Dedicated to Professor Mircea Diudea
on the Occasion of His 65th Anniversary

BAND GAP MODULATION OF GRAPHENE AND GRAPHYNE VIA TETRACYANOETHYLENE ADSORPTION

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ABSTRACT. Adsorption of tetracyanoethylene molecule on graphene and graphyne was investigated in view of finding an effective way to control their electronic properties. The electronic properties of graphene, α-, β- and γ- graphyne were studied by using the density functional theory. The binding energy, equilibrium adsorption distance, amount of charge transfer, electronic band structure, and density of states were calculated. The small adsorption energy and large adsorption distance identified physisorption of tetracyanoethylene molecule on graphene and graphyne sheets. It was found that charge is transferred from sheets to tetracyanoethylene molecule. In the presence of this acceptor molecule, the graphene and α-, β- and γ-graphynes, with semimetallic properties, show semiconducting behaviour. The tetracyanoethylene molecule has no considerable effect on the semiconducting property of γ-graphyne. Our results reveal that adsorption of organic molecules, such as tetracyanoethylene, is a proper method to open a band gap in graphene and graphyne.

Keywords: Organic molecule, Graphene, Graphyne, Band gap, Density functional theory.

INTRODUCTION

Graphene is a class of two dimensional nanomaterials with exceptional electronic properties which make it a promising material for the next generation electronics [1].

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The graphene structure is composed of carbon atoms packed into planar honeycomb lattice. Recently, new two dimensional carbon allotropes named graphyne were formed by introducing acetylenic linkages within the hexagonal lattice of graphene [2]. By varying concentrations of acetylenic linkages, several forms of graphyne so called α-, β- and γ- graphyne with different properties have been proposed [2-4]. It is found that α- and β- graphyne analogous to graphene are zero band gap semimetals while γ-graphyne is a semiconductor. It should be mentioned that lack of a band gap largely limits the application of graphene and graphyne in electronics. Thus, a band gap must be opened for the practical applications of these materials [5]. In the recent years, many physical and chemical approaches were suggested to open a band gap and provide suitable semiconducting properties in graphene [6-11]. For instance, it was found that chemical functionalization of graphene is a proper way to modify the electronic properties of graphene [6]. In addition, the use of underlying substrate such as silicon dioxide produced the shift from semimetal to semiconductor with a small energy band gap [7]. An alternative strategy is the organic molecule adsorption on graphene which may cause dramatic changes in electronic properties of graphene and induce a band gap. It is found that adsorption of organic molecules, such as tetracyanoethylene (TCNE), tetrakisdimethylamino-ethylene (TDAE), and tetracyanoquino-dimethane (TCNQ) provide a nondestructive way for controlling the carrier type and concentration of graphene via charge transfer between sheet and the adsorbed molecule [8, 11]. This result motivated us to study the effect of organic molecules on the electronic properties of graphene and graphyne; in the present work, we studied the adsorption of tetracyano-ethylene molecule on graphene and graphyne using density functional theory (DFT).

METHOD

The DFT calculations were performed using the openMX code [12]. The generalized gradient approximation (GGA) as parameterized by the Perdew-Burke-Ernzerhof (PBE) was used to take into account the exchange and correlation energy [13]. The cutoff energy was set to 150 Ry. The systems were relaxed until the residual forces arrived below 0.01 eV/Å. Charge transfer between the adsorbed molecule and sheet was estimated by Mulliken charge analysis. For calculations of the electronic properties, 51 k-points were used along of each high symmetry line. The graphene, α-, β- and γ- graphyne were selected as the host material for molecular adsorption. We have considered supercells of graphene and graphyne sheets as shown in Figure 1.

The periodic boundary condition was applied. A void with the height of 15 Å was put above the sheet to ensure that the distance between adjacent sheets

