# First Principles Study of Bio-Conjugated Boron Nitride Nanostructures

**A THESIS**

**SUMMARY**

**SUBMITTED TO**
**THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA**

**FOR THE AWARD OF THE DEGREE OF**

## Doctor of Philosophy

*IN*

## *Physics*


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**MARCH-2019**

# Summary

The present thesis is organized in the following manner. The ***Chapter 1*** is all about the recent trends which are developed to shrink the dimensionality of materials for the access of desire unique material properties for their application in the novel field electronics, optical and biomedical applications. Nanomaterials have a large surface area to volume ratio which plays a significant role in determining their chemical and physical properties. The properties of nanostructures strongly depend on their size, shape and chemical compositions. Interfacing the biomolecules, typically called 'soft' molecules, with the generally 'hard' nanostructured materials requires control of both the nature and spatial distribution of the molecular interactions that take place between the two to ensure that the former retain their remarkable properties. When the biomolecules are deoxyribonucleic Acid (DNA) or protein/peptide, the task is particularly challenging because of the heterogeneous chemical nature of nucleotide/peptide surface. They possess many exciting and novel properties. Low-dimensional nanomaterials like BNNT, BNNR and new member in the row haeckelite-BN have many applications depending on their dimensionality and electronic properties. The properties of nanostructures can also be tuned by functionalization; understanding of which will be applicable for fabricating new hybrid nanomaterials.

Theoretical description of computational methodology used throughout the work is presented in ***Chapter 2***. Formalism of density functional theory (DFT) by discussing Kohn-Sham equation to its implementation in Plane Wave Pseudopotential code - Quantum Espresso is discussed. An important theoretical description of dispersion corrections to DFT is also discussed. ***Chapter 3*** is devoted to understand the underlying physics behind the interaction of

biomolecules (caffeine and nicotine) with the boron nitride nanomaterials (BNNs) to use them practically as bio-nanomaterials.

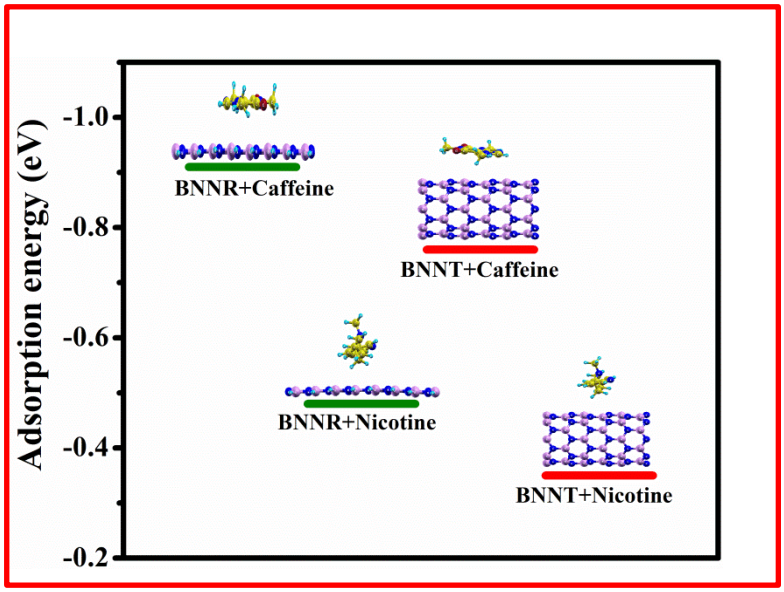


***Figure 1:*** *Adsorption energy of alkaloids over BNNR and BNNT depicting superiority of BNNR than BNNT.*

The investigation of the electronic structures and adsorption properties of alkaloids (Caffeine and Nicotine) over boron nitride nanotube (BNNT) and boron nitride nanoribbon (BNNR) is carried out under the frame work of density functional theory based first principles calculations. The study of density of states (DOS) along with partial density of states (PDOS) depicts major contributions of both molecules caffeine and nicotine in top of the valance band. The PDOS reveals that the ‘s’ orbital of nitrogen and boron do not contribute significantly. Suitability of BNNs as filtration or sensing of alkaloids is also checked by adsorption energy calculation of both molecules over BNNT and BNNR, and found BNNR as superior candidate than BNNT for the filtration/sensing. For incorporating the dispersion correction in the

