Magnesium Adsorption on B/N/P-Doped Graphene Nanoribbons: A DFT Investigation of Structural and Electronic Modifications

Himanshu Pundir[a], Gaurav Sapra[b], Preetika Sharma[c]

UIET, Panjab University, Chandigarh, India.

[a] erhimanshu003@gmail.com
[b] gaurav.sapra@pu.ac.in
[c] preetitkamadhav@yahoo.co.in

Abstract

Heteroatom(s) doping and introduction of functional groups into nanoribbons proposes a promising pathway to exploit their electronic and quantum transport characteristics. In this work, doping of armchair graphene nanoribbons (AGNRs) is accomplished to explore its potential for switching applications. Doping is done using Boron (B), Nitrogen (N) and Phosphorous (P) dopants in concentration of 3.125% individually. B outshines the other two dopants N and P in terms of its metallic character and offers minimum threshold voltage (V_{th}). Further, to examine its switching potential, Magnesium (Mg) is adsorbed on hollow sites of the doped structures. The stability of both Mg adsorbed doped structures as well as doped structure without adsorption are analysed in terms of band structure, density of states (DOS), bond length variations, adsorption energy and current-voltage (I–V) characteristics using Density Function Theory (DFT). Each AGNR structure showed an appreciable shift in threshold voltage. However, N and P doped AGNR both yield semiconducting nature noting that N doped AGNR given high threshold voltage while P doped distorts the I-V behaviour. The results show that due to most metallic nature and lowest threshold voltage out of all three structures, the B doped AGNR with Mg adsorption can be excellent for transistor switching applications.

Keywords: Adsorption, DFT, Doping, Switching, Threshold Voltage.
Received 28 January 2025; First Review 10 February 2025; Accepted 16 February 2025

*** Address of correspondence**
Preetika Sharma
UIET, Panjab University, Chandigarh, India.

Email: preetitkamadhav@yahoo.co.in

How to cite this article
Himanshu Pundir, Gaurav Sapra, Preetika Sharma, Magnesium Adsorption on B/N/P-Doped Graphene Nanoribbons: A DFT Investigation of Structural and Electronic Modifications, J. Cond. Matt. 2024; 02 (02): 59-63.

Available from:
https://doi.org/10.61343/jcm.v2i02.82

Introduction

Diverse carbon derives especially nano ribbons have fascinated immense research interests driving exploration into their potential for numerous future electronic applications [1-4]. Electrical properties of these materials can be tailored through many ways hence, tunability makes them further versatile and attractive [5-6]. Band gap engineering using doping and adsorption are common practices to harvest the fascinating properties. One involves substituting or interstitially fitting the foreign atoms suitably into nano ribbons, on the other hand adsorption demands attaching these molecules onto the surface of adsorbent surface [7-10]. A DFT study is used to investigate the interactions of the magnesium on graphene, a wonder 2D material. The outcome suggests that the binding nature of the Mg ions (Mg^{+} and Mg^{2+}) was caused by charge transfer interactions and Mg interacts with graphene surfaces via Van Der Waals forces [11]. The interaction of graphene surfaces with magnesium atoms is reported using a direct molecular dynamics approach and the Mg atoms were observed to bind at hollow site positioned at 2.02 Å from the surface of graphene. [12]. It is also found that graphene increases the Mg adsorption energies on certain surfaces and improve the cycling stability and is a very promising electrode material for Mg rechargeable ion batteries [13-14]. The kinetic properties and electronic conduction due to Mg adsorption can provide excellent electrode material for battery applications. The above literature confirms the Mg adsorption on carbon surfaces to be promising. However, there is limited research on the interaction mechanism between metal-atom-doped graphene nanoribbon. To the best of author's knowledge, there is no work done on finding the lowest threshold values for doped AGNR though Mg adsorption. Hence, we explored the electronic and transport behaviour of doped AGNR structures before and after Mg adsorption and tried to depict the role of Mg through theoretical perspective for switching applications.

