First Principles Study of Bio-Conjugated Boron Nitride Nanostructures

A

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Introduction

In recent years, graphene a flat monolayer of carbon atoms with tightly packed honeycomb lattice and basis for all carbon allotropes has become an exciting material for research due to its fascinating physical properties, such as quantum electron transport [1-2], a tunable bandgap [3], high carrier mobility [1-2,4-5], high elastic behaviour [6] and excellent electrochemical properties [7] that make it a promising material for nano-bioelectronic devices, biosensing and biomedical applications [8-10]. Furthermore, the bioconjugated nanostructure materials including nanotubes [11-15], nanowires [16], fullerene [17] and nanoparticles [18-19] have emerged as a new class of materials for biosensing and medical diagnostics applications. For example, while DNA- decorated carbon nanotubes showed effectiveness for chemical sensing of various odours [20], the probing of conformational changes in DNA in triggered by a change in the surrounding ionic concentration [21]. The structure specific binding property of biomolecules has been used to sort carbon nanotubes of different kinds [22]. Recently, a functionalized multi-walled carbon nanotube (CNT) attached to an atomic force microscope was used as tip to penetrate cell membranes and deliver "cargo" to the interior of the cell [23]. A properly handled nanotube can be useful to target a cell accurately and hence raises a hope of using the nano-needle or injector as a high precision delivering vehicle for transporting biological molecules to a variety of cells and may eventually contribute to the treatment of disease. Apart from all the astonishing properties of carbon based nanomaterial, their cytotoxicity became a major hurdle in the path of its bio application [24]. This encourages researcher to explore other two dimensional material (2D material) having bio compatibility. Boron nitride has immerged as a suitable candidate for biological application.

Boron nitride (BN) is a compound with an equal number of alternative boron and nitrogen which are covalently linked. Similar to carbon allotropes BN exist in several crystalline varieties: cubic BN (c-BN) which is analogous to diamond, wurtzite BN (w-BN) which is similar to the lonsdaleite, and two sp^2-bonded layered configurations, i.e. hexagonal BN (h-BN) in AB stacking and rhombohedral BN (r-BN) in ABC stacking, corresponding to h-graphite and r-graphite, respectively.

In all of the above, h-BN has becomes the milestone model for the understanding of low dimensional layer materials because of its electrical neutrality. The development of the boron nitride nanostructure is closely linked with the carbon nanostructures as BN fullerene and nanotube were developed in 1990s [25-27] similar to the time at which carbon nanotube (CNT) and fullerene (C60) were made. Similarly white graphene was developed in 2000s [28], nanomesh, nanowire and nanoribbon are also followed after the development of similar carbon counterpart [29-32].

It is noteworthy that the present work focuses in understanding the interactions between boron nitride nanostructure and biomolecules which is at preliminary stage. However, the full potential of boron nitride in biotechnology is yet to be realized. Its physical and chemical properties make it a potential carrier for nanoscale diagnostic tools and sensors; support for heterogeneous and template biocatalytic reactions; vector for delivering of pharmaceuticals or genes; and foundation for field phase and combinational synthesis of biomolecules.

Bioconjugated (hybrid organic-inorganic) compounds are an emerging class of new materials that hold significant promise [11-15, 33-35]. These complex structures, based on molecular scale composite of organic and inorganic (such as carbon allotropes and boron nitride allotropes) allow the combination of properties of biomaterials and nanostructures in a unique material. Inorganic compounds, typically characterized by covalent and ionic interactions, provide a wide range of electronic properties: high electrical mobility, wide range of band gap e.g. designing insulators, semiconductors and metals, interesting magnetic and dielectric properties, thermal stability, and mechanical hardness. On the other hand, organic component or biomaterials are an arising class of new materials that hold significant promise, typically interact through weaker interactions van der Waals (vdW) forces or hydrogen bonding, offer the potential of high luminescence efficiency, large polarizability, plastic mechanical properties, and in some cases exhibit conducting properties. Hybrid organic-inorganic or bioconjugated compounds are considered innovative advanced materials. Promising applications are expected in many fields including optics, electronics, mechanics, protective coatings, catalysis, sensors, biology, and others. The tuning of the electronic structure of bioconjugated materials at nanoscale can lead to unique electronic and optical properties that are typical neither of the organic nor of the inorganic component alone. In addition, the nanostructure provides large surface for interactions involving biomolecules which further offers a promising pathway to combine biomolecular functionality with unique electronic and optical attributes of nanostructure for creation of hybrid nano scaffolds. Such scaffolds with specific features are of particular interest in recognition and modulation of biomolecules, protein interaction, protein-nucleic acid interaction, enzyme activity and biometric reactions etc. The boron nitride nanotubes and other boron nitride derivatives such as boron nitride sheet, boron nitride ribbon, etc. are structural analogy to the carbon allotropes (tube, sheet, ribbon etc.) and expected that its physical and chemical properties will make it a potential vehicle for nanoscale diagnostic tools and sensors, support for heterogeneous and coupled biocatalytic reaction, vector for delivery of pharmaceutical or gene and foundation for solid-phase and combinational synthesis of biomolecules. However, the link between boron nitride derivatives and biological systems are missing.

