

Enhancement of the surface reactivity of zigzag boron nitride nanoribbons by chlorine gas decoration: A computational study

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ABSTRACT

In this study, we explored the field emission and chlorine sensing mechanisms of zigzag boron nitride nanoribbons (ZBNNRs). First principle calculations were used to investigate the surface reactivity of ZBNNRs within the framework of the density functional theory based on the local density approximation and generalized gradient approximation. Six different possibilities were considered for chlorine-gas termination and adsorption on ZBNNRs. The band gap of the ZBNNRs decreased monotonically as the ribbon width increased. The charges on the functional groups and corresponding bond lengths, i.e., B(N)-X and X-X (Cl-Cl), were dependent on the adsorption sites (B or N edge) and the types of functional groups, but independent of the ribbon width. Chlorine gas (Cl₂) induced electrons into the conduction band and their consequent electronic states over the Fermi level enhanced the electrical conductivity. Transmission spectra demonstrated the spin-dependent electron tunneling from the valence band to the conduction band. Charge density analysis indicated the charge trapping behavior of the ZBNNRs. Cl₂ introduced excess negative charges onto the active surfaces of the ZBNNRs to enhance their surface reactivity. Therefore, Cl₂-decorated ZBNNRs can be employed as Cl₂ sensors and they may also be useful in field emission applications.

1. Introduction

The latest development of graphene is attracting much attention because of its excellent characteristics in terms of the electronic, electrochemical, thermal, and mechanical properties, which make it a promising candidate for use in various technological applications [1–4]. Boron nitride is also a well-known ceramic material with excellent properties, such as low density, a high melting point, excellent thermal conductivity, high dielectric strength, and good electrochemical resistance in both hazardous and moist environments [5,6]. Boron (2p¹) and nitrogen (2p³) are neighboring elements to carbon, and the electronic structure of boron nitride is identical to that of carbon (2s²2p²) [6], which also demonstrates why their structural polymorphs are analogous to carbon polymorphs [7]. Hexagonal boron nitride (h-BN) comprises boron and nitrogen atoms in a honeycomb arrangement with an sp² hybridized two-dimensional structure [8]. h-BN has interesting characteristics including a large surface area, lubricating nature, wide band gap, very low dimensional porosity, high anisotropy, excellent thermal and optical properties, chemical inertness, light emission in the deep ultraviolet region, and negative electron affinity (NEA) [8–11]. Boron nitride nanoribbons (BNNRs) have been synthesized successfully

with several methods and employed in different technological applications [12–14]. A one-dimensional thick strip is carved out of two-dimensional h-BN to form BNNRs [15]. According to the earlier convention used for graphene nanoribbons, BNNRs are classified based on the number of zigzag chains or lines over the ribbon width, which are represented as N_z-ZBNNR. In contrast to armchair structures, the number of dimer lines over the width of the BNNRs is denoted as N_A-ABNNR [15,16].

In general, nanoribbons comprise vacancies, unsaturated bonds along both edges of the ribbon, and dangling bonds, where their linear combinations lead to eigenstates in the vicinity of the Fermi level. Both edges are the only active sites for the chemical modification of nanoribbons [16,17]. Recently, several theoretical studies have investigated BN structures with different morphologies. Mirzaei et al. studied the effects of oxygen termination and sulfur doping on the electronic structure, quadrupole coupling constants, and bond lengths of zigzag BN nanotubes [18–22]. Loh et al. reported the enhancement of NEA when a boron nitride nanofilm was exposed to hydrogen [23]. Wu et al. described the effects of chemical decoration using various functional groups on the band gap of ZBNNRs [24]. The chlorine (Cl) sensing properties of ZBNNRs and negative differential resistance in bare-

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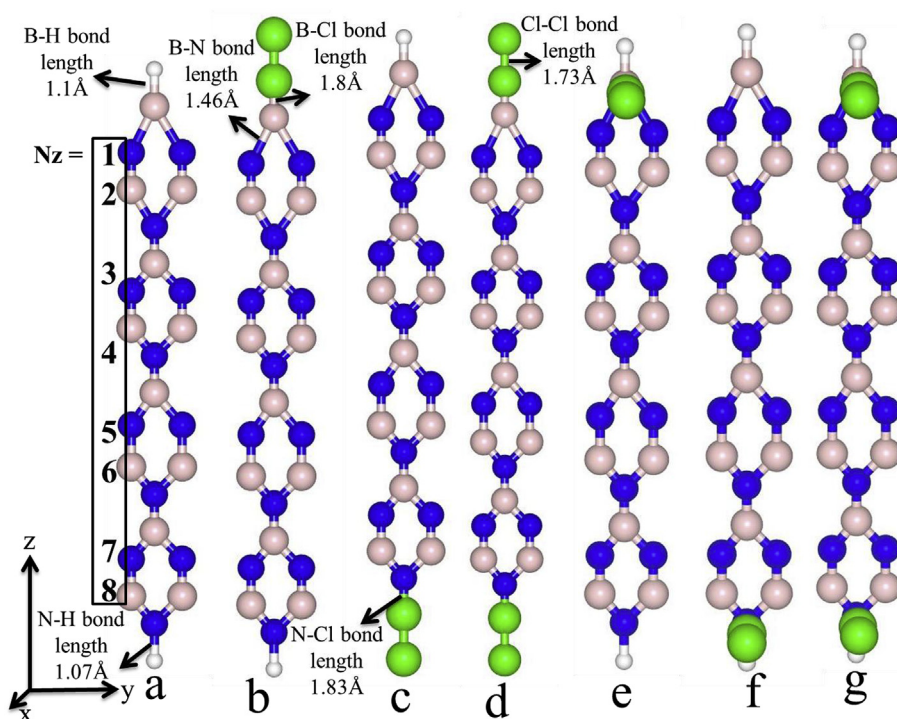