Computational Details

An AGNR with 32 carbon atoms doped individually with B/N/P and later adsorbed with Mg is explored using Quantum ATK (Synopsis) (P-2019.03-SP1) based on Density Functional Theory (DFT). The calculations are simulated using generalised gradient approximations (GGA) which represent the exchange correlation in the calculations. During geometry optimisations, a double Zeta polarised basis set has been chosen for all atoms of Mg, B, N, P, C and H to obtain the best results. The structures are analysed with 1*1*70 uniformly placed k-points. Edge passivation of AGNRs hydrogen atoms is done. The structural stability of the AGNRs was evaluated by optimizing the cohesive energy, where a negative cohesive energy confirmed stability. The cohesive energy calculations are done using the formula given below by equation (1)

$$\boldsymbol{E_{coh}} = E_{Total} - \Sigma n_x E_x / N \qquad (1)$$

Where, E_{coh} is the cohesive energy of the doped AGNR with Mg adsorption, E_{Total} = total energy of doped AGNR with adsorbed alkali earth metal ion (Mg), n is the no. of atoms, E is the energy of an individual atom, x represents the individual atom while, N is the total no. of atom resent in the system. On the other hand, adsorption energy (E_{ad}) is calculated using the formula mentioned in equation (2) below to further support the investigation

$$\boldsymbol{E_{adsorption}} = E_{Total} - E_{adsorbent\ Surface} - E_{adsorbent\ ion} \qquad (2)$$

Where, E_{Total} is total energy of doped AGNR with adsorbed alkali earth metal ion (Mg), $A_{dsorbent}$ surface is total energy of doped AGNR surfaces, $A_{dsorbent}$ ion is total energy of single Mg. Variations in bond lengths between carbon and adsorbent were analysed and tabulated. Further, the I-V characteristics are plotted to further investigate the transport behaviour. Two electrodes at both sides of the ribbon are formed and a potential of 0-2 V is applied to get I-V plots.

Geometric Structures and stability

To estimate the threshold values of n and p type doped AGNRs with Mg adsorption afterwards is done. Front and top view of the geometric structures including hydrogen passivated pristine (undoped) AGNR and B/N/P individually doped AGNRs are shown in figure 1 respectively.

Though, geometrically optimized structures of each doped AGNR including Mg adsorption are given separately in figure 2. Here, figure 2(a) fixed position and dopant concentration of 3.125% is used in each. The change in bond length in these optimized structures w. r. t. individual dopant with Mg adsorption is also shown clearly. The modification in bond length is noted maximum in case of N doped AGNR, secondly moderate variation in case of P doped AGNR and lastly B doped AGNR shown minimum variations after adsorption of Mg. These modifications in bond lengths are due to the varying atomic radius of each dopant. To analyse the structural stability in all it is also observed that as size of the dopant is varying there is a change in the value of corresponding bond lengths and cohesive energy value respectively. Boron and Nitrogen doped AGNRs with Mg adsorption given almost close values of the cohesive energy to each other, while phosphorous doped AGNR with Mg adsorption shown a least value among all with clear deformed AGNR. Adsorption energy of all three structures is calculated to further confirm the adsorption competence. The value of adsorption energies clearly shows that phosphorous doped Mg adsorbed AGNR shown least value signifying poor adsorption. Nitrogen doped AGNR structure with Mg adsorption holds second place, while boron stands-up tall with highest adsorption energy among all. The values of calculated cohesive energies, bond lengths and adsorption energy are further provided.

