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Metal decorated graphdiyne: A first principle study

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ABSTRACT

In this work, we performed first principles calculations based on self-consistent charge density functional tight-binding to investigate mechanical and electronic properties of the optimized graphdiyne sheet, nanoribbons and transition metal decorated with Ag, Fe and Co atoms in the different sites. Then we calculated electronic properties of the graphdiyne sheet under uniaxial elastic strain in two different crystal directions. It is shown that the carbon bond length values for the graphdiyne structure are agreeable with experimental and other theoretical values. Our results show that the charge transferred to the graphdiyne from Ag and Fe atoms but to the Co decorated charge transferred to the Co atom from the graphdiyne. From the results, it can be seen that the graphdiyne is a direct semiconductor with doubly degenerated for both the valence band maximum and the conduction band minimum in the 6C hole site. Also, by Metal decorated of the graphdiyne, the structures become also direct semiconductor for the Ag decorated and indirect for Co and Fe decorated for the 6C- hole, top and bridge sites while the structure have metallic behavior for the 18C- hole site. Our results from the band structure of the GDY nanoribbons with the size of N = 1, 2, 3 and 4, indicate that all of them are nonzero band gaps at the Γ point. It can be seen that the energy gap decreases with increasing of nanoribbons size. Finally, we found that the gap energy increase with applying strain and also the structure remain direct semiconductor.

1. Introduction

Graphene, a two-dimensional with a hexagonal structure, is one of the most important materials in science due to its unique and remarkable electromechanic properties [1–6]. However, graphene is zero band gap materials, what limits its use in some electronic devices and band gap engineering. Therefore, some other graphene like 2D materials are interested such as silicene [7–10], phosphorene [11–13] and MoS_2 [14–16]. Beside of these materials, there are carbon allotropes family of 2D structures can be used in optoelectronic application such as graphyne [17,18] and graphdiyne [19]. But among these structures, only the graphdiyne was successfully synthesized [19–22].

Graphdiyne (GDY) can be described as a lattice of benzene rings connected by diacetylene bonds, which are composed of sp and sp^2 hybridized carbon atoms [18,19,23,24] (see Fig. 1).

As for carbon allotrope material, previous theoretical and experimental studies have shown semiconductor behavior for GDY [20,25], which make it as a possible application in the future nanoelectronics.

Some theoretical works have studied the properties of the GDY, such as the band gap [26,27], charge mobility [28], structural [25,28–31], electronic [32–37], optical [38], mechanical [39–42], magnetic properties [43,44].

For example, Long et al. found that GDY and its nanoribbon have high electron mobility [28]. Furthermore, the band gap of GDY nanoribbon can be tuned by either ribbon width or electric field [36,45]. In addition, the application of GDY in photocatalyze is also reported [46]. Pei et al. [47] investigated the effect of strain to the electronic properties of GDY by first-principles calculations. They found that the band gap of GDY is tunable under uniform strain. Cranford et al. [33] predicted some mechanical properties of monolayer graphdiyne by employing the classical molecular dynamics (MD) method and reported that the in plane stiffness of GDY is equal to 170.4 N/m (532.5 GPa for a thickness of 0.32 nm). Kang et al. [34] studied the mechanical and electronic properties of the GDY by using the density functional theory (DFT) method with the VASP package. These authors used GGA–PBE functional and reported an in-plane stiffness and band gap of 165.8 N/m and 0.46 eV for the GDY, respectively. Long et al. [28] used a similar approach to study the GDY at room temperature (300 K) and obtained an in-plane stiffness of 158.6 N/m. The band gap of the GDY has also been calculated by Zhou et al. [27], who used the DFT method with the GGA–PBE exchange correlation functional and the DMOL3 package. These researchers concluded that the GDY with a length of 26.16 Å has a band gap of 0.49 eV. Finally Lu et al. [48] presented a study electronic structure of

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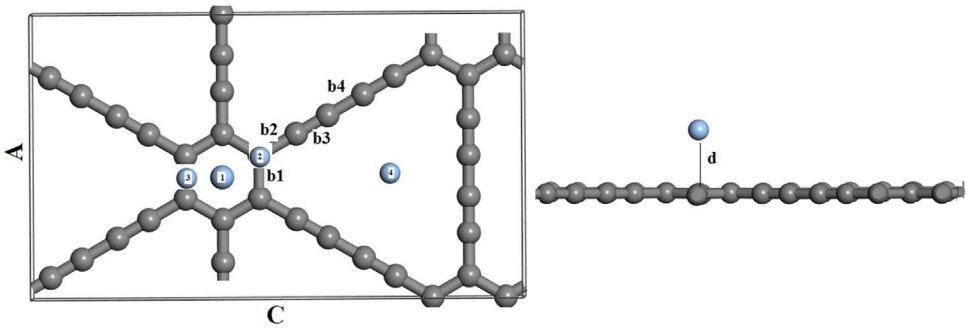

Fig. 1. Top and side view of the graphdiyne with metal decorated super cell.

