Investigation of Optical Properties of (2, 2) Zigzag Graphdiyne Nanotube in the Presence of Lithium and Nitrogen Dopant: Density Functional Theory Approach

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Abstract

In the study, the structural and electronic properties of zigzag Graphdiyne nanotube (2, 2) in the pure state and in the presence of lithium and nitrogen impurities were studied using the density functional theory method. The structure investigation shows that the pure Graphdiyne nanotube is a semiconductor with a direct band gap of 0.65eV at gamma point. By inserting the lithium and nitrogen impurities, nanotubes exhibit the metallic behavior. The optical properties of all nanotubes above-mentioned were examined and computed using SIESTA package and based on Kramers–Kronig relations. Optical investigations show that placing the lithium atom in the center of the nanotube has little effect on the optical properties, but, by substituting the nitrogen atoms for carbon atoms, the optical properties significantly change.

Key Words: Graphdiyne Nanotube, Impurities, DFT, Optical Properties.

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Introduction

During the past two decades, organic materials have been recognized as promising candidates to be used in fabricating new generation of electronic and optoelectronic devices. Among these materials, carbon-rich molecules have attracted much more attentions for using in nanotechnology and the related area (1-4).

Single-layer Graphdiyne, fig 1, is a two-dimensional structure composed of sp and sp^2 hybrids of carbon atoms. The carbon atoms with the sp^2 hybrid form a hexagonal ring, which are connected together by di-acetylene sp connections (5-10).

Graphdiyne nanotubes were first designed in 2003-2004. Graphdiyne nanotubes are produced by rolling the Graphdiyne sheets (plates).

Similar to carbon nanotubes, the denomination (n, m) can be used for Graphdiyne nanotubes. According to this denomination, (n, n) and (n, 0) represent zigzag and arm chair structures, respectively (11-18).

Graphdiyne nanotubes are expected to be used in the next generation of lithium-ion batteries, electronic and optoelectronic components (19-24). Therefore, the study investigated the optical properties of zigzag Graphdiyne nanotube (2, 2) in the presence of lithium and nitrogen impurities.

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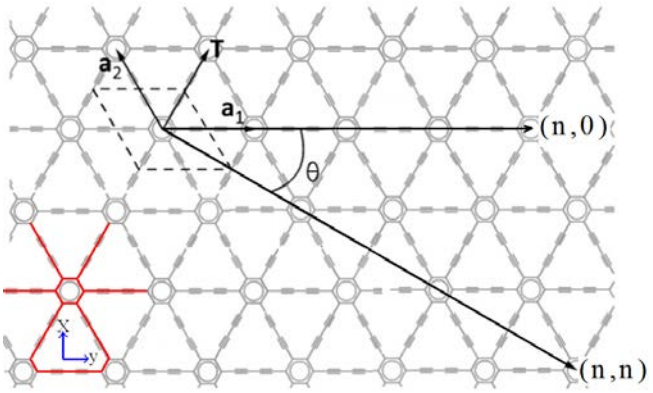


Figure 1. Chiral vector of zigzag (n, n) and armchair (n, 0) graphdiyne nanotube. The unit cell of the graphdiyne sheet is shown in rhombic black dots. The unitcell of graphdiyne nanotube is marked with red lines in the left-hand corner of the figure.

Computational Method

The computations were performed based on the density functional theory (*DFT*) and the exchange-correlation potential with the generalized gradient approximation (GGA) presented by *Perdew–Burke–*Ernzerhof (*PBE*)(25). SIESTA codewas used to perform the computations(26). In order to achieve proper accuracy in computing and minimizing the total energy, a Monkhorst–Pack gridwith points (1×1×5) was applied.The optimal cutoff energyof 200Ry was also used in the computations. A vacuum layer that is large enough in non-periodic directions was considered to avoid interactions between two adjacent nanotubes. Then, by applying these parameters, the system was completely relaxed to decrease the force applied less than 0.01eV/Å to each atom. The energy range in which the optical properties are investigated was selected from zero to 40eV. In optical computations, the spin-orbit interaction is neglected because it will not have much impact on the results. In all the structures studied, the polarized light and its propagation *along the x direction* were considered.

