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PAPER

Graphane versus Graphene: A Computational Investigation of the Interaction of Nucleobases, Aminoacids, Heterocycles, Small Molecules (CO₂, H₂O, NH₃, CH₄, H₂), Metal Ions and Oniom Ions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Graphane has emerged as a two-dimensional hydrocarbon with interesting physical properties and potential applications. Understanding the interaction of graphane with various molecules and ions is crucial to appreciate their potential applications. We investigated the interaction of nucleobases, aminoacids, saturated and unsaturated heterocycles, small molecules, metal ions and oniom ions with graphane by using density functional theory calculations. The preferred orientations of these molecules and ions on the graphane surface have been analysed. The binding energies of graphane with these molecules have been compared with the corresponding binding energies of graphene. Our results reveal that graphane forms stable complexes with all the molecules and ions yet showing lesser binding affinity when compared to graphene. As an exemption, the preferential strong binding of H₂O with graphane than graphene reveals the fact that graphane is more hydrophilic than graphene. Charge transfer between graphane and the molecules and ions have been found to be an important factor in determining the binding strength of the complexes. The effect of the interaction of these molecules and ions on the HOMO-LUMO energy gap of graphane has also been investigated.

1. Introduction

Carbon nanostructures such as carbon nanotubes, graphene and fullerene are considered to be the rising stars in the field of nano science owing to their extraordinary physical and chemical properties.^{1, 2} The scope of applications that they can be used for has escalated sharply in recent years. Graphene is a two-dimensional hexagonal lattice of carbon atoms and its extended π -network is the basic building block for other carbon allotropes such as graphite, nanotubes and fullerenes. Although graphene is known theoretically since many years, the experimental discovery of free-standing graphene is achieved by Novoselov et al. in the year 2004.³ Functionalization of graphene has been found to be a potential tool to tune the properties of graphene for desired applications. Covalent and noncovalent functionalization of graphene have been recently reviewed by Kim and co-workers.⁴ Our group has done comprehensive studies on the noncovalent interactions of carbon nanotubes and graphene including cation- π type of interactions with metal ions,⁵⁻⁷ π - π interactions with aromatics and bio-molecules⁸⁻¹⁰ and other XH... π type of interactions with various small molecules.¹¹ Since the advent of graphene, the interest in low dimensional materials has increased significantly.

Graphane is the upcoming new player in the field of carbon nanomaterials. It is a saturated hydrocarbon with sp³ hybridized carbon atoms forming a hexagonal arrangement derived from graphene.^{12, 13} Sofo et al. predicted the structure and stability of graphane by computational studies.¹⁴ The chair conformation of graphane has been found to be more stable than the boat conformation. Experimental realization of graphane occurred when Elias et al. demonstrated the formation of graphane by exposing pristine graphene to hydrogen plasma.¹⁵ While the structure of graphene is a planar sheet, the stable graphane is a puckered chair-like structure with hydrogen atoms on both sides of the sheet. Thus graphene and graphane are the striking examples for the successful prediction of theoretical methods.

Several studies have been performed to understand the structure and properties of graphane and doped graphane in recent years.¹⁶⁻²⁵ Band gap engineering of graphane and its derivatives have also been explored.²⁶⁻²⁹ Pumera and co-workers have done extensive studies on the synthesis, electrochemistry and bio-sensing ability of graphane.³⁰⁻³³ The interaction of graphane-graphene dimer and their band structures have been investigated.³⁴ A recent study demonstrated that the graphane-graphene association is driven by dispersion and orbital interactions.³⁵ The stability of graphane nanotube has also been explored in a theoretical study.³⁶ Besides pristine graphane, Si, Ge, and Sn analogues of graphane are emerging as a new class of two-dimensional materials with novel structure, stability, and properties.³⁷⁻³⁹ Hydrogenation of graphene to form graphane is reversible in nature and consequently graphane gained instant research interest in hydrogen storage.¹⁵ Metal doped graphane has been predicted to be a potential candidate for gas

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Electronic Supplementary Information (ESI) available: Optimised geometries, binding energies, charge transfer, HOMO-LUMO energy gap values.

DOI: 10.1039/x0xx00000x

storage.⁴⁰⁻⁴³ Hence developments in graphene based research are expected to push the boundaries of the field of advanced hydrogen storage technologies. The applications of graphene in the area of transistors⁴⁴ and sensors⁴⁵ have also been explored. Halogenated graphene derivatives appear to be promising materials with applications in graphene-based electronic devices.⁴⁶⁻⁴⁹ The CO₂ adsorption thermodynamics of pristine graphene and the N□substituted graphene have also been evaluated.⁵⁰

Understanding the interaction of carbon materials with various molecules and ions is a topic of outstanding interest in order to appreciate their potential applications in various fields.⁵¹⁻⁵³ Extensive studies have been done to understand the interaction of biomolecules with graphene.⁵⁴⁻⁶³ Aromatic hydrocarbons are well known for their noncovalent interactions namely cation- π , π - π and XH... π interactions.⁶⁴⁻⁷¹ Graphene with its extended π -system exhibits a variety of noncovalent interactions with molecules and ions.^{72, 73} However, the noncovalent interactions of saturated hydrocarbons have also gained significant research interest in recent years. Schreiner and co-workers have demonstrated that σ/σ and π/π interactions are equally important and thus proposed the possibility of multilayered graphanes.⁷⁴ A recent study from our group has revealed that cation-alkane interactions are strong noncovalent interactions.⁷⁵ We have also quantified the dispersion interactions of various linear and cyclic alkane dimers.⁷⁶ Besides, the interactions of saturated and unsaturated hydrocarbons with carbon nanostructures have also been investigated in our recent study.¹⁰ Thus quantifying the interaction of graphene with molecules and ions is interesting in its own right. The current study provides a comprehensive and comparative analysis of the interaction of nucleobases, aminoacids, heterocycles, small molecules, metal ions and oniom ions with graphene and graphene. The study of graphene-nucleobase interactions is expected to provide insights into the feasibility of employing graphene in DNA sequencing. It is very important to study the interaction of aminoacids with graphene in order to understand the graphene-protein hybrids. As most of the drug molecules contain heterocycles, the study of their interactions with graphene will be helpful to understand the prospective of graphene as drug carriers. In addition, understanding the interactions of all these systems with graphene provides valuable guidelines to employ graphene as sensors. The study of the interaction of metal ions with graphene will be supportive to appreciate the possibility of using graphene as a sorbent to remove metal ion pollutants from water. The orientations of these molecules and ions on the graphene surface and their binding strength have been estimated. The charge transfer and the HOMO-LUMO energy gap of the complexes have been analysed. The binding strength of graphene has been compared with that of graphene in all the cases.