Fig. 1. Schematic of various ZBNNR configurations: (a) ZBNNR_{2H}, (b) ZBNNR_{Cl₂B}, (c) ZBNNR_{Cl₂N}, (d) ZBNNR_{Cl₂B-Cl₂N}, (e) ZBNNR_{AdCl₂B}, (f) ZBNNR_{AdCl₂N}, and (g) ZBNNR_{AdCl₂B-AdCl₂N} (blue, brown, white, and green spheres are N, B, H, and Cl, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

ZBNNRs were investigated by Srivastava et al. [25]. However, to the best of our knowledge, there have been no previous studies of the effects of Cl₂ decoration on the surface reactivity of ZBNNRs.

Therefore in the present study, we investigated whether Cl₂ decoration can change the electronic properties, transport properties, and surface reactivity of single edge Cl₂-terminated ZBNNRs (ZBNNR_{Cl₂B} and ZBNNR_{Cl₂N}), both edge Cl₂-terminated ZBNNRs (ZBNNR_{Cl₂B-Cl₂N}), single edge Cl₂-adsorbed on ZBNNRs (ZBNNR_{AdCl₂B} and ZBNNR_{AdCl₂N}), and both edge Cl₂-adsorbed on ZBNNRs (ZBNNR_{AdCl₂B-AdCl₂N}). The various ZBNNR configurations are shown in Fig. 1. It should be noted that two layers of Cl₂ adsorption are possible on ribbons, where adsorption may occur on the upper surface of the ribbon or on the opposite surface of the ribbon (Fig. S1). However, in the case of termination, two layers cover the two edges of the ribbon (Fig. 1(d)). We conducted calculations to determine the potential of band gap engineering for ZBNNRs with Cl₂. Electronegativity (EN) has a considerable impact on charge distribution analysis so it is useful to know the relevant value. The EN values for chlorine (Cl), nitrogen (N), hydrogen (H), and boron (B) are 3.16, 3.04, 2.2, and 2.04, respectively [24].

2. Computational details

To investigate the electronic, transport, and charge density properties of Cl₂-decorated ZBNNRs, we conducted first principles calculations based on the two exchange-correlations comprising the local density approximation (LDA) and generalized gradient approximation (GGA) within the framework of density functional theory (DFT), as implemented in the atomistic tool kit-virtual nano lab (ATK-VNL) computational package [26]. LDA was applied as proposed by Perdew and Zunger [27]. GGA in the Perdew–Burke–Ernzerhof form was employed as the exchange-correlation [28]. All the configurations of the ZBNNR model were considered within the supercell and they were separated by 10 Å to avoid inter-ribbon interactions. To optimize the geometry, we used LDA and GGA as exchange-correlations, with the double- ξ basis set to solve the Kohn–Sham equations under these exchange-correlations, 100 Rydberg as the density mesh cut-off energy of the expanded wave function, a force tolerance of 0.05 eV/Å, stress of 0.01 GPa, step size of 0.2 Å, the fast Fourier transform as the Poisson

solver for density measurement, the limited Broyden–Fletcher–Goldfarb–Shanno method for optimization based on 200 iterations, and the Pulay mixer algorithm. Using the Monkhorst–Pack grid, k-points sampling was set to $1 \times 1 \times 100$ in the Brillouin zone along the x, y, and z directions, respectively. The periodicity of the ribbon was maintained along the z-axis. To calculate the band structure (BS), we selected 20 points per segment and considered all of the bands above the Fermi level.

For the density of state (DOS) calculations, the spin up and down components were calculated with respect to 8×8 grid points and an energy range of -10 to $+10$ eV. The transport properties were investigated according to the Wolfsberg weighting scheme using the extended Hückel calculator without biasing. In the extended Hückel calculator, we selected the Hückel basis set with self-consistent calculations and an energy range of -8 to $+8$ eV. Recursion was used for the self-energy calculator. The spin up and down components were calculated with respect to 8×8 k-points sampled in the x and y directions, respectively, which were periodic in nature. The ZBNNR along the z-axis was considered as the central region, which was finite and non-periodic along the transport direction.

All of the configurations were optimized without any constraints until the force on each atom was less than 0.01 eV/Å. After complete optimization under both LDA and GGA, the bond lengths of B–N, B–H, and N–H were 1.46, 1.06, and 1.1 Å, respectively, which are highly consistent with the previously reported values (1.43, 1.02, and 1.20 Å) [15,24]. We calculated the total energies with respect to the equilibrium (optimized) states of the configurations considered. The binding energies were calculated using equation (1):

$$E_B = E_T - E_{\text{bare}} - n E_i, \quad (1)$$

where E_T is the total energy of the ZBNNR with impurity atoms (H and Cl₂), E_{bare} is the total energy of the bare ZBNNR, n is the number of impurity atoms, and E_i is the total energy of an isolated impurity atom [17].

The termination/adsorption energies of impurities (H and Cl₂) were calculated using equation (2):

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