# Theoretical study on the Photo-catalytic properties of the doped Carbon–Nitride (C<sub>3</sub>N<sub>4</sub>) Systems

M. Sc. Thesis

By

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# DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE June 2015

# Theoretical study on the Photo-catalytic properties of the doped Carbon-Nitride (C<sub>3</sub>N<sub>4</sub>) Systems

### A THESIS

Submitted in partial fulfilment of the requirements for the award of the degree of Master of Science

> *by* **Twinkle Yadav**



DISCIPLINE OF CHEMISTRY INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2015



# INDIAN INSTITUTE OF TECHNOLOGY INDORE CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Theoretical study** on the photo-catalytic properties of the doped carbon-nitride (C<sub>3</sub>N<sub>4</sub>) systems in the partial fulfilment of the requirements for the award of the degree of **MASTER OF SCIENCE** and submitted in the **DISCIPLINE OF CHEMISTRY**, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2014 to June 2015 under the supervision of Dr. Biswarup Pathak, Assistant Professor, IIT Indore. The matter presented in this thesis has not been submitted by me for the award of any other

degree of this or any other institute.

# Signature of student with date Twinkle Yadav

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

Signature of the Supervisor of M. Sc. thesis (with date) Dr. Biswarup Pathak

Twinkle Yadav has successfully given her M. Sc. oral examination held on 1<sup>st</sup> July 2015.

Signature of Supervisor of M.Sc. thesis Date:

Convener, DPGC Date:

Signature of PSPC Member #1	Signature of PSPC Member#2
Date:	Date:

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#### ABSTRACT

Photo-catalytic water splitting is gaining attention among researcher in recent few years for the generation of  $H_2$  from water. Varieties of materials have proposed for this process but these are very far from practical application due to the less efficiency and low conversion rate. So, in this project, we have studied some materials by Density functional theory (DFT) calculations which can be used as a metal free photo-catalytic material for water splitting. We have also designed some new materials by the art of theoretical techniques to improve the efficiency of photo-catalysis. We have thoroughly investigated their electronic properties like density of states (DOS) and work function. Graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is used as starting materials which can be used as photo-catalysts. In this project, B-doping was done in g-C<sub>3</sub>N<sub>4</sub> to change the photo-catalytic properties of g-C<sub>3</sub>N<sub>4</sub>. By this doping we have achieved to tune the band gap and work function of g-C<sub>3</sub>N<sub>4</sub> which will be very fruitful for designing efficient metal free photo-catalyst.

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#### **CHAPTER-1**

#### 1. INTRODUCTION:

The diminution of fossil fuels and its harmful effects on environment caused by their combustion is a serious issue. Use of fossil fuels cannot be stopped because it produced a significant amount of energy per unit weight. The calculated amount of energy consumed or required per year is 14 TW/Y [1]. Taking into account the economic development and constantly increasing population, demand of energy will be doubled in coming years i.e. 28-30 TW/yr. About 96% of the energy used globally for transportation purpose is supplied from crude oil fuels. It is not a good sign as petroleum reserves and other fuels are limited and they will deplete with time. Estimated time for expenditure of remaining fuels is 150-200 years. But depletion of fossil fuels is not only problem, combustion of these fuels released many poisonous gases like carbon dioxide, sulphur dioxide, carbon monoxide and many more gases.

Release of carbon dioxide in atmosphere disturb the balance between CO<sub>2</sub> released to environment and gas absorbed that can be absorbed by plants. According to the reports, if the consumption of fuels and emission of carbon dioxide goes with the same speed then after 20-30 years carbon dioxide level will rise to 40 billion Mg per year [1]. So, researchers start working on this field and they find out that water splitting is the most promising approach to this problem as it can solve both energy and environmental problem simultaneously. H<sub>2</sub>O is used to produce hydrogen and oxygen as it is a clean, cheap, renewable and safe. Photocatalytic water splitting is considered as a significant way of production of hydrogen from resources because solar energy is renewable energy. By using TiO<sub>2</sub> photoelectrochemical (PEC) hydrogen production initiation in this field was done by Fujishima and Honda [2]. Eventually, interest of researcher's shifted towards photocatalytic water splitting and many research paper and reviews have published in many journals [3]. But inspite of all the hard work done, direct photocatalyst for water splitting faces few challenging issues. For example, (i) rare and expensive materials have used for many photocatalysts (ii) some show poor stability (iii) some have low quantum efficiency [4].

