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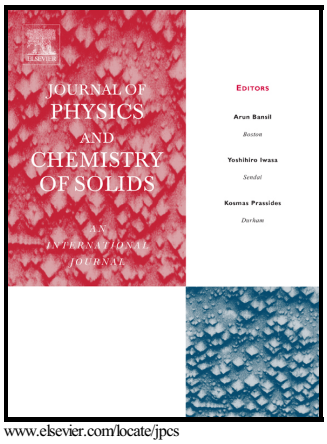

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A DFT study of 5-fluorouracil adsorption on the pure and doped BN nanotubes

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Abstract

The electronic and adsorption properties of the pristine, Al-, Ga-, and Ge-doped BN nanotubes interacted with 5-fluorouracil molecule (5-FU) were theoretically investigated in the gas phase using the B3LYP density functional theory (DFT) calculations. It was found that the adsorption behavior of 5FU molecule on the pristine (8, 0) and (5, 5) BNNTs are electrostatic in nature. In contrast, the 5FU molecule (O-side) implies strong adsorption on the metal-doped BNNTs. Our results indicate that the Ga-doped presents high sensitivity and strong adsorption with the 5-FU molecule than the Al- and Ge-doped BNNTs. Therefore, it can be introduced as a carrier for drug delivery applications.

Keywords: A. Nanostructures, **C.** Ab initio calculations, **D.** Electronic structure, **D.** Surface properties

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1. Introduction

Boron nitride nanotubes (BNNTs) is a nanostructure with similar morphology and different properties from carbon nanotubes (CNTs), being introduced as a capable tool for biomedical adsorption due to its high amount of bonding energy based on the previous reports [1-6]. The CNT's helicity and central layers are different in characteristics, representing a wide variety of electronic properties, whereas BNNTs are semiconductor, regardless of their diameter and chirality [7, 8]. Two factors of chemical inertness and structural stability of BNNTs made these materials nontoxic to health and environment that make their applications more possible for medical uses especially for drug delivery process [9]. BNNTs' own physical properties are suited for wide range of applications as an inorganic analog of CNTs [1, 10]. 5-fluorouracil molecule (5-FU) is a fluorinated pyrimidine analogue chemotherapeutic agent using as solid cancer treatment like esophagus, stomach, intestines, carcinoma [11-13]. 5-FU is applied for regional drug delivery by analytical methods. 5-FU has emerged excellent anticancer activity in human breast cancer cells (MCF-7) using multi-walled carbon nanotube adapted graphite electrode that applies cyclic voltammetry (CV) and potentiometric stripping analysis [14-16]. Recently, Deka and co-worker reported the interaction of (10, 0) and (5, 5) BN nanotubes functionalized with isoniazid (INH) drug molecule, they have shown that the binding energy of INH upon (5, 5) BNNT is slightly considerable than that of (10, 0) BNNT [17]. Pandey et al. demonstrated the adsorption of tryptophane (nonpolar amino acid), asparatic acid and argenine (polar amino acids) upon the surface of BN nanotubes, indicating for a strong binding energy with polar amino acids, asparatic acid and argenine, on the tube surface [1]. Baei and coworker performed the adsorption and electronic structure study of Imidazole molecule functionalized (6, 0) BN nanotube in gas and solvent phases. They found that the adsorption of Imidazole molecule has no significant

effects upon the electronic structure of BN nanotube [18]. Yang et al. [19] introduced the interaction between boron nitride nanotubes (BNNTs) with a variety of biological molecules using DFT calculations. Anota and co-workers introduced the interaction between BN nanotubes with metformin drug using DFT [20]. Recently, the interaction of Uracil molecule with ultra-small (n, 0) BN nanotubes were investigated by Mirzaei et al. [21]. In this work, we report a systematic theoretical investigation into the interactions of an isolated 5FU molecule (O- and F-sides) with the Ge-, Ga-, and Al-doped (8, 0) zigzag single-walled BN nanotubes. It was found that systems are covalently functionalized with 5FU drug molecule through its carbonyl oxygen active site (O-side) and is stabilized in comparison with its carbon-fluorine active site (F-side). Besides, we studied the effects of 5FU drug adsorption on the structural and electronic properties of Ge-, Ga-, and Al-doped BNNTs.

2. Computational methods

First principle calculations of all the geometry optimizations, geometric structures, density of states (DOS), natural bond orbital (NBO), and frontier molecular orbitals (FMO) analyses for 5FU drug interacted with pristine and Ge-, Ga-, and Al-doped (8, 0) *zigzag* BNNT are performed using GAMESS software [22] at the level of density functional theory (DFT) with B3LYP/6-31G* basis set [23-25]. The length and diameter of relaxed pristine (8, 0) BNNT were calculated to be about 9.34 and 6.32 Å, respectively. The diameter and length of the pristine (5, 5) BNNT are about 6.84 and 6.90 Å, respectively. The NBO charges on B and N atoms in the nano-cage are 1.17 and -1.17|e|, indicating strong ionicity nature of B-N bonds. The charge of the Ge, Al, and Ga atoms in the (8, 0) BNNT are about 0.526, 0.539, and 0.494e, respectively. Spin multiplicity of the gas molecules were set to one with relevance to its molecular orbital of ground

state (its ground electronic state is $^1\Sigma^+$). The adsorption energy (E_{ad}) between the drug molecule and metal-doped BNNTs was computed using the following expression:

$$E_{ad} = E_{5FU/BNNT} - [E_{BNNT} + E_{5FU}] \quad (1)$$

$$E_{ad} = E_{5FU/Al\text{-}BNNT} - [E_{Al\text{-}BNNT} + E_{5FU}] \quad (2)$$

$$E_{ad} = E_{5FU/Ga\text{-}BNNT} - [E_{Ga\text{-}BNNT} + E_{5FU}] \quad (3)$$

$$E_{ad} = E_{5FU/Ge\text{-}BNNT} - [E_{Ge\text{-}BNNT} + E_{5FU}] \quad (4)$$

where $E_{5FU/BNNT}$, $E_{5FU/Al\text{-}BNNT}$, $E_{5FU/Ga\text{-}BNNT}$, and $E_{5FU/Ge\text{-}BNNT}$ are the total energies of the E_{BNNT}, $E_{Al\text{-}BNNT}$, $E_{Ga\text{-}BNNT}$, and $E_{Ge\text{-}BNNT}$ interacted with 5FU drug molecule, E_{5FU}, E_{BNNT}, $E_{Al\text{-}BNNT}$, $E_{Ga\text{-}BNNT}$, and $E_{Ge\text{-}BNNT}$ are the total energy of the pristine 5FU, BNNT, Al-BNNT, Ga-BNNT, and Ge-BNNT, respectively. For 5FU drug molecule adsorbed upon BN nanotubes, the quantum molecular descriptors [26] such as ionization potential (IP), vertical electron affinity (EA), global hardness (η), global softness (S), electronic chemical potential (μ), electronegativity (χ), and electrophilicity index (ω) were calculated.