2. Computational methods

The model systems used to represent graphene and graphene have been shown in the Fig. 1. The relatively stable chair conformation has been adopted for the graphene model. Hydrogen atoms have been added to passivate the dangling atoms at the truncated ends of graphene and graphene to avoid spurious end effects. The

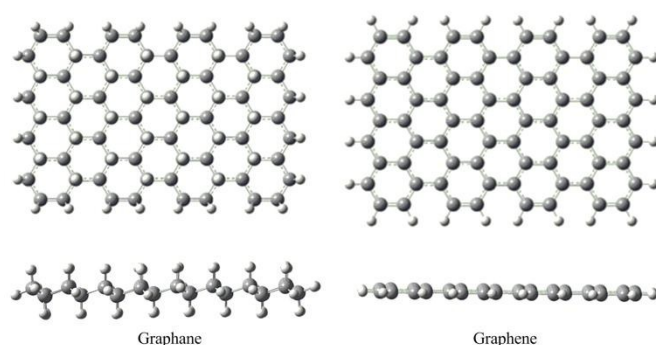


Fig. 1 Top view and lateral view of the graphene and graphene model systems considered in this study.

optimization of the complexes were carried out using the two layer ONIOM approach as it has been well employed to study the interactions of graphene with various molecules and ions in the literature.^{8-11, 77, 78} All the complexes have been optimised at ONIOM (M06-2X/6-31G*:PM6) level otherwise mentioned. We have selected model systems of similar dimensions for graphene and graphene in order to compare their binding affinity. The interacting surface of graphene with the molecules were treated at the M06-2X/6-31G* level and the remaining atoms were treated at low level using semiempirical PM6 Hamiltonian.^{79,80} Various atoms of graphene and graphene treated at different methods are shown in Fig. S1 in the Electronic Supplementary Information (ESI). All the other molecules and ions have been considered as high layer in the geometry optimization of their corresponding complexes. The stationary points obtained in the geometry optimization have been categorized as minima by verifying the presence of all real frequencies. Single point calculations have been done at M06-2X/6-311G** level in order to fine tune the energy. BSSE correction has not been included as the M06-2X functionals have been shown to perform better in the absence of BSSE.⁸¹ Binding energy (BE) has been calculated as the difference between sum of the total energies of graphene/graphene (E_G) and the molecules/ions (E_X) and the total energy of the complex (E_{G_X}) as given in (1)

$$BE = (E_G + E_X) - E_{G_X} \quad (1)$$

Natural population analysis has been done to calculate the charge transfer during the complex formation of graphene and graphene with various molecules and ions. The charge transfer has been considered as the sum of the charges of all the atoms in the graphene/graphene model system. Positive charge transfer values indicate the transfer of charge from graphene to the molecules/ions, while negative charge transfer values indicate the transfer of charge from the molecules/ions to graphene. The HOMO-LUMO energy gap of the pristine graphene/graphene as well as their complexes has been calculated at M06-2X/6-311G** level. All the calculations were done in the Gaussian 09 suite of programs.⁸²

3. Results and discussion

The current study comprises the noncovalent interaction of molecules and ions with graphene and graphene. We have divided

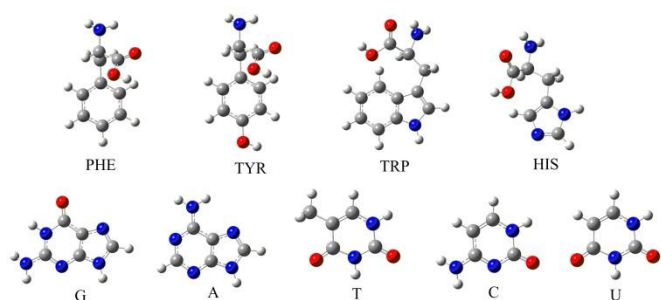


Fig. 2 Structure of biomolecules (amino acids and nucleobases) considered in the study.

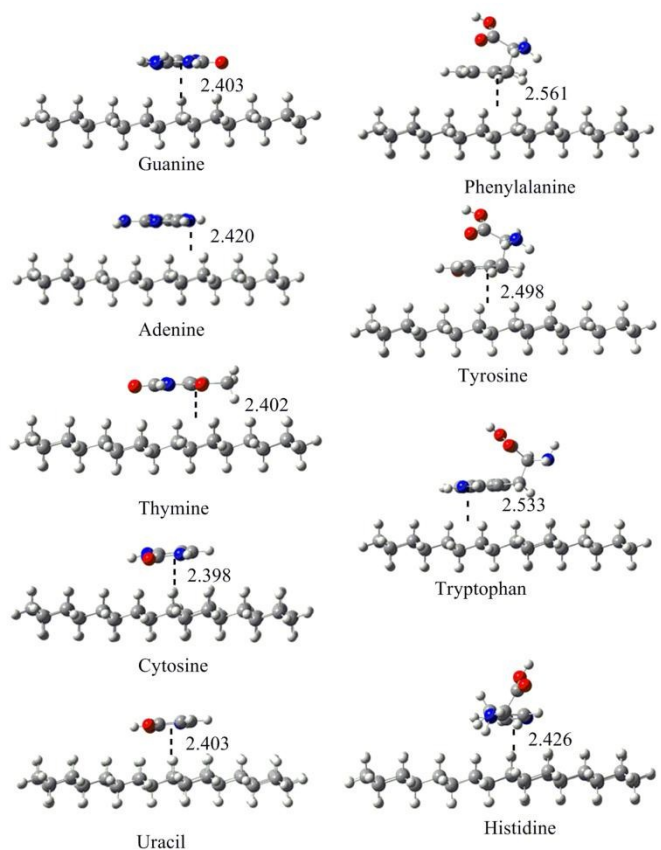


Fig. 3 Optimized structures and distances (Å) of the complexes of graphane with nucleobases and aminoacids.

the results and discussion in to four subsections describing the interaction of biomolecules, heterocycles, small molecules and cations respectively. In each section, the geometry of the complexes, binding energy, charge transfer and HOMO-LUMO energy gap have been discussed. This is followed by a comparative analysis of the binding affinity of graphane and graphene.

3.1 Interactions with biomolecules

A systematic study has been carried out to understand the interaction of biomolecules such as nucleobases and aromatic aminoacids with graphane (Fig. 2). There exist two possible modes of orientations for nucleobases and aminoacids while interacting with graphane which bring the aromatic motifs into parallel and perpendicular orientations with respect to the graphane plane. We

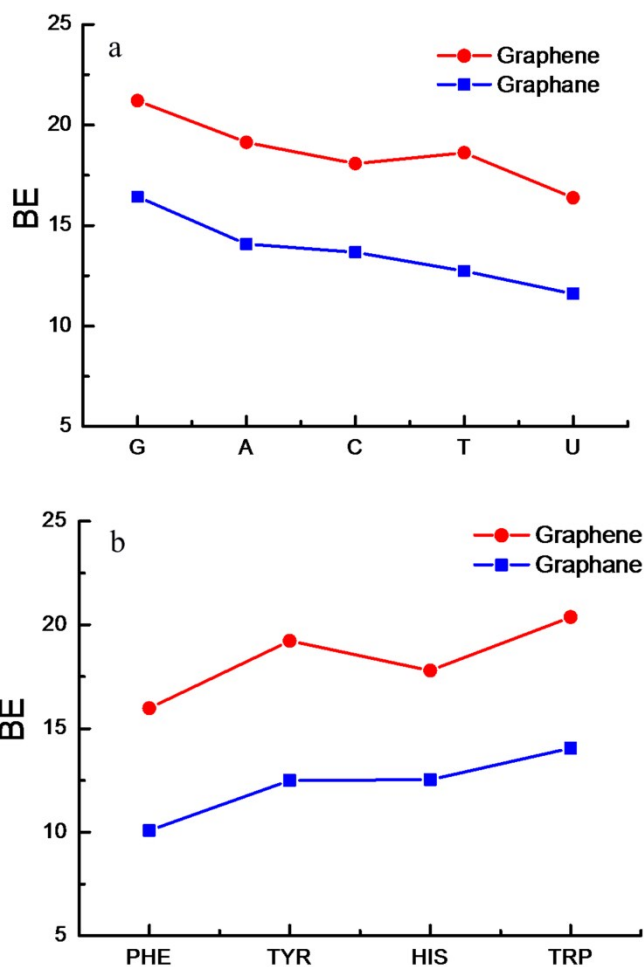


Fig. 4 Binding energies (kcal/mol) of (a) nucleobases and (b) aminoacids with graphane and graphene.