In the past few years, inorganic phototalyst containing transition metals especially Ti (i.e. titanium oxide) gained everyone's attention most because it is sensitive to ultraviolet light due to its large band gap, powerful oxidation properties, non- toxicity, inexpensive and its

photostability can be maintained for a long period of time but photocatalytic reduction of  $H_2O$  by using pure  $TiO_2$  is not fair enough for practical use which makes less suitable for artificial photosynthesies.

In last few years, large number of work was done on graphene and graphitic-carbon nitride (g- $C_3N_4$ ).  $C_3N_4$  is analogous to graphene. Scientists are interested about these carbon-nitrogen based graphene analogs because of the abundance of C and N in nature than the tansition metals. On the other hand C based materials are cheaper and easily handalable then transition metals. So, we chose the C<sub>3</sub>N<sub>4</sub> analogous for our initial study. C<sub>3</sub>N<sub>4</sub> is found in many forms like cubic C<sub>3</sub>N<sub>4</sub>, pseudocubic C<sub>3</sub>N<sub>4</sub>, alpha-C<sub>3</sub>N<sub>4</sub>, beta-C<sub>3</sub>N<sub>4</sub>, graphitic-C<sub>3</sub>N<sub>4</sub>. Among all these forms, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is the most stable phase with band gap 2.70 eV and absorbes light upto 450 nm. g-C<sub>3</sub>N<sub>4</sub> can be prepared by polycondensation of melamine in hydrazine solvent under supercritical condition or by using tri-s-triazine [5-9]. On investigation, it has been anticipated that it shows exceptional semiconducting properties and visible light absorption. It can be used as a metal free photocatalyst for water splitting and  $CO_2$  reduction using solar energy but one big disadvantage of g-C<sub>3</sub>N<sub>4</sub> is that it has low carrier mobility and absorption of sunlight is inadequate which affect the efficiency of energy conversion rate. Also due to its high level of the top of the valence band it shows a moderate water oxiadaton ability [10]. The modification is needed in the electronic structure and in surface properties to improve its ability and to make it a better semiconductor. In last few years, many people doped transition metals which is one of the possible way to tune the band gap and electronic property of g-C<sub>3</sub>N<sub>4</sub>.

In present work, I have modelled some structures by substituting C atom with some main group elements like N and B by first principle calculations. We prefer main group elements (N and B) over transition metal because of its abundance. We also investigate its electronic properties of the modelled structure like work function, band structure, density of state (DOS) and partial density of state (PDOS).

## **1.2. COMPUTATIONAL METHODS AND APPROXIMATIONS**

#### (i) Schrodinger wave equation

This equation is used to describe how the quantum state of a molecule changes with time [11]. It is the basic tool for calculating the properties of atoms and molecules. Commonly, the time

independent Schrödinger Equation is used to evaluate the different properties of materials. Time independent equation is given below.

$$H\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_M) = E\Psi(\boldsymbol{r}_1,\ldots,\boldsymbol{r}_N,\boldsymbol{R}_1,\boldsymbol{R}_2,\ldots,\boldsymbol{R}_M)$$
(1.2.1)

Where H is Hamiltonian operator and  $\psi$  is the wave function which contains all information about nuclei and electrons of atoms in the system. The Hamiltonian operator can be expressed as follows:

$$H = -\frac{h^2}{2m_e} \sum_{i} \nabla_i^2 - \sum_{I} \frac{h^2}{2M_I} \nabla_I^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I \neq j} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|},$$
(1.2.2)

 $M_I$ ,  $R_I$  and  $Z_I$  are the masses of nuclei, position of nuclei and nuclear charge,  $m_e$  is mass of electrons. Kinetic energy of both electron and nuclei are represented in both first and second term respectively, following by the terms of electron-electron repulsion and nuclei-nuclei repulsion after which term of attraction is there. According to Born-Oppenheimer approximation, kinetic energy term for nuclei can be neglected as mass of nuclei is more than that of electron. So the equation becomes

$$H = -\frac{h^2}{2m_e} \sum_{i} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|},$$
(1.2.3)

#### (ii) Density Functional Theorem

It is not possible to solve Schrödinger wave equation accurately in a real system. Hohenberg and Kohn proposed an alternate method in which an electron charge density plays an important role for the whole system. This is known as Density functional theory (DFT).