3. Results and discussion

First of all, we discussed the structural and electronic properties of the *zigzag* (8, 0) single-walled BN nanotubes coupled to 5-fluorouracil (5FU) molecule (see Fig. 1). The optimized structure of the pristine BNNT has the B-N bond length 1.45 Å while the B-N-B and N-B-N angles are 118.96 and 119.93˚, respectively. The presented results in this work are in agreement with previous reports provided by Li and Ahmadi [26, 27]. The dipole moment value (D_M) for an isolated (8, 0) BNNT is 11.44 Debye, suggesting a hydrophilic property for this tube. Whereas the dipole moment value for 5FU molecule is 3.90 Debye. Therefore, the selection of a polar 5FU molecule exhibits how the polarity of a molecule can be useful in the reactivity of tube. The

DOS plot reveals that the energy gap (E_g) of (8, 0) BNNT is about 5.69 eV, whereas BN nanotube has an energy gap of 5.5 eV, complying with previous results [28, 29]. As shown in Fig. 1, the negative value of 5FU adsorption upon BNNT (-0.13 eV) typically indicates for a physisorption process with the interaction distance of 3.17 Å, having an electron transfer about 0.039 electron calculated by the NBO population charge analysis (Fig. 1). This result implies that this interaction is weak and should be considered as a physisorption. Likewise, the 5FU is slightly deformed so the length of C-O bond of 5FU is slightly elongated from 1.216 Å in the pure model to 1.218 Å after the adsorption process. The value of dipole moment for 5FU-BNNT complex is 12.73 Debye implying relatively weak binding with the tubular wall of (8, 0) BNNT.

As shown in Fig. 2, we calculated the interaction of 5FU molecule with (5, 5) BNNT at the B3LYP/6-31G* level of theory. For 5FU/(5, 5) BNNT complex, the binding energy and distance are -0.11 eV and 2.97 Å, respectively. There is observed that in the 5FU/ (5, 5) BNNT system, the decreasing of binding energy on the surface of nanotube indicating that 5FU molecule cannot significantly be adsorbed upon this site and undergoes weakly physical adsorption owing to van der Waals forces. Our result shows that the 5FU molecule is bound to the *armchair* BNNT weaker than *zigzag* BNNT, and the energy difference between 5FU molecule and (5, 5) BNNT is slightly smaller than (8, 0) BNNT. The dipole moment value for (5, 5) BNNT is increased from 0.006 Debye in the pure (5, 5) BNNT to 5.08 Debye in the 5FU/(5, 5) BNNT complex. Besides, this result reveals that the 5FU molecule added to (5, 5) BNNT leads to increase of the polarization.

<Fig. 1>

<Fig. 2>

To improve the adsorption conditions, we have used the Ge, Ga, and Al-doped (8, 0) BNNTs, improving the sensitivity of tube to 5FU molecule. In previous work, we were reported that the Al- and Ga-doped can improve the sensitivity of BNNT to gas molecule [30]. In addition, we were investigated the substitution effects of one B atom by an Al, Ga, and Ge atoms in the skeleton of BN nanotube on the adsorption of 5FU molecule. The bond lengths are 1.823, 1.835, and 1.876 Å, respectively, after the optimization of 5FU/ Ge-, Ga-, and Al-doped BNNT systems, the Al-N, Ga-N, and Ge-N bond length are longer than those of the pristine models (1.822, 1.804, and 1.758 Å). The calculated adsorption energies of the 5FU (O-side) upon the Ge-, Ga-, and Al-doped BNNTs are -0.53, -1.50, and -1.86 eV and the distances between the molecule and dopant atoms are 2.59, 2.01, and 1.88 Å, respectively. The net electron transfer from the 5FU to the Ge-, Ga-, and Al-doped BNNTs are about 0.067, 0.299, and 0.674 electrons, respectively, revealing considerable charge transfer founded for 5FU molecule in the interaction with Al-doped BNNTs in compared with the Ge- and Ga-doped BN nanotubes. Calculations of the bond length and NBO charge analysis indicates that the Al- and Ga-doped BN nanotubes interacting with 5FU molecule are stronger than the Ge-doped BNNT (Fig. 3). Accordingly, the chemisorption of 5FU on the Al- , Ga-, and Ge-doped BN nanotubes leads to the rehybridization of dopant atoms transferring from sp^2 to sp^3. In comparison with pure BNNTs, the adsorption processes of the 5FU represents stronger binding towards Ge-, Ga-, and Al-doped BNNTs, this can be attributed to the catalytic reactivity and the incomparable properties of the stabilized Ge-, Ga-, and Al-doped BN nanotubes. The binding energy values for the F atom of 5FU molecule interacted with Ge-, Ga-, and Al-doped BN nanotubes are -0.46, -0.72, and -1.07 eV,

respectively, showing that the adsorption value for O atom of 5FU is much stronger than the F atom of molecule. The intermolecular interactions between 5FU and Al-, Ga-, and Ge-doped BN nanotubes are similar to the intermolecular hydrogen bonding, especially the F atom of 5FU. Zhao and et al. [31] have shown hydrogen bonding in the electronic excited state on internal conversion (IC), electronic spectral shifts (ESS), photoinduced electron transfer (PET), fluorescence quenching (FQ), intramolecular charge transfer (ICT), and metal-to-ligand charge transfer (MLCT). Their results showed the nature of hydrogen bonding by delineating the interaction between hydrogen bonds and photons, thereby providing a basis for excited-state hydrogen bonding studies in photophysics, photochemistry, and photobiology. Also, Zhang, and et al. [32] have theoretically shown modification of *n*-type organic semiconductor performance of perylene diimides by substitution in different positions by hydrogen bonding. Their results showed the hydrogen bonds formed at the imide positions are responsible for the large mobility. Our results indicating that the 5FU can be adsorbed on the metal-doped BN nanotube via the π–π stacking interactions with moderate adsorption energy [33].