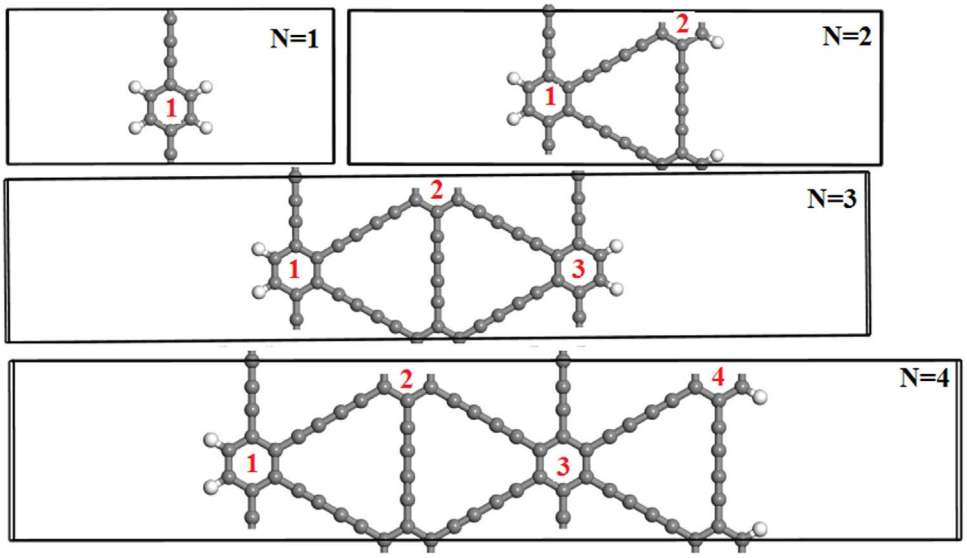

Fig. 2. The geometric structures of the graphdiyne nanoribbons with different width from N = 1 to N = 4.

Table 1
Geometry parameters for relaxed GDY and GDY decorated with Ag, Co and Fe in the 6C-hole site.

	GDY sheet	Ag Decorated	Co Decorated	Fe Decorated
Unit cell (Å^2)	9.481*16.421	9.492*16.441	9.505*16.468	9.506*16.466
b1 (Å)	1.417	1.428	1.437	1.444
b2 (Å)	1.422	1.421	1.423	1.419
b3 (Å)	1.217	1.218	1.217	1.218
b4 (Å)	1.370	1.370	1.370	1.369
d (Å)	–	2.413	1.633	1.817

Table 2
The transferred charge and interaction energy between the GDY and Ag, Co and Fe in the 6C-hole site.

	Ag Decorated	Co Decorated	Fe Decorated
Charge transferred (e)	+ 0.002 (donor)	− 0.015 (acceptor)	+ 0.135 (donor)
Interaction Energy (eV)	− 0.612	− 2.73	− 2.17

atoms adsorbed on the GDY. They investigated the mobility of the Novel Metal atoms on the GDY and possibility of these structures to be applied as single metal catalysts or gas molecule sensors.

Based on our knowledge, little information about the electronic properties of the GDY which is decorated with the transition metal atoms with a partially filled d electron sub-shell has been reported. Therefore, in this work, we have studied electronic and mechanical properties of the decorated GDY with Ag, Fe and Co atoms using self-consistent charge density functional tight-binding (SCC-DFTB) formalism with DFTB+ package [49]. Also, we have studied the electronic properties of GDY nanoribbons and the effect of applying a uniaxial tension on the band gap of GDY sheet. For this, we first carried out a geometry optimization of pure GDY sheet, Ag, Fe and Co decorated GDY. Then we calculated the band structure and density of states of these structures to show how metal atoms on the GDY can effected on energy gaps and electronic properties of GDY. At the next step we obtained gap energy and density of state for relaxed GDY nanoribbons. Finally, the gap and total energy of GDY sheet under uniaxial tension obtained.

We organized this paper is as follows: in the Section 2 we presented a brief explanation of the computational methods. In Section 3, we discuss the crystal parameters, the energy gaps and density of state for the GDY sheet and effecting of metal decorated on these parameters. Also, we studied charge transferred and binding energy between metal atom and GDY. For GDY nanoribbons, we investigated the effect of nanoribbons size on gap energy and density of state. Also in this section, we studied the gap and total energy of GDY sheet under two different tensions. The Section 4 is a brief conclusion of our work.

2. Simulation method

To study of electronic and mechanical properties of the GDY sheet and metal decorate of the GDY, we considered a typical GDY sheet with