

Comparative Analysis of Hydrogen Molecule Interaction with B-Au and N-Au Co-Doped Graphene Nanoribbons: DFT Insights

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Abstract

In the present study, B and N atoms are co-doped with Au atom in graphene nanoribbons and has been analysed for hydrogen molecule interaction with the aid of Density Functional Theory. A comparative analysis is carried out between N-AuG and B-AuG substrate towards H₂ molecule. The structural as well as electronic properties of the optimized structures have been studied. Different theoretical parameters which include adsorption energy, charge redistribution, and bandgap analysis have been computed to determine the effectiveness of substrate.

Keywords: Dft; Co-Doped; Gnrs; B-Aug; N-Aug.

1. Introduction

With the development of a global hydrogen economy, it is evident that the scope of hydrogen use would expand and disperse. The challenge of hydrogen-based technology is particularly significant as it is combustible over a broad array of concentrations (4-75%) in the air at a typical atmospheric temperature [1, 2]. There is a critical need for effective and economical hydrogen gas sensing materials to benefit from its advantages of operating as a clean energy carrier along with shifting to the hydrogen economy. Sensors like these are needed whenever hydrogen gas is generated or used, especially to assure the safety of hydrogen gas fuelling stations [3]. In the fabrication of gas sensors, the selection of sensing material is the primary step. Different materials including conducting polymer, semiconducting metal-oxide, and carbon nanomaterials have been reported recently for the development of hydrogen gas sensors [4, 5]. Graphene being a one-atom-thick sheet of carbon atoms has been recognized as having the potential to unleash a new wave of revolutionary technological innovation since its discovery in 2004. Monolayer graphene has been viewed as an "academic" substance for a long period because it has been illustrated that the semi-metallic phase is fragile in 2D [6]. It was

first discovered by mechanical exfoliation of graphite by Andre Geim and Konstantin Novoselov with tape which involves isolation of a single layer of graphite with the thickness of one atom [7]. The interest of researchers worldwide in graphene stems mostly from the multifunctionality of this 2D-atomic crystal, which combines unusual features. The σ orbitals contribute to the mechanical stability of graphene [8]. The electrical characteristics of graphene, alternately, are attributable to the delocalized π bond. The physical as well as chemical characteristics of graphene are influenced by the pz orbital. It has been reported that electronic mobility in graphene is extremely high, with theoretical potential limits of 250,000 cm²/Vs [9]. The other distinguishing characteristics of graphene include high thermal conductivity (~5000W/mK) as structural holes let phonons pass through unhindered; huge specific surface area (2630m²/g); large electrical conductivity which makes it appealing to be utilized in a broad array of applications like field effect transistors, strain sensors, hydrogen sensors and storage devices, electrochemical systems [10]. However, the usage of graphene is challenging in specific applications as it is a zero-band gap material. It's

primarily because electrons act like massless relativistic particles. In light of this, several efforts have been made to change its band gap and tweak its electrical properties. One of the approaches to alter the band gap of graphene is the finite termination of graphene width resulting in ribbon-like structures, referred to as graphene nanoribbons (GNR). The main determinants of electronic properties in finite dimensions are shape and size, electronic correlations, and corresponding boundary conditions. This approach provides required control over the band gap depending upon the width of GNR. The GNR band structure is significantly influenced by both width and direction, which results in a variety of electrical properties [11]. To improve the device utility of GNRs, a variety of chemical modification strategies have been developed. The electronic characteristics of graphene and GNRs can be altered by structural changes such as vacancy defects, bond twisting, or the insertion of foreign atoms i.e. dopants. By altering the band gap, the insertion of such heteroatoms frequently modifies the electronic characteristics. Transition metal doping is subject of much research due to their favorable optical, catalytic, and electronic abilities in increasing the gas sensing efficacy of graphene-based gas sensors [12]. The modeling of gas sensors employing graphene nanoribbons as well as other nanomaterials, on the other hand, has been the subject of several theoretical and modeling investigations. Some of this research used quite comparable modeling techniques, introducing fitting parameters to match the proposed models to experimental data [13, 14]. In the present analysis, the structural and electronic properties of B and N atoms doped with Au atom in graphene nanoribbons (GNRs) have been examined followed by determination of hydrogen adsorption properties.

