

Structural and Electronic Properties of Graphdiyne Nanotubes

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Abstract

The sp^2 hybridized carbon allotropes such as fullerenes and graphene are scientifically and technologically significant because of their unique elastic and electronic properties. These properties make them useful in a wide variety of applications. Recently, experimentalists have synthesized sp - sp^2 hybridized carbon tubular arrays of two-dimensional carbon films, referred to as graphdiyne. To explore the possible existence of an sp - sp^2 hybridized one-dimensional carbon allotrope, we investigate graphdiyne nanotubes' structural and electronic properties using dispersion-corrected density functional theory calculations. Graphdiyne nanotubes display unique porous characteristics and remarkable stability, which may promote them as a novel class of carbon materials.

Introduction

Carbon can form sp , sp^2 , and sp^3 hybridized bonds. Over the years, sp^2 hybridized carbon allotropes with low dimensionality, exemplified by Buckminsterfullerenes (zero-dimension), carbon nanotubes (one-dimension), and graphene (two-dimension), have been successfully synthesized [1-3]. These carbon nanomaterials have attracted a great deal of attention. Recently, a two-dimensional carbon graphdiyne film composed of mixed sp and sp^2 hybridized (sp - sp^2) carbon atoms has been synthe-

sized via a cross-coupling reaction using hexaethynylbenzene on a copper surface. Remarkably, sp - sp^2 hybridized graphyne and graphdiyne have intrinsic semiconducting properties, which is in stark contrast to sp^2 hybridized graphene with inherent zero band gap characteristics [4-7]. Experimentally synthesized graphdiyne has high-temperature stability and mechanical properties similar to graphene [8-19].

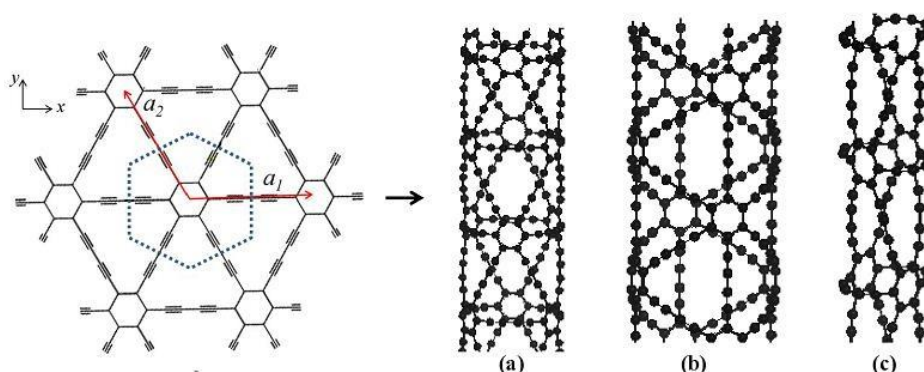


Figure 1: Schematic chemical structure and unit cell representation for β -graphdiyne sheet. The lattice vectors are given by $a_1 = ax$ and $a_2 = a(-x/2 + \sqrt{3}y/2)$. The unit cell of β -graphdiyne sheet has 18 atoms, and the structural relationship between graphdiyne sheets and single-wall graphdiyne nanotubes for sheets of graphdiyne (a) armchair, (b) zigzag, and (c) chiral.

Graphdiyne is a 2D single-layered carbon sheet containing sp and sp² carbon atoms [5]. Graphdiyne can be viewed as a structure in which one-third of the C-C bonds in the graphene are inserted with two -C≡C- units (di-acetylenic). Since graphdiyne is an intrinsic semiconductor, a graphdiyne nanotube is expected to display semiconducting characteristics, making these potential nanotubes candidates in electronic devices [20-21].

Given the successful synthesis of these sp-sp² hybridized one-dimensional carbon tubular arrays and two-dimensional carbon films, a natural question arises as to whether it is possible to create graphdiyne nanotubes [22].