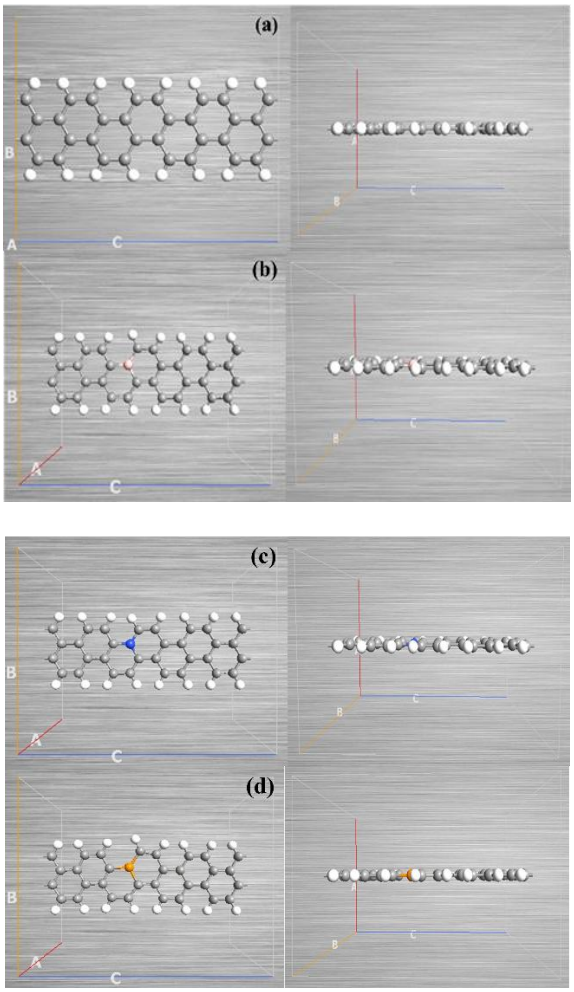

Figure 1: Geometric optimized structures (front view and top view) (a) Pristine AGNR, (b) Boron doped, (c) Nitrogen and (d) Phosphorous doped AGNR respectively.

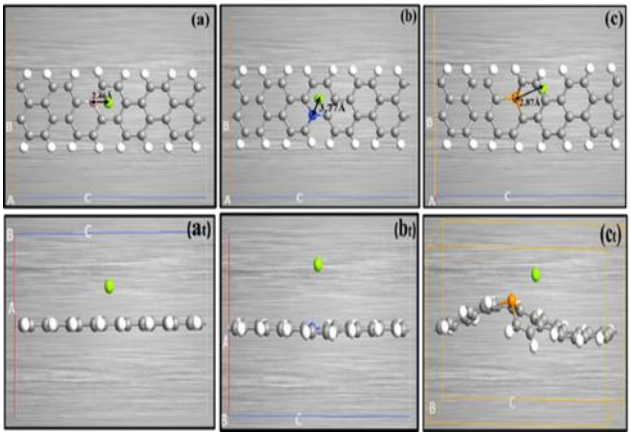

Figure 2: Geometric optimized structures (front view and top view) (a), (at) B doped AGNR with Mg adsorption (b), (bt) N doped AGNR with Mg adsorption and (c), (ct) P doped AGNR with Mg adsorption respectively.

Results and discussions

Band structures and Density of states

Intentional addition of solo dopants or doping introduces the impurity atoms and influence position of fermi level either near to valence band or conduction band for p-type and n-type dopants respectively. We have explored DOS and band structures of each doped AGNR structure. The band structures and corresponding density of states for pristine AGNR and all doped AGNR structures are depicted in figure no.3 respectively. At first, the band gap of pristine AGNR is found to be 2.55 eV presenting it as semiconductor in compliance with DOS value of 0 eV^{-1} nearly in range of -1.25 eV to +1.25 eV as shown in Figure 3.

Band gap engineering is performed through substitutional doping of B/N/P dopants individually on AGNR. Respective band gaps are noted and well tabulated in table 1. It is apparent that doping offers transitional density of states in doped AGNR structures which were absent in case of pristine AGNR. In comprehensive view firstly the p type dopant (boron) incorporated insignificantly small band gap of 0.02 eV with sufficient no. of energy states appearing in the valence band below the fermi level confirms the p type doping. Though substitution of n-type dopants (N and P) atoms respectively additionally provided bandgap modifications. The presence of phosphorus n-type dopants introduced the band gap of 2.24 eV, which is slightly lesser than pristine AGNR keeping the nature as semiconducting. The dopant (P) shifted the fermi level in the conduction band justifying the effective doping. Moreover, the DOS plot demonstrates the energy state immediate to fermi level further confirming a doping of n-type. Nitrogen(N) another n-type dopant used, offer a reasonable band gap value of 0.41 eV introducing major modifications in band gap value and density of states correspondingly.