Table 1 Binding energy (kcal/mol), charge transfer (amu) and HOMO-LUMO energy gap (eV) of graphane complexes with biomolecules

Biomolecules	Binding energy	Charge transfer	HOMO-LUMO energy gap
Nucleobases			
G	16.43	-0.030	7.61
A	14.08	-0.026	7.32
C	13.67	-0.027	6.98
T	12.73	-0.020	6.90
U	11.60	-0.019	6.78
Aminoacids			
PHE	10.08	-0.009	7.62
TYR	12.50	-0.014	7.53
TRP	14.06	-0.016	7.19
HIS	12.53	-0.014	8.07

found that parallel orientations are preferred than the perpendicular orientations. This is in agreement with our earlier observation in the case of graphene.⁹ All attempts to locate a stationary point in the perpendicular orientation resulted in the parallel orientation. Hence graphane exhibits CH $\cdots\pi$ type of interaction with the aromatic biomolecules. Fig. 3 displays the

optimized structures of the complexes of graphane with nucleobases and aminoacids. The distance value is determined from the centre of the 6-membered rings in the biomolecules to the plane of the hydrogen atoms in the graphane. It is clear from the figure that the distance between the biomolecules and graphane in their optimized structure is 2.4 Å to 2.5 Å. Table 1 shows the binding energy, charge transfer and the HOMO-LUMO energy gap of the graphane complexes with nucleobases and aminoacids. It is evident from the table that graphane binds with nucleobases in the order $G > A > C > T > U$ and with aminoacids in the order as $\text{Trp} > \text{Tyr} \sim \text{His} > \text{Phe}$. The order of binding observed is clearly reflected in the charge transfer value. Fused rings molecules (G, A and Trp) show higher binding energy than the isolated ring molecules. The ability to tune the energy gap by functionalization is one of the primary requirements for carbon nanostructures to be used in nanoelectronics. The HOMO-LUMO energy gap of our model system of graphane computed at M06-2X/6-311G** level is found to be 8.46 eV. Interestingly, the energy gap of graphane has been found to be decreased on binding with aminoacids and nucleobases as shown in Table 1.

Subsequently, we studied the interaction of nucleobases and aminoacids with the unsaturated counterpart graphane. The optimized geometry, distances, binding energy, charge transfer and energy gap of the complexes have been given in the Fig. S2 and Table S1 in the ESI. The distance values are determined from the centre of the 6-membered rings in the biomolecules to the surface of graphane. The binding energy values of nucleobases and aminoacids with graphane are in the order $G > A > T > C > U$ and $\text{Trp} > \text{Tyr} > \text{His} > \text{Phe}$ respectively. Fig.4 compares the binding energy of graphane and graphane with nucleobases and aminoacids. It has been shown that graphane exhibits stronger binding energy than graphane in both the cases of nucleobases and aminoacids. However, the charge transfer in the graphane complex formation is very less when compared to graphane. The HOMO-LUMO energy gap of the pristine graphane model has been found to be 0.78 eV at M06-2X/6-311G** level. Our results indicate that there is no significant change in the HOMO-LUMO energy gap of graphane on binding with nucleobases (Table S1 in the ESI).

3.2 Interactions with heterocycles

In this section, we discuss the interaction between 5- and 6-membered heterocyclic compounds with graphane. A set of saturated and unsaturated heterocycles has been considered in the study as shown in Fig. 5. The nomenclature used in this discussion for heterocycles are U_nX and S_nX respectively for unsaturated and saturated hydrocarbons, where n stands for the number of atoms in the ring and X corresponds to the heteroatom. The binding energy, charge transfer and HOMO-LUMO energy gap of the complexes of graphane with heterocycles have been given in Table 2. As noticed earlier with biomolecules, graphane exhibits $\text{CH}\cdots\pi$ type of interaction with the unsaturated hydrocarbons. The decreasing order of binding energy with unsaturated heterocyclic compounds is $U5N > U5S > U5C > U5O$ and $U6S > U6O > U6N > U6C$ respectively for 5- and 6-membered rings. The optimized geometries of the complexes of graphane with unsaturated heterocyclic compounds have been given in Fig. 6. The reported distance values have been

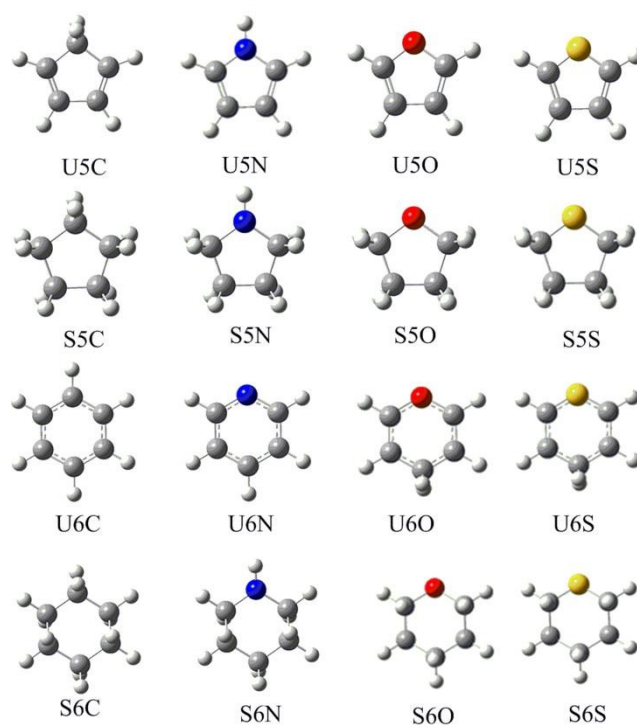


Fig. 5 Saturated and unsaturated 5- and 6-membered heterocyclic hydrocarbons.

Table 2 Binding energy (kcal/mol), charge transfer (amu) and HOMO-LUMO energy gap (eV) of graphane complexes with heterocyclic compounds

Heterocycles	Binding energy	Charge transfer	HOMO-LUMO energy gap
Unsaturated			
U5C	6.82	-0.007	7.55
U5N	7.78	-0.014	8.06
U5O	6.51	-0.010	7.62
U5S	7.43	-0.016	7.73
U6C	7.88	-0.009	7.73
U6N	7.92	-0.010	7.22
U6O	8.04	-0.011	8.12
U6S	9.12	-0.016	7.43
Saturated			
S5C	4.54	-0.001	8.28
S5N	7.93	-0.014	8.21
S5O	8.00	-0.012	8.25
S5S	5.87	-0.013	8.18
S6C	4.32	-0.002	8.24
S6N	7.36	-0.014	8.18
S6O	7.06	-0.011	8.24
S6S	5.07	-0.011	8.18

calculated from the ring centre of the heterocycles to the plane of the hydrogen atoms in graphane. Saturated heterocycles interact via $\text{CH}\cdots\text{HC}$ type of interaction which has been recently shown to be a considerable strong interaction.⁸³ For saturated heterocyclic compounds, the order of binding energy is $S5O > S5N > S5S > S5C$

