Tailoring electronic properties of bilayer tri-s-triazine C₃N₄ using spatial modification: An ab-initio study

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Abstract. In the present work, change in electronic properties due to structural modification of bilayer g-C₃N₄ using density functional theory has been studied. We have considered shifting and rotation of one layer parallel to the second fixed layer and optimised three different arrangements. The stability of the bilayer was examined by calculating the total energy of all the structures. Specific bilayer arrangement having 180° rotation has been found most stable. The study of density of states reveals band gap of this structure to be 0.60 eV. From HOMOLUMO and partial density of states it is seen that the stability and properties of bilayer g-C₃N₄ highly depends on the arrangement of N-2p and C-2p orbitals in both the layers. The inclusion of van der Waals (vdW) interaction changes the properties in z axis due to coupled orbital and columnic interaction between the layers and individual orbitals.

1. Introduction
In search of novel eco-friendly, non-toxic, polymorphic, low cost material with earth abundant elemental composition, wide range band gap tunability, fidelity for spin based properties, multi-doping sites for cations and anions brings us to graphitic carbon nitride (g-C₃N₄) which is also known for its weak van der Waals (vdW) interlayer interaction which facilitates easy exfoliation [1]. Band gap for g-C₃N₄ bilayer is low as compared to monolayer and also C, N 2p orbital overlapping in the bilayer gives us opportunity to explore the applications on the basis of structural modifications [2]. Carbon self-doped g-C₃N₄ has shown ferromagnetic and half-metallic nature, which shows its application in spintronics, memory devices and dilute magnetic semiconductors [3]. Due to the easy tuning of the optical absorption edge, g-C₃N₄ films are also proposed as efficient solar cell material [4]. g-C₃N₄ based organic LEDs are good alternatives of gallium (Ga) and indium (In) based LEDs owing to their low cost earth abundant materials and its high quantum yield (QY) of 17.9% [5]. g-C₃N₄ is also used as sensing fluorescent probes, UV detectors, and in biomedical applications [6].

The interlayer interaction, excitonic effects, interface recombination and their synergistic effects play a crucial role in enhancing the electronic, optical and magnetic properties of g-C₃N₄, making it potential candidate for the metal-free organic multifunctional material. Here, in this work, we have studied the stability of bilayer g-C₃N₄ to understand interlayer coupling and its effect on electronic properties that could be a step closer in the field of tuning of properties on basis of layered arrangement as a keen field of study for experimentalist.

2. Methodology
For the present work, we have used the QUANTUM ESPRESSO code [7] which is based on projected augmented wave pseudopotentials. We have performed all the computations using Perdew–Burke–Ernzerhof functional under generalized gradient approximation [8]. vdW interaction is also included...
for the accurate estimation of interlayer interaction [9]. For structural and electronic properties calculations, Γ-centered k-mesh grid of 5×5×2 is used. Cut-off for wave function and charge density are used as 60 Ry and 540 Ry, respectively. Interlayer spacing of 3.27 Å and vacuum of 16.73 Å is given in z direction to ensure the bilayer nature of the structures. In the present work, three different structures named as C₃N₄-AA, C₃N₄-AB and C₃N₄-AB’ where C₃N₄-AA denotes two monolayers of C₃N₄ stacked on each other; for C₃N₄-AB, upper layer is rotated with 180° with the fixed lower layer and for C₃N₄-AB’atomic displacement of upper layer in x-y plane is considered so that the void of the lower layer is above the web of the upper layer as mentioned in Figures 1 (a-c). All the structures are geometrically optimized to minimize the force between the atoms. Effective mass of electrons and holes were calculated by fitting the energy bands using second degree polynomial method.

![Figure 1](image1.png)

**Figure 1.** Top and side view of C₃N₄ bilayer with (a) AA, (b) AB and (c) AB’ stacking.

3. Results

Structural optimization and total energy analysis have been performed for C₃N₄-AA, C₃N₄-AB and C₃N₄-AB’ structures. The change in total energy with structural modifications are presented in Figure 2. Among the studied structures, most stable structures is identified as g-C₃N₄-AB. No axial distortion is observed after inclusion of vdW in any of the bilayers. The calculated values of lattice parameters a=b and c and interlayer distance (d) are presented in Table 1. The value of lattice parameters a=b is found to be constant for AA, AB and AB’ structures while the value of c parameter was changed with different stacking. The d value of C₃N₄-AA, -AB and -AB’ stacking are found to be 3.52, 3.17 and 3.18 Å, respectively. Larger d value shows that the repulsive force between the two layers in the case of the AA-stacking is much stronger than that in the AB and AB’ stacking. Therefore, AA-stacking has lower binding energy as compared to AB stacking. Based on that, the AB-stacking is a more stable arrangement compared to the AA-stacking. The repulsive interaction between the layers of the AA-stacking leads to a larger interlayer distance. From the difference in c value the most stable structure have its least value signifying the proportionality of stability with the separation distance combined with the non-bonding planar orbital interaction.