2. Computational Details

The optimized GNR consist of 42 carbon atoms terminated with 16 hydrogen atoms for neutralization of dangling bonds. This configuration has been utilized in previously

reported studies [15, 16, 17]. The DFT computations were performed using B3LYP calculation method and LANL2DZ basis set in GAUSSIAN 09 software. Frequency calculations were done to ensure stability and no imaginary frequency. The adsorption energy is calculated using the following equation:

$$\Delta E_{\text{ads(H}_2\text{-DG)}} = E_{\text{H}_2\text{-DG}} - (E_{\text{DG}} + E_{\text{H}_2}) \quad (1)$$

where $E_{\text{H}_2\text{-DG}}$ and E_{DG} represents the energies of optimized geometries of doped GNR with and without hydrogen molecule, and E_{H_2} corresponds to the energy of optimized geometry for hydrogen molecule, respectively. Moreover, the observations of LUMO (Lowest Unoccupied Molecular Orbital) energy, HOMO (Highest Occupied Molecular Orbital) energy are based on the aforesaid basis set. The band gap (E_g) is calculated from the following equation:

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (2)$$

3. Results and Discussion

3.1. Adsorption Energy and Bonding Distance

All the computations of chosen geometry were accomplished using the above-mentioned basis set with the help of density of functional theory. One carbon atom in pure GNR was replaced by Au atom. As Au atom has size larger in comparison to the carbon atom, it protrudes out of the surface and dangling bonds are formed making the site more reactive. The hydrogen molecule interacts with Au doped GNR (AuG) more effectively as compared to the pristine GNR. In order to enhance H_2 interaction, AuG is further co-doped with B and N atoms. A comparative analysis is done between N-AuG and B-AuG for H_2 interaction.

Table 1 Adsorption Energies of the Substrates

Substrate	E_{ads} (eV)	d (Å)	$d_{\text{H-H}}$ (Å)
Au-G	-0.29	1.99	0.77
B-AuG	-0.06	2.54	0.75
N-AuG	-0.39	1.83	0.81

The adsorption energies and bonding distances for the optimized substrates revealed the N-AuG

substrate is better than B-AuG substrate for H₂ molecule interaction as nitrogen is an electronegative atom in Table 1 and Figure 1.

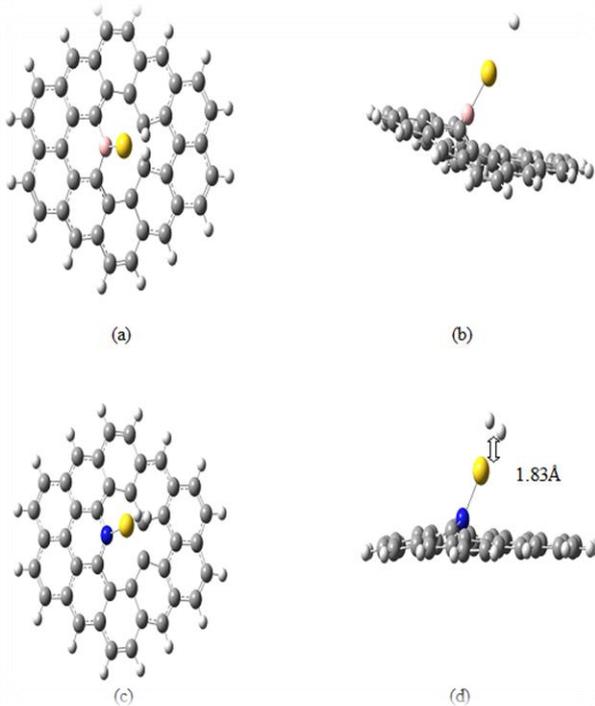


Figure 1 Hydrogen Interaction with B-AuG and N-AuG

3.2. Bandgap Analysis

It is an imperative parameter to determine the gas sensing capability of the substrate. Charge transfer is followed by changes in bandgap which results in increase or decrease in conductivity of material. As H₂ is reducing in nature, there is decrease in conductivity and hence increased bandgap values after H₂ adsorption. The band gap values have been determined in accordance with eq. (2) i.e. HOMO-LUMO gap and mentioned in the following table 2.

Table 2 Band Gap

Substrate	E _g (eV)
Au-G	1.170
H ₂ -AuG	2.135
B-AuG	2.593
H ₂ -B-AuG	2.677
N-AuG	1.468
H ₂ -N-AuG	2.355

Conclusions

From the above research work carried out, we conclude that Transition metal doping Because of its catalytic activity, Au in graphene improved H₂ contact with the substrate. Because of the enormous size of the Au atom, the geometry of Au-G is deformed. Since both H₂ and Au are electron donors, hydrogen adsorption in N-AuG (-0.39eV) substrate is better than in B-AuG (-0.06eV) substrate because the nitrogen atom connected has an electronegative character that allows it to acquire electrons and boost H₂ adsorption efficiency.

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