STUDY OF THE EFFECT OF MONO VACANCY OF GRAPHENE HEXAGONAL BORON NITRIDE HYBRID WITH DIAMOND SHAPED h-BN ISLAND

BY

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Outline

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Density functional theory

- Computational method for solving the many body **Schrödinger equation.**

- All the information of the system is contained in the electron density

- With **DFT** we can obtain
  - Structure beyond the current capability of experiment.
  - Predict properties at a resolution and length scale currently inaccessible to experiments.
  - We are in control of the degree of freedom.
  - We know our model, so we know exactly what we are measuring.

Fundamentals of DFT
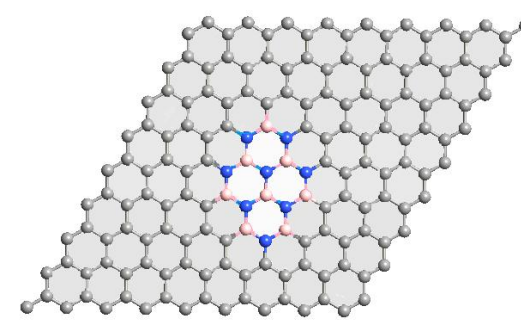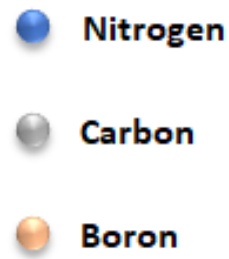
- DFT is base on two very fundamental theorems

THEOREM 1: The ground state energy E is a unique functional of the electron density:
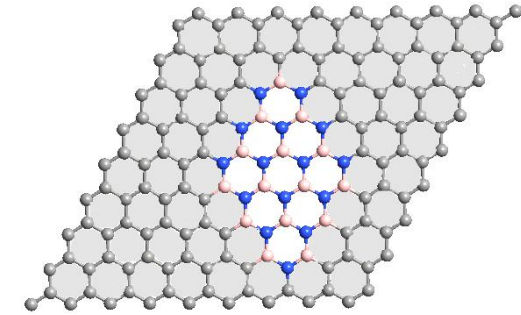
$$E = E[n(r)]$$

THEOREM 2: The electron density that minimizes energy of the overall functional is the true ground state electron density.

$$E = E[n(r)] > E_0[n_0(r)]$$

Introduction

Nitrogen
Carbon
Boron

- We generated a graphene island of various sizes in the h-BN layout and vice versa. Each of pristine and defective GBN hybrids involves a diamond shaped island with size X and the size of island (X) is 4, 9 or 16.