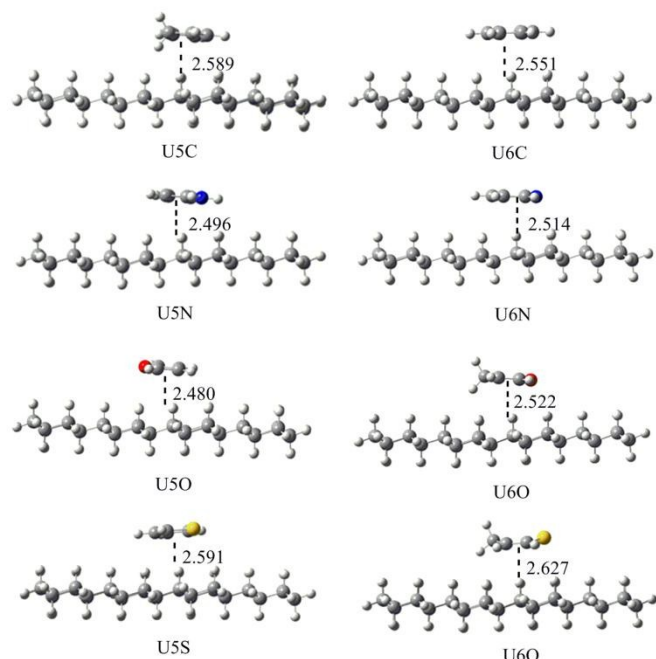


Fig. 6 Optimized structures and distances (Å) of the complexes of graphene with various unsaturated heterocyclic compounds.

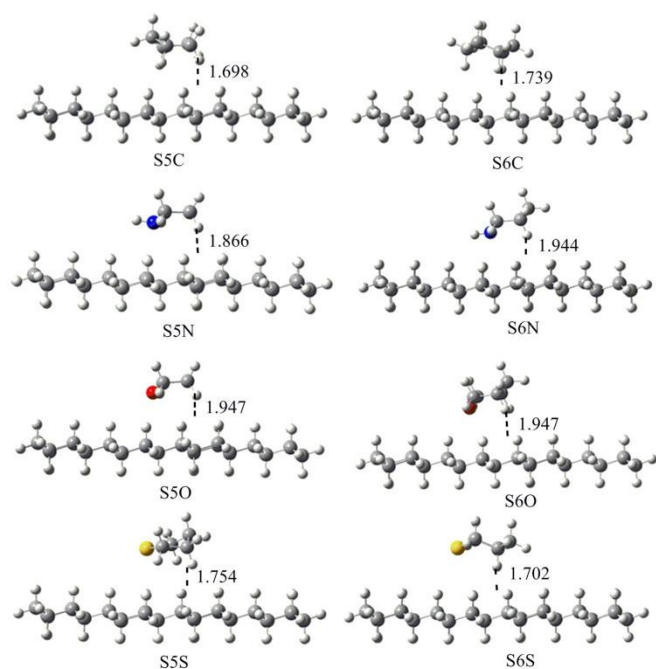


Fig. 7 Optimized structures and distances (Å) of the complexes of graphene with various saturated heterocyclic compounds.

and $S6N > S6O > S6S > S6C$ for 5- and 6-membered rings respectively. The optimized geometries of the saturated heterocyclic complexes have been given in Fig. 7 and the reported distance values have been measured from the nearest atom of the heterocycles to the plane of the hydrogen atoms in graphene. Charge transfer analysis indicates that these heterocycles act as charge donors to graphene in the complexes. Graphene exhibits $CH\cdots\pi$ type of interaction with unsaturated heterocycles (UnX) and

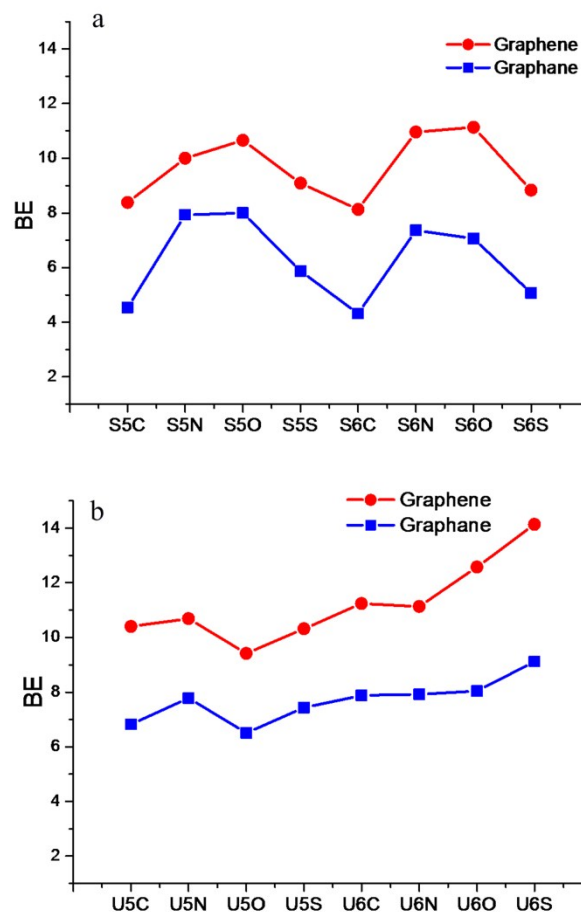


Fig. 8 Binding energies (kcal/mol) of (a) saturated and (b) unsaturated hydrocarbons with graphene and graphane.

a comparatively weaker $CH\cdots HC$ type of interaction with saturated heterocycles (S_nX). Hence in the 6-membered heterocycles complexes, $U6X$ show higher binding energy values when compared to $S6X$. However there is no such trend observed in the case of 5-membered heterocycles. We also noted a decrease in the HOMO-LUMO energy gap of graphene on binding with the heterocyclic compounds as shown in Table 2.

For graphene, the binding energy of unsaturated heterocyclic compounds is in the order $U5N > U5C > U5S > U5O$ and $U6S > U6O > U6C > U6N$ for 5- and 6-membered rings respectively as shown in Table S2 in the ESI. It is also noticeable from the table that the order of binding energy of 5- and 6-membered saturated heterocyclic compounds with graphene are $S5O > S5S > S5N > S5C$ and $S6O > S6N > S6S > S6C$ respectively. The optimized geometries of all the complexes of graphene with heterocycles have been given in Fig. S3 and Fig. S4 of the ESI. It is evident from Fig. 8 that graphene shows stronger binding affinity than graphane in both the cases of saturated and unsaturated heterocycles. However charge transfer and the change in the HOMO-LUMO energy gap in the case of graphene complexes are negligible when compared to graphane (Table S2 in the ESI).

3.3 Interactions with small molecules

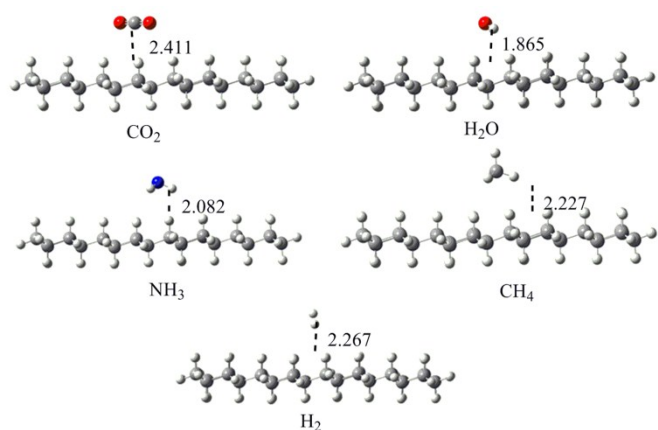


Fig. 9 Optimized structures and distances (Å) of the complexes of graphene with small molecules.