<Fig. 3>

In order to appreciate the most stable adsorption configurations of 5FU upon the applied nanotubes, we representing the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) plots for the most energetic configurations summarized in Table 1. The HOMO and LUMO values in the pristine BN nanotube are -6.54 and -0.85 eV, respectively. After the adsorption process, the HOMO value slightly increased to -6.08 eV, while the LUMO value in this system significantly reduced to -2.9 eV. After the adsorption of molecule, the

energy gap value is reduced from 5.69 eV in the pure model to 5.07 eV in 5FU-(8, 0) BNNT complex. As shown in Fig. 4, the HOMO of 5FU molecule interacted with Al- and Ga-doped BNNTs are located upon the N atoms of tube, while the LUMO of these complexes are located upon the aromatic ring of drug molecule. For 5FU/Ge-doped BNNT system, the HOMO is located on the N and Ge atoms vicinity to drug molecule and also is located on the C-C orbitals of molecule while its LUMO is situated on 5FU molecule. Localization of electron density in HOMO exhibits that the particular site is more nucleophilic whereas the LUMO is electrophilic in nature [34].

<Fig. 4>

<Table 1>

The DOS plots revealed that the energies of HOMO in the Ge-, Ga-, and Al-doped BNNTs are increased from -5.84, -6.53, and -6.53 eV to -5.33, -5.99, and -6.08 eV after the adsorption processes, whereas the energies of LUMO are reduced from -0.79, -1.4, and -1.84 eV to -1.74, -3.13, and -2.90 eV, respectively (see Table 1). These results imply that the energy levels of LUMO are reduced while the energy levels of HOMO are slightly increased due to the adsorption processes along with the decrement in energy of Fermi level for all systems, demonstrating that the Fermi level changes over the valence level of the material. As shown in Fig. 3, upon the interaction of 5-fluorouracil molecule with the Ge-, Ga-, and Al-doped BNNTs, the electronic properties of tube undergoes significant changes. The DOS plots revealed 5.05, 5.13, and 4.69 eV energy gaps for the pure Ge-, Ga-, and Al-doped BNNTs, respectively,

showing a low conductivity. After the adsorption of 5-fluorouracil molecule upon the Ge-, Ga-, and Al-doped BNNTs, E_g is reduced with the energies of about 3.59, 2.86, and 3.18 eV, respectively. Therefore, the changes of 1.46, 2.27, and 1.51 eV in E_g occurred for Ge-, Ga-, and Al-doped BNNTs, respectively, implying that the systems are more sensitive toward the 5-fluorouracil adsorption (see Fig. 5). This result shows a significant increase in electrical conductivity of the system, computed as follows [35]:

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right)$$

where σ is the electric conductivity of the system and k is the Boltzmann's constant. According to the above equation, smaller energy gap (E_g) values lead to the larger electric conductivity at a given temperature. These results of the DOS plots reveal that the adsorption of 5FU with the preferable O site on the Ga-, Ge-, and Al-doped BNNTs have undergone distinct changes in compared with that of the pure BNNT. We are finding that the doping of Ga atom in BN nanotube is caused more sensitivity of the adsorbate to the presence of 5FU drug with the changes in the energy gap (ΔE_g= -39.02 eV) in comparison with the Al (-38.01 eV) and Ge (-28.01 eV) atoms. Chi and Zhao introduced that Al-doped graphene can be expected to be a suitable sensor for H_2CO detection [36]. The calculated Fermi levels of the semiconducting nanotube after the adsorption processes for pristine; Al-, Ga-, and Ge-doped BNNTs are -3.69, -3.96, -4.18, and -3.31 eV, respectively. The values of Fermi level in the above mentioned systems are -3.92, -4.49, -4.56, and -3.53 eV, respectively. This finding reveals that the 5FU molecule has strong reactions with doped-BNNTs, resulting in a specific hybridization between the respective orbitals of adsorbate and adsorbent. The DOS plots represented that the 5FU/Ga-,

Ge-, and Al-doped BN nanotubes near the Fermi level are affected upon the adsorption processes.

<Fig. 5>

We have calculated the total electron density plots of the electronic density for 5FU drug molecule interacted with the Ga-, Ge-, and Al-doped BNNTs implying that it is chemically adsorbed upon the doping atoms. As shown in Fig. 6, the 5FU drug molecule is coupled to the Ga-, Ge-, and Al-doped BNNTs that have effected on the electronic charge distribution of dopant atoms of tube; so, considerable charge transfer takes place between the drug molecule and nanotube. As shown in Table 2, the global hardness is generally diminished for all three adsorption systems as 5FU adsorbed on Al, Ga, and Ge-doped BNNTs where the biggest change is revealed at 5FU/Al-doped BNNT system (from 2.56 to 1.59 eV) confirming by a reasonable decrease in the value of energy gap presuming good reactivity along with low stability for Al-doped BNNT compared with other complexes. These conclusions along with the increased results of electron affinity for Al-BNNT (from 1.40 to 2.90 eV) suggested that there can be easily picks up electrons from 5FU molecule. The electrophilicity index of 5FU/Ga-doped BNNT is 7.27 eV, exhibiting greater change in comparison with the pristine tube (3.73 eV). The high value of electrophilicity index indicates higher electrophilic character of the molecule [37].