- We likewise investigated the size effects of diamond shaped island on the electronic and magnetic properties of pristine GBN in-plane hybrids.
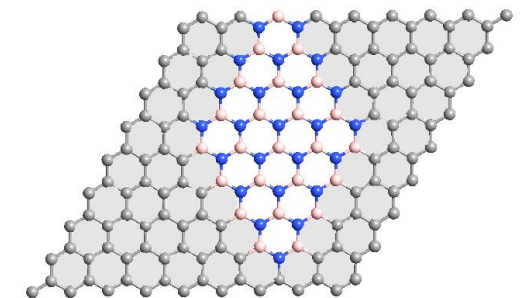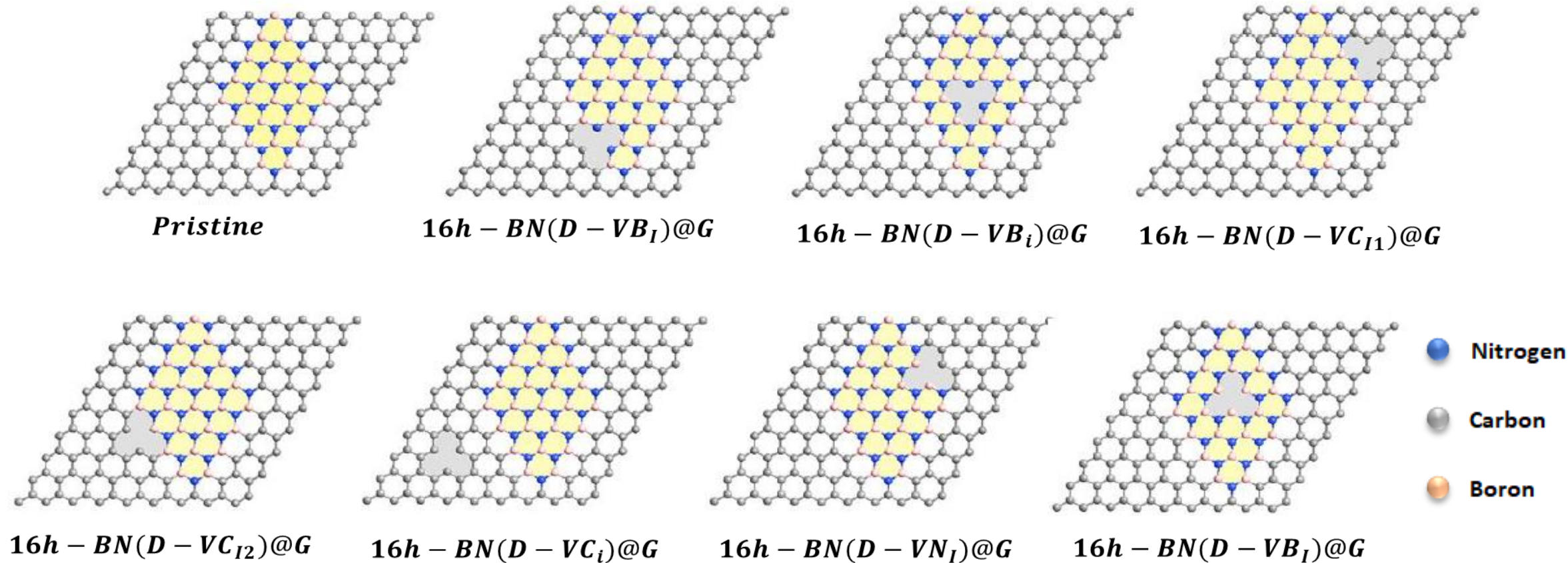
$4h - BN@G$

$9h - BN@G$

$16h - BN@G$

pristine $h - BN@G$ for the 3 different island sizes band gap increase with increase island size

- By ejecting a single carbon, boron or nitrogen atom in the GBN nanosheet, we created a vacancy defected GBN hybrid.
- We next calculated the defect formation energy and material properties of defective hybrids such as band gap energy and magnetic moment.
- The Single vacancy created alters the electronic properties of the system.

Pristine 16h − BN(D − VB_I)@G 16h − BN(D − VB_i)@G 16h − BN(D − VC_{I1})@G

16h − BN(D − VC_{I2})@G 16h − BN(D − VC_i)@G 16h − BN(D − VN_I)@G 16h − BN(D − VB_I)@G

● Nitrogen
● Carbon
● Boron

$VN_{\text{I (Interface)}}$: nitrogen vecancy at the interface
$VB_{\text{L (Layout)}}$: boron vacancy at the layout
$VC_{\text{I (Interface (1))}}$ = carbon vacancy at the interface N bonded atom
$VC_{\text{I (Interface (2))}}$ = carbon vacancy at the interface B bonded atom

$VC_{\text{i (Idle)}}$: carbon vacancy at the middle of carbon atoms
$VN_{\text{I (Interface)}}$: nitrogen vacancy at the interface
$VN_{\text{L (Layout)}}$: nitrogen vacancy at the layout

Introduction

- We investigated the effects of mono vacancy on the electronic and magnetic properties of defective GBN nanosheet.
- We searched for the energetics of 7 distinct C, B and N mono vacancies created at various places GBN hybrid.
- We carried through the self-consistent calculations for k-point mesh convergence, the energetics and non-self consistent DOS calculations using tetrahedron method with Bloch corrections.

Methodology

- Geometry optimizations, electronic and density of states (DOS) calculations were conducted by using **VASP**.

- Static self-consistent calculation were performed to obtain the charge density and total energies of the systems after the geometry optimization.