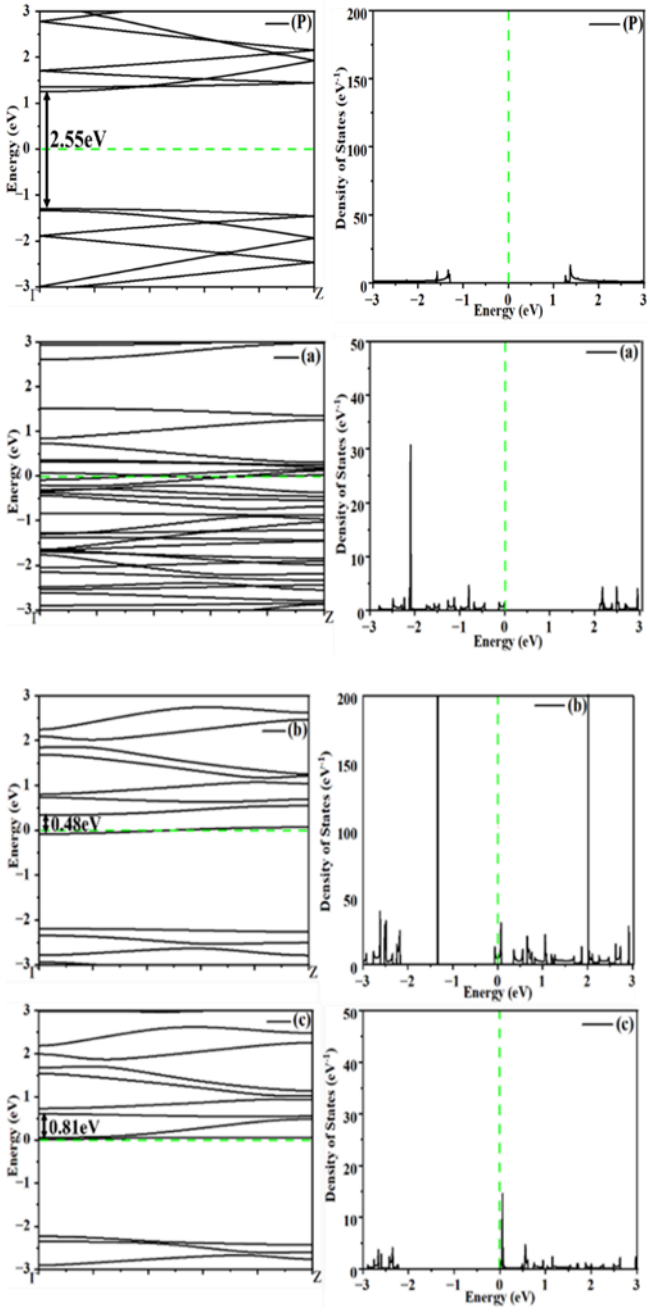

Figure 2: Band Structures and density of states (P) pristine AGNR (a) B doped AGNR (b) N doped AGNR and (c) P doped AGNR

Indeed, both n and p type dopants has tailored the band gap efficiently. Accordingly, observed, a nearly metallic band structure of B atom doped AGNR, while a semiconducting one by N and P dopants respectively. In addition, complete behaviour profiling is accomplished by visualising Mg adsorption on these doped AGNRs. The obtained modified band structures and DOS plots on Mg adsorption are given away in figure 4.

Adsorption of Mg on B doped AGNR notably modifies its electronic properties by bringing significant modifications in its band structure as well as density of states. It is evident from the band structure that the behaviour of AGNR has turned metallic with no band gap but presence of available

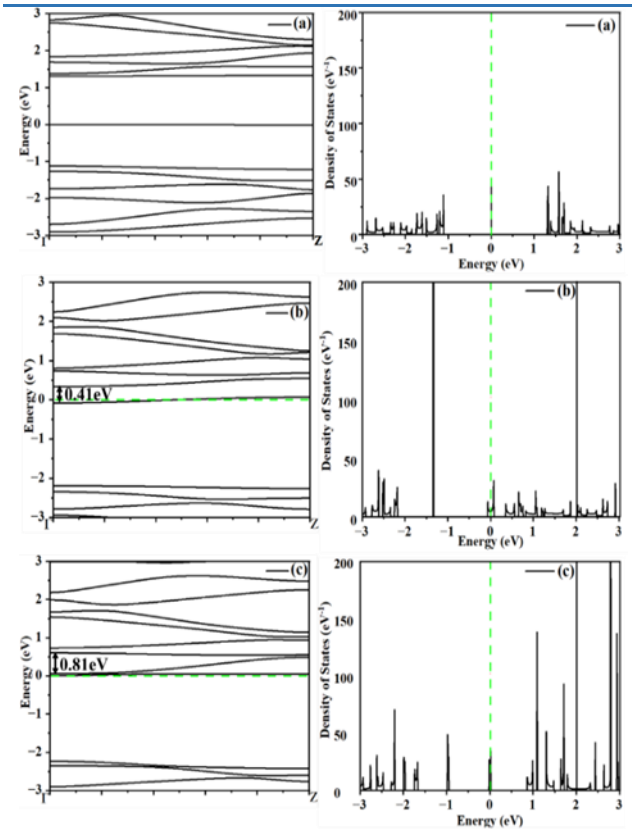

Figure 4: Band Structures and density of states (a) B doped Mg adsorbed AGNR (b) and (c) N and P doped Mg adsorbed AGNRs respectively.

