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Theoretical study of graphyne- γ doped with N atoms: The quest for novel catalytic materials

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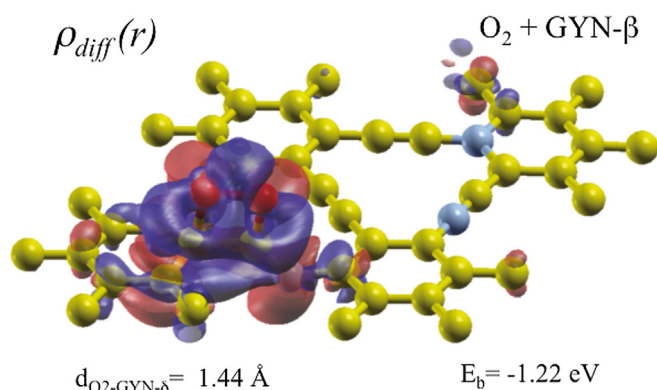
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GRAPHICAL ABSTRACT



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ABSTRACT

In this theoretical work, we present the results from Density Functional Theory (DFT) calculations on novel systems formed by graphyne- γ (GY- γ) with defects, and Nitrogen-doped graphyne (GYN) systems. Systems with vacancy defects present a widening on the band gap. We found that the electronic properties of the GYN family may be tuned, from a semiconducting to a metallic character. This may be due to the presence of Nitrogen atoms (N) in acetylenic linkages. The N-doping was shown to generate thermodynamically stable systems with different electronic properties, which can be further confirmed by *ab initio* Molecular Dynamics simulations. In this work, we also analyzed the chemical stability and reactivity with the following criteria: hardness, chemical potential, and electronic density. The GYN system with defects (GYN-def) presents the lowest-energy of formation and cohesion, indicating that it may correspond to the most energetically stable system. The catalytic character of the series of graphyne systems under study was tested by assessing the capability to adsorb the O_2 molecule on the graphyne substrate. It was discovered that the GYN- β and - δ systems represent models able to achieve O_2 molecular chemisorption onto the surface, due to the modified electronic structure after N-doping. We found activation barriers below 0.70 eV. This addresses that the process might occur spontaneously at room temperature. Such graphyne systems represent potential candidates to be implemented as catalysis in devices such as fuel cell cathode materials.

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1. Introduction

Nowadays, the unique ability of carbon to form different structures is well known [1,2]. In recent years, carbon allotropes have attracted much attention. They have been synthesized and characterized in forms such as the fullerenes [3], carbon nanotubes (CNTs) [4] and graphene (G) [5]. Since it was possible to exfoliate a carbon sheet of graphite [5], G has been the most extensively studied material because of its high versatility on several applications such as energy storage [6], conversion [7–10], and solid-state devices [11]. However, one of the disadvantages of G is the absence of a band gap, this character is a drawback in some applications, such as organic photovoltaic devices (OPVs) [12]. A strategy that has been widely studied to introduce a band gap is through the interaction of metallic atoms, metal clusters, and metallic oxides [6,13–15] and by doping with N-atoms [16]. As an alternative material of two-dimensional (2D) hierarchy, the GY was predicted by Baughman et al. [17] as one of the new carbon allotropes, which has a native band gap. The structure was obtained when acetylenic linkages ($-C\equiv C-$) were introduced between all carbon atoms, between pairs of sp^2 hybridization and among the vertices of the aromatic rings. The presence of acetylene groups indicates that GY can be formed in architectures other than the hexagonal G lattice. Within the three high symmetry geometries reported on GY- (α , β and γ); the GY- α and GY- β are semimetallic, while GY- γ is semiconducting [18]. Due to its electronic structure properties, GY has opened a new field of research in the study of new carbon-based 2D materials for electronic devices [2,19–24]. Li et al. [25] successfully synthesized a graphdiyne (graphyne- γ with diacetylene groups) on a copper substrate. In this context, based on the different methods of synthesis that have been proposed on the design of this material, it is very likely that the synthesis on laboratories may be produced in the coming years [26–30], with extended surfaces, as it has been done with current carbon allotropes. In this context, GY- γ may be used in practical applications, such as those of carbon materials of the same hierarchy.

In this regard, with the aid of *ab initio* calculations, it has been possible to predict some of their electronic structure properties. First-principle calculations have indicated that GY- γ has a natural band gap, in contrast to the null band gap of graphene. Baughman et al. [17] estimated the band gap to be 0.79 eV using the extended Hückel level of theory. Narita et al. [18] obtained a band gap of 0.52 eV using the local spin density approximation (LSDA). Enyashin and Ivanovskii [31] modeled several types of GY systems and reported a band gap of 1.42 eV using density-functional-based tight binding method (DF-TB). Using DFT calculations, different models of GY monolayer systems have been obtained, such as $C_{24}H_{12}$ [32], $C_{66}H_{18}$ [33], $C_{86}H_{22}$ [34] and $C_{162}H_{30}$ [35] with band gaps of 2.20, 4.97, 1.7 and 2.25 eV, respectively. Thus, it is understandable to have different band gap values for the GY- γ , which depend to a large extent on the system size and level of theory used in the calculations.