- We performed the **DFT** by adopting the **GGA** together with the Perdew-Wang parametrization (PW91) for the exchange correlation potential.

- We used the projected augmented wave (PAW) method for the treatment of electron-core interactions.

- Sampling of Brillouin zone was done using Γ point centered Monkhorst-Pack grids.

Methodology

- Optimum k-point mesh, which is required for the geometry relaxation, was converged as the difference in total energy between two successive iterations is below 10 meV.

- The optimized k-point meshes for pristine samples are as follows.

  - Graphene unit cell: $10 \times 10 \times 3$,
  - graphene supercell: $4 \times 4 \times 1$,
  - h-BN unit cell: $8 \times 8 \times 1$,
  - h-BN supercell: $3 \times 3 \times 1$.
  - Pristine and vacancy defected GBN supercells: $3 \times 3 \times 1$ or $4 \times 4 \times 1$ resp.

Methodology

- The adapted criteria for the energy convergence and the total force on each atom are $0.1\mu eV$ and $4 \times 4 \times 1$ V/Å, respectively.

- In the case of DOS calculations, the optimum size of k-point mesh is $9 \times 9 \times 1$ for both pristine and defective hybrids.

- Band structure and DOS of the optimum structure were calculated non-self consistently with the charge density obtained from the self-consistent calculation.

- We carried out spin unpolarized (**NSP**) and spin polarized (**SP**) calculations for each of the pristine and defective hybrids to find out its ground state and magnetic moment.

Methodology

- We then formed a single vacancy by removing a boron or nitrogen atom at the interface of **G** and **h-BN** regions, or in the h-BN layout. (we did the same for h-BN@G hybrids)

- The GBN hybrids with a missing carbon atom at the G-BN interface or in the middle of graphene island were taken into account. (same for h-BN@G hybrids)

- We investigated 42 defective GBN hybrids in all. As we did in the geometrical optimization of pristine samples, the atoms of defective hybrids as well as the lattice vectors of supercell were relaxed into their ground state.

Results

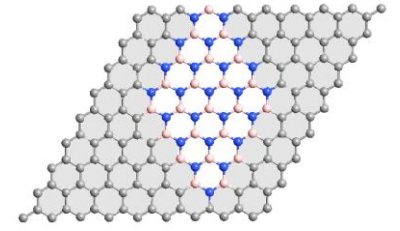## Magnetization energy

- The difference of total energies of a system in the NSP and SP states is called as the **magnetization energy** ΔE_M i.e.

$$\Delta E_M = E_{NSP} - E_{SP}$$

- A positive ΔE_M expresses that the system has an SP ground state. otherwise it is NSP.
- The higher the magnetization energy, the more stable magnetism the system has.

Results

Island formation energy

- The minimum and maximum values of G and h-BN island formation energy through a solid-state reaction is:

- $\varepsilon_{if_{min(for\ h-BN@G)}} = (E_{h-BN@G} + (Y+Z) \times \mu[C_{bulk}] - (E_{G_{162}} + Y \times \mu[B_{atom}] + Z \times \mu[N_{atom}])$

- $\varepsilon_{if_{(for\ h-BN@G)}} = (E_{h-BN@G} + (Y+Z) \times \mu[C_{atom}] - (E_{G_{162}} + Y \times \mu[B_{bulk}] + Z \times \mu[N_{bulk}])$

- where $E_{h-BN_{162}}$ and $E_{G@h-BN}$ are the respective total energies of h-BN nanosheet and h-BN layout involving a graphene island.

Results

- **Defect formation energy**

- A vacancy defect can exist in these systems either by nature during the synthetization process or can be formed on purpose under particle (electron, ion) irradiation.

$$E_{df}(VY) = E_T^D(VY) - E_T^P + \mu_Y ....(8)$$

where $E_T^D(VY)$ is the total energy of vacancy-defected hybrid, E_T^P is the total energy of pristine hybrid, and μ_Y is the chemical potential of the missing lattice atom.

Results

- Structural reconstruction was not observed after the optimization except that dangling bonds of atoms around the vacancy site introduced local in/out-plane distortions in the hybrid nanosheet.