<Fig. 6>

<Table 2>

However, in order to investigate the thermodynamic feasibility of the 5FU adsorption upon the pristine and doped BN nanotubes, the changes of enthalpies (ΔH_{ad}), free Energies (ΔG_{ad}), and entropies (ΔS_{ad}) of the most stable configurations are computed from the frequency calculations according to the following equations:

$$\Delta H_{ad} = H_{5FU/BNNT} - H_{5FU} - H_{BNNT} \quad \text{Eq. (9)}$$

$$\Delta S_{ad} = S_{5FU/BNNT} - S_{5FU} - S_{BNNT} \quad \text{Eq. (10)}$$

$$\Delta G_{ad} = G_{5FU/BNNT} - G_{5FU} - G_{BNNT} \quad \text{Eq. (11)}$$

Calculated values of ΔS_{ad}, ΔH_{ad}, and ΔG_{ad} for the configurations are reported in Table 3. The calculations on Al- and Ga-doped BNNTs implied that the changes of ΔS_{ad}, ΔH_{ad}, and ΔG_{ad} have negative values, whereas these values for the Ga-doped BNNT are -40.27, -32.95, and -20.95 kcal/mol and about -41.58,-42.07, and -28.87 kcal/mol for the Ga-doped BNNT, respectively. The results indicating that the adsorption of 5FU toward Al- and Ga-doped BNNTs are thermodynamically notable in comparison with the pristine BNNT and the 5FU show a strong adsorption upon Al-doped BNNT. However, the less value of ΔG in comparison with that of ΔH is owing to the entropic effect [38].

<Table 3>

4. Conclusions

In summary, we investigated the structural and electronic properties of 5FU drug molecule through interaction with the pristine; Al-, Ga-, and Ge-doped BN nanotubes based on the first-principle density functional theory calculations. It was found that the 5FU can be physically adsorbed upon the wall of (8, 0) and (5, 5) BN nanotubes with the energy values of -0.13 and -0.11 eV, respectively. The adsorption energy values of 5FU molecule in the interaction with the Ge-, Ga-, and Al-doped BN nanotubes are calculated to be -0.53, -1.50, and -1.86 eV, and the changes of energy gap in these systems are -28.01, -39.02, and -38.01 eV, respectively. The results of adsorption properties and NBO charge analysis exhibited that substitution of Al and Ga atoms with the B atoms of BN nanotube improves the interaction energies between the 5FU molecule and the BN nanotubes. The obtained results shown that the Ga-doped BNNT can be reliable to perform as a carrier for 5FU molecule in drug delivery.

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Figure captions:

Fig. 1 Optimized structures of (8, 0) BNNT and 5FU/BNNT complex and their density of states.

Fig. 2 Optimized structures of (5, 5) BNNT and 5FU/(5, 5) BNNT complex and their density of states.

Fig. 3 Optimized configurations for the 5FU molecule upon the Al-, Ga-, and Ge-doped BNNTs.

Fig. 4 Charge distributions of HOMO and LUMO orbitals for the 5FU/Al-, Ga-, and Ge-doped BNNTs complexes.

Fig. 5 DOS plots for the applied systems.

Fig. 6 Isosurfaces of the total electron density for the 5FU/Al-, Ga-, and Ge-doped BNNTs complexes.

Table captions:

Table 1 The calculated adsorption energies (E_{ad}), HOMO and LUMO energies, Energy Gap (E_g), and Fermi Level (E_F) of systems. All parameters are in units of eV.

Table 2 The calculated quantum molecular descriptors of complexes. All parameters are in units of eV.

Table 3 Calculated thermodynamic data [ΔH, ΔG (kcal/mol), and ΔS (Kcal/mol)] and minimum and maximum vibrational frequencies (cm^{-1}) for the studied systems.

Table 1

Configuration	E_{ad} /eV	E_{HOMO}/eV	E_{LUMO}/eV	E_g /eV	ΔE_g (%)	E_F/eV	D_M/Debye
(8, 0) BNNT	-	-6.54	-0.85	5.69	-	-3.69	11.45
BNNT/5FU	-0.13	-6.46	-1.39	5.07	-10.89	-3.92	12.73
(5, 5) BNNT	-	-6.40	-0.09	6.31	-	-3.24	0.00
BNNT/5FU	-0.11	-6.31	-0.05	6.26	0.8	-3.18	5.08
Al-BNNT	-	-6.53	-1.40	5.13	-	-3.96	11.80
Al-BNNT/5FU	-1.86	-6.08	-2.90	3.18	-38.01	-4.49	19.13
Ga-BNNT	-	-6.53	-1.84	4.69	-	-4.18	11.69
Ga-BNNT/5FU	-1.50	-5.99	-3.13	2.86	-39.02	-4.56	16.37
Ge-BNNT	-	-5.84	-0.79	5.05	-	-3.31	11.51
Ge-BNNT/5FU	-0.53	-5.33	-1.74	3.59	-28.91	-3.53	13.42

Table 2

Configuration	I/eV	A/eV	η/eV	μ/eV	S/eV	χ/eV	ω/eV
(8, 0) BNNT	6.54	0.85	2.84	-3.69	0.17	3.69	2.39
BNNT/5FU	6.46	1.39	2.53	-3.92	0.19	3.92	3.03
Al-BNNT	6.53	1.40	2.56	-3.96	0.19	3.96	3.06
Al-BNNT/5FU	6.08	2.90	1.59	-4.49	0.31	4.49	6.34
Ga-BNNT	6.53	1.84	2.34	-4.18	0.21	4.18	3.73
Ga-BNNT/5FU	5.99	3.13	1.43	-4.56	0.35	4.56	7.27
Ge-BNNT	5.84	0.79	2.52	-3.31	0.19	3.31	2.18
Ge-BNNT/5FU	5.33	1.74	1.79	-3.53	0.28	3.53	3.48

Table 3

Structure	ΔH_{ad}	ΔG_{ad}	ΔS_{ad}	υ_{min}	υ_{max}
5FU	-	-	-	116.99	3644.30
(8,0) BNNT	-	-	-	57.94	3560.47
5FU/ (8, 0) BNNT	-2.58	8.36	-36.69	-2.80	3643.39
Al-doped BNNT	-	-	-	56.66	3560.53
Ga-doped BNNT	-	-	-	55.16	3560.90
5FU/ Al-doped BNNT	-42.07	-28.87	-41.58	16.10	3620.96
5FU/ Ga-doped BNNT	-32.95	-20.95	-40.27	10.02	3622.33

Highlights

► 5-fluorouracil adsorption over the pristine and doped BN nanotubes was studied.

