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Investigation of NH_3 adsorption behavior on graphdiyne nanosheet and nanotubes: A first-principles study

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ABSTRACT

The electronic properties of zigzag graphdiyne nanosheet and nanotube are investigated using first-principles studies. The adsorption behavior of ammonia molecules on graphdiyne nanosheet are studied using density functional theory. The density-of-states spectrum gives insights on transfer of charge upon interaction of NH_3 gas molecules on graphdiyne nanostructures. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap vary upon interaction with ammonia gas molecules on graphdiyne nanostructure. The adsorption properties of NH_3 molecules on graphdiyne nanostructures are studied in terms of natural bond orbital, HOMO-LUMO gap, adsorption energy and average energy gap variation. The structural stability of graphdiyne base material is confirmed with the help of formation energy. A shorter recovery time is observed in graphdiyne sensor material during adsorption and desorption process of ammonia molecules. The most favorable adsorption sites of NH_3 on graphdiyne are investigated in an atomistic level. The interaction of NH_3 on graphdiyne nanosheet is observed to be more prominent rather than graphdiyne nanotube. The findings of the present study support the use of zigzag graphdiyne nanosheets for the detection of ammonia molecules.

1. Introduction

Carbon is one of the abundant elements, which forms different types of allotropes. It possesses different hybridized states such as sp., sp^2 & sp^3. Moreover, the element carbon possesses different bonding states and capable to bond itself or to other species. The well-known allotropes of carbon include carbon nanotubes [1,2], graphene [3], nanotubes [4], fullerenes [5] and nanobuds [6]. The synthesis and discovery of novel carbon allotropes with new bonding characteristics, high stability, unique properties and applications will be of current interest among materials scientists for synthesis and processing [1]. Furthermore, the single-atomic layer of carbon elements forms honeycomb lattice [7], graphene is the strongest materials among other carbon allotropes, which have been confirmed with Young's modulus and stiffness studies [8]. Owing to the high saturation velocity and carrier mobility, graphene may be a good candidate for ultrahigh-speed radio frequency electronics [9].

Recently, the novel form of carbon allotropes (non-natural) compared to graphene/graphite, graphdiyne and graphyne is in focus among researchers due to their fascinating optical, electronic and mechanical properties with unique structures [10]. Moreover, these materials may be a promising base material for energy storage and nanoelectronics applications [11]. The structure of graphdiyne slightly differs from graphyne, which contains one additional acetylenic linkage in all individual unit cells when compared to graphyne that has only one acetylenic linkage. Due to the two acetylenic linkages in graphdiyne, the carbon chain length becomes twice as that of graphyne allotropes and linking with hexagonal rings [12]. Graphdiyne is a softer material rather than graphene and graphyne with a thickness value of 0.320 nm [12]. Haley et al. [13] predicted graphdiyne first in 1997, from first-principles study using the VASP package. Pei et al. [14] reported that the energy band gap of graphdiyne as 0.47–1.12 eV, which can be tuned upon applying strain. Experimentally, different techniques are utilized for synthesis of graphdiyne on various substrates [15,16]. Recently, Li et al. [16] have successfully synthesized the large-area graphdiyne film through cross-coupling reaction on copper surface in 2010 and reported that the graphdiyne film with porosity shows effective semiconducting properties. Furthermore, graphdiyne has been investigated in more potential applications, including lithium-ion battery [17], spintronics [18], transistors [19], photocatalysis [20] and metal-free catalysis [21]. In addition, graphdiyne is a good candidate for diffusion of CO, H_2 and CH_4, which is confirmed by density functional theory technique [22]. Pari et al. [23] proposed the structural stability and electronic properties of both zigzag and armchair graphdiyne carbon-nanotubes using DFT method. Chen et al. [24] predicted the graphdiyne as a good candidate for sensing the amino acid molecules. The state-of-the-art in design and development of graphdiyne as chemical nanosensor is of the current interest among scientific community.

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Previously, we have proposed the electronic and adsorption behavior of different toxic gas/vapor molecules on two-dimensional nanomaterials [25–28]. The present study is an attempt to investigate the interaction of gas/vapor on graphdiyne base material for chemical nanosensor. In the present study, the structural stability, electronic properties and adsorption behavior of ammonia (NH_3) molecules on both zigzag nanosheet and nanotube form of graphdiynes are investigated for the first time and results are discussed.

2. Computation methods

The structural relaxation and electronic properties of zigzag graphdiyne nanosheets (ZGNS) and zigzag graphdiyne nanotubes (ZGNR) were studied using the Gaussian 09 package [29]. During the relaxation process, hybrid Perdew-Burke-Ernzherof (PBE) generalized gradient approximation [30] with suitable basis set double-ζ polarized 6–31 g (d) [31] is used. We optimized the pristine graphdiyne nanosheet and nanotube with various exchange-correlation (XC) functional as shown in Table 1 using 6–31 g (d) basis set. The different exchange-correlation functional such as B1LYP, M-06, B3LYP, PBE and X3LYP functional has been utilized to compute the HOMO-LUMO gap with various percentages of Hartree-Fock (HF) exchange (X) in the present work [32–36]. Furthermore, the HOMO-LUMO gap value for graphdiyne nanostructure gradually increases with the increase of HF exchange functional, which is in good agreement with previously reported work [37]. After being optimized, force constant is calculated with the similar basis set utilizing the Gaussian 09 package. The interactions of ammonia on both ZGNS and ZGNR are also investigated with this package. Fig. 1 (a) and (b) represents the optimized ZGNS and ZGNR with applied periodic boundary conditions respectively [38]. To study the electronic properties and structural stability of graphdiyne allotropes, selection of suitable basis set is a significant criterion. Zhang et al. [39] have selected the similar basis set 6–31 g (d) to investigate graphdiyne nanostructure. Furthermore, the PBE/6–31 g (d) combination provides the effective output with pseudo potential approximation [40,41]. The highest occupied molecular orbital (HOMO) & lowest unoccupied molecular orbital (LUMO) including density of states (DOS) spectrum were computed using Gauss Sum 3.0 package [42]. While optimizing the graphdiyne nanostructure, self-consistent force and energy convergence limit is adjusted in the order of 0.002 eV/Å and 10^{-6} eV respectively, while relaxing zigzag graphdiyne nanostructures.