- The h-BN nanosheet with VB defect has a higher amount of ΔE_M, and hence it can be more stable for both systems (i.e G(D)@h-BN and h-BN(D)@G.)

- The interface is the energetically most favorable place for the generation of mono vacancy.

- In general, we could not observe any correlation between the island size and the vacancy formation energy.
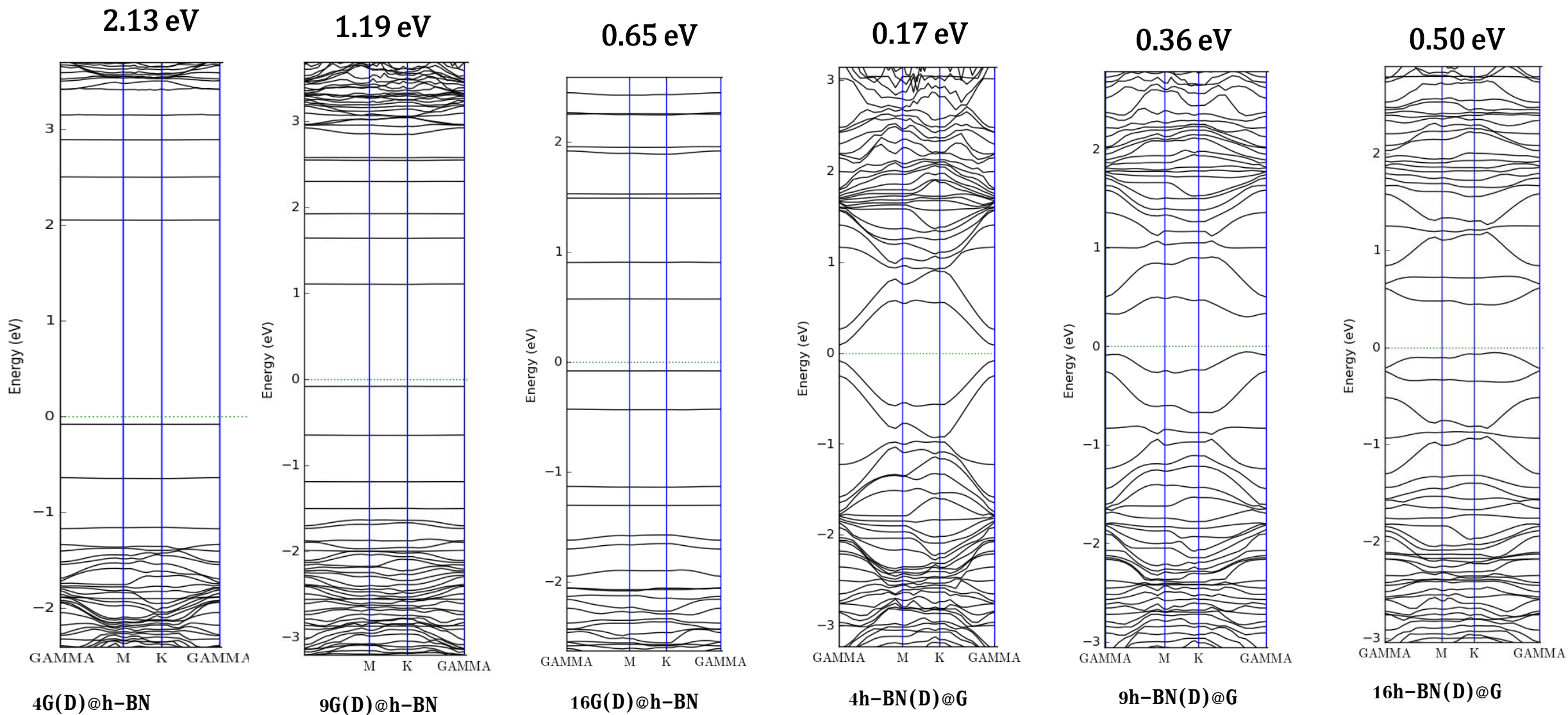
Table 3. Magnetization energy ΔE_m, Magnetic moment μ, Defect formation energy E_{df} and Band gap E_g of all the pristine and defective hybrids of h-BN@G