calculation to consider proper long range van der Waals interaction, we used DFT-D2 with GGA-PBE scheme which increases the accuracy of adsorption energy calculation. Physisorption of both molecules over BNNs has been seen as the adsorption energy ranging between -0.35 and -0.76 eV, and -0.45 and -0.91 eV for caffeine and nicotine over BNNT and BNNR respectively. The most beneficial orientation of caffeine and nicotine over BNNT and BNNR is hetero atoms facing in-parallel for adsorption. Figure 1 clearly indicates the large adsorption energy of both alkaloids over BNNR than BNNT. Charge transfer analysis between BNNs and the adsorbed alkaloid molecules has also been checked by Lowdin charge analysis which depicts negligible charge transfer between BNNs and alkaloid molecules. Both BNNT and BNNR are sensitive towards both alkaloids which are observed from density of states, electronic structure calculations and quantum conductance. Our analysis shows that the BNNR strongly interacts with both alkaloids. Absence of any covalent interactions between the considered alkaloids and BNNs species (BNNT/BNNR) confirms its superiority as sensing materials. From our study one may conclude that the boron nitride nanostructures may be useful in designing sensitive alkaloids sensing device.

In ***Chapter 4,*** we have systematically investigated structural, vibrational and electronic properties of newly predicted allotrope of BN with octagonal and square ring morphology, haeckelite BN (haeck-BN). We further explore its applicability as biosensor by investigating the adsorption mechanism of most important basic building block of DNA i.e. nucleobases adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U). For the appropriate consideration of long distance van der Waals interaction, dispersion correction (DFT-D2) is

included in our calculation. The adsorption energy over haeck-BN for all five nucleobases has the following order: G > T > A ≈ C > U.

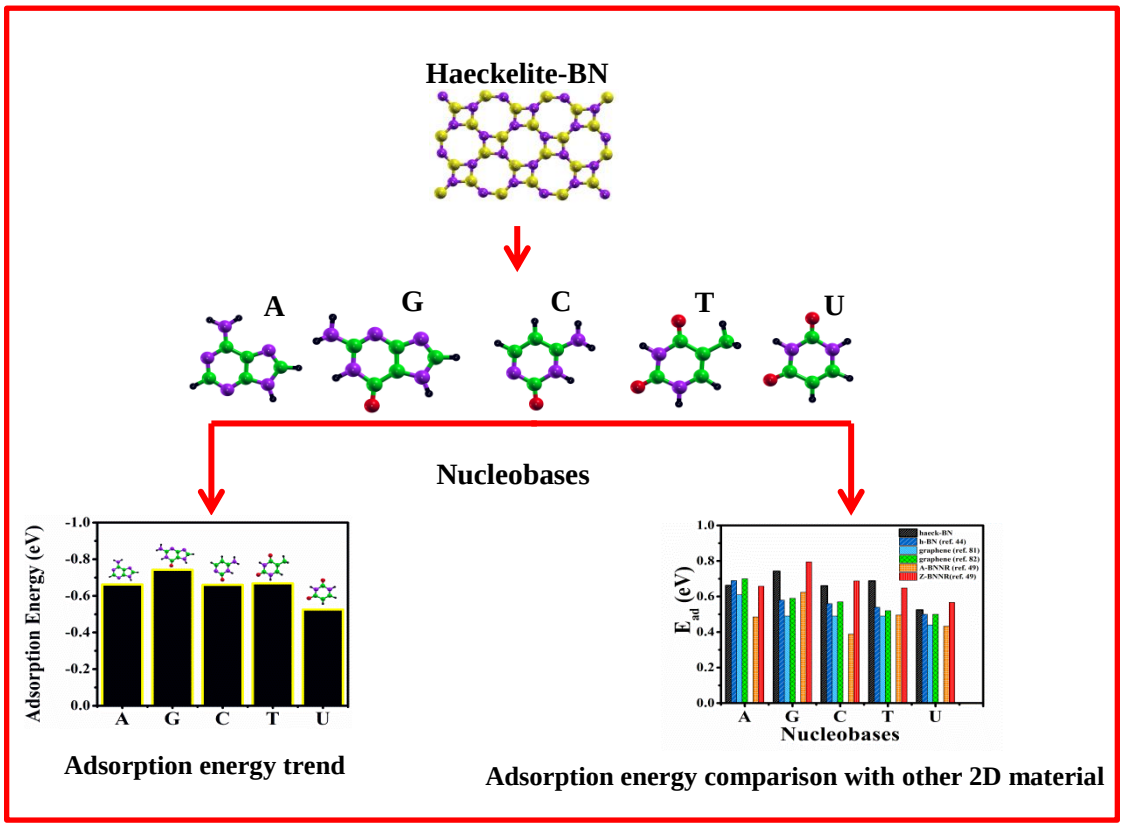


***Figure 2:*** *Schematic of adsorption energy trend of nucleobases over haeck-BN and comparision with other 2D materials.*