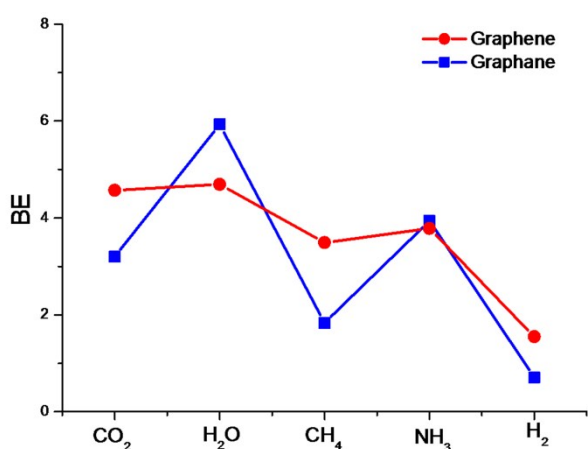


Fig. 10 Binding energies (kcal/mol) of various small molecules with graphene and graphane.

Graphene has been broadly explored for the fabrication of gas sensors. To study the feasibility of graphene as gas sensors, we have studied the interaction of various small molecules, such as CO₂, H₂O, NH₃, CH₄ and H₂ with graphene. Various possible orientations of these molecules on the surface of graphene have been considered and only the minimum energy orientations are reported. Fig. 9 shows the optimized structures of the complexes of graphene with small molecules. The nearest distance between the molecules and the plane of the hydrogen atoms in graphene has also been given in the figure. CO₂ molecule can have two possible orientations on the graphene surface which brings the molecule in parallel and perpendicular orientations. Our results reveal that the parallel orientation of the CO₂ molecule is more feasible than the perpendicular orientation. The distance between the CO₂ molecule and the hydrogen atom plane of the graphene sheet is found to be 2.411 Å. H₂O orients itself above the graphene surface at a distance of 1.865 Å. In the complexes of CH₄ and NH₃, the orientation where three hydrogen atoms are pointing towards the graphene have been found to be more stable as given in the Fig. 9. From the surface of the graphene sheet, the nearest distance of the CH₄

Table 3 Binding energy (kcal/mol), charge transfer (amu) and HOMO-LUMO energy gap (eV) of graphene complexes with small molecules

Small molecules	Binding energy	Charge transfer	HOMO-LUMO energy gap
CO ₂	3.20	-0.003	8.33
H ₂ O	5.93	-0.015	8.11
CH ₄	1.83	-0.001	8.31
NH ₃	3.94	-0.016	8.18
H ₂	0.71	0.002	8.43

molecule is 2.227 Å, while the distance of NH₃ molecule is 2.082 Å. The H₂ molecule aligns itself perpendicular to the graphene surface at 2.267 Å. Table 3 shows the binding energy, charge transfer and the HOMO-LUMO energy gap of the graphene complexes with the small molecules. The order of binding energy with graphene has been found as H₂O > NH₃ > CO₂ > CH₄ > H₂. All these molecules act as charge donors to the graphene except H₂ which acts as a charge acceptor from graphene. There is a slight decrease in the HOMO-LUMO energy gap of the graphene on binding with these molecules.

We then evaluated the interaction of these molecules with graphane. All the considered molecules exhibit similar orientations with graphane as observed in the case of graphene (Fig. S5 in ESI). However, the order of binding energy is found to be different from that of graphene. It is evident from the Table S3 that the decreasing order of binding energy is H₂O > CO₂ > NH₃ > CH₄ > H₂. All these molecules act as charge donors to the graphane except H₂ and virtually there is no change in the HOMO-LUMO energy gap of graphane on binding with these molecules. Fig. 10 shows the binding energy trend of graphane and graphene with these molecules. A cursory look at the figure reveals that graphane exhibit stronger binding energy than graphene with all of these molecules except NH₃ and H₂O. For NH₃, there is not much difference between the binding energies of graphane and graphene. However, for H₂O graphane exhibits stronger binding energy than graphene as shown in the figure. The higher binding energy for H₂O has been attributed to the higher charge transfer value as given in the Table 3. Thus our studies reveal that graphane is more hydrophilic than graphene. The binding energy of graphane with the small molecules are found to be smaller compared to the other species and this could be overcome by suitable functionalization of graphane such as covalent functionalization, hetero atom doping and metal ion doping on pristine graphane.⁴⁰⁻⁴³

3.4 Interactions with cations

In order to understand the interaction of cations with graphene, we have considered a set of metal ions (Li⁺, Na⁺, K⁺, Be²⁺, Mg²⁺, Ca²⁺) and a set of oniom ions (NH₄⁺, NMe₄⁺, OH₃⁺, OMe₃⁺, SH₃⁺, SME₃⁺). Graphane interacts with cations by cation-alkane type of interaction that has been shown to be a strong noncovalent interaction in the literature.⁷⁵ Fig. 11 shows the optimized structures and distances (Å) of the complexes of graphene with various cations. In the case of metal ions, the distance has been measured from the metal ion to the surface of the hydrogen atoms in graphene. For, an oniom ion, the distance is considered from the nearest atom of the oniom ions to the surface of the hydrogen

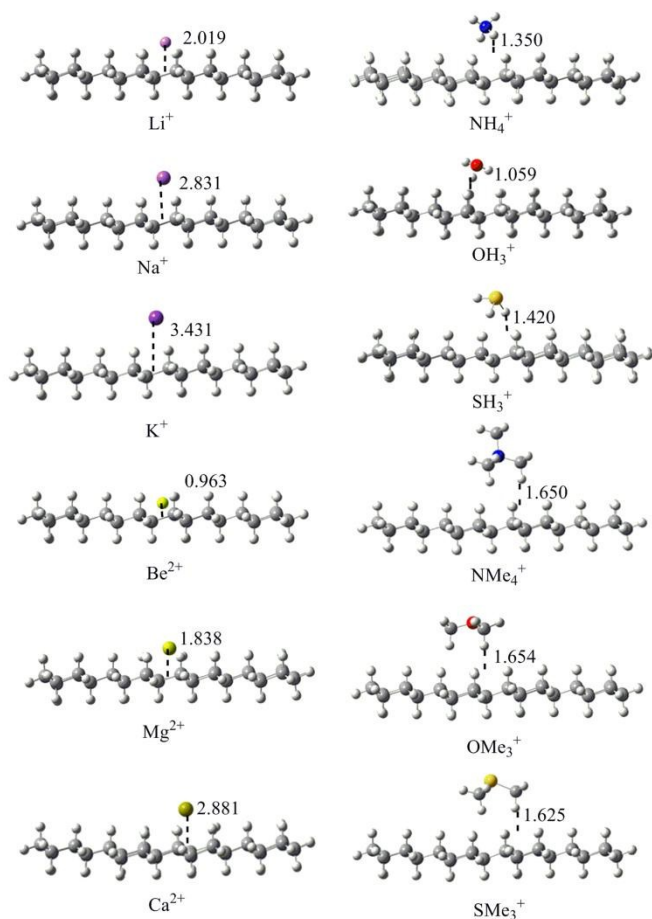


Fig. 11 Optimized structures and distances (Å) of the complexes of graphane with cations.