#### (iii) The Local Density Approximation (LDA)

It is most widely used approximation. It is used for the determination of ground state properties of materials. It is good for predicting geometrical quantities such as bond length lattice parameters and mostly gives values of electron densities and frequencies [12].

#### (iv) The Generalized Gradient Approximation (GGA)

Perdew, Burke and Ernzeroh proposed GGA. It gives a better prediction of bulk modulus, bond length, adsorption and binding energies as compared with the LDA. Although, there are chances of error in the band gap estimation in GGA also.

#### (v) The Projector Augmented Wave Method

The wave function of electron changes in space depending on the position of electron, whether it is close to nucleus or in the bonding region. The Projector Augmented Wave method is based upon a linear transformation operator, T which transfers all electron wave function to pseudo-wave function.

#### (vi) Hybrid Density Functional

GGA, LDA and HF (Hartree-Fock) are not accurate for band gap prediction of semiconductors and insulators, while hybrid functional generally provides a better estimation of the band gap. The local and semi local density approximations can be improved by using a well-established strategy of hybrid functional that includes a certain amount of non-local Hartree-Fock exchange. Thus, the resulting exchange correlation energy expression for PBE0 takes the following form.

$$E_{xc}^{PBE0} = aE_x^{HF} + (1-a)E_x^{PBE} + E_c^{PBE}$$
(1.2.4)

For the PBE0 hybrid function, this mixing parameter is set to a = 1/4, which is determined by perturbation theory [13].

#### (vii) GW Approximation

Many body perturbation theories are used to determine quasi-particle excitations in solid materials, especially for accurate calculation of electronic band structure. In the GW approximation, HF approximation has been replaced the exchange correlation which is based on the concept of screened Coulomb interaction. By the introduction of the screening of interaction between particles in a many body system, this leads to the concept of quasi-particles. A quasi-particle is defined as it is simply an electron with the screening cloud.

#### **CHAPTER-2**

#### **2.1. COMPUTATIONAL DETAILS:**

We have used the Vienna ab initio simulation package (VASP) [14] to do all the calculations. The exchange-correlation interaction was treated in the level of the GGA using the Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation functional [15]. The projected augmented wave (PAW) method [16] employed using an energy cut-off of 470 eV to describe the electronic wave function. In all the calculations, self-consistency was achieved with a tolerance in the total energy was set to  $10^{-4}$  eV.

The total systems consist of 7 atoms in which different combinations of Nitrogen, carbon and boron atoms were optimised with a distance of 15 Å between the adjacent Sheets to avoid any kind of structural interactions. The Brillion zone was integrated using Monkhorst-Pack generated sets of  $12 \times 12 \times 1$  k-points [17]. For the density of states calculations we have used Gamma generated sets of  $48 \times 48 \times 1$  k-points with a Gaussian smearing of 0.003 eV. We have calculated the work function for all the systems.

### **CHAPTER-3**

#### **3. RESULTS AND DISCUSSION:**

We have considered seven atom unit cell of  $C_3N_4$ , whose hardness is greater than diamond. Teter and Hemley have proposed different structures for  $C_3N_4$  (cubic, pseudo-cubic, alpha, beta, graphitic) [18]. g-C<sub>3</sub>N<sub>4</sub> is considered as an analogue of graphene as it also has 2D sheet like structure same as graphene. We have started with g-C<sub>3</sub>N<sub>4</sub>. The structure was fully relaxed and calculated carbon-Nitrogen bond length is 1.46 Å and 1.32 Å which matches well with the other previous theoretical calculations [19]. The Electronic structure of  $C_3N_4$  (or graphitic-C<sub>3</sub>N<sub>4</sub>) has some interesting properties and we have calculated the electronic structure and the total density of states (TDOS) for C<sub>3</sub>N<sub>4</sub>.