is large enough and interaction between them is negligible. The size of the simulation box, numbers of unit cell and carbon atoms in each supercell are listed in Table 1.
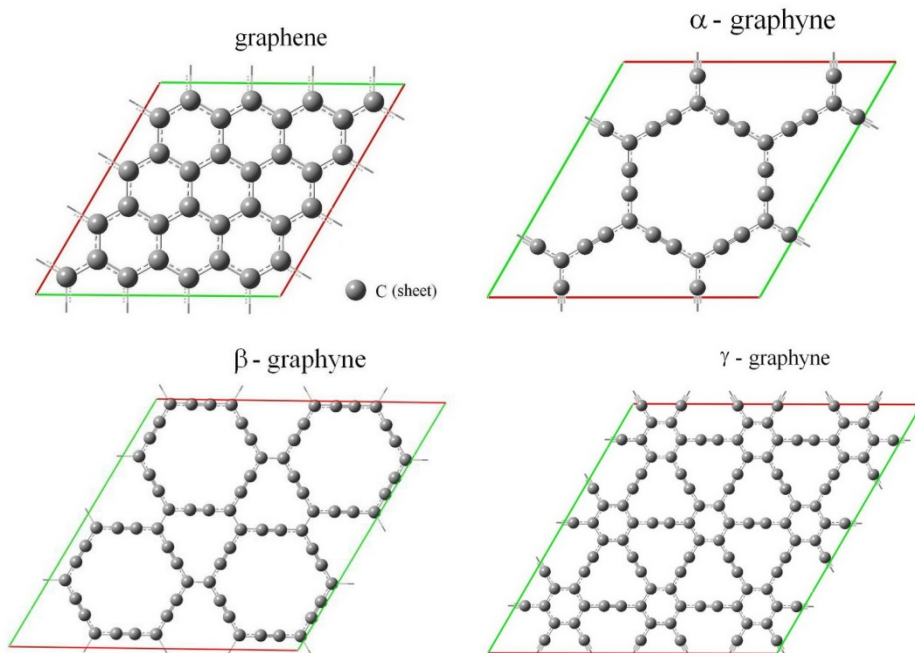
Figure 1. Structure of graphene and α-, β- and γ- graphynes.

Table 1. Size of simulation box, $a×b×c$, number of unit cell, n_u, and number of carbon atoms, n_C, per supercell.

| Structure	$a×b×c$ (Å³)	n_u	n_C
graphene	9.85×9.85×15	4×4	32
α- graphyne	13.96×13.96×15	2×2	32
β- graphyne	19.0×19.0×15	2×2	72
γ- graphyne	20.65×20.65×15	3×3	108

RESULTS AND DISCUSSIONS

To evaluate adsorption state of tetracyanoethylene on sheets, the binding energy was calculated by $E_b = E_{sheet+TCNE} - (E_{sheet} + E_{TCNE})$. Here $E_{sheet+TCNE}$ and E_{sheet} are the total energies of sheet with and without tetracyanoethylene molecule,

respectively. The energy of an isolated tetracyanoethylene molecule is represented by E_{TCNE}.