Results and Discussion

Zigzag nanotubes have a larger diameter than the armchair nanotubes, so they appear to be a better option for inserting impurities into the nanotube. In order to reduce the volume of computations, among the zigzag Graphdiyne nanotubes with different diameters, thesmallest nanotube, zigzag Graphdiyne nanotube (2, 2) was selected to insert lithium and nitrogen impurities.

A lithium atom was placed in the center of the nanotube, in order to investigate the impurity effect, and its electronic properties were examined. First, we placed a lithium atom in the center of the nanotube, which was then incorporated into the wall of the nanotube after relaxation(Fig 1). In the next step, nitrogen impurities were inserted into the nanotube so that two nitrogen atoms were replaced by carbon atoms in each hexagon. The relaxed structure of these nanotubes is shown in Fig 1. As shown in Fig2, the nanotube structure did not change by inserting the lithium and nitrogen and had a symmetric circular cross-section.

The band structure of the zigzag Graphdiyne nanotube (2,2) without impurity and in the presence of lithium and nitrogen impurities is plotted in Fig 1. In these diagrams, zero energy represents the position of the Fermilevel. As clearly shown in these Figures, the pure Graphdiyne nanotube is a semiconductor with the direct band gap of 0.65eV at the point Γ of the first Brillouin zone. This result is in agreement with the results of other researchers (2). By inserting lithium and nitrogen impurities, the band gap becomes zero and the doped nanotubes exhibit a metallic behavior.

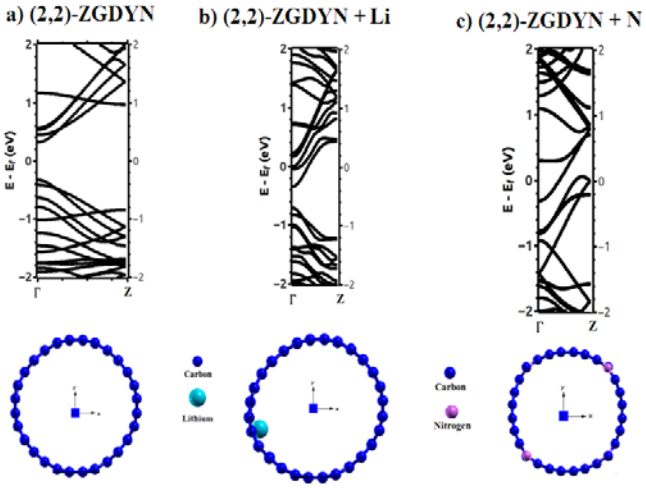


Figure 2. Geometric Structure and Band Structure of the Zigzag Graphdiyne Nanotube (2,2), (a) In a Pure State; (b) In the Presence of a Lithium Atom in the Center of the Nanotube; (c) Two Nitrogen Atoms in Each Hexagon.

Optical Properties of Graphdiyne Nanotubes

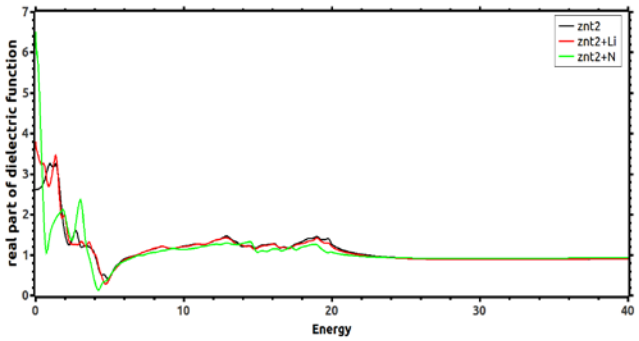
Dielectric Function

The complex dielectric functiondescribes the optical properties of solids. This function is used to describe the crystal response to electromagnetic fields, which depends on the band structure of crystal (6). The curves of real and imaginary partof the dielectric function of the zigzag Graphdiyne nanotube (2, 2) in the pure state and in the

presence of lithium and nitrogen impurities are shown in Fig 3. The imaginary part of the dielectric function partly represents the actual transfers between occupied and unoccupied states. We also know that the inter-band transition is due to excitation at the absorption edges, and the intra-band transition is due to volumetric plasmons (absorption by free electrons). Therefore, the relatively large increase in energy values less than5eV in the imaginary part of the dielectric function, as well as the almost constant behavior at energies above 20eV confirm these absorption approaches.By comparing the dielectric function of the zigzag Graphdiyne nanotube (2,2) in the pure state and in the presence of impurities, we conclude that the presence of lithium inside the nanotube does not change the dielectric function but the replacement of carbon atomswith nitrogen causes much variation in the dielectric function.