The goal of the proposed thesis is to provide the missing link between different derivative of boron nitride and biomolecules by providing the insight about the underlying physics and chemistry behind the biomolecules interaction with boron nitride nanostructures. First-principles calculations, based on density-functional theory (DFT), can provide a significant physical understanding into the real mechanisms of the contact formation and consequently into the structural, electronic as well as transport properties of the resulting hybrid nanostructures interfaces. It is believed that in near future, the hybrid nanostructure based bioconjugates are expected to play a significant role in applications that require low cost, large area and flexible devices useful for biomedical applications. The structure-dynamics property relation of these materials are not known and theoretical study focusing on electronic and vibrational dynamics is expected to contribute to the determination of these relations and the development of new materials.

Objectives

The present work aims to investigate the site selective/specific interaction (binding) of biomolecules with boron nitride nanostructure such as boron nitride nanotubes (BNNT), boron nitride nanoribbons (BNNR), boron nitride Nanosheet (BNNS) etc., by using the quantum chemical calculations based on first principles calculations under the frame work of density functional theory. To provide the knowledge of underlying physics and chemistry behind, biomolecule interactions with the boron nitride nanostructures and the complexity of biomolecules will also be discussed. With increased activities in their synthesis, growth, integration in technology and consumer products, there has also been increased concern about their biological and environment effects. Therefore, as the production and applications of engineered bioconjugated materials continue to increase, it is deemed critically important and timely to develop an understanding of their health and environmental effects, also to unfold new materials. The specific objectives of the present work are following:

1. To obtain a better understanding of the binding mechanism between boron nitride nanostructure and biomolecules.
2. To assess the exquisite differences in the adsorption strength of several biomolecules on boron nitride nanostructures, this in turn will allow us to draw the interaction of biomolecules with BN nanostructures.
3. To perform a first principles calculation of electronic band structure and density of sates.
4. To analyse the results of electronic properties in terms of conducting behaviour for possible transport applications and also sensing mechanisms of biomolecule over nanosurface.
5. To investigate theoretically the vibrational properties and understand the structure-dynamics-property relation.

Summary of Research Work

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 DFT by discussing Kohn-Sham equation [36] to its implementation in Plane Wave basis code - Quantum Espresso [37] is discussed. An importance theoretical description of dispersion corrections to DFT is also discussed.

In **Chapter 3** systematic study is described about the interaction mechanism of two alkaloids caffeine and nicotine molecules with boron nitride nanostructures (BNNT and BNNR) and its possible use for the application of sensing of these molecules using first principles calculations within dispersion corrected density functional theory. A detailed and systematic investigation is performed to obtain the stable geometrical properties, adsorption energy, electronic structure, charge transfer and quantum conductance for two alkaloids. It is shown that the caffeine and nicotine molecules are strongly adsorbed over BNNR than BNNT. The binding strength of these molecules is found to be stronger with the incorporation of dispersion correction and hence reinforces that the dispersion correction is essential for an accurate description of the adsorption process. No noticeable charge transfer is observed between the molecules and BNNT/BNNR. The caffeine presents stronger physisorption with both nanostructure but more with BNNR as compared to nicotine. The change in the DOS is due to adsorption of charge donor molecules. More sensitivity of the electronic properties of BNNR in the presence of caffeine and nicotine indicates that the BNNR as promising nanostructures for detection of these molecules. The present study emphasizes that the BNNR is an effective substrate to non-covalently binding alkaloid molecules [38]. The reliable conclusions drawn in this study will encourage experimentalists to explore and use these nanostructures as alkaloid carriers, filters and sensors.