Different initial configurations of tetracyanoethylene molecule adsorbed on sheets were considered and their binding energies were compared. The most stable configurations with the lowest binding energies are shown in Figure 2. The parameters of binding energy, equilibrium distance between molecule and sheet (defined as the nearest distance between molecule and sheet), and charge transfer are listed in Table 2. The small binding energy and large adsorption distance indicate that tetracyanoethylene molecule is physisorbed on graphene and graphyne sheets. The charge analysis demonstrates that electrons transfer occurred from sheets to tetracyanoethylene molecule. Such adsorption and charge transfer are similar to those reported in reference [8].
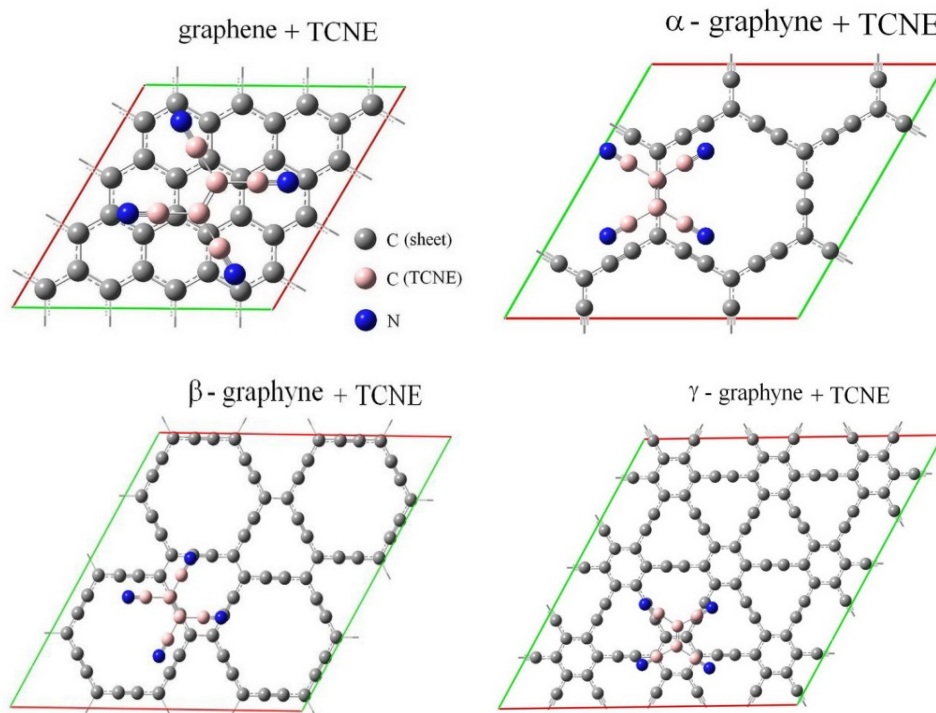
Figure 2. The most stable adsorption configurations
of tetracyanoethylene on graphene and
α-, β- and γ- graphynes.
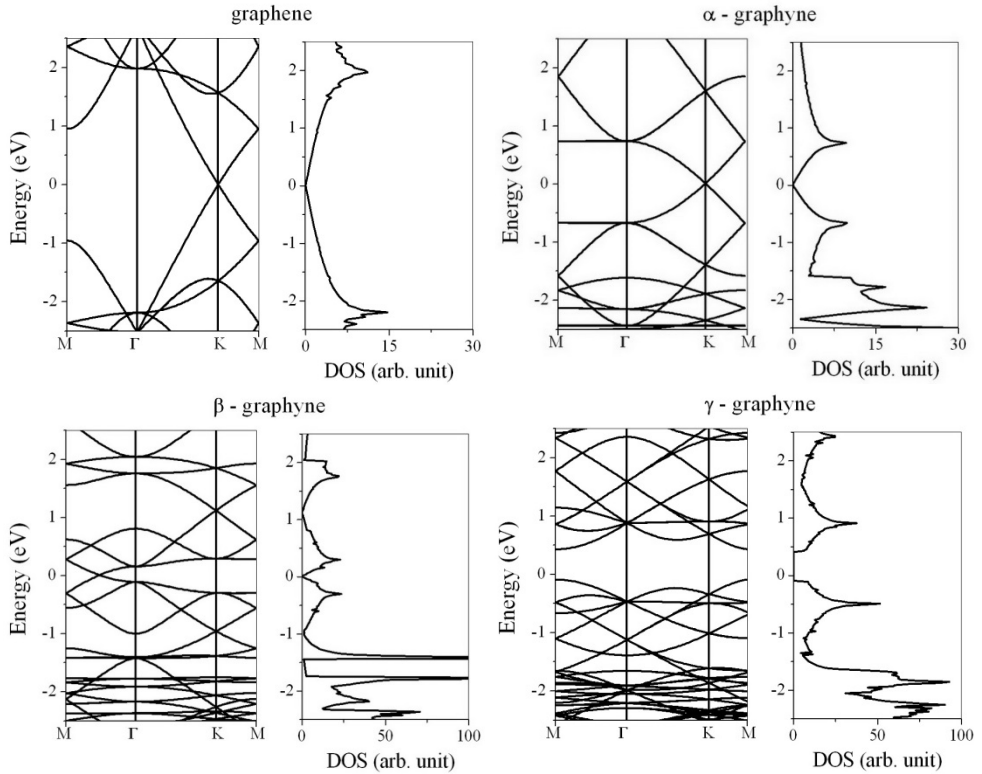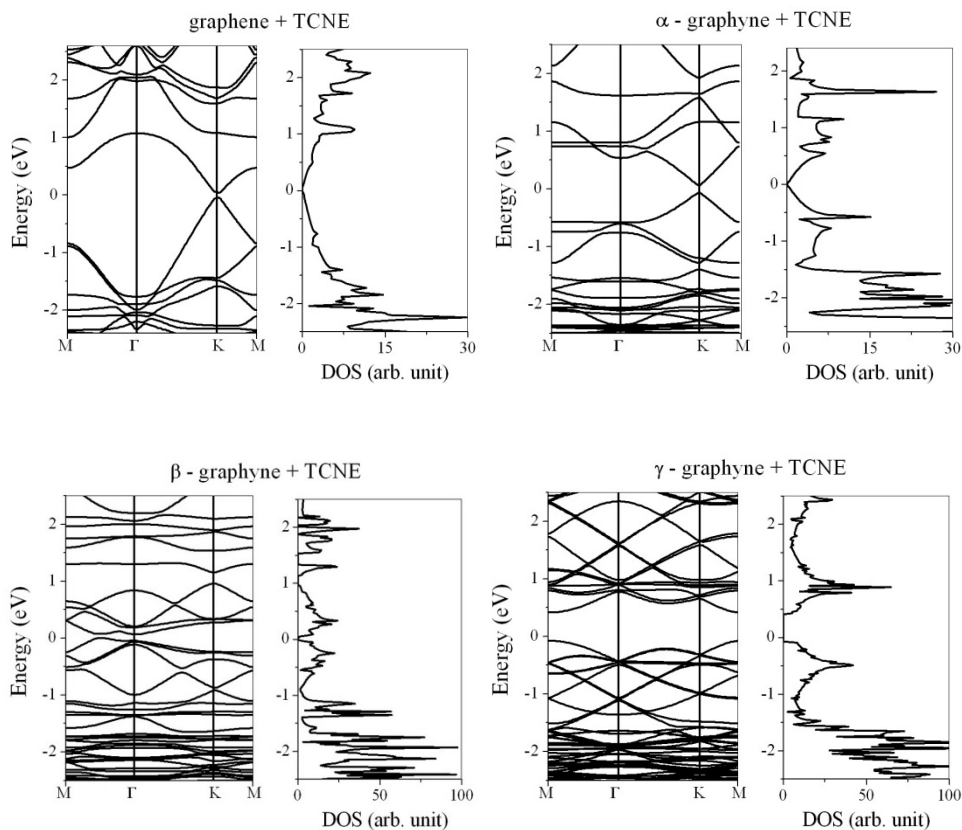
Figure 3. Electronic band structures and DOS of graphene and
α-, β- and γ- graphynes. (The Fermi level is set to 0 eV.)