- The higher the magnetization energy the more stable the defective structure is
- From all indications systems with B vacancy seems to be more stable against thermal excitation.
- Apart from the pristine hybrids, the nonmetallic hybrids are those with C vacancy

$E_{TOTAL}[D(i)] = $ **total E of defective hybrid**
$E_{TOTAL}[D(0)] = $ **total E of non defective hybrid**
4 = no of hexagons involve in the island
9 = no of hexagons involve in the island
16 = no of hexagons involve in the island
$G = $ **Graphene**
$D = $ **Pristine hybrid**
$h - BN = $ **hexagonal boron nitride**

System	Name	$\Delta E_m (eV)$	$\mu (\mu_B)$	$E_{df} (eV)$	$E_g (meV)$
$C_{154}B_7N_8$	4h-BN(D-VB$_L$)@G	-0.1	NM	-	0.17
$C_{154}B_7N_8$	4h-BN(D-VB$_L$)@G	-231.8	2.2	8.43	Metallic
$C_{154}B_7N_8$	4h-BN (D-VB$_l$)@G	-9.9	NM	7.30	Metallic
$C_{153}B_8N_8$	4h-BN (D-VC$_{I2}$)@G	-42.4	NM	6.81	Metallic
$C_{153}B_8N_8$	4h-BN (D-VC$_{I1}$)@G	-3.2	NM	5.67	258.0
$C_{153}B_8N_7$	4h-BN (D-VC$_i$)@G	-300.8	1.6	7.71	Metallic
$C_{154}B_8N_7$	4h-BN (D-VN$_L$)@G	-29.6	1.0	7.50	Metallic
$C_{132}B_{15}N_{15}$	9h-BN(D-VB$_L$)@G	-2.9	NM	-	0.36
$C_{132}B_{14}N_{15}$	9h-BN (D-VB$_L$)@G	-545.2	2.0	8.45	Metallic
$C_{132}B_{14}N_{15}$	9h-BN (D-VB$_l$)@G	-1.4	0.4	7.34	Metallic
$C_{131}B_{15}N_{15}$	9h-BN (D-VC$_{I2}$)@G	-29.7	NM	5.61	0.32
$C_{131}B_{15}N_{15}$	9h-BN (D-VC$_{I1}$)@G	-5.1	0.1	6.76	Metallic
$C_{131}B_{15}N_{15}$	9h-BN (D-VC$_i$)@G	-144.8	1.5	7.67	Metallic
$C_{132}B_{15}N_{14}$	9h-BN (D-VN$_L$)@G	-5.8	1.0	7.47	Metallic
$C_{144}B_{24}N_{24}$	16h-BN(D-VB$_L$)@G	2.9	NM	-	0.49
$C_{144}B_{23}N_{24}$	16h-BN (D-VB$_L$)@G	-665.9	2.2	8.96	Metallic
$C_{144}B_{23}N_{24}$	16h-BN (D-VB$_l$)@G	-	1.0	7.40	Metallic
$C_{143}B_{24}N_{24}$	16h-BN (D-VC$_{I2}$)@G	-33.6	-0.3	5.95	Metallic
$C_{143}B_{24}N_{24}$	16h-BN (D-VC$_{I1}$)@G	-12.9	0.4	6.83	Metallic
$C_{144}B_{24}N_{24}$	16h-BN (D-VC$_i$)@G	-14.50	NM	7.34	0.23

Comparison between non defective G@h-BN and **h-BN@G** hybrids

2.13 eV	1.19 eV	0.65 eV	0.17 eV	0.36 eV	0.50 eV

4G(D)@h−BN   9G(D)@h−BN   16G(D)@h−BN   4h−BN(D)@G   9h−BN(D)@G   16h−BN(D)@G

These flat bands arise from the dangling bonds of atoms around the vacancy site.

Fig. 3 Showing the changes in band gap with change in island size, flat band near fermi level for G@h-BN

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Thank you