Figure 1: Fully relaxed sheet of g-C<sub>3</sub>N<sub>4</sub>





Figure 2: total density of states of  $g-C_3N_4$  using (a) GGA approximation (b) hybrid functional method and work function of  $g-C_3N_4$  (c) GGA approximation (d) hybrid functional method

The band gap of g-C3N4 is 1.55 eV (Figure 1) according to GGA calculation and 2.57 eV according to hybrid calculations which again agrees well with the theoretical value of 2.50 eV. Calculated work functions are 3.83 eV according to GGA and 3.47 eV according to hybrid function. Therefore the level of theories we have used is good enough for our further study. Then we want to study the structure of doped  $g-C_3N_4$  and the electronic properties.

#### **3.1.** B-doped g-C<sub>3</sub>N<sub>4</sub> (C replaced by B)

We thought to study the effect of doping on g-C<sub>3</sub>N<sub>4</sub>, therefore we doped g-C<sub>3</sub>N<sub>4</sub> with boron as it is an electron deficient atom we were expecting some interesting result. Doping is done in a pattern. At first we dope one boron atom in 7 atomic unit cell, which corresponds to 14.28% of boron doping then percentage of B-doping increases from 14.28% to 28.57% then to 42.85%. We have fully relaxed the B-doped g-C<sub>3</sub>N<sub>4</sub> structure (Figure-3) and then calculated it's density of states for our electronic structure study. We found that these electronic structures show unusual behaviour. All these structure behaves as a degenerate semiconductor. Degenerate semiconductor is that in which the Fermi level entering the valance (conduction) bands in case of p-type (n-type) doping [20].









Figure-3: Boron doped structures (a)  $B_3N_4$  sheet (b)  $B_2CN_4$  sheet (c)  $BC_2N_4$  sheet





Figure 4: total density of states of  $B_3N_4$  using (a) GGA approximation (b) hybrid functional method and work function of  $B_3N_4$  (c) GGA approximation (d) hybrid functional method



Figure 5: total density of states of  $B_2CN_4$  using (a) GGA approximation (b) hybrid functional method and work function of  $B_2CN_4$  (c) GGA approximation (d) hybrid functional method



Figure 6: total density of states of BC<sub>2</sub>N<sub>4</sub> using (a) GGA approximation (b) hybrid functional method and work function of BC<sub>2</sub>N<sub>4</sub> (c) GGA approximation (d) hybrid functional method

### 3.2. B-Doped g-C<sub>3</sub>N<sub>4</sub> (N replaced by B)

After replacing C from B, we saw some interesting results. Therefore we thought to dope B by replacing more electro-negative atom so we replaced N by B. At first we dope one boron atom in the 7 atoms unit cell of  $C_3N_4$  which corresponds to 14.28% of boron doping. Then two boron atoms were doped which corresponds to 28.57% boron doping, then percentage of doping increased to 42.85% to 57.14%. At 57.14% all nitrogen atoms were replaced by boron. All the electronic structures were optimized. We have fully relaxed B-doped g- $C_3N_4$  structures (Figure-7). We found that after doping some structures have isomers. We have plotted the total density of

states for 14.28%, 28.57%, 42.85% and 57.14% of B-doped g-C<sub>3</sub>N<sub>4</sub> by using GGA and hybrid functional method. We found that GGA calculation and hybrid calculations were showing different results.



Figure 7: Fully relaxed sheet of C<sub>3</sub>N<sub>3</sub>B (a) Isomer 1 (b) Isomer 2



Figure 8: total density of states of  $C_3N_3B$  using (a) GGA (b) hybrid functional method and work function of  $C_3N_3B$  (c) GGA approximation (d) hybrid functional method



Figure 9: Total density of states of  $C_3N_3B$  (2<sup>nd</sup> isomer) using (a) GGA approximation (b) hybrid functional method and work function of  $C_3N_3B$  (2<sup>nd</sup> isomer) using (c) GGA approximation (d) hybrid functional method

We have seen that in  $1^{st}$  isomer when total density of state was calculated by GGA calculations no energy gap was observed but when total density of states for the same  $1^{st}$  isomer was calculated by using hybrid functional calculations band gap was observed. We have observed that  $C_3N_3B$  ( $1^{st}$  isomer) behaved as a p-type semiconductor with band gap of 0.94 eV and calculated work function was 4.28 eV. Whereas, in  $2^{nd}$  isomer of  $C_3N_3B$  slightly different but when TDOS calculated by hybrid functional calculations it exhibited band gap of 0.73 eV and it also behaved as a p-type semiconductor with work function of 4.64 eV.