► Natural bond orbital and dipole moment for 5-aminolevulinic with BN nanotube is also calculated.

► Adsorption of 5-fluorouracil on Al-doped BN nanotube is more notable than Ga- and Ge-doped BN nanotube.

► The energy gap of Ga-doped BN nanotube has changed over functionalization in comparison with Al and Ge-doped.

Fig. 1.

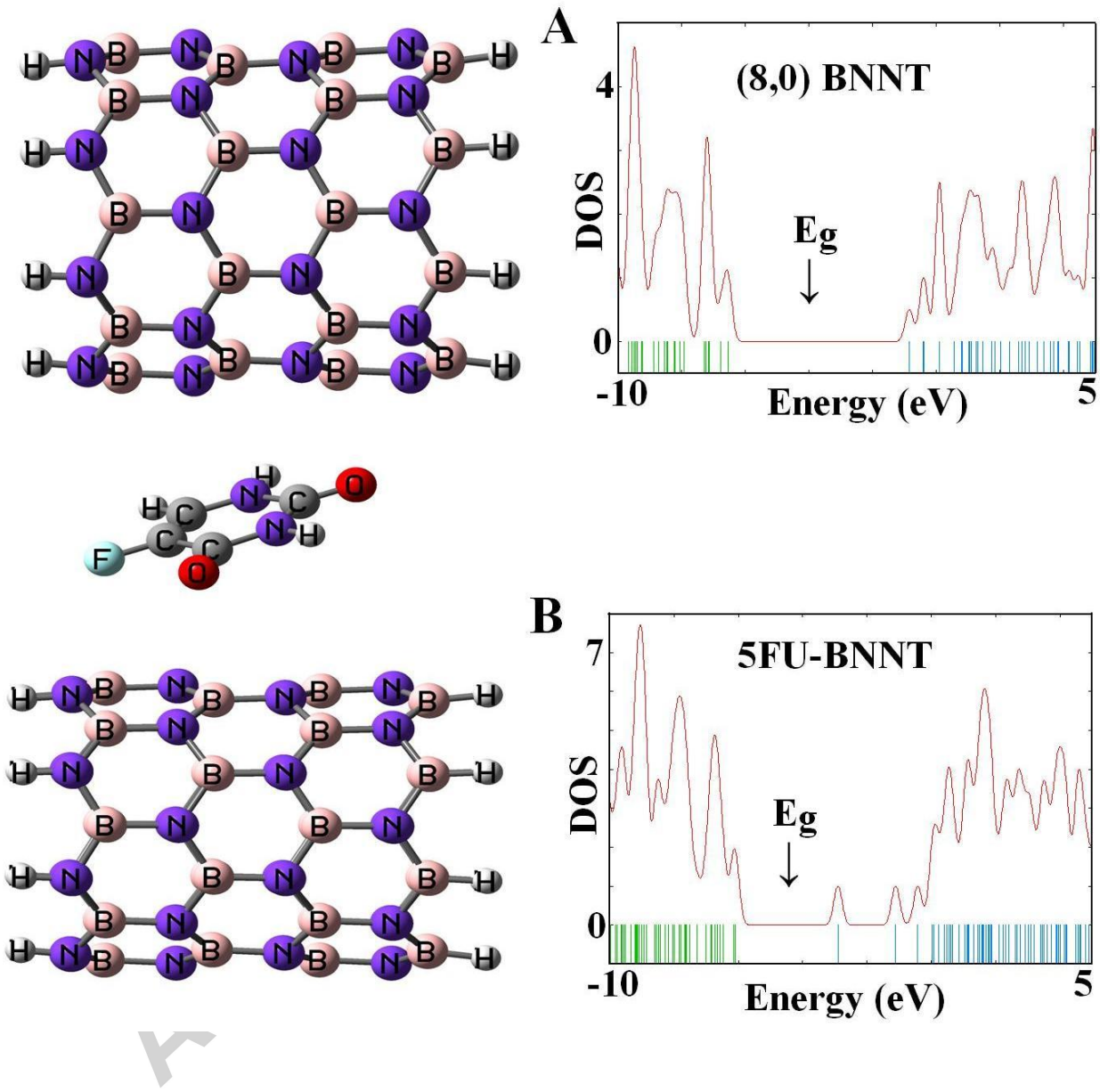

A
(8,0) BNNT
DOS
Eg
4
0
-10
Energy (eV)
5
B
5FU-BNNT
DOS
Eg
7
0
-10
Energy (eV)
5

Fig. 2.