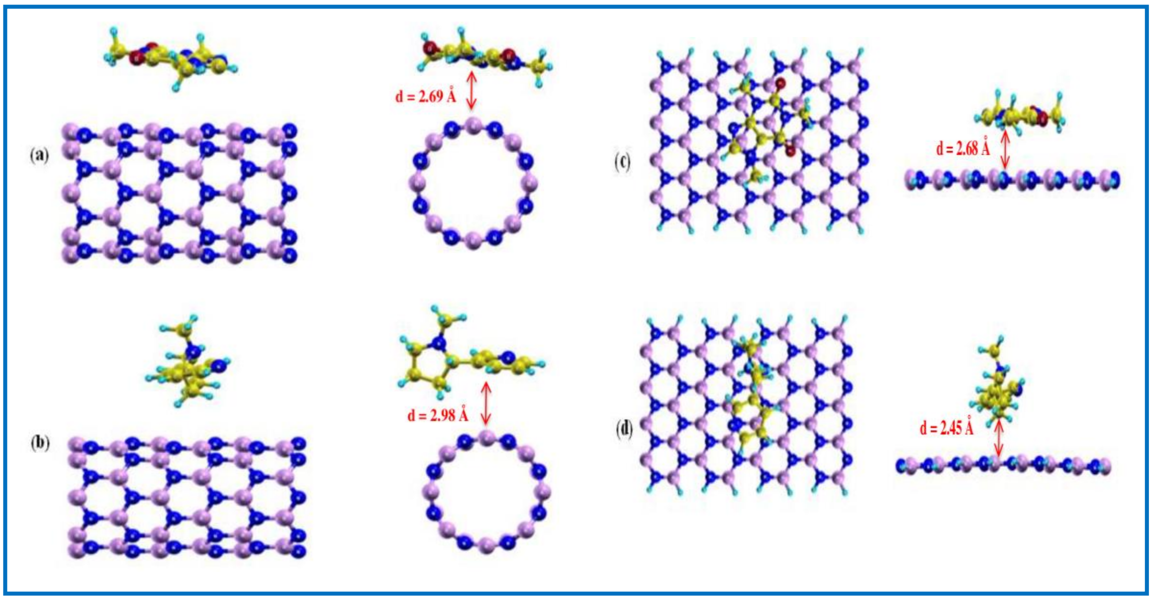

Figure 1: Equilibrium geometry of physisorbed Caffeine and Nicotine molecules on (a-b) BNNT and (c-d) BNNR. The figure also shows the side view of optimized structures of functionalized BN nanostructures with alkaloids.

In **Chapter 4**, using the state-of-the-art first principles calculations based on density functional theory, we investigated the electronic properties of relatively newly proposed Haeckelite BN (haeck-BN) comprising of square and octagonal rings. The kinetic stability of this haeckelite monolayer has been confirmed by phonon dispersion curves and the phonon density of states. There is not a single mode with imaginary frequency in the entire BZ. The calculated electronic properties of this new BN haeckelite form illustrate its direct bang gap semiconducting behaviour which is the main advantage of any material to utilize in chemical as well as biosensor. To understand the adsorption behaviour of the nucleobases on haeck-BN surface, we have employed van der Waals correction (DFT-D2) to the density functional theory.