The calculated adsorption energy for G, A, C, T and U is -0.742 eV, -0.662eV, -0.660eV, -0.668 eV and -0.525 eV respectively which is higher in comparison to h-BN, graphene and BNNT. The adsorption energy trend of nucleobases over haeck-BN and its comparison with other 2D material are illustrated in Figure 2. The adsorption of nucleobases is confirmed by the significant variation seen from the calculated values of electronic properties,

density of states and work function. We have also calculated the recovery time because it confirms reusability of a sensor. The calculated recovery time depicts ultrafast recovery times (in millisecond) of 292 ms, 130 ms, 120 ms, 160 ms and 0.6 ms for G, A, C, T and U adsorbed haeck-BN systems respectively. Our finding suggests superiority of haeck-BN over boron nitride nanotubes, h-BN and graphene for the detection of nucleobases which makes it a good candidate to be utilized as an improved biosensor.

***Chapter5*** contains results of the structural and electronic properties of two significant neurotransmitters dopamine (DA) and adrenaline (AD) adsorbed over boron nitride

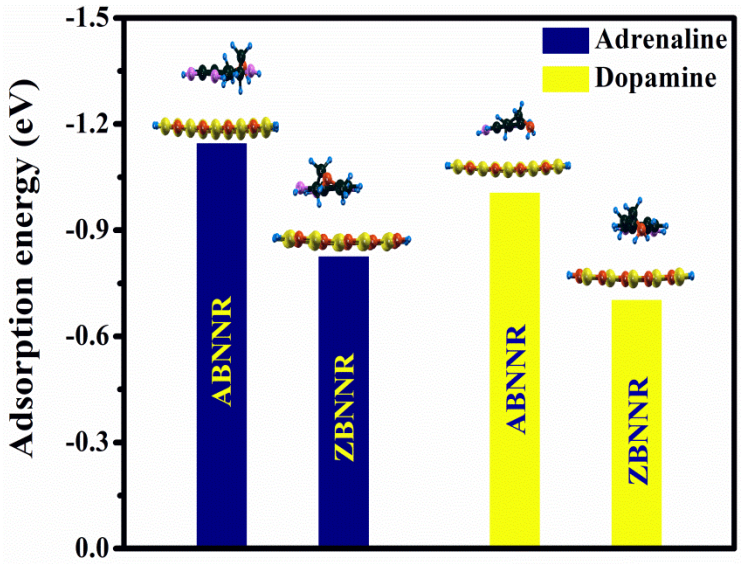


***Figure 3:*** *Adsorption energy plot of neurotransmitter over ABNNR and ZBNNR.*

nanoribbons (BNNRs) for investigating the feasibility of BNNRs as neurotransmitter carrier. A comparative study of adsorption mechanism is performed on armchair BNNR (ABNNR) and zigzag BNNR (ZBNNR) using dispersion corrected density functional theory to check the superiority in adrenaline and dopamine adsorption among both BNNRs.

Both neurotransmitters adsorption effectively modulate the electronic structure of ZBNNR and ABNNR. Significant reduction of 0.992 eV and 1.135 eV in bandgap is observed in case of ABNNR adsorbed by DA and AD respectively while in case of ZBNNR reduction of 0.769 eV and 0.942 eV in the band gap is observed by DA and AD respectively. A strong interaction of neurotransmitters (DA and AD) is observed with BNNRs (ABNNR and ZBNNR). Adrenaline and dopamine have higher adsorption energy with ABNNR (-1.144 eV and-1.013eV) as compared to ZBNNR (-0.824eV and -0.701eV). Figure 3 shows the adsorption energy of both neurotransmitters have higher magnitude over ABNNR compared to ZBNNR Significant modulation in the work function is seen for dopamine and adrenaline adsorbed pristine BNNRs. The 32% (becomes 3.350eV) of reduction in the work function of ZBNNR (4.970eV) is observed after the adsorption of DA while it reduces up to 26 % (becomes 3.661eV) in case of AD adsorption. Moreover, 26 % (become 3.057eV) and 25 % (become 3.111 eV) reduction in work function in case of ABNNR (4.152 eV) after DA and AD adsorption is observed. The present study helps in understanding the underline physics behind the interaction between BNNRs and neurotransmitters and possibility to explore BNNRs as a carrier for these neurological medicines. The present results will help researchers to design new sequencing material for human health as well as live cells.