Methods

Herein, we investigate the structural and electronic properties of sp-sp² hybridized graphdiyne nanotubes. The calculations were based on a dispersion-corrected density-functional theory (DFT) approach. Specifically, we employed general gradient approximation (GGA) with the exchange-correlation of Perdew-BurkeErnzerhof (PBE) parametrization [5]. We used the dispersion correction utilizing Tkatchenko-Scheffler (TS) scheme, which exploits the relationship between polarizability and volume [6]. To model the graphdiyne nanotubes, we used a graphdiyne sheet with different cells intercepted. A kinetic energy change of 3×10^{-4} eV in the orbital basis and appropriate Monkhorst-Pack k-point grids of $6 \times 6 \times 1$ were sufficient to converge with the integration of the charge density. Optimizing the atomic positions proceeded until the change in energy was less than 1×10^{-5} eV per cell.

The schematic structure of the graphdiyne is shown in Figure 1. The C≡C units form acetylenic linkages. The shape of the unit cell of graphdiyne is a rhombus analogous to graphene. The geometrical and electronic properties of graphdiyne were calculated using first-principle density functional theory (DFT) calculations. The optimized side length of the rhombus is 7.67 Å. Graphdiyne is a semiconductor with a direct band gap of 1.14 eV at the band center. These results agree with experimental extracted values and previous theoretical calculation results [5].

We illustrate in Figure 2 the calculated band structure of planar graphdiyne, along with the charge density for the VBM and CBM, respectively. As seen in Figure 2, a band gap at the band center indicates a semiconducting behavior. The charge distribution shows that for VBM, the charge is predominantly confined at (C≡C) carbon triple bond, while for CBM, the charge is mainly confined in (C-C) carbon single bond. The single and triple bonding corresponds to the anti-bonding and bonding states, respectively. The calculated band structure of graphdiyne is presented in Figure 2. As seen from Figure 2, the Dirac cone of graphdiyne is shifted 2.4 eV above the Fermi level at the K point. This is to be contrasted to graphene, a semimetal with linear dispersed π and π^* bands crossing at the K point. Therefore, the graphdiyne nanotubes are semiconducting tubes. This is a unique feature for promising applications in electronics devices.

A perfect hexagon was assumed for the β -graphdiyne sheet with bond lengths of 1.418 and 1.236 Å for the single and triple bonds (see Figure 1), respectively. The construction of graphdiyne nanotubes can be done analogously to the case of carbon nanotubes [23-30]. Specifically, defining the chiral vector as $C_h = na_1 + ma_2 = (n, m)$ (n, m being integers), zigzag and armchair β -graphdiyne nanotubes are defined by $(2m, m)$ and $(n, 0)$, respectively. There are two graphene sheets with the same space group as graphene, referred to as α -graphdiyne and β -graphdiyne. The latter is a modification of the α -graphdiyne where double bonds covalently interconnect the hexagons [31]. However, experimentally, findings demonstrated that the hexagons are covalently interconnected by triple bonds instead of double bonds. As such, in this paper, we investigate the properties of the β -graphdiyne sheet and label the graphdiyne nanotubes accordingly. The diameter of graphdiyne nanotube is of the following empirical form:

$$D = \frac{a}{\pi} \sqrt{n^2 + nm + m^2} \quad [7]$$

where a is the single-triple bond length of 9.54 Å.

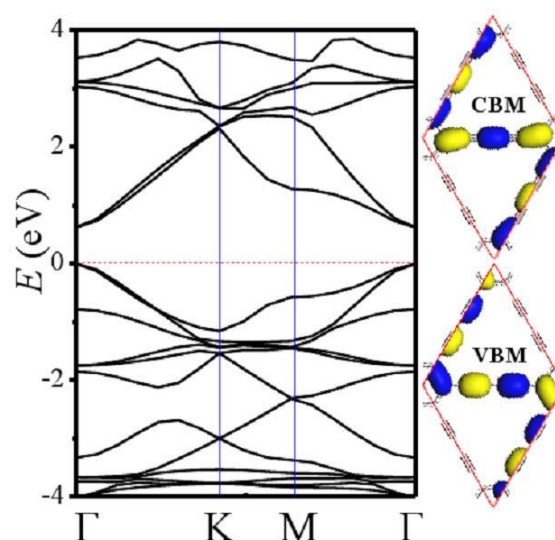


Figure 2: Calculated band structure in graphdiyne, along with isosurfaces of the valence band maximum (VBM) and conduction band minimum (CBM) for the graphdiyne. $\Gamma = (0, 0) \pi/a$, $K = (-\pi/3a, 2\pi/3a)$, $M = (0, \pi/2a)$, where $a = 9.54$ Å. The Fermi level, highlighted by the dashed red line, is shifted to 0 eV.