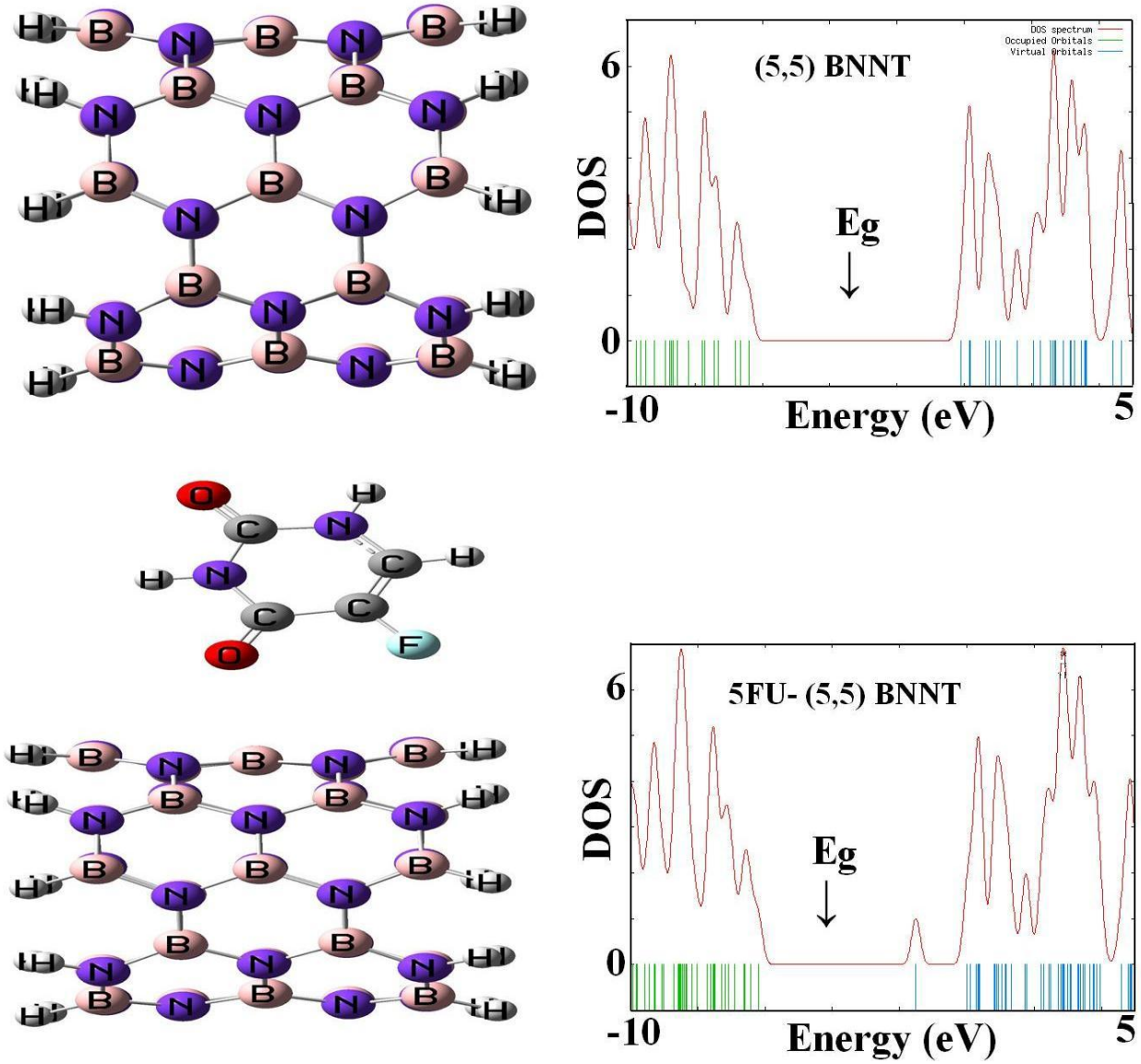

(5,5) BNNT
DOS spectrum
Occupied Orbitals
Virtual Orbitals
DOS
Eg
6
0
-10
Energy (eV)
5
5FU- (5,5) BNNT
DOS
Eg
6
0
-10
Energy (eV)
5

Fig. 3.

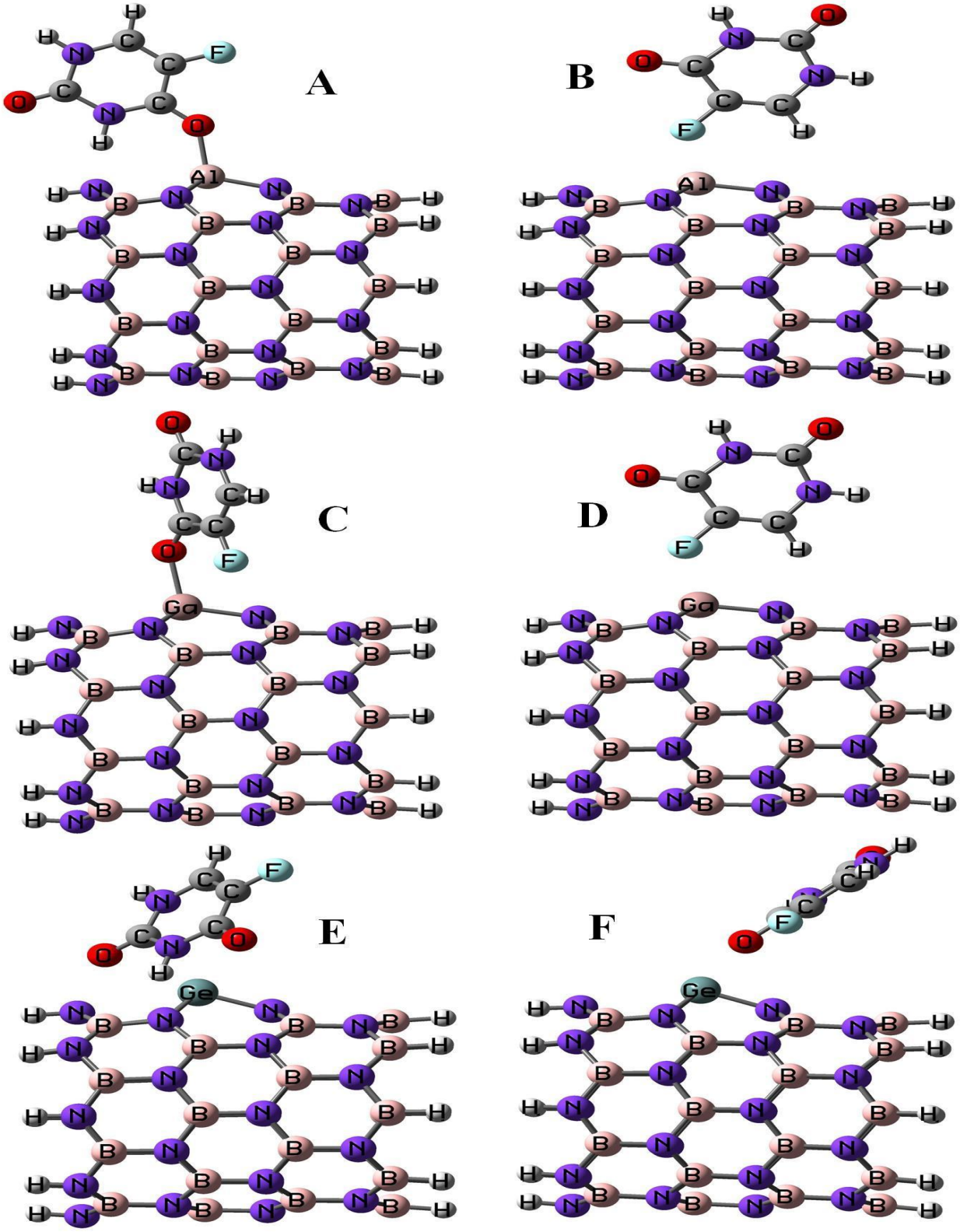


Fig. 4.

