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Nanotube Connections in Bilayer Graphene with Elongated Holes

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Structures, stability and electronic properties of AA-stacking bigraphene with holes are studied using molecular mechanic and DFT method calculations. It has been shown the zig-zag edges of considered elongated holes lead to armchair sp^2-nanotube-type connection between these two edges forming all sp^2-structure. We consider similar periodic structures with (n,n) nanotubes formed among elongated holes and connected with bigraphene fragments, which edges are also closed edges. The stability and electronic properties of these structures are investigated. Band structures of considered materials have energy gaps 0.20-0.27 eV in the direction of tube axes through jumpers on the connections, and Dirac-like point views in the opposite direction.

Keywords: Bigraphene, Molecular Mechanics, DFT, Carbon Nanostructure.

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1. INTRODUCTION

Graphene is one sheet of hexagonal lattice of carbon atoms, which can be presented as a basic material for many allotropic form of carbon. However, in addition to the unique properties, it has one drawback - the lack of band gap, making it difficult to use in nanoelectronics.

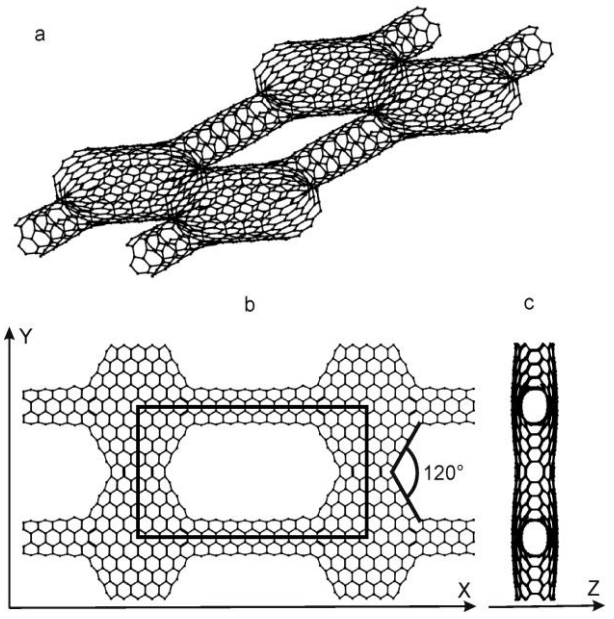

Fig. 1 – Example of periodic structures with CNT(4,4) connected with small bigraphene fragments: a) – common view, b) view in Z-direction with rectangular unit cell, c) view in X-direction. The nanotube consists of 9 unit cells.

The alternative is bilayer graphene, in which the band gap is observed when electric and magnetic fields are exposed [1-2], or graphene mesh [3]. In this work another opportunity is offered to get a bandgap in AA-stacking bigraphene by creation holes with zig-zag edges. The edges have free bonding and layers of bigraphene should connect together forming sp^2-bonded armchair nanotube-type connecting sections [4-5]. The possible way to prepare such structure is making holes by STM lithography previously used to create different edges in graphene [6].

One of the considered structures with CNT(4,4) connected with small bigraphene fragments is shown on the Fig.1. We have used the fact that in the experiments [5] sp^2-bonded armchair nanotube-type sections connected at the angle of 120 degrees.

2. METHODS OF CALCULATIONS

Geometry optimization of the structures was carried out using molecular mechanic method in a software package *GULP* [7]. This method uses Lennard-Jones and Brenner potentials for describing van der Waals and covalent interactions respectively. Electronic band structures were performed by *DFT* (*density functional theory*) method in the *Siesta* package [8]. Both program packages allow performing calculations with periodic boundary conditions.

3. RESULTS AND DISCUSSION

Structures with different geometric parameters were investigated. We changed length (numbers of unit cells) and diameter of nanotube between bigraphene areas. Geometric parameters and atom numbers in calculated cells for structure with (4,4) nanotube are shown in the Table 1. Translation parameter b is the distance between axes of adjacent nanotubes. Axis X coincides with the axis of nanotube.

Structures with (4,4), (6,6), (8,8) and (10,10) nanotubes which consisted of 9, 11 and 13 unit cells were modeled. (4,4) nanotube is the minimal nanotube which can be obtained by connecting graphene layers with zig-zag edges (Fig.1). Bigraphene area has length 16.6 Å for all investigated structures.

All structures were optimized by the molecular mechanics and total energies on the carbon atom shown in

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the Table 2. Energy of structure decreases with the length decreasing and with the diameter increasing. The minimal value of total energy corresponds to structure with 13 unit cells of (10,10) nanotube. Discuss in more details the structure with 9 unit cells of (4,4) nanotube. The distance between axes of adjacent nanotubes is 21.12 Å. The length of calculated cell is 39.02 Å. Calculated cell consists of 412 carbon atoms. Initial state was bigraphene with holes and edges of graphene layers were connected. The areas of connecting had octagonal defects. The distance between layers was 3.6 Å as in bigraphene. After optimizing the structure has changed: the distance between layers increased and nanotube deformed. Graphene layers were distanced to 7.2 Å. This is due to the fact that it was taken too small area of bilayer graphene. This distance is the characteristic of all above structures. Electronic band structures were obtained for the smallest structures (Fig.2). Calculating the electronic properties of bigger structures is impossible because the number of atoms in the calculated cell is very big. Direction X-Γ corresponds to axes of nanotubes. Dependence in values of energy gap wasn't found, however, nearest to Fermi energy levels were straight lines as in the band structure of quantum dots. Behaviour of electrons is caused by the fact that the bigraphene areas are the potential barrier and electrons are trapped in carbon nanotube. The difference between the lowest unoccupied molecular orbital and the highest occupied molecular orbital E_{LUMO}-E_{HOMO} is equal 0.20-0.27 eV. These structures are metal in direction perpendicular axes of nanotubes and have Dirac-like point electronic structure.