We have first studied the electronic properties of graphene and α-, β- and γ- graphyne sheets. The electronic band structures and density of states (DOS) of graphene and graphyne are presented in Figure 3. For graphene and α- and β- graphyne, the valence and conduction bands touch linearly at the Dirac cone and DOS is zero. Hence, graphene and α- and β- graphyne are semimetals with zero band gap. It is found that γ- graphyne is a semiconductor with a small energy band gap of 0.5 eV.

Next, we studied the effect of tetracyanoethylene molecule on the electronic properties of graphene and graphyne. The electronic band structures and DOS of graphene and α-, β- and γ- graphynes with tetracyanoethylene molecule are shown in Figure 4. In electronic band structures of graphene and α- and β- graphynes, small band gaps appeared, due to the presence of tetracyanoethylene molecule. The energy band gaps are listed in Table 2.

Therefore, graphene and, α- and β- graphynes show semiconducting behaviour in the presence of tetracyanoethylene molecule. This can be explained by the fact that adsorption of an acceptor molecule such as tetracyanoethylene decreases the carrier concentration and consequently the electrical conductivity of graphene and graphyne sheets with semimetallic properties. In contrast, adsorption of tetracyanoethylene has no considerable effect on the electronic band structure and energy band gap of γ- graphyne near the Fermi level. Hence, this type of graphyne is semiconductor before and after tetracyanoethylene adsorption.

Figure 4. Electronic band structures and DOS of graphene and
α-, β- and γ- graphynes in the presence of tetracyanoethylene.
(The Fermi level is set to 0 eV.)

Table 2. Binding energy, E_b, adsorption distance, d, charge transfer, q, and band gap, E_g.

Structure	E_b (eV)	d (Å)	q (e)	E_g (eV)
graphene	1.8	2.6	0.85	0.1
α- graphyne	1.5	2.5	0.86	0.14
β- graphyne	0.8	2.5	0.16	0.07
γ- graphyne	1.1	2.6	0.03	0.5

CONCLUSIONS

Adsorption of tetracyanoethylene molecule on graphene and α-, β- and γ- graphynes was studied using DFT. The binding energy, equilibrium adsorption distance, charge transfer, electronic band structure, and DOS were calculated. The results show that tetracyanoethylene molecule is physisorbed on graphene and graphyne. The charge is transferred from sheets to tetracyanoethylene molecule. Adsorption of this acceptor molecule has a significant effect on the electronic properties of graphene and α- and β- graphyne sheets. These sheets with semimetallic character switch to semiconducting behaviour in the presence of tetracyanoethylene molecule. In contrast, the effect of tetracyanoethylene on electronic properties of γ- graphyne, with a priori semiconducting property, is not considerable. Our results provide an effective way to generate a band gap and produce semiconducting graphene and graphyne. This opens a gate for enormous technological and industrial areas for graphene and graphyne.

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