Optical Conductivity

Due to the photon absorption, the electrons of occupied states are excited to the unoccupied states above the Fermi level. This inter-band transition (known as the Droud transition) is called the optical conductivity, and the absorption of photons by electrons is called inter-band absorption. Fig 4 shows the changes of optical conductivity of the zigzag Graphdiyne nanotubes in the pure state and in the presence of lithium and nitrogen impurities for the polarized light in the direction of x-axis, compared to the incident photon energy. As can be seen, the diagram of optical conductivity is proportional to the imaginary part of the dielectric function. Generally, in the energies that present in the imaginary part of the peak of dielectric function, these peaks are seen in the real part of the optical conductivity. In this spectrum, the conductivity increases up to 20eV and then decreases, and at energies with the highest absorption, we have the optical conductivity maximum.



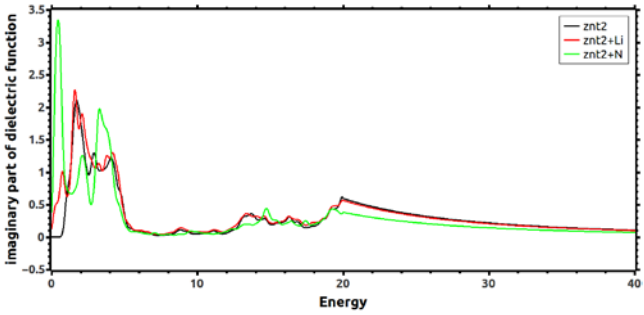


Figure 3. (a) The Real Part and, (b) the Imaginary Part of the Dielectric Function of the Zigzag Graphdiyne Nanotube (2,2) in a Pure State and in the Presence of Lithium and Nitrogen Impurities for Polarized Light in the Direction of X-Axis.

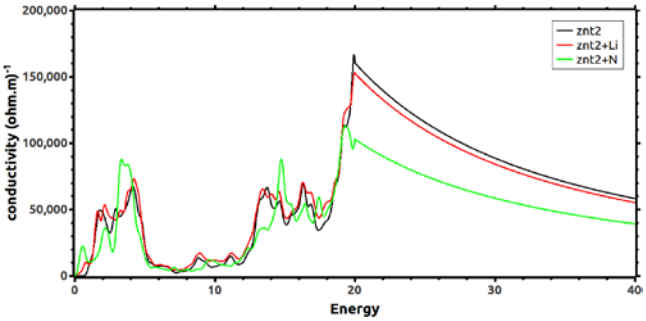


Figure 4. The Diagram of Optical Conductivity of Zigzag Graphdiyne Nanotube (2,2) in a Pure State and in the Presence of Lithium and Nitrogen Impurities for Polarized Light in the Direction of X-Axis.

Abosorption coefficient

(Fig 5) shows the absorption coefficient of these nanotubes. This fig shows the permitted optical transitions of the electron between the occupied states of the valence band and theempty states of the conduction band. The transition energy in the absorption spectrum corresponds to the band gap value in the band structure of graphdiyne nanotubes, which means that the electrons are excited and transient by receiving at least energy greater than the band gap value.The graph shows that the presence of lithium atom causes a very small decrease in the absorption spectrum of zigzag graphdiyne nanotubes (2,2), but the presence of nitrogen atoms significantly reduces the absorption spectrum.

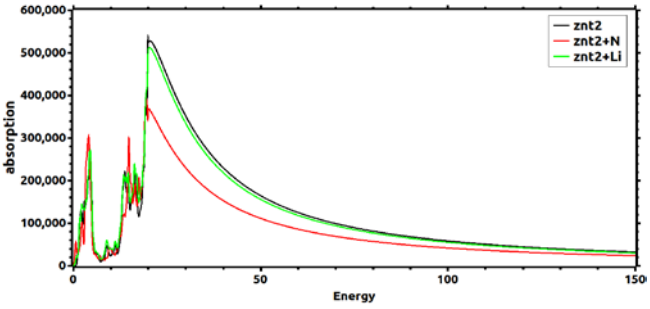


Figure 5. Absorption coefficient of pure, N- doped and Li-doped of zigzag graphdiyne nanotube (2, 2).