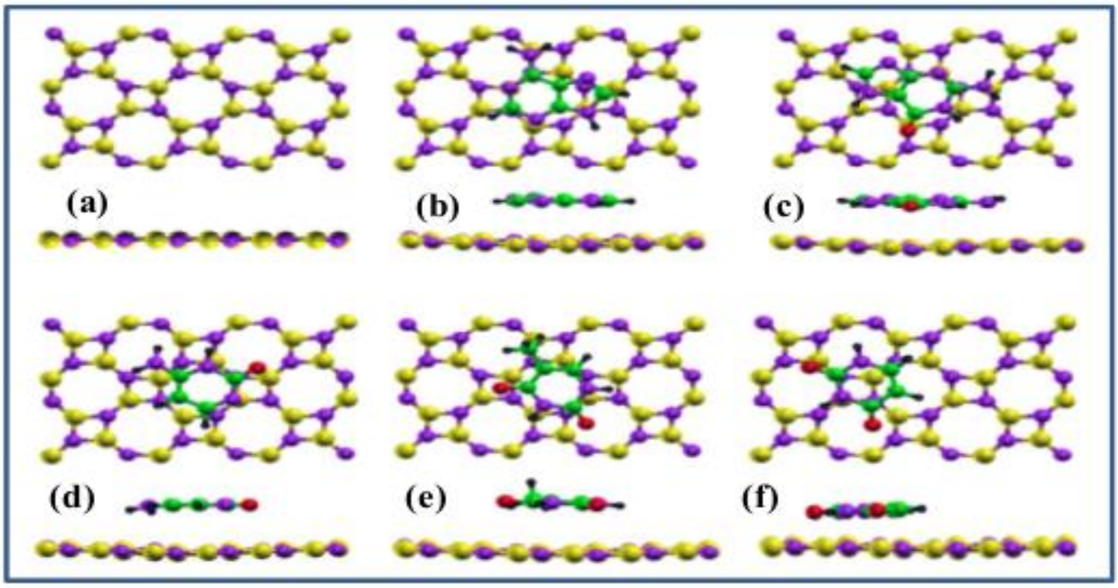

Figure 2: Optimized structures of (a) pristine haeck-BN and nucleobases adsorbed haeck-BN (b) Adenine (c) Guanine (d) Cytosine (e) Thymine (f) Uracil (top and side view).

The comparative analysis of the adsorption mechanism of nucleobases with graphene, BNNT and haeck-BN is discussed in detail and showed superiority. Our result depicts the physisorption of nucleobases on the surface of haeck-BN with the interactions order of G > T > A ≈ C > U respectively. The change in work function after the adsorption of nucleobases are also calculated and found the changes in order G (3.135eV) > A (2.076eV) ≈ U (2.058) > C

(1.517eV) ≈ T (1.469eV) respectively which is different from both graphene and BNNT, confirms its sensitivity towards the nucleobases. To further confirm the novelty of the haeck-BN as biosensor we have calculated the recovery time. Very less recovery time of 292 ms, 130ms, 120ms, 160ms and 0.6ms is predicted for G, A, C, T and U respectively which reinforced the possibility of haeck-BN for reusable biosensor [39]. The large change in the electronic properties gives the idea of the interaction and its possible use for the detection of these bio molecules. Thus from our results, one may conclude that the haeck-BN may act as an alternative candidate for the sensing application of nucleobases as well as DNA sequencing other than h-BN and graphene systems. We hope that our results will motivate more experimental and theoretical studies on new layered III-V semiconducting materials for biosensing applications.

In **Chapter 5,** we have discussed in detail about the interaction between the neurotransmitters and the boron nitride nanoribbon (ABNNR and ZBNNR). Neurotransmitters are the main chemicals involve to transmit the signal from one neuron cell to other where the message have to be send [40]. It acts as a chemical messenger in our nervous system which passes the information by relaying it across synapses by mean of excitation of near neuron or the targeted tissue [41]. Among all neurotransmitters dopamine (DA) and adrenaline (AD) have a significant importance. The sensing ability of BNNRs toward these biologically important hormones is studied by electronic properties, adsorption energy and change in work function [42].

The results of our systematic investigation on electronic and vibrational properties of various hybrid bioconjugated systems have been summarized in **Chapter 6**. Variation of properties of conjugated material compared to their pristine form has been concluded discussing possible applications in science and technology followed by a brief discussion on possible future work.