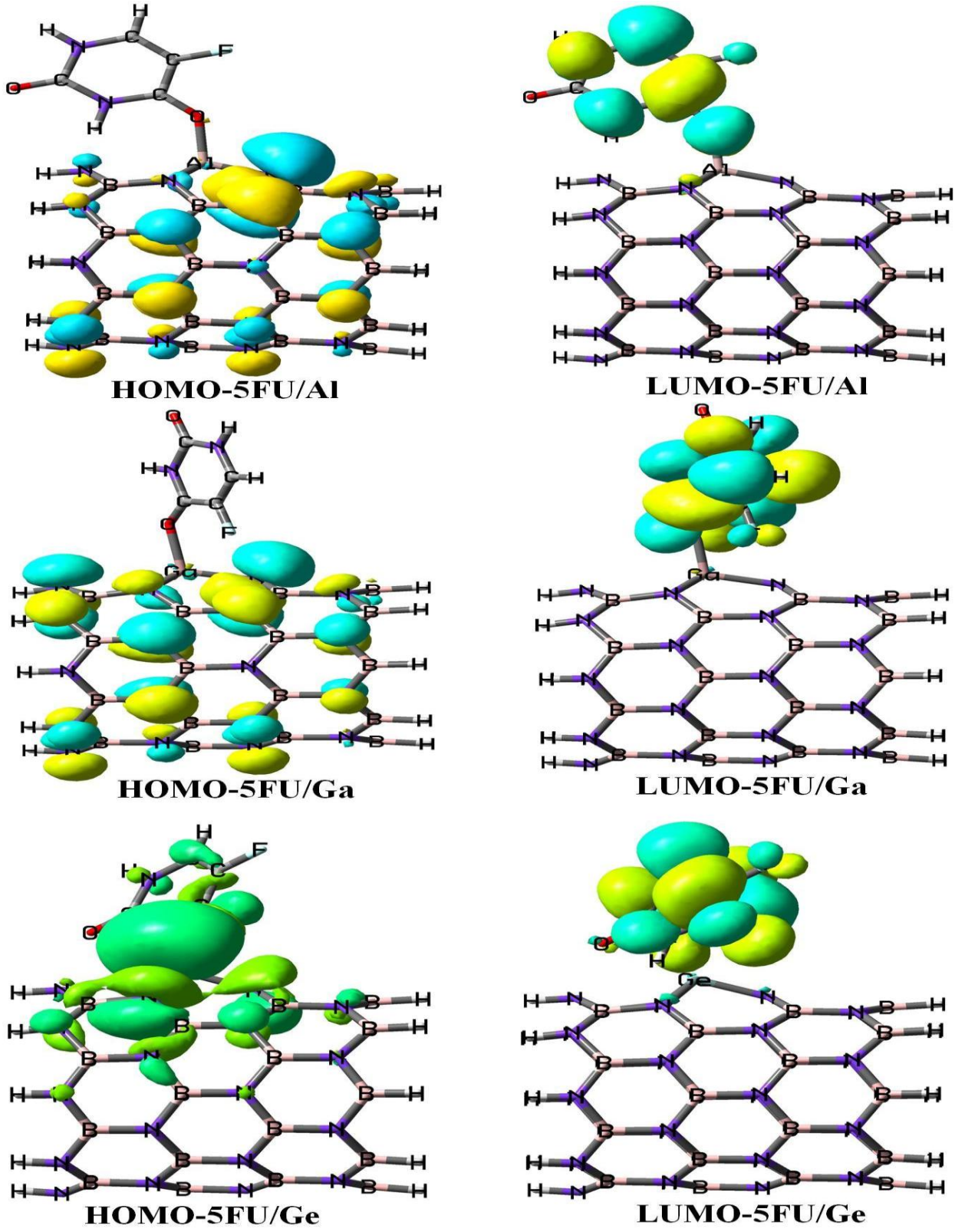

HOMO-5FU/Al
LUMO-5FU/Al
HOMO-5FU/Ga
LUMO-5FU/Ga
HOMO-5FU/Ge
LUMO-5FU/Ge

Fig. 5.