energy state is evident. This is supported by DOS plot showing the presence of electronic state on the fermi level confirming the strong influence of p-type dopant B. Moving to another case N-doped AGNR, significantly modified the band structure corresponding to a band gap value of 0.41 eV making it semi conducting. Adsorption of Mg on P-doped AGNR introduced a band gap of 0.81 eV with observing energy state very close to fermi level. Though discrete energy bands are seen in the conduction band of the DOS plot. Band structures and DOS plots of all the three B/N/P doped AGNR with Mg adsorption are given in figure.4. B doped AGNR on adsorption of Mg results into a DOS plot with an occupied state on the fermi level, justifying the metallic character and likewise offering much more available state for electronic conduction. Furthermore, in N and P doped AGNRs on Mg adsorption band gap is noted with presence of much denser electronic states in the conduction band region in DOS plot aiding strong interaction of N-type dopants with Mg.

It is evident from the band structure that the behaviour of AGNR has turned metallic with no band gap but presence of available energy state is evident. This is supported by DOS plot showing the presence of electronic state on the fermi level confirming the strong influence of p-type dopant B. Moving to another case N-doped AGNR, significantly modified the band structure corresponding to a band gap value of 0.41 eV making it semi conducting. Adsorption of

Table 1: Tabulates band gaps of B/N/P doped AGNR, band gap of B/N/P doped AGNR with Mg adsorption, cohesive energy, adsorption energy and bond lengths before and after optimizations respectively.

Dopant	Band gap of doped AGNR (eV)	Band gap of doped AGNR with adsorbed Mg (eV)	Cohesive energy (eV)	Adsorption Energy (eV)	Bond length before optimization (Å)	Bond length after optimization (Å)
B	0.02	0	-7.223	-3.37	2.42	2.46
N	0.41	0.41	-7.241	-2.86	2.38	3.77
P	2.24	0.80	-7.166	-0.21	2.40	2.87

Mg on P-doped AGNR introduced a band gap of 0.81 eV with observing energy state very close to fermi level. Though discrete energy bands are seen in the conduction band of the DOS plot. Band structures and DOS plots of all the three B/N/P doped AGNR with Mg adsorption are given in figure.4. B doped AGNR on adsorption of Mg results into a DOS plot with an occupied state on the fermi level, justifying the metallic character and likewise offering much more available state for electronic conduction. Furthermore, in N and P doped AGNRs on Mg adsorption band gap is noted with presence of much denser electronic states in the conduction band region in DOS plot aiding strong interaction of N-type dopants with Mg.

I-V Characteristics

Introduction of Mg adsorption on B doped AGNR significantly reduced the threshold voltage. The results indicate the lowering of threshold voltage in Mg adsorbed B doped AGNR.

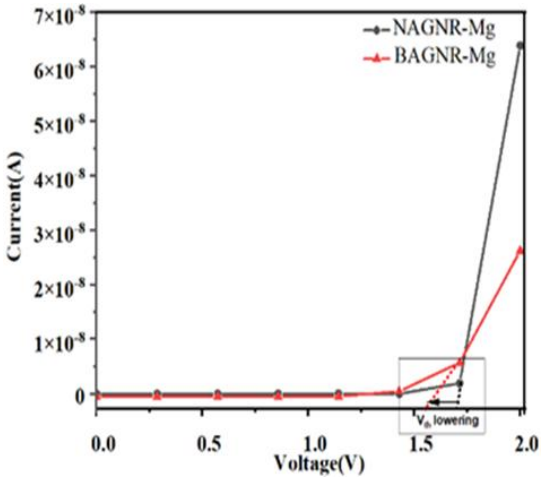

Figure 5: IV Plots for B doped AGNR with and without Mg adsorption

The threshold voltage lowers down appreciably making device ON state characteristics more promising. Lower threshold voltage is important for faster switching in transistors which lead to enhanced circuit performance at low power consumption. Doping causes a lowering in threshold voltage as it can be used to fine-tune the performance of a device through band gap engineering. Hence, the doped structures were showing better values for

threshold voltage as the structures turned nearly metallic. However, due to the metallic nature of B doping, the N and P were not taken for IV characteristics. Further, the adsorption caused more variations in threshold voltage because application of adsorption on doped structures reduces the band gap further. Thus, after adsorption the threshold voltage is markedly lowered. Figure 5 depicts the I-V characteristics of B and N doped structures with Mg adsorption.