Table 4 Binding energy (kcal/mol), charge transfer (amu) and HOMO-LUMO energy gap (eV) of graphane complexes with cations

Cations	Binding energy	Charge transfer	HOMO-LUMO energy gap
Metal ions			
Li ⁺	42.46	0.179	5.73
Na ⁺	25.60	0.108	5.07
K ⁺	17.16	0.073	5.36
Be ²⁺	321.79	1.011	4.57
Mg ²⁺	185.72	0.356	2.92
Ca ²⁺	121.13	0.218	2.84
Oniom ions			
NH ₄ ⁺	18.37	0.030	5.78
NMe ₄ ⁺	10.95	0.020	6.80
OH ₃ ⁺	29.47	0.088	5.43
OMe ₃ ⁺	12.28	0.021	6.45
SH ₃ ⁺	19.75	0.051	5.15
SMe ₃ ⁺	12.57	0.022	6.45

atoms in graphane. The binding energy, charge transfer and HOMO-LUMO energy gap of the complexes of various cations with graphane have been given in Table 4. It is evident from the table that, in the case of alkali metal ions the binding energy is in the

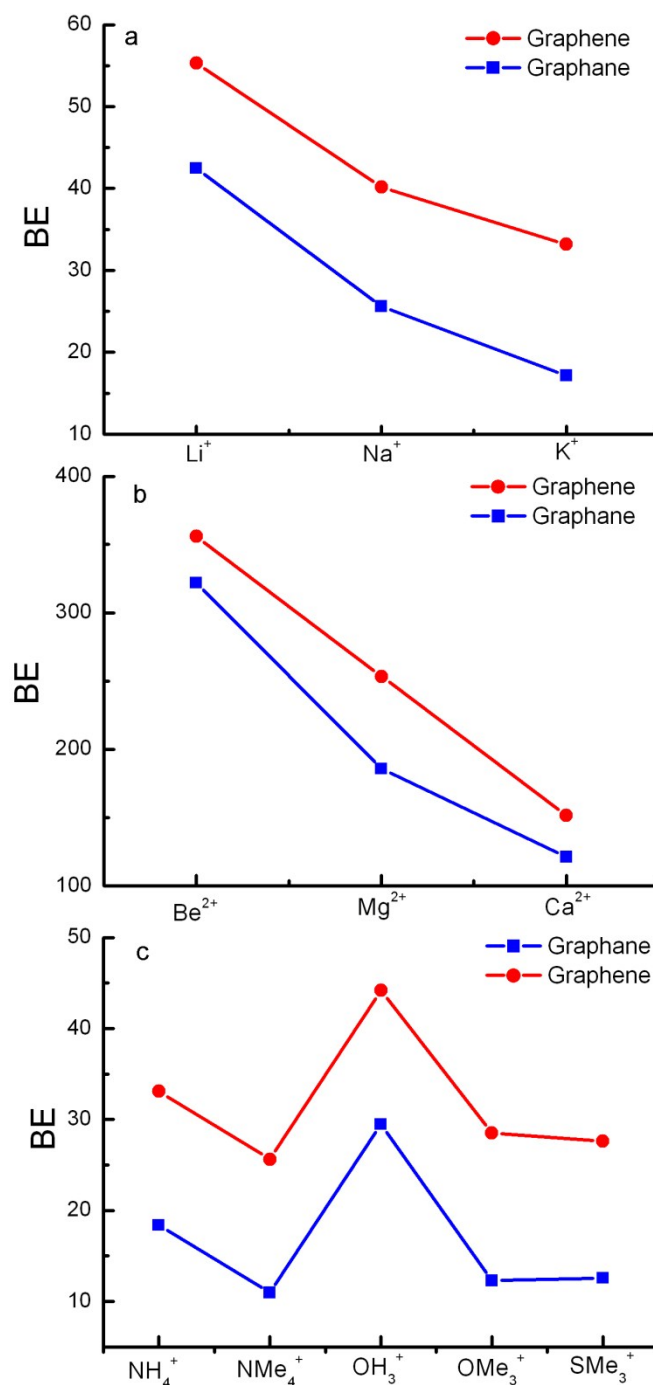


Fig. 12 Binding energies (kcal/mol) of (a) alkali metal ions and (b) alkaline earth metal ions (c) oniom ions with graphane and graphane.

order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$; while in the case of alkaline earth metal ions the order is $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}$. This may be attributed to the electronegativity and charge-to-mass ratio trends of the metal ions. Table 4 also shows the amount of charge transfer from graphane to the metal ions which clearly reflect the order observed in the binding energy. Oniom ions bind with graphane in the order $\text{OH}_3^+ > \text{SH}_3^+ > \text{NH}_4^+ > \text{SMe}_3^+ > \text{OMe}_3^+ > \text{NMe}_4^+$. Graphane shows stronger binding affinity with the simple oniom ions (OH_3^+ , SH_3^+ , NH_4^+) when compared to their methyl substituted analogues (OMe_3^+ , SMe_3^+ , NMe_4^+). The amount of charge transfer from graphane to the oniom

ions is in good agreement with the above mentioned order of binding energy. The interaction energies for the complexes formed by divalent cations are larger than those for the complexes involving monovalent cations. A cursory look at the Table 4 reveals that graphene exhibit stronger binding with the metal ions than the oniom ions considered in the study. We further studied the change in HOMO-LUMO energy gap of graphene before and after complex formation with the cations. Our results reveal that there is significant decrease in the HOMO-LUMO energy gap of graphene on binding with the cations. Hence doping of graphene with metal ions and oniom ions can be used as a tool to fine tune the energy gap of graphene which is an essential characteristic for its application in nano electronics. We have also studied the cation complexes of the unsaturated counterpart graphene. Metal ions generally form cation- π type of complexes with graphene, however for oniom ions in addition to cation- π , there is also a possibility for proton transfer to graphene. In order to understand this, graphene-cation complexes have been fully optimized at M06-2X/6-31G* level followed by single point calculations at M06-2X/6-311G**. The optimized structure of all the graphene-cation complexes considered have been given in Fig. S6 in ESI. Our results reveal that all the oniom ions form cation- π type of complexes with graphene except SH_3^+ which involves a proton transfer. The binding energy, charge transfer and HOMO-LUMO energy gap of all the cation- π complexes of graphene have been given in Table S4 in the ESI. The order of binding for metal ions and oniom ions have been observed as $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+$ and $\text{OH}_3^+ > \text{NH}_4^+ > \text{OMe}_3^+ > \text{SMe}_3^+ > \text{NMe}_4^+$ respectively. The HOMO-LUMO energy gap value of graphene decreases on binding with cations except in the case of alkaline earth metal ions where there is an increase in the energy gap. Fig. 12 compares the binding energy of cations with graphene and graphene. It is evident from the figure that graphene exhibit stronger binding affinity than graphene towards the cations.