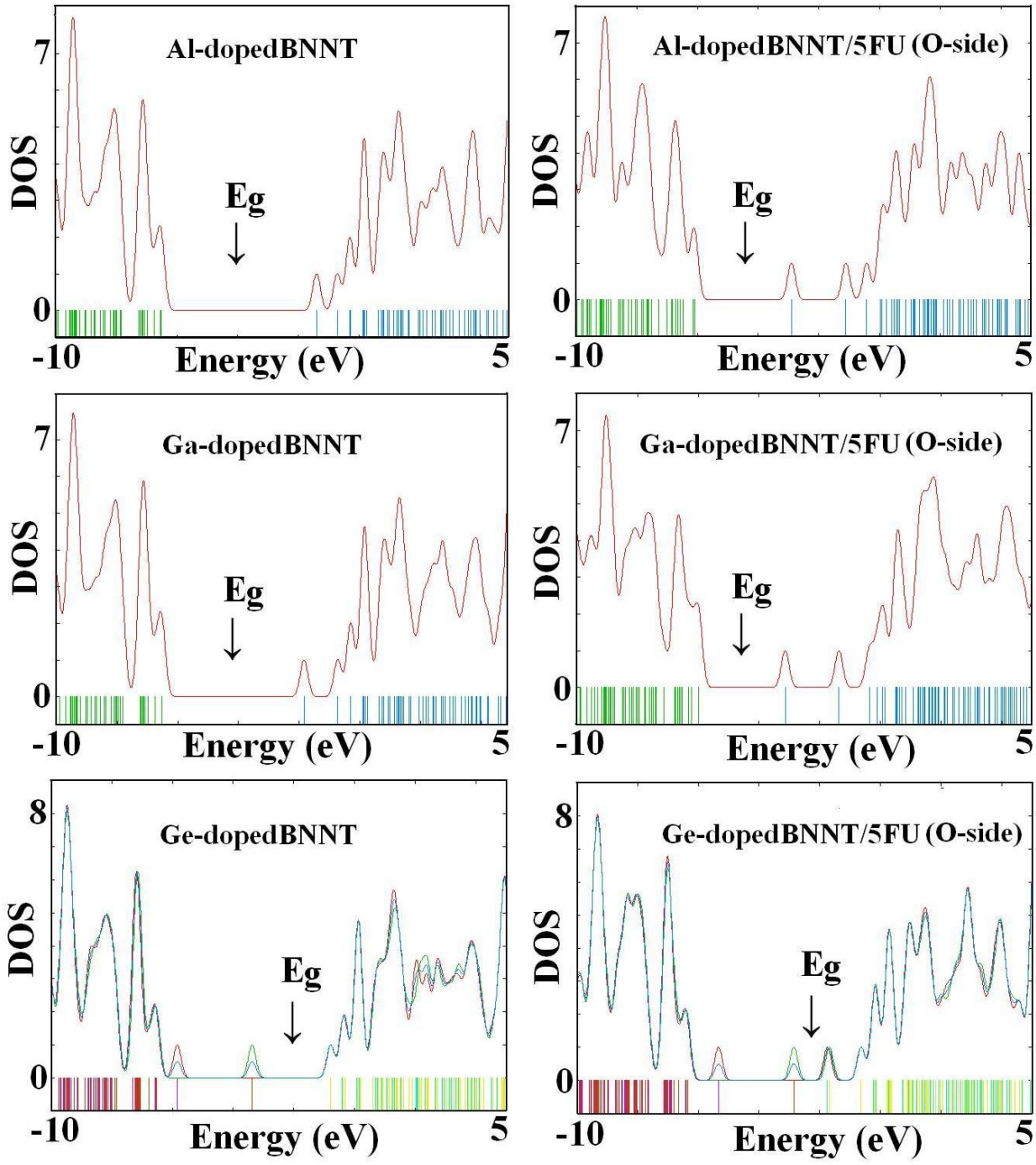
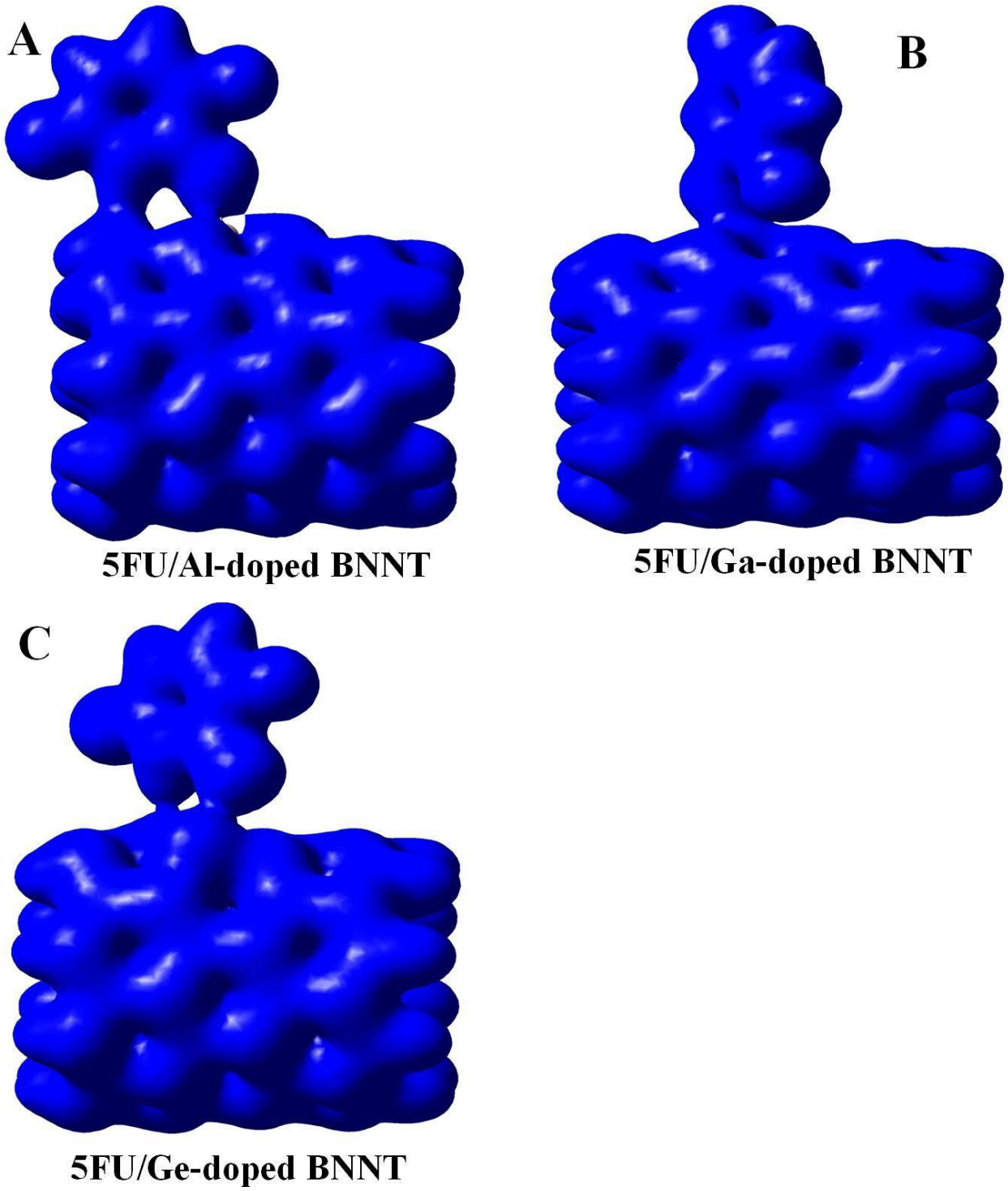

Al-dopedBNNT
Al-dopedBNNT/5FU (O-side)
Ga-dopedBNNT
Ga-dopedBNNT/5FU (O-side)
Ge-dopedBNNT
Ge-dopedBNNT/5FU (O-side)
DOS
Eg
Energy (eV)
-10
5
0
7
8

Fig. 6.



Graphical Abstract