Theoretical studies have corroborated the structural stability of GY- γ , when it is subjected to a high pressure and temperature [36–38]. Therefore, the study of electronic properties of GY- γ by the substitution with doping-atom impurities has attracted enormous attention in the scientific community since it is a subject of research that has not yet been deeply explored. Omidvar and Mohajeri [39] studied a GY- γ ($C_{66}H_{18}$) substrate, decorated with B and N atoms in the six-membered rings. They reported favorable adsorption energy with the CO molecule. Yun et al. [40] based on first-principle calculations, studied the effect of doping with B and Al atoms on the GY- γ surface with interesting magnetic properties. Liu et al. [41] performed DFT calculations, and they discovered stable structures of GY- γ doped with a Ge atom, reporting a band gap of 0.965 eV. Liang et al. [42] investigated BN-substituted graphyne nanoribbons (NRs) using DFT. They found structural stability using Molecular Dynamics (MD) calculations at temperatures of 600 K. Felegari and Hamedani [34] explored the influence of adatoms such as B, N, and Si on the activity of graphyne towards phosgene

adsorption by DFT calculations. Asadpour et al. [43] studied the mechanical properties of GY- γ -BN sheet, where carbon atoms were substituted with N and B atoms in order to form the network. Its corresponding bulk modulus value is 107.451 N/m. Ruiz-Puigdollers and Gamallo [44] carried out a DFT study on the role of N- and B-doping on the structure of doped GY- γ . It was found that the addition of a dopant of 1–3 atoms per unit cell, changes the character from a semiconductor to a metal system. Bhattacharya et al. [45] performed first principle calculations, where it was studied the possibility of tuning the optical properties of GY- γ by systematic BN doping at different sites. The results showed that the doped-systems exhibited a strong absorption peak in wide UV region. Bhattacharya and Sarkar [46] explored the effect of B and N doping in different concentrations for the formation of six and twelve membered rings. They reported that the B- or N-doped GY- γ showed a strong absorption in the UV region. The latter may be due to a direct band gap. Kang and Lee [47] studied the oxygen reduction reaction by the interaction of O_2 and H_2 molecules on the surface of GY- γ . Cortés-Arriaga [48] performed a DFT study on the GY- γ ($C_{86}H_{22}$) system and its interaction with polycyclic aromatic hydrocarbons, the results showed a strong electrostatic character in the interaction of these systems. Chen et al. [49] performed first-principle calculations based on DFT/GGA. They studied a GY- γ ($C_{66}H_{18}$) substrate, which was single-doped with B and N, exhibiting a possible catalytic activity in the process of oxygen reduction reaction as a cathode material. Ma et al. [50] performed first-principles calculations to systematically study the stable configuration and its corresponding electronic structures of hydrogenated GY- γ , the results indicated that the most stable configuration is the one with sp^3 hybridization on the carbon atoms. Ahmadi et al. [51] analyzed the mechanical properties of Na and Pt decorated arrays of 2D structures (GY- γ -BN sheet). Peyghan et al. [52] studied the electronic sensitivity of pristine, Ni- and Si-doped GY- γ ($C_{86}H_{22}$) to ammonia (NH_3) molecule. They reported charge transfer from the NH_3 to the $C_{86}H_{22}$ system. Therefore, the diversity of theoretical works have predicted stability and high reactivity of GY- γ substrates. However, the application to catalysis is only limited to systems formed by the addition of metal atoms [53,54].

The porosity of the GY- γ is a potential feature to effectively yield gas adsorption. Due to the intrinsic electronic properties, this material exhibits other potential applications such as membranes to separate molecules, substrates as single-atom catalysts [53,54], hydrogen storage [55] media nanocapacitors [56], nanostructures for application in optoelectronics [57–60] and anode materials in lithium-ion batteries [61], as well as a cathode material for fuel cells (oxygen reduction reaction) [47].

Recently, theoretical and experimental works have been performed with three different N-doped graphene systems: (i) pyridinic (ii) pyrrolic and (3) graphitic [16,20]. Based on the previous ideas, some important questions emerge: (1) what is the influence of a defect point of the N-doped GY- γ systems after considering the correct valence in the unit cell? (2) Is it possible to obtain a vacancy defect in the structure of the GY- γ ? (3) Is it possible to form a surface of GY- γ with a pyridine-type defect? (4) The effect of defect points can favor the interaction with O_2 molecules, as a catalyst on the substrate?

The objectives of this work are: (1) To modify the intrinsic properties of the GY- γ through doping with N-atoms (GYN) forming new surfaces with defect points. (2) To evaluate the stability of the substrate by incorporating a vacancy defect in the unit cell of GY- γ , and also by adding two N-atoms into the unit cell (forming a pyridine-like-doped defect) (3) To study the interaction of O_2 molecules with the novel systems, as a support material in a possible catalytic process within the framework of fuel cells applications.

2. Computational details

DFT was used within the general gradient approximation (GGA) [62] and the Quantum ESPRESSO code [63]. For the exchange-

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