Static Refractive Index

The value of the refractive index at zero energy is called the static refractive index, which is equal to the static dielectric constant. The value of static refractive index of zigzag graphdiyne nanotube (2, 2) in the presence of lithium and nitrogen impurities is presented in Table 1. By inserting the impurities, the static refractive index increases. The graph of refractive and extinction index of graphdiyne nanotubes in the presence and absence of impurities is plotted in Fig 6 and 7, respectively. As can be seen in this graph, the refractive index reaches its lowest value at energies between 4 and 6 eV, so the reflection is increased, which is in consistent with Fig 5. It can be seen that the introduction of lithium atom does not have a significant effect on the refractive and extinction index, but the substitution of nitrogen atoms results in significant changes in the refractive and extinction index.

Table 1. Static Refractive Index of Zigzag Graphdiyne Nanotube (2, 2) in the Presence of Lithium and Nitrogen Impurities

nanotube	ZGDYN	ZGDYN+ Lithium	ZGDYN +Nitrogen
Refractive index	1.62	1.94	2.55

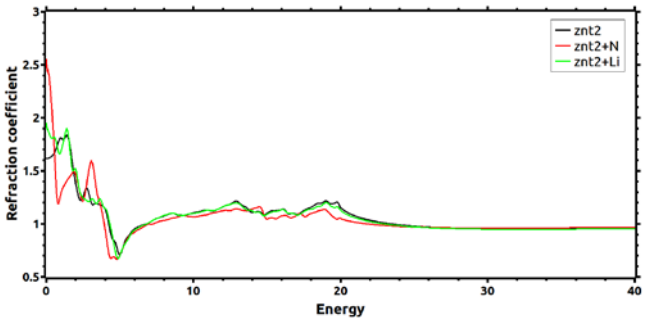


Figure 6. Refraction coefficient of pure, N- doped and Li-doped of (2, 2) zigzag graphdiyne nanotube.

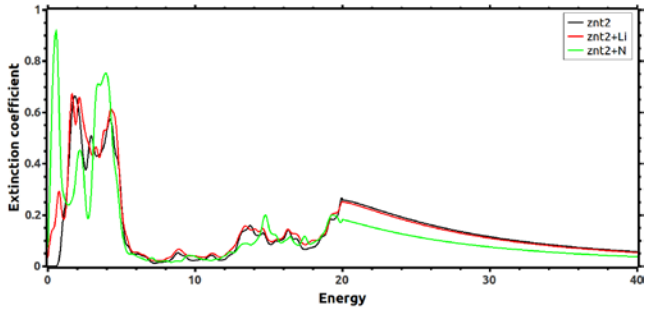


Figure 7. Extinction coefficient of pure, N- doped and Li-doped of (2,2) zigzag graphdiyne nanotube.

Conclusion

In this study, the structural, electronic and optical properties of pure, lithium and nitrogen doped of (2, 2) zigzag graphdiyne nanotube were investigated in the framework of Density Functional Theory (DFT) with Generalized Gradient Approximation (GGA), employing siesta code. The results show that the pure nano tube exhibited semiconducting behavior. By entering the lithium and nitrogen dopant, the nanotube shows a metallic behavior. Optical properties such as dielectric function, optical conductivity and refraction coefficient were calculated and investigated.

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References

Wang A, Li L, Wang X, Bu H, Zhao M. Graphyne-based carbon allotropes with tunable properties: From Dirac fermion to semiconductor. Diamond and related materials 2014; 41: 65-72.

Ozkan C, Buehler M, Pugno N, Wang K. De Novo carbon nanomaterials: Opportunities and challenges in a flat world 2013.

Lin ZZ, Wei Q, Zhu X. Modulating the electronic properties of graphdiyne nanoribbons. Carbon 2014; 66: 504-510.

Shohany BG, Roknabadi MR, Kompany A. Computational study of edge configuration and the diameter effects on the electrical transport of graphdiyne nanotubes. Physica E: Low-dimensional Systems and Nanostructures 2016; 84: 146-151.

Cranford SW, Buehler MJ. Selective hydrogen purification through graphdiyne under ambient temperature and pressure. Nanoscale 2012; 4(15): 4587-4593.