The structural modification also affects the electronic structure due to the variation in the bond length, charge density and interlayer orbital interaction which is also seen in Figure 2. A significant change in band gap value is observed by changing stacking from AA to AB/AB’ while similar band gap is observed in AB and AB’ stacking. The calculated value of band gaps is also mentioned in Table 1. Total and partial density of states (TDOS and PDOS, respectively) are presented in Figures 3 (a-c). From TDOS (top panel of figures 3 a-c), it is seen that by layer arrangement significant change is seen in conduction region whereas valence region is almost similar. In PDOS, we have considered the bay and corner C atoms denoted as C₁ and C₂, respectively, and double and triple bonded N atoms represented by N₁ and N₂, respectively from each of the layer selected in a way that atoms over each others are selected for the study of orbital interaction. For the atoms of upper layer subscript U is used while for lower layer L subscript is used in PDOS. In AA stacking, all the C and N atoms of both the
layers show almost similar DOS while on changing layer arrangement (for AB and AB’ stacking) due to orbital interaction upper and lower layers show different DOS. Major contribution in the VB is mainly due to the N$_1$ atom of lower layer while N$_2$ atom and both the C atoms show significant contribution in CB. From the change in intensities of VB and CB, it is seen that a significant change in bonding takes place on changing the layer arrangement in bilayer g-C$_3$N$_4$ and the electronic properties can be tuned accordingly.

Figure 2. Calculated values of relative total energy and band gap for AA, AB and AB’ stacking of C$_3$N$_4$-bilayer. Solid lines are drawn to guide the eyes.

Figure 3. Total and partial density of states for (a) C$_3$N$_4$-AA (b) C$_3$N$_4$-AB and (c) C$_3$N$_4$-AB’, where subscript L and U represent the lower and upper layer atoms, respectively. Shaded region is for s orbital of respective atoms.

To recognize the orbital contribution in the band edges, we have presented the HOMO and LUMO (with top and side view) for AA, AB and AB’ stacking of C$_3$N$_4$ bilayer in Figure 4 (a-c). In case of AA stacking, the HOMO covers all N$_1$ atoms, and the LUMO is mainly distributed on C$_1$ and C$_2$ atoms and moderately occupies N$_2$ atoms, which confirms the PDOS. For AB stacking, the redistribution of HOMO and LUMO occurred in the lower layer only while for AB’ significant change in HOMO and LUMO is observed due to the change in interlayer interaction.
Figure 4. Top and side view of HOMO and LUMO for (a) AA, (b) AB and (c) AB’ stacking of bilayer C$_3$N$_4$

Table 1 is also collated with values of effective mass for electrons ($m_e^*m_0$) and holes ($m_h^*m_0$) calculated from the band structure calculation for AA-, AB- and AB’-C$_3$N$_4$ here $m_0$ denotes the rest mass of free electron. An indirect band gap is obtained with the increment of band gap values as one move towards the bilayer stability. The lower effective mass denotes higher mobility and easy migration of charge carrier over the surface, from the effective mass we observed the high electron mobility in AB and AB’ structure as compared to AA while the mobility of hole in all the three structures remains almost similar. The effective mass ratio corresponds to the rate of recombination of the charge carriers whose value is inversely proportional. Here the effective mass ratio for AB and AB’ show promising features in terms of lower rate of recombination of the electron hole pair.
Table 1. Lattice parameters, band gap and effective mass ratio with separate values of charge carriers.

| Structure   | Optimised Lattice Parameters (Å) | Interlayer distance (Å) | Band gap (eV) | Effective Mass  |
|-------------|---------------------------------|-------------------------|--------------|----------------|
|             |                                 |                         |              | Electron (m_e/m_0) | Hole (m_h/m_0) | Ratio (m_e/m_e) |
| C_3N_4-AA   | a=b=7.12, c=20.72               | 3.52                    | 0.42         | 0.31           | 0.76          | 2.43           |
| C_3N_4-AB   | a=b=7.12, c=19.64               | 3.17                    | 0.60         | 0.19           | 0.73          | 3.70           |
| C_3N_4-AB'  | a=b=7.12, c=19.67               | 3.18                    | 0.60         | 0.19           | 0.75          | 4.00           |

4. Conclusions
The stability and electronic properties of three different layer arrangements for bilayer C_3N_4 were calculated using density functional theory. Stability of bilayer depends on the interlayer orbital interaction of C and N and their positions, as studied by density of states. N-2p and C-2p orbitals play a major role in interlayer interaction. Hence, the structure with C-N atoms stacked over each other show p-p hybridization making it most stable that should be used for the further studies to reduce the interface recombination of e^-h^+ pair for C_3N_4 bilayer as an efficient metal free multifunctional material with rich electron density. The present study works as an initial step towards the design of an efficient material based on C_3N_4 bilayer for photo-assisted applications.

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