Figure 10: Fully relaxed sheet of  $C_3N_2B_2$  (a) Isomer 1 (b) Isomer 2



Figure 11: Total density of states of  $C_3N_2B_2$  (1<sup>st</sup> isomer) using (a) GGA (b) hybrid functional method and work function of  $C_3N_2B_2$  (1<sup>st</sup> isomer) (c) GGA approximately (d) hybrid functional method



Figure 12: Total density of states of  $C_3N_2B_2$  (2<sup>nd</sup> isomer) using (a) GGA (b) hybrid functional method

The electronic structure with 28.57% boron doping again had two isomers. Total density of states for 1<sup>st</sup> isomer was when calculated by GGA no band gap was seen but when hybrid functional calculation was used for calculating TDOS, band gap of 0.42 eV (p-type) was observed with work function 4.54 eV. The 2<sup>nd</sup> isomer did not show any band gap.



Figure 13: Fully relaxed sheet of C<sub>3</sub>NB<sub>3</sub> (a) Isomer 1(b) Isomer 2



Figure 14: Total density of states of  $C_3NB_3$  (1<sup>st</sup> isomer) using (a) GGA (b) hybrid functional method and Work function of  $C_3NB_3$  (1<sup>st</sup> isomer) (c) GGA approximation (d) hybrid functional method







Figure 15: Total density of states of  $C_3NB_3$  (2<sup>nd</sup> isomer) using (a) GGA approximation (b) hybrid functional method and work function of  $C_3NB_3$  (2<sup>nd</sup> isomer) (c) GGA approximation (d) hybrid functional method

When we calculated the total density of states of  $1^{st}$  isomer of  $C_3NB_3$  by using GGA calculation band gap of 0.71 eV was observed with work function 4.92 eV whereas by using hybrid calculation TDOS changes to 0.38 eV with work function 5.37 eV. On the other hand TDOS calculation of  $2^{nd}$  isomer of  $C_3NB_3$  by using GGA calculation exhibited band gap of 0.42 eV with work function 4.25 eV and by hybrid calculation band gap reduced to 3.85 eV with work function of 5.41 eV. In this case we have seen that in GGA calculations both the isomers were showing different band gap but in hybrid calculations band gaps were approximately equal.



Figure 16: Fully relaxed sheet of C<sub>3</sub>B<sub>4</sub>



Figure 17: Total density of states of  $C_3B_4$  using (a) GGA approximation (b) hybrid functional method and work function of  $C_3B_4$  (c) GGA approximation (d) hybrid functional method

In this case we were expecting some band gap as all electronegative atoms were replaced by boron and as boron has one electron less than carbon we are expecting for a p-type semiconducting behaviour but after calculating TDOS using both GGA calculations and hybrid calculation we saw that  $C_3B_4$  did not show any band gap and hence  $C_3B_4$  was metallic.

#### **3.3. N-DOPED SHEET**

After all this doping we thought to use  $C_3B_4$  for doping because it's a kind of analogue of  $g-C_3N_4$ and we doped carbon of  $C_3B_4$  by more electronegative atom nitrogen as nitrogen has one more valance electron than carbon therefore such doping lead to n-type semiconductor. So, we doped one nitrogen which corresponds to 14.28% of nitrogen doping then percentage of doping increased to 28.57% that means two nitrogen atoms were doped in  $C_3B_4$  then percentage increased to 42.57% which means all carbon atoms of  $C_3B_4$  were replaced by nitrogen.Thereafter we have fully relaxed the structure and calculated their total density of states. We have plotted the total density of states for 14.28%, 28.57% and 42.57% of N-doped  $C_3B_4$ .