Conclusion

In the conclusions of this investigation, the structural and electronic modifications of AGNR on doping and adsorption of Mg in terms of cohesive and adsorption energy,bond length variations along with band structures,density of states and IV characteristics are presented.Notably,boron doped AGNR shown best adsorption with highest value of -3.37 eV of adsorption energy. In contrast phosphorus doped AGNR got completely distorted on adsorption of Mg with least adsorption energy. However structural stability of the same is further accredited by cohesive energy and minute variation in bond length from 2.42Å to 2.46 Å whereas nitrogen shows the wider variation. Indeed band structures and therefore electronics properties are significantly modified of all three AGNR structures. It is observed that boron doped AGNR turned metallic with Mg interaction, although the N and P doped AGNR showed semiconducting nature after Mg adsorption. Mg adsorption leads to variation of threshold voltage in all three AGNR structures. The boron doped AGNR outperforms due to its least threshold voltage of 1.6 eV and hence can be excellent choice for transitor switching applications.

References

1. Wang S, Liu X and Zhou P, *"The Road for 2D Semiconductors in the Silicon Age"*, Advanced Materials, 2022, 34.
2. Zou X, Xu Y and Duan W, *"2D materials: Rising star for future applications"*, Innovation, 2021, 2.
3. Schwierz F, Pezoldt J and Granzner R, *"Two-dimensional materials and their prospects in transistor electronics"*, Nanoscale, 2015, 7 8261-83.
4. Ares P and Novoselov K S, *"Recent advances in graphene and other 2D materials"*, Nano Materials Science, 2022, 43-9.
5. Ajeel F N, Mohammed M H and Khudhair A M, *"Energy bandgap engineering of graphene nanoribbon by doping phosphorous impurities to create nano-heterostructures: A DFT study"*, Physica E Low Dimens Syst Nanostruct, 2019, 105, 105-15.
6. Chaves A, Azadani J G, Alsalman H, da Costa D R, Frisenda R, Chaves A J, Song S H, Kim Y D, He D, Zhou J, Castellanos-Gomez A, Peeters F M, Liu Z, Hinkle C L, Oh S H, Ye P D, Koester S J, Lee Y H, Avouris P, Wang X and Low T, *"Bandgap engineering of two-dimensional semiconductor materials NPJ 2D"*, Mater Appl 4, 2020.
7. Sharma P, Singh S, Gupta S and Kaur I, *"Enhancing linearity in I–V characteristics by B/N doping in graphene for communication devices"*, Journal of Materials Science: Materials in Electronics, 2017, 28, 7668-76.
8. Shinde P V, Tripathi A, Thapa R and Sekhar Rout C, *"Nanoribbons of 2D materials: A review on emerging trends, recent developments and future perspectives"*, Coord Chem Rev, 2022, 453.
9. Wang L, Zheng J, Zhou J, Qin R, Li H, Mei W N, Nagase S and Lu J, *"Tuning graphene nanoribbon field effect transistors via controlling doping level"*, Theor Chem Acc,2011, 130, 483-9.
10. Chen L N, *"Electronic properties of armchair graphene nanoribbons with BN-doping"*, Solid State Commun, 2014, 191, 59-65.
11. Kato K, Iyama T and Tachikawa H, *"Density functional theory study on the interaction of magnesium ions with graphene surface Jpn"*, J Appl Phys, 2014, 53.
12. Li Y, Pei X, Zhang H and Yuan M, *"A First-Principle Study of Interactions between Magnesium and Metal-Atom-Doped Graphene"*, Nanomaterials, 2022, 12 834.
13. Riyaz M, Garg S, Kaur N and Goel N, *"Boron doped graphene as anode material for Mg ion battery: A DFT study"*, Comput Theor Chem, 2022, 1214.
14. Tayyab M, Hussain A, Asif Q ul A and Adil W, *"Band-gap tuning of graphene by Mg doping and adsorption of Br and Be on impurity: A DFT study"*, Computational Condensed Matter, 2020, 23.