Proposed Content of Thesis

Chapter 1: Introduction

1.1 Bioconjugated Nanomaterials

1.2 Low dimensional carbon and its derivatives

1.3 Boron Nitride Nanostructure

1.4 Research objectives

1.5 Structure of the Present Thesis

References

Chapter 2: Background of Density functional theory

2.1 Basic Origin

2.1.1 Born-Oppenheimer Approximation

2.1.2 Hartree-Fock Approximation

2.1.3 Thomas-Fermi Theory

2.1.4 Schrodinger Equation

2.1.5 Electron Density

2.2 Many Body Problems

2.2.1 Wave Function Based Methods

2.2.2 Density Based Method - Density Functional Theory

2.2.3 The Kohn-Sham Approach

2.3 Exchange and Correlation Functional Forms

2.3.1 Generalized-Gradient Approximation

2.3.2 Local Density Approximation

2.4 Density Functional Perturbation Theory

References

Chapter 3: Sensing properties of boron nitride nanostructures towards alkaloids

3.1. Introduction

3.2. Computational Details

3.3. Results and Discussions

3.4. Conclusions

References

Chapter 4: ‘‘Haeckelite’’, a new low dimensional cousin of boron nitride for biosensing

Chapter 5: Boron nitride nanoribbon conjugated with neurotransmitter

Chapter 6: Summary

Curriculum Vitae and List of Publications

References

1. K. S. Novoselov, A. K Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, A. A. Firsov, Nature, **438**, 197 (2005).
2. Y. Zhang, Y. W. Tan, H. L. Stormer, P. Kim, Nature, **438**, 201 (2005).
3. M. Y. Han, B. Oezyilmaz, Y. Zhang, P. Kim, Phys. Rev. Lett., **98**, 206805 (2007).
4. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, Science, **306**, 666 (2004).
5. C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, et al. Science, **312,** 1191 (2006).
6. C. Lee, X. Wei, J. W. Kysar, J. Hone, Science, **321**, 385 (2008).
7. M. Pumera, A. Ambrosi, A. Bonanni, E. L. K. Chng, H. L. Poh, Trends Anal. Chem**., 29,** 954 (2010).
8. A. H. C. Neto, Guinea, F. N. M. R Peres, K. S. Novoselov, A. K. Geim, Rev. Mod. Phys., **81**, 109 (2009).
9. J. S. Bunch, A. M. Van der Zande, S. S. Verbridge, I. W. Frank, D. M. Tanenbaum, J. M. Parpia, H. G. Craighead, P. L. McEuen, Science, **315,** 490 (2007).
10. R. M. Westervelt, Science, **320**, 324 (2008).
11. R. J. Chen, S. Bangsaruntip, K. A. Drouvalakis, N. W. S. Kam, M. Shim, M. Y. Li, W Kim, P. J. Utz, H. Dai, J. Proc. Natl. Acad. Sci. U.S.A., **100,** 4984 (2003).
12. R. J. Chen, Y. G. Zhang, D. W. Wang, H. J. J. Dai, J. Am. Chem. Soc., **123**, 3838 (2001).
13. Y. Kang, Y. C. Liu, Q. Wang, J. W. Shen, T. Wu, W. J. Guan, Biomaterials, **30,** 2807 (2009).
14. D. Pantarotto, C. D. Partidos, R. Graff, J. Hoebeke, J. P. Briand, M. Prato, A Bianco, J. Am. Chem. Soc., **125**, 6160 (2003).
15. S. S. Wong, .E. Joselevich, A. T. Woolley, C. L. Cheung, C. M. Lieber, Nature, **394**, 52 (1998).
16. Y. Cui, Q. Q. Wei, H. K. Park, C. M. Lieber, Science, **293**, 1289 (2001).
17. H. Benyamini, A. Shulman-Peleg, H. J. Wolfson, B. Belgorodsky, L. Fadeev, M. Gozin,. Bioconjugate Chem., **17**, 378 (2006).
18. R. Hong, N. O. Fischer, A. Verma, C. M. Goodman, T. Emrick, V. M. Rotello, J. Am. Chem. Soc., **126,** 739 (2004).
19. C. C. You, S. S. Agasti, M. De, M. J. Knapp, V. M. Rotello, J. Am. Chem. Soc. **128,** 14612 (2006).
20. C. Staii, A. T. Johnson, Nano Lett. **5**, 1774 (2005).
21. D. A. Heller, E. S. Jeng, T. K. Yeung, B. M. Martinez, A. E. Moll, J. B. Gastala, M. S. Strano, Science, **311,** 508 (2006).
22. M. X. Tu, S. Manohar, A. Jagota, M. Zheng, Nature, **460**, 250 (2009).
23. X. Chen, A. Kis, Azettl, C. R. Bertozzi, Proc. Nat. Acad. Sci. **104,** 8218 (2007).
24. G. Jia, H. Wang, L. Yan, X. Wang, R. Pei, T. Yan, Y. Zhao, X. Guo, Environ. Sci. Technol., **39**, 1378 (2005).
25. S. Gowtham, R. H. Scheicher, R. Pandey, S P Karna, R. Ahuja, Nanotechnology, **19**, 125701 (2008);

