Selectivity of a Graphene Nanoribbon-Based Trinitrotoluene Detector: A Computational Assessment

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ABSTRACT: A computational study investigating the suitability of zigzag graphene nanoribbons to serve as selective chemical detectors for trinitrotoluene is presented. Using lithium adatoms as surface anchoring sites, we find that chemisorption of different chemical precursors serving in the trinitrotoluene synthesis process induces unique and distinguishable fingerprints on the electronic structure of the underlying nanoribbon. Furthermore, mixed adsorption of trinitrotoluene and its various chemical precursors may allow the determination of the specific synthesis route used to produce this commonly used explosive material. The understanding of the contaminant adsorption process gained in this study suggests that lithium-decorated graphene nanoribbons may serve as selective chemical detectors.

INTRODUCTION

In recent years, increased security and safety considerations have raised interest in the selective and sensitive detection of nitro-aromatic explosives, such as trinitrotoluene (TNT). This has led to the development of a number of new analytical methods for TNT detection including fluorescence, ion mobility spectroscopy, mass spectrometry, gas chromatography, and surface plasmon resonance. Apart from sensitivity, one of the fundamental reliability requirements from any such detection technology is the ability to selectively detect molecules with minimal occurrence of false alarms (positive and/or negative).

Low-dimensional nanomaterials have long been considered as promising candidates to serve as highly sensitive chemical detectors. Specifically, the ultimate detection sensitivity has recently been achieved with graphene, where room-temperature single-molecule detection has been experimentally demonstrated. With this respect, graphene nanoribbons (GNRs) offer a wealth of unique physical characteristics including tunable bandgaps that may enhance the robustness of graphene-based detection devices. Their, in principle, infinite surface-to-volume ratio allows for efficient adsorption of gas molecules on their surface and edges. The influence of such adsorption events on the electronic properties of the underlying ribbon can, in turn, be harnessed to achieve sensitive detection capabilities.

A major challenge that needs to be overcome when considering the utilization of GNRs as chemical detectors for nitro-aromatic explosives and their chemical precursors is the inert nature of their surface. This problem may be addressed via chemisorption at their reactive edges or on lattice defects such as Stone–Wales defects and atomic vacancies. Alternatively, strongly binding metal atoms may serve as anchoring sites for the chemisorption of otherwise weakly binding molecules. Lithium has been identified as the strongest graphene binding alkali-metal atom. This has been attributed to its small atomic radius allowing for the partially positively charged adatom to closely approach the graphene plane, thus enhancing the attractive metal-cation/π interactions. Based on this understanding we have recently proposed using lithium adatoms to anchor aromatic compounds to the surface of GNRs. As a proof of concept, the lithium-mediated adsorption of benzene on GNRs was studied, demonstrating substantial substrate electronic transport response leading to ultrahigh detection sensitivity.

In the present study, we aim to assess the selectivity of the suggested device. To this end, we define TNT to be the target molecule and study the electronic response of lithiated zigzag graphene nanoribbons (ZGNRs) toward the individual adsorption of TNT and several of its molecular precursors, as well as their mixed adsorption schemes. Furthermore, we compare the response of the system toward the adsorption of the target contaminant and its molecular derivatives to the fingerprints of other background molecules, such as water and carbon dioxide. We find that the electronic and spintronic properties of the substrate are sensitive to the specific chemical identity of the adsorbate, thus indicating the potential selectivity of the suggested sensing device under ambient conditions. The recent fabrication of suspended GNRs and synthesis of highly pristine narrow ZGNRs may therefore lead to the realization of ultrasensitive and selective GNR-based chemical detectors.

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METHODS

Our density functional theory (DFT) calculations have been carried out utilizing the Gaussian suite of programs. Spin-polarized calculations have been performed within the screened-exchange hybrid density functional of Heyd, Scuseria, and Ernzerhof (HSE) that has been shown to reproduce experimental optical bandgaps of bulk semiconductors and to describe the physical properties of graphene-based materials with much success. We use the double-$\zeta$ polarized 6-31G** basis set noting that the effects of basis-set superposition errors (BSSEs) in this type of systems have been recently studied in detail and shown to be of minor importance at this level of theory. The effects of inclusion of long-range dispersion interaction corrections on the optimal geometries and calculated band gaps are found to be of minor importance (see Supporting Information) and are hence neglected in the present study.

We annotate the GNR unit-cell by $(N \times M)$, where $N$ stands for the number of zigzag chains along the armchair edge and $M$ for the number of carbon dimer chains along the zigzag edge. Using this notation we choose the $(8 \times 12)$ supercell (see Figure 2(a)) with a single lithium–molecule complex calculated at the doublet spin state. The singlet and triplet states are then obtained by duplicating the unit-cells along the periodic zigzag direction, creating an $(8 \times 24)$ supercell (see Figure 6). For these spin states, we consider two lithium–molecule complexes located on opposite sides of the ZGNR sheet, that is, one above the center of a hexagon of the ZGNR sheet and the other below the center of another hexagon distant from the first one.

For TNT and all its derivatives considered herein, apart from toluene, the doublet spin state was found to be more energetically stable than both the singlet and the triplet states (see Supporting Information). In the case of toluene, the doublet and triplet spin states are nearly energetically degenerate, slightly favoring the triplet configuration. Hence, for all systems involving the adsorption of individual contaminants the doublet spin configuration was considered.

RESULTS AND DISCUSSION

In order to demonstrate the selectivity of the proposed detection device we start by considering its electronic response toward the individual adsorption of the various TNT synthesis intermediates presented in Figure 1. First, we determine the energetically favorable configuration of each molecule by placing their ring center atop the lithium adatom and pointing the methyl side group in four possible directions (along (1), ortho (2), meta (3), and para (4)) with respect to the hydrogenated zigzag edge as shown in Figure 2(a). After full geometry optimization, all contaminants considered presented either ortho or para favorable orientations, with energy differences typically smaller than 0.1 eV/supercell between the different configurations (see Figure 3). Specifically, geometry optimization starting from the ortho orientation was found to yield