In analogous to carbon nanotubes, the graphdiyne nanotubes are uniquely characterized by the chiral indices (n, m) and the diameter. Figure 3 the optimized structures of various armchairs, zigzag, and chiral graphdiyne nanotubes. As seen in Figure 3, these nanotubes vary in diameters. However, using the average of maximum and minimum diameters as the characterization, the extracted average diameter d is in excellent agreement with the predicted values from the empirical formula for d_0 .

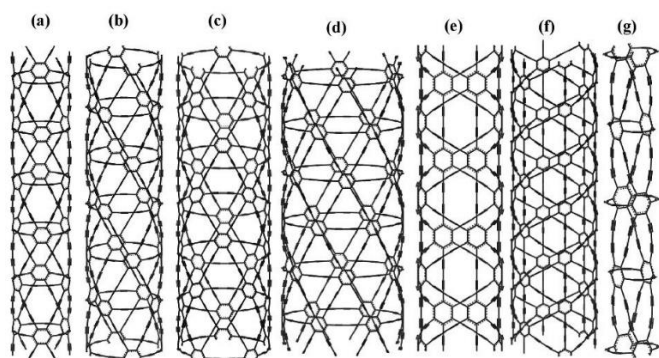


Figure 3: Two-dimensional view of (a), (b), (c), and (d): armchair nanotubes labeled as (3,0), (4,0), (5,0), (6,0), respectively (e) and (f): zigzag nanotubes labeled as (4,2) and (6,3), and (g): chiral (2,1) nanotubes.

Results

We show in Figure 4 the calculated band structures for various graphdiyne nanotubes. One of these characteristics is the effective mass and its dependence on the nanotube diameter for the armchair, zigzag, and chiral tubes. Differences in effective mass can lead to different optical and electronic transport properties for the various graphdiyne nanotubes. Interestingly, the zigzag graphdiyne tubes have a smaller effective mass than the armchair counterparts. The chiral tubes have an enormous effective mass, as exemplified by (2,1), with a nearly flat valence band maximum. The almost flat band implies charge confinement on the linkage and virtually localized electrons. By contrast, the link forms a chain along the zigzag direction for zigzag tubes, thereby promoting the charge transport along the path.

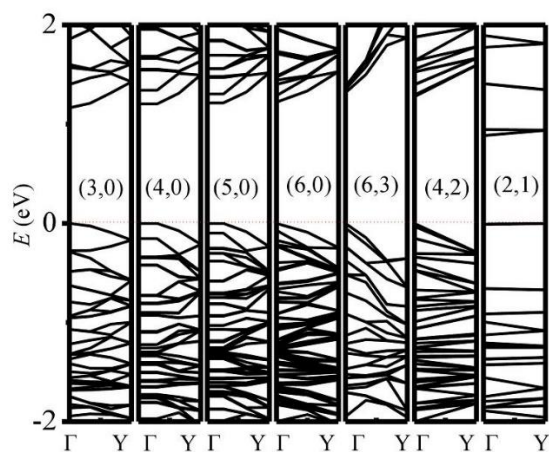


Figure 4: Calculated band structure armchair nanotubes with labeling as (3,0), (4,0), (5,0), (6,0), zigzag nanotubes labeling as (4,2) and (6,3), and chiral (2,1) nanotubes based on a graphdiyne. $\Gamma = (0, 0) \pi/a$, $Y = (0, \pi/2a)$, where $a = 36.8 \text{ \AA}$. The Fermi level, highlighted by the dashed line, is shifted to 0 eV.

