitting curve obtained with a parabolic polynomial function. A total energy minimum was observed at a lattice constant of 9.89 Å. The ideal monolayer of BN in a (4 × 4) unit cell has a lattice constant of 10.08 Å and that of free standing g-C4N3 in a (2 × 2) unit cell is 9.68 Å. Therefore, a newly found lattice constant of g-C4N3 was 9.89 Å, which is approximately 2% lower and larger than to those of free standing BN and g-C4N3, respectively.

We now discuss the adsorption energy. The adsorption energy ($E_{\text{ads}}$) was calculated as: $E_{\text{ads}} = E_{\text{BN}} + E_{g\text{-C4N3}} - E_{g\text{-C4N3}/\text{BN}}$, where $E_{\text{BN}}$ and $E_{g\text{-C4N3}}$ denote the total energies of the free standing systems, and $E_{g\text{-C4N3}/\text{BN}}$ represents the total energy of the hybridized system. To calculate the total energy of free standing layers, the corresponding lattice constants of (2 × 2) unit cell for g-C4N3 and (4 × 4) unit cell for BN were used. The calculated total energies of the free standing BN and g-C4N3 are 248.685 eV and 199.699 eV, respectively. The horizontal line in Fig. 2 represents the sum of the energies of the free standing systems, i.e., $E_{\text{BN}} + E_{g\text{-C4N3}}$. Thus, the total energy of the g-C4N3/BN hybridized system should be below the horizontal line. Based on the calculated total energy curve in Fig. 3, the g-C4N3/BN hybridized system is unstable when the g-C4N3/BN structure has a lattice constant similar to that of either BN or g-C4N3 because the resulting total energy is larger than the sum of the free standing systems energies. The total energy minimum of the hybridized system was obtained at a lattice constant of 9.89 Å, which corresponds to a 2% contraction and expansion with respect to that of BN and g-C4N3, respectively. The ground state lattice constant obtained herein is comparable with the calculated average of the respective lattice constants of the free standing g-C4N3 and BN layers; the lattice changes enables adsorption of g-C4N3 layer on the BN layer. The calculated adsorption energy was 0.67 eV. Another interesting aspect is the structural behavior of the g-C4N3/BN system. According to previous theoretical prediction13, the free standing...
$g\text{-C}_3\text{N}_3$ surface is believed to show a $(2 \times 2)$ reconstructed geometry owing to surface buckling. However, herein, we observed that the surface reconstruction is absent on the BN layer and the $g\text{-C}_3\text{N}_3$ layer becomes flat layer with the interlayer spacings presented in Table I. We have found using Bader charge analysis\textsuperscript{20–23} that no significant charge transfer takes place between two layers. However, the van der Waals interaction between these two layers significantly influences the surface structure. Owing to this geometric effect, the lattice constant of $g\text{-C}_3\text{N}_3$/BN will be 4.945 Å in a $(1 \times 1)$ unit cell.

For the configuration depicted in Fig. 1(g), magnetic moments of N$_1$ and C$_2$ are 0.26 $\mu_B$ and 0.028 $\mu_B$, respectively. The calculated total magnetic moment per unit cell is 4 $\mu_B$, indicating the half metallic nature of $g\text{-C}_3\text{N}_3$. Fig. 4 shows the electronic band structure. The valence bands of majority spin states are located below the Fermi level, whereas the minority spin bands cross the Fermi level. These finding confirms that the half metallic nature of the metal free $g\text{-C}_4\text{N}_3$/BN system. Fig. 5(a) and (b) show the m-resolved density of states (m-DOS). As observed, the spin polarized state mainly originates from the px,y orbitals of the N$_1$ atoms in the $g\text{-C}_3\text{N}_3$ layer. In contrast, no significant spin polarization was found in the px orbital. Moreover, this result indicates that the top of the valence involves the planar px,y orbitals. In Fig. 6 the calculated spin polarized charge density of $g\text{-C}_4\text{N}_3$/BN. As inferred, the planar px,y orbitals contribute to the magnetic moment. Additionally, observed spin polarization in planar orbitals indicates that the K-edge X-ray magnetic circular dichroism (XMCD) measurement, using normal incidence beam, can verify our predictions because the magnetism of $g\text{-C}_3\text{N}_3$/BN originates from the 2p$_{x,y}$ orbital. In contrast, no XMCD signals would be detected with a grazing incidence beam because the selection $\Delta m = \pm 1$ is not satisfied.

In conclusion, we explored adsorption, structural, and magnetic properties of $g\text{-C}_3\text{N}_3$/BN. The hybridized system had a new lattice constant, which is different from those of free standing BN and $g\text{-C}_3\text{N}_3$ layers and this lattice change was responsible for adsorption of $g\text{-C}_3\text{N}_3$ on BN layer. In addition, the surface reconstruction feature found in free standing layer disappeared due to the interaction with BN layer. The magnetic moment arises from the N atoms in $g\text{-C}_3\text{N}_3$ layer, whereas the C atoms show negligible spin polarization. Very interestingly, half metallic behavior is preserved even on BN layer and the half metallicity originates mainly from the 2p$_{x,y}$ planar orbitals of N atoms in $g\text{-C}_3\text{N}_3$ layer. We suggest that this spin polarization from 2p$_{x,y}$ orbitals can be verified with the K-edge XMCD measurement using normal incidence beam. Overall, this metal free half metallic behavior even on a supporting material will enable the development of new and intriguing properties that show potential for next generation spintronics.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education, Science and Technology(No. 2013R1A1A2006071).

Author contributions

J.H. reviewed and wrote the manuscript. A.H. prepared figures 1–6.
Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Hashmi, A. & Hong, J. Metal free half metallicity in 2D system: structural and magnetic properties of γ-C3N3 on BN. Sci. Rep. 4, 4374; DOI:10.1038/srep04374 (2014).

This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-nd/3.0