4. Summary

The present study has made a systematic effort to examine the binding affinity of graphene with various molecules and ions. Graphene forms stable complexes with all the systems considered yet exhibits lower binding energies when compared to graphene. The summary of the results is as follows,

- 1) Graphene binds with nucleobases in the order $\text{G} > \text{A} > \text{C} > \text{T} > \text{U}$, while it binds with aminoacids in the order $\text{Trp} > \text{Tyr} \sim \text{His} > \text{Phe}$.
- 2) Saturated heterocyclic compounds exhibit binding energy with graphene as $\text{S5O} > \text{S5N} > \text{S5S} > \text{S5C}$ and $\text{S6N} > \text{S6O} > \text{S6S} > \text{S6C}$ for 5- and 6-membered rings respectively. The orders of binding energy of graphene with unsaturated heterocyclic compounds are $\text{U5N} > \text{U5S} > \text{U5C} > \text{U5O}$ and $\text{U6S} > \text{U6O} > \text{U6N} > \text{U6C}$ for 5- and 6-membered rings respectively.
- 3) The order of binding energy of small molecules with graphene has been found as $\text{H}_2\text{O} > \text{NH}_3 > \text{CO}_2 > \text{CH}_4 > \text{H}_2$.
- 4) Graphene binds with metal ions in the order $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Li}^+ > \text{Na}^+ > \text{K}^+$ and with oniom ions in the order $\text{OH}_3^+ > \text{SH}_3^+ > \text{NH}_4^+ > \text{SMe}_3^+ > \text{OMe}_3^+ > \text{NMe}_4^+$. Pristine oniom ions bind stronger with graphene when compared to their methyl substituted analogues. Graphene exhibit stronger binding with the metal ions compared to the oniom ions considered in the study.
- 5) Charge transfer in the graphene complexes are in good correlation with the observed binding energies. All the neutral molecules considered in this study act as charge donors to graphene excluding H_2 which acts as a charge acceptor from graphene. Metal ions and oniom ions act as charge acceptors.
- 6) HOMO-LUMO energy gap of the graphene decreases on binding with the molecules and ions to a dramatic extent in the later case. Hence we propose that the energy gap of graphene may be tuned by functionalization.
- 7) Graphene exhibits stronger binding affinity than graphene with nucleobases, aminoacids, heterocycles, small molecules, metal ions and oniom ions except H_2O . Hence our results reveal that graphene in more hydrophilic than graphene.

Thus, the current study provides insight into the interaction of graphene with various molecules and ions. We hope that our comparative study of graphene with graphene will provide valuable guidelines to develop graphene based advanced materials that could satisfy the demand in various fields.

Acknowledgements

We thank the 12th five year plan project of CSIR (INTELCOAT and MSM) for financial assistance.

References

1. D. Umadevi, S. Panigrahi and G. N. Sastry, *Acc. Chem. Res.*, 2014, **47**, 2574-2581.
2. T. C. Dinadayalane and J. Leszczynski, *Struct. Chem.*, 2010, **21**, 1155-1169.
3. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva and A. A. Firsov, *Science*, 2004, **306**, 666-669.
4. V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chem. Rev.*, 2012, **112**, 6156-6214.
5. D. Umadevi and G. N. Sastry, *J. Phys. Chem. C*, 2011, **115**, 9656-9667.
6. D. Umadevi and G. N. Sastry, *Chem. Phys. Lett.*, 2012, **549**, 39-43.
7. A. S. Mahadevi and G. N. Sastry, *Chem. Rev.*, 2013, **113**, 2100-2138.
8. D. Umadevi and G. N. Sastry, *J. Phys. Chem. Lett.*, 2011, **2**, 1572-1576.
9. D. Umadevi and G. N. Sastry, *ChemPhysChem*, 2013, **14**, 2570-2578.
10. D. Umadevi and G. N. Sastry, *Front. Chem.* 2014, **2**:75.
11. D. Umadevi and G. N. Sastry, *Curr. Sci.*, 2014, **106**, 1224-1234.
12. J. Agbenyega, *Mater. Today*, 2009, **12**, 13.