The band gaps for various graphdiyne nanotubes are shown in Table 1. The band gaps of the armchair graphdiyne nanotubes increase when their diameter increases. This is attributed to the charge transfer associated with different electron affinities of the hexagonal ring and the $C_{(sp)} \equiv C_{(sp)}$ segments. Figure 5 shows the wave functions of the highest occupied and lowest unoccupied states to pursue the charge transfer behavior further. As seen from Figure 5, the isosurfaces associated with the valence band maximum (VBM) and conduction band minimum (CBM) of graphdiyne nanotubes are primarily confined at the sp^3 linkages rather than located on benzene carbon rings.

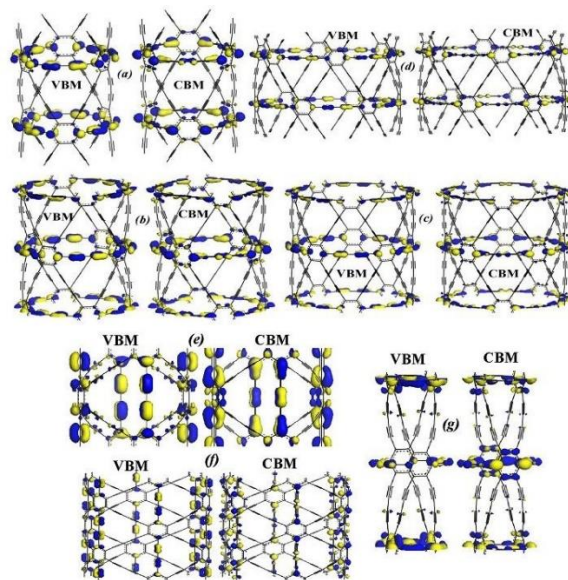


Figure 5: Isosurfaces of the valence band maximum (VBM) and conduction band minimum (CBM) (a–d) for an armchair with graphdiyne nanotubes labeled as (3,0), (4,0), (5,0), and (6,0) respectively, (e–f) for zigzag with graphdiyne nanotubes labeled as (4,2) and (6,3), and (g) for chiral (2,1) graphdiyne nanotubes. The isovalue is 0.2 a.u.

As the charges are primarily confined in the triple and single bond for VBM and CBM, the electronic characteristics are mainly determined by the "bonding" behavior of the graphdiyne. A unique feature of the graphdiyne nanotubes is that there are energy gaps for armchair, zigzag, and chiral tubes, which are to be contrasted to carbon nanotubes, whose electronic properties depend upon tube chirality.

Table 1: Calculated binding energy (E), diameter (d), diameter using the empirical formula (d_0), number of atoms (N) in graphdiyne or graphdiyne nanotubes, along with the extracted band gap (E_g).

| (n,m) | N | E (eV) | d Å | d_0 Å | E_g (eV) |
|------------|-----|----------|-------|---------|------------|
| graphdiyne | 18 | -7.219 | | | 1.84 |
| (3,0) | 108 | -7.122 | 9.13 | 9.11 | 1.17 |
| (4,0) | 144 | -7.148 | 12.21 | 12.15 | 1.21 |
| (5,0) | 180 | -7.159 | 15.42 | 15.19 | 1.21 |
| (6,0) | 216 | -7.163 | 18.24 | 18.22 | 1.24 |
| (2,2) | 72 | -7.142 | 10.61 | 10.52 | 1.31 |
| (3,3) | 216 | -7.153 | 15.78 | 15.78 | 1.30 |
| (2,1) | 72 | -6.795 | 7.14 | 7.41 | 0.88 |

In summary, the armchair, zigzag and chiral graphdiyne nanotubes present semiconducting behavior independent of the nanotube diameter for one type of graphdiyne nanotubes. These unusual properties can be experimentally investigated. Graphdiyne nanotubes can be used for many electronic applications. Due to graphdiyne nanotube's superior mechanical properties, many structures have been proposed, including sports gear, combat jackets, and space elevators. In electrical circuits, graphdiyne nanotubes can be used as field-effect transistors, which can operate as a digital switcher. Graphdiyne nanotubes behave like semiconductors; hence they can be used as solar cells. In addition, graphdiyne nanotubes can also store electric energy such as hydrogen to be used as a fuel source.

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