The most real structures for fabrication, of course, should have larger size of holes and therefore length of nanotubes and areas of bigraphene. Larger area of bigraphene will keep the distance between layers as in intact bigraphene. As an example, the structures with significantly large areas of bigraphene and longer nanotubes were considered (Fig.3). Bigraphene fragment was 71 Å, nanotube length was being changed from 22.40 Å (9 unit cells of nanotube) to 39.36 Å (16 unit cells). Two types of tubes were considered: (8,8) and (10,10). The distance between layers remained as in intact bilayer graphene 3.40 Å. Total energies and translation parameters are shown in the Table 3. The most stable structures are structures with shorter nanotubes. It is connected with the difference between energies of bigraphene and nanotube. Nanotube has larger energy than graphene. The ratio of the number of nanotube atoms to the number of bigraphene atoms determines the total energy of the system. Therefore, structure with shorter nanotube with biggest diameter is the most stable structure.

Table 1 – Geometrical parameters of structures with carbon nanotube (4,4)

Translation parameter *a*, Å	39.02	43.98	48.92
Translation parameter *b*, Å	21.12	21.12	21.12
unit cell Number of (4,4)CNT	9	11	13
L_{CNT}, Å	22.40	27.34	32.30
Numbers of carbon atom in the calculated cells, N	412	444	476

Table 2 – Energies of investigated structures per atom

	Total energies of structures, eV/atoms			
Indexes of NT, (k,l) → Length of NT, Å ↓	(4,4)	(6,6)	(8,8)	(10,10)
22.40	-7.26	7-.31	-7.33	-7.34
27.34	-7.25	-7.31	-7.33	-7.34
32.30	-7.25	-7.30	-7.33	-7.34

Table 3 – Number of atoms in structure, total energies per atom and parameters of translation

Type of structure	Number of atoms	Length of a CNT fragment, Å	E_{tot}, eV/atom	Superlattice parameters	
				X, Å	Y, Å
(10,10)	3652	39,52	-7,37	112,79	46,86
(8,8)	2180	39,62	-7,36	112,78	30,01
CNT(8,8)			-7,33		
CNT(10,10)			-7,34		
Bigraphene			-7,40		

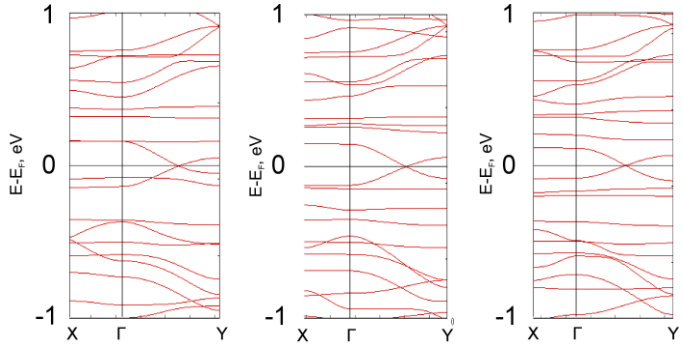

Fig. 2 – Electronic band structures for structures with 9 (left), 11 (middle) and 13 unit cells of (4,4) nanotube

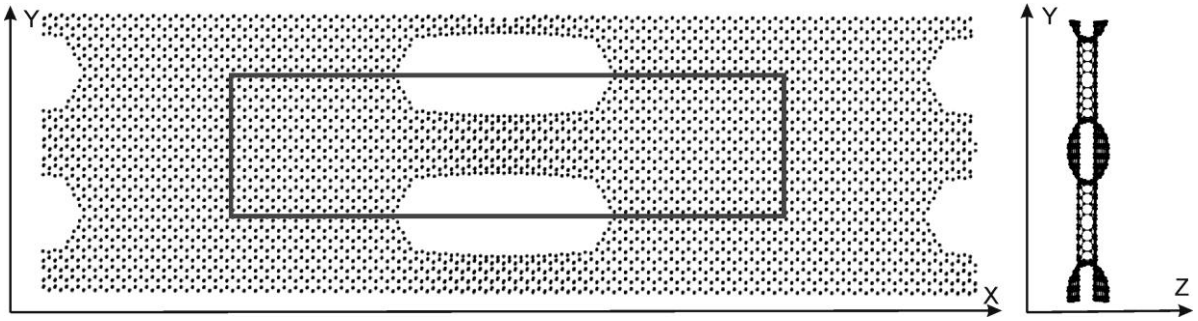

Fig. 3 – Structure with 16 unit cells of CNT(8,8). The rectangle is calculated supercell

4. CONCLUSION

New sp^2 carbon structures were investigated by molecular mechanics method and *DFT* calculations. These structures are bigraphene with holes and they can be imagined as periodically arranged nanotube fragments which are connected by bigraphene areas. Structures with biggest bigraphene areas have smallest energies. Structures with small bigraphene areas have energy gap in the direction of CNT and Dirak-like point electronic structure in perpendicular direction. All structures are stable.

Band structures of considered materials have energy gaps 0.20-0.27 eV in the direction of tube axis in spite of metallic types of CNT, and Dirac-like point views in the opposite direction. This behavior can be explained by finite CNT lengths and electron scatterings on the jumpers containing topological defects similar to CNT connections [9].

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