3. Results and discussions

3.1. Geometric relaxation of zigzag graphdiyne nanosheet and nanotube structures

The optimized structure of zigzag graphdiyne nanosheet and nanotube are shown in Fig. 1 (a) and (b) respectively. In the relaxed unit cell, the calculated lattice parameters a = b = 9.41 Å, which perfectly matches with the reported work [43]. Moreover, like graphyne, the two- dimensional graphdiyne possess two kinds of pores: one is the quasi-triangular pore on acetylenic linkers; the other is the hexagonal pore on six-member carbon ring [44]. The bond length of C—C on graphdiyne nanosheet and nanotube were found to be 1.42 Å and 1.41 Å respectively. In order to build the graphdiyne nanotube, initially the above mentioned zigzag graphdiyne nanosheet were built. Next wrapping-up the graphdiyne nanosheet towards the direction of chiral vector, the graphdiyne nanotubes were built by joining its terminated end as shown in Fig. 1 (b). Furthermore, like carbon nanotube (CNT), graphdiyne nanotube has two types of edge structures, namely armchair and zigzag edges. Based on the proposed work, Pari et al. [23] demonstrated the structural properties of zigzag and armchair graphdiyne nanotubes. In this reported work, the authors studied the chiral angle and chiral vector for zigzag and armchair graphdiyne nanotubes. The present work is highly related and validated with the previously reported work of Pari et al. for building zigzag graphdiyne nanotubes. The main concentration of the present work is to calculate and study the formation energy, HO-molecular orbital and LU-molecular orbital gap (HLG), electron density and density of states spectrum of zigzag graphdiyne nanosheet and nanotubes in order to study the structural stability and electronic properties of the material. The atomic position coordinates for both zigzag graphdiyne nanosheet and nanotube are available in electronic supplementary information (ESI).

Table 1
HOMO-LUMO gap of graphdiyne nanosheet and nanotube with various percentage of Hartree-Fock exchange.

Basis set	Graphdiyne nanosheet E_g (eV)	Graphdiyne nanotube E_g (eV)	Exchange correlation functional	Percentage of HF exchange (X)
M-06	0.36	0.51	Hybrid-metal-GGA	27
B1LYP	0.29	0.46	Hybrid GGA	25
PBE0	0.28	0.44	Hybrid GGA	25
X3LYP	0.17	0.35	Hybrid GGA	21.8
B3LYP	0.12	0.29	Hybrid GGA	20

3.2. Structural stability and electronic properties of zigzag graphdiyne nanostructures

The structural stability of zigzag graphdiyne nanosheet and nanotube can be described in terms of formation energy [45,46] as expressed in Eq. (1):

$$E_{form} = 1/n\,[E(GDN) - n\,E(C)] \quad (1)$$

where E (GDN) represents the total energy of graphdiyne nanostructure (nanosheet or nanotube). E(C) refers the energy of the isolated C atom. 'n' is the total number of carbon atoms in graphdiyne nanostructures. The formation energies of ZGNS and ZGNR are tabulated in Table 2. The formation energy of zigzag graphdiyne nanosheet and nanotube are found to be −7.32 and −7.37 eV respectively, which proves the stability of graphdiyne nanostructures. The dipole moment (DM) provides the perception on distribution of charge along graphdiyne nanostructures. The DM value of both zigzag graphdiyne nanosheet and nanotube is observed to be zero Debye, which reveals the even charge distribution on graphdiyne nanostructures and enhance the adsorption properties of NH_3 on the base system. Moreover, the even charge distribution of graphdiyne results in the free transfer of electrons between graphdiyne material and NH_3 gas molecules, which is more suitable for chemical sensor. C_S group is noticed in graphdiyne nanosheet, which exhibits both mirror plane and identity operation; whereas graphdiyne nanotube exhibits C_1 point group, which adopt only identity operation without symmetry.

The electronic properties of graphdiyne nanosheet and nanotube are investigated in terms of DOS spectrum and HO-molecular orbitals & LU-molecular orbitals [47,48]. The HO- and LU-molecular orbital energy gap of isolated zigzag graphdiyne nanosheet and nanotube is observed to be 0.28 and 0.44 eV respectively, which is in good agreement with proposed work [14]. Furthermore, the adsorption of NH_3 gas leads to increase in the HOMO-LUMO gap in graphdiyne nanosheet but not in the case of graphdiyne nanotube owing to the morphological effect. Hence, the property of different morphological systems leads to various applications of graphdiyne. From the first-principles calculations, the peak maximum arose on HOMO and LUMO level owing to the overlapping of molecular orbitals between carbon atoms in graphdiyne nanostructures in different energy intervals. The density-of-states (DOS) spectrum gives the perception of charge localization in different energy intervals across graphdiyne nanosheet. The visualization of HOMO-LUMO gap and DOS spectrum of graphdiyne nanosheet and nanotube is shown in Fig. 2(a) & (b) respectively. From the observation of