Figure 19: Total density of states of  $C_2NB_4$  using (a) GGA approximation (b) hybrid functional method and work function of  $C_2NB_4$  (c) GGA approximation (d) hybrid functional method

When only one nitrogen atom was doped no band gap was seen by using both the calculations therefore  $C_2NB_4$  is metallic.



Figure 20: Fully relaxed sheet of CN<sub>2</sub>B<sub>4</sub>



Figure 21: Total density of states of  $CN_2B_4$  using (a) GGA approximation (b) hybrid functional method and work function of  $CN_2B_4$  (c) GGA approximation (d) hybrid density method

No band gap was seen when only 14.28 % nitrogen doping was done but when doping increased to 28.57 % doping i.e. two nitrogen atoms were doped band gap was seen. By using GGA calculation band gap was 1.38 eV with work function of 4.89 eV and when hybrid functional was used it increased to 1.64 eV with work function 5.11 eV.



Figure 23: Total density of states of  $N_3B_4$  using (a) GGA approximation (b) hybrid functional method and work function of  $N_3B_4$  (c) GGA approximation (d) hybrid functional method

We found when total density of state of  $N_3B_4$  was calculated by GGA calculation band gap was 3.53 eV with work function 2.68 eV and when TDOS calculated by hybrid functional calculation it increased to 3.78 eV with work function 3.23 eV (n-type ).

# 3.4. C-DOPING IN N<sub>3</sub>B<sub>4</sub>

We thought to dope carbon in  $N_3B_4$  by replacing boron. We started by doping one carbon and we found two isomers then we doped two carbon atoms. Thereafter, we have fully relaxed the structure and calculated their total density of states. We have plotted the total density of states for 14.28% and 28.57% C-doped  $N_3B_4$ .



Figure 24: Fully relaxed sheet of N<sub>3</sub>B<sub>3</sub>C (a) Isomer 1 (b) Isomer 2





Figure 25: Total density of states of  $N_3B_3C$  (1<sup>st</sup> isomer) using (a) GGA approximation (b) hybrid functional method and work function of  $N_3B_3C$  (1<sup>st</sup> isomer) (c) GGA approximation (d) hybrid functional method

When total density of states of 1<sup>st</sup> isomer was calculated, band gap was observed by both the calculations. By using GGA calculation band gap was 0.74 eV and work function was 3.83 eV whereas by using hybrid calculation band gap of 0.94 eV was observed with work function 3.63 eV.



Figure 26: Total density of states of  $N_3B_3C$  (2<sup>nd</sup> isomer) using (a) GGA approximation (b) hybrid functional method

 $2^{nd}$  isomer of  $N_3B_3C$  did not show any band gap by using both calculations and hence act as metallic.



Figure 28: Total density of states of  $N_3B_2C_2$  using (a) GGA approximation (b) hybrid functional method and work function of  $N_3B_2C_2$  (c) GGA approximation (d) hybrid functional method

When two carbon atoms were doped in  $N_3B_4$  band gap was seen by GGA calculation around 0.84 eV and work function was 4.21 eV and by hybrid calculation it increased to 0.94 eV and work function to 3.63 eV.

#### **CHAPTER-4**

#### **CONCLUSION:**

In this project we have thoroughly studied the role of different dopant (like B, N etc.) on g-C<sub>3</sub>N<sub>4</sub>. We have studied their electronic properties by their total and partial density states (TDOS and PDOS) and work function calculations. By replacing C with B we can tune the band gap of g-C<sub>3</sub>N<sub>4</sub> from 2.57 eV to ~5.0 eV by introducing 42.85% B doping. Then we have replaced N with B atom and find different type of isomers among them some are metallic, some are semiconductors. We also use two different methods to determine the proper band gap opening and changes in work function due to the different doping. We also find that the work function can also be tuned by this different doping. So, our study reveals that by changing different doping concentration as well as the position of the dopant (B in place of C or N) we can easily tune the electronic property of g-C<sub>3</sub>N<sub>4</sub> which will be helpful to model some metal free photocatalyst for future applications.

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