26. O. Stephan, Y. Bando, A. Loiseau, F. Willaime, N. Shramchenko, T. Tamiya, T. Sato, Appl. Phys. A: Mater. Sci. Process. **67**, 107 (1998).
27. D. Golberg, Y. Bando, O. Stephan, K. Kurashima, Appl. Phys. Lett., **73**, 2441 (1998).
28. N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, A. Zettl, Science, **269,** 966 (1995).
29. K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, A.K. Geim, P. Natl. Acad. Sci. U.S.A. **102**, 10451 (2005).
30. M. Corso, W. Auwarter, M. Muntwiler, A. Tamai, T. Greber, J. Osterwalder, Science, **303,** 217 (2004).
31. K. F. Huo, Z. Hu, F. Chen, J. J. Fu, Y. Chen, B. H. Liu, J. Ding, Z. L. Dong, T. White, Appl. Phys. Lett., **80,** 3611 (2002).
32. Y. J. Chen, H. Z. Zhang, Y. Chen, Nanotechnology, **17,** 786 (2006).
33. Z. G. Chen, J. Zou, G. Liu, F. Li, Y. Wang, L. Z. Wang, X. L. Yuan, T. Sekiguchi, H. M. Cheng, G.Q. Lu, ACS Nano, **2**, 2183 (2008).
34. G. Ciofani, Expert Opin. Drug Deliv, **7**, 889 (2010).
35. S. Gowtham, R. H. Scheicher, R. Ahuja, R. Pandey, S. P. Karna, Phys. Rev. B **76**, 033401 (2007).
36. W. Kohn, L. J. Sham, Phys. Rev. B. **140,** 1133 (1965).
37. P. Giannozzi et al., QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. J. Phys. Condens. Matter **21,** 395502 (2009); URL: http://www.quantum-espresso.org
38. B. Roondhe, S. D. Dabhi, P. K. Jha, Applied Surface Science **441**, 588 (2018).
39. B. Roondhe and P. K. Jha, ‘‘Haeckelite’’, a new low dimensional cousin of boron nitride for biosensing with ultra-fast recovery time: a first principles investigation J. Mater. Chem. B, 2018, DOI: 10.1039/C8TB01649F.
40. S. K. Jackowska, P. Krysinski, Anal. Bioanal. Chem., **405**, 3753 (2013).
41. T. Mele, M. Carman-Krˇ zan, D. M. Juriˇ c, Int. J. Dev. Neurosci., **28,** 13 (2010).
42. B. Roondhe, P. K. Jha “Boron nitride nanoribbon conjugated with neurotransmitter: utilization as biological cargo carrier.” (In communication).

LIST OF PUBLICATIONS

1. B. Roondhe, S. D. Dabhi and P. K. Jha Sensing properties of pristine boron nitride nanostructures towards alkaloids: A first principles dispersion corrected study. *Appl. Surf. Sci.* 441 (2018) 588–598.
2. B. Roondhe and P. K. Jha “Haeckelite” a new nanoscale member of boron nitride family for biosensing: A first principles investigation (in communication).
3. B. Roondhe and P. K. Jha “Ultrahigh Sensitive Neurotransmitter Sensor Based on BNNRs” (in preparation).
4. S. D. Dabhi, B. Roondhe and P. K. Jha Nucleobases Decorated Boron Nitride Nanoribbon for Electrochemical Bio-sensing: A Dispersion Corrected DFT Study. Phy. Chem. Chem. Phy. 20 (2018) 8943-8950.

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