13. C. Zhou, S. Chen, J. Lou, J. Wang, Q. Yang, C. Liu, D. Huang and T. Zhu, *Nanoscale Res. Lett.*, 2014, **9**, 26.
14. J. O. Sofo, A. S. Chaudhari and G. D. Barber, *Phys. Rev. B*, 2007, **75**, 153401.
15. D. C. Elias, R. R. Nair, T. M. G. Mohiuddin, S. V. Morozov, P. Blake, M. P. Halsall, A. C. Ferrari, D. W. Boukhvalov, M. I. Katsnelson, A. K. Geim and K. S. Novoselov, *Science*, 2009, **323**, 610-613.
16. H. Şahin, C. Ataca and S. Ciraci, *Phys. Rev. B*, 2010, **81**, 205417.
17. Y. Li, Z. Zhou, P. Shen and Z. Chen, *J. Phys. Chem. C*, 2009, **113**, 15043-15045.
18. N. Lu, Z. Li and J. Yang, *J. Phys. Chem. C*, 2009, **113**, 16741-16746.
19. L.-F. Wang, T.-B. Ma, Y.-Z. Hu, H. Wang and T.-M. Shao, *J. Phys. Chem. C*, 2013, **117**, 12520-12525.
20. Q. Peng, C. Liang, W. Ji and S. De, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2003-2011.
21. S. Costamagna, M. Neek-Amal, J. H. Los and F. M. Peeters, *Phys. Rev. B*, 2012, **86**, 041408.
22. Y. Li, F. Li and Z. Chen, *J. Am. Chem. Soc.*, 2012, **134**, 11269-11275.
23. H. Da, Y. P. Feng and G. Liang, *J. Phys. Chem. C*, 2011, **115**, 22701-22706.
24. X.-D. Wen, L. Hand, V. Labet, T. Yang, R. Hoffmann, N. W. Ashcroft, A. R. Oganov and A. O. Lyakhov, *Proc. Nat. Acad. Sci.*, 2011, **108**, 6833-6837.
25. J. J. Hernández Rosas, R. E. Ramírez Gutiérrez, A. Escobedo-Morales and E. Chigo Anota, *J. Mol. Model.*, 2011, **17**, 1133-1139.
26. Y. H. Lu and Y. P. Feng, *J. Phys. Chem. C*, 2009, **113**, 20841-20844.
27. B. S. Pujari and D. G. Kanhere, *J. Phys. Chem. C*, 2009, **113**, 21063-21067.
28. L. F. Huang, X. H. Zheng, G. R. Zhang, L. L. Li and Z. Zeng, *J. Phys. Chem. C*, 2011, **115**, 21088-21097.
29. Y. Zhang, X. Wu, Q. Li and J. Yang, *J. Phys. Chem. C*, 2012, **116**, 9356-9359.
30. H. L. Poh, F. Sanek, Z. Sofer and M. Pumera, *Nanoscale*, 2012, **4**, 7006-7011.
31. H. L. Poh, Z. Sofer and M. Pumera, *Electrochem. Commun.*, 2012, **25**, 58-61.
32. M. Pumera, A. Ambrosi, A. Bonanni, E. L. K. Chng and H. L. Poh, *TrAC, Trends Anal. Chem.*, 2010, **29**, 954-965.
33. M. Pumera and C. H. A. Wong, *Chem. Soc. Rev.*, 2013, **42**, 5987-5995.
34. Y. Li and Z. Chen, *J. Phys. Chem. Lett.*, 2012, **4**, 269-275.
35. C. Wang, Y. Mo, J. P. Wagner, P. R. Schreiner, E. D. Jemmis, D. Danovich and S. Shaik, *J. Chem. Theor. Comp.*, 2015, **11**, 1621-1630.
36. X.-D. Wen, T. Yang, R. Hoffmann, N. W. Ashcroft, R. L. Martin, S. P. Rudin and J.-X. Zhu, *ACS Nano*, 2012, **6**, 7142-7150.
37. S. Jiang, M. Q. Arguilla, N. D. Cultrara and J. E. Goldberger, *Acc. Chem. Res.*, 2015, **48**, 144-151.
38. J. C. Garcia, D. B. de Lima, L. V. C. Assali and J. F. Justo, *J. Phys. Chem. C*, 2011, **115**, 13242-13246.
39. C. J. Rupp, S. Chakraborty, R. Ahuja and R. J. Baierle, *Phys. Chem. Chem. Phys.*, 2015, **17**, 22210-22216.
40. H. Tanveer, P. Biswarup, M. Tuhina Adit, A. Carlos Moyses, H. S. Ralph and A. Rajeev, *EPL Europhys. Lett.*, 2011, **96**, 27013.
41. T. Hussain, B. Pathak, M. Ramzan, T. A. Maark and R. Ahuja, *Appl. Phys. Lett.*, 2012, **100**, 183902.
42. L. Y. Antipina, P. V. Avramov, S. Sakai, H. Naramoto, M. Ohtomo, S. Entani, Y. Matsumoto and P. B. Sorokin, *Phys. Rev. B*, 2012, **86**, 085435.
43. T. Hussain, P. Panigrahi and R. Ahuja, *Phys. Chem. Chem. Phys.*, 2014, **16**, 8100-8105.
44. B. Gharekhanlou, S. B. Tousaki and S. Khorasani, *J. Phys. Conf. Ser.*, 2010, **248**, 012061.
45. H. Tanveer, P. Puspamitra and A. Rajeev, *Nanotechnology*, 2014, **25**, 325501.
46. F. Karlický, K. Kumara Ramanatha Datta, M. Otyepka and R. Zbořil, *ACS Nano*, 2013, **7**, 6434-6464.
47. M. N. Amini, O. Leenaerts, B. Partoens and D. Lamoen, *J. Phys. Chem. C*, 2013, **117**, 16242-16247.
48. M. Nava, D. E. Galli, M. W. Cole and L. Reatto, *Phys. Rev. B*, 2012, **86**, 174509.
49. S. Tang and X. Cao, *Phys. Chem. Chem. Phys.*, 2014, **16**, 23214-23223.
50. J. Xiao, S. Sitamraju and M. J. Janik, *Langmuir*, 2014, **30**, 1837-1844.
51. J. Leszczynski, *Nat. Nano*, 2010, **5**, 633-634.
52. M. K. Shukla, M. Dubey, E. Zakar, R. Namburu, Z. Czyznikowska and J. Leszczynski, *Chem. Phys. Lett.*, 2009, **480**, 269-272.
53. S. K. Min, W. Y. Kim, Y. Cho and K. S. Kim, *Nat. Nano*, 2011, **6**, 162-165.
54. K. Balamurugan, E. R. A. Singam and V. Subramanian, *J. Phys. Chem C*, 2011, **115**, 8886-8892.
55. S. Gowtham, R. H. Scheicher, R. Ahuja, R. Pandey and S. P. Karna, *Phys. Rev. B: Condens. Matter*, 2007, **76**, 033401.
56. H. Vovusha, S. Sanyal and B. Sanyal, *J. Phys. Chem. Lett.*, 2013, **4**, 3710-3718.
57. S. Mogurampelly, S. Panigrahi, D. Bhattacharyya, A. K. Sood and P. K. Maiti, *J. Chem. Phys.*, 2012, **137**, 054903.
58. S. Panigrahi, A. Bhattacharya, S. Banerjee and D. Bhattacharyya, *J. Phys. Chem. C*, 2012, **116**, 4374-4379.
59. S. K. Mudedla, K. Balamurugan and V. Subramanian, *J. Phys. Chem. C*, 2014, **118**, 16165-16174.
60. N. Varghese, U. Mogera, A. Govindaraj, A. Das, P. K. Maiti, A. K. Sood and C. N. R. Rao, *ChemPhysChem*, 2009, **10**, 206-210.
61. J. Prasongkit, A. Grigoriev, B. Pathak, R. Ahuja and R. H. Scheicher, *Nano Lett.*, 2011, **11**, 1941-1945.
62. G. Zuo, X. Zhou, Q. Huang, H. Fang and R. Zhou, *J. Phys. Chem. C*, 2011, **115**, 23323-23328.
63. T. Nelson, B. Zhang and O. V. Prezhdo, *Nano Lett.*, 2010, **10**, 3237-3242.
64. M. Chourasia, G. M. Sastry and G. N. Sastry, *Int. J. Biol. Macromol.*, 2011, **48**, 540-552.
65. S. Panigrahi and G. N. Sastry, *RSC Advances*, 2014, **4**, 14557-14563.

66. A. S. Reddy and G. N. Sastry, *J. Phys. Chem. A*, 2005, **109**, 8893-8903.
67. B. Sharma, D. Umadevi and G. Narahari Sastry, *Phys. Chem. Chem. Phys.*, 2012, **14**, 13922-13932.
68. D. Vijay, H. Sakurai, V. Subramanian and G. N. Sastry, *Phys. Chem. Chem. Phys.*, 2012, **14**, 3057-3065.
69. D. Vijay and G. N. Sastry, *Phys. Chem. Chem. Phys.*, 2008, **10**, 582-590.
70. M. A. Hussain, A. S. Mahadevi and G. N. Sastry, *Phys. Chem. Chem. Phys.*, 2015, **17**, 1763-1775.
71. S. Saha and G. N. Sastry, *J. Phys. Chem. B*, 2015, **119**, 11121-11135.
72. N. Li, G. Lee, J. W. Yang, H. Kim, M. S. Yeom, R. H. Scheicher, J. S. Kim and K. S. Kim, *J. Phys. Chem C*, 2013, **117**, 4309-4313.
73. E. Munusamy and S. E. Wheeler, *J. Chem. Phys.*, 2013, **139**, 094703.
74. A. A. Fokin, D. Gerbig and P. R. Schreiner, *J. Am. Chem. Soc.*, 2011, **133**, 20036-20039.
75. J. R. Premkumar and G. N. Sastry, *J. Phys. Chem. A*, 2014, **118**, 11388-11398.
76. J. R. Premkumar, D. Umadevi and G. N. Sastry, *Indian J. Chem., Sect A*, 2014, **53A**, 985-991.
77. K. Balamurugan and V. Subramanian, *J. Phys. Chem. C*, 2013, **117**, 21217-21227.
78. K. Balamurugan, P. Baskar, R. M. Kumar, S. Das and V. Subramanian, *Phys. Chem. Chem. Phys.*, 2014, **16**, 24509-24518.
79. Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
80. J. J. P. Stewart, *J. Mol. Model.*, 2007, **13**, 1173-1213.
81. Y. Liu, J. Zhao, F. Li and Z. Chen, *J. Comput. Chem.*, 2013, **34**, 121-131.
82. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Journal*, 2009.
83. J. Echeverría, G. Aullón, D. Danovich, S. Shaik and S. Alvarez, *Nat. Chem.*, 2011, **3**, 323-330.