He J, Ma SY, Zhou P, Zhang CX, He C, Sun LZ. Magnetic properties of single transition-metal atom absorbed graphdiyne and graphyne sheet from DFT+ U calculations. The Journal of Physical Chemistry C 2012; 116(50): 26313-26321.

Ivanovskii AL. Graphynes and graphdyines. Progress in Solid State Chemistry 2013; 41(1-2): 1-19.

Li G, Li Y, Liu H, Guo Y, Li Y, Zhu D. Architecture of graphdiyne nanoscale films. Chemical Communications 2010; 46(19): 3256-3258.

Pan LD, Zhang LZ, Song BQ, Du SX, Gao HJ. Graphyne-and graphdiyne-based nanoribbons: density functional theory calculations of electronic structures. Applied Physics Letters 2011; 98(17): 173102.

Pei Y. Mechanical properties of graphdiyne sheet. Physica B: Condensed Matter 2012; 407(22): 4436-4439.

Kang J, Wu F, Li J. Modulating the bandgaps of graphdiyne nanoribbons by transverse electric fields. Journal of Physics: Condensed Matter 2012; 24(16): 165301.

Peng Q, Dearden AK, Crean J, Han L, Liu S, Wen X, De S. New materials graphyne, graphdiyne, graphone, and graphane:

review of properties, synthesis, and application in nanotechnology. Nanotechnology, science and applications 2014; 7: 1.

Jiao Y, Du A, Hankel M, Zhu Z, Rudolph V, Smith SC. Graphdiyne: a versatile nanomaterial for electronics and hydrogen purification. Chemical Communications 2011; 47(43): 11843- 11845.

Drogar J, Roknabadi MR, Behdani M, Modarresi M, Kari A. Hydrogen adsorption on the α-graphyne using ab initio calculations. Superlattices and Microstructures 2014; 75: 340-346.

Srinivasu K, Ghosh SK. Graphyne and graphdiyne: promising materials for nanoelectronics and energy storage applications. The Journal of Physical Chemistry C 2012; 116(9): 5951-5956.

Luo G, Zheng Q, Mei WN, Lu J, Nagase S. Structural, electronic, and optical properties of bulk graphdiyne. The Journal of Physical Chemistry C 2013; 117(25): 13072-13079.

Bu H, Zhao M, Zhang H, Wang X, Xi Y, Wang Z. Isoelectronic doping of graphdiyne with boron and nitrogen: stable configurations and band gap modification. The Journal of Physical Chemistry A 2012; 116(15): 3934-3939.

Narita N, Nagai S, Suzuki S, Nakao K. Optimized geometries and electronic structures of graphyne and its family. Physical Review B 1998; 58(16):11009.

Andrew RC, Mapasha RE, Ukpong AM, Chetty N. Mechanical properties of graphene and boronitrene. Physical review B 2012; 85(12): 125428.

Shohany BG, Roknabadi MR, Kompany A. Electrical Investigation of Armchair Graphene-Graphdiyne-Graphene Nanoribbons Heterojunctions. Communications in Theoretical Physics 2016; 65(1): 99.

Long M, Tang L, Wang D, Li Y, Shuai Z. Electronic structure and carrier mobility in graphdiyne sheet and nanoribbons: theoretical predictions. ACS nano 2011; 5(4): 2593-2600.

Malko D, Neiss C, Görling A. Two-dimensional materials with Dirac cones: Graphynes containing heteroatoms. Physical Review B 2012; 86(4): 045443.

Shohany BG, Roknabadi MR, Kompany A. DFT-NEGF simulation of graphene-graphdiyne-graphene resonant tunneling transistor. Computational Materials Science 2018;144: 280-284.

Kang J, Li J, Wu F, Li SS, Xia JB. Elastic, electronic, and optical properties of two-dimensional graphyne sheet. The Journal of Physical Chemistry C 2011; 115(42):20466- 20470.

Perdew JP, Burke K, Ernzerhof M. Phys rev lett 77: 3865. Errata: (1997) Phys Rev Lett., 1996; 77(18): 1396.

Hao H, Zheng X, Jia T, Zeng Z. Room temperature memory device using single-molecule magnets. RSC Advances 2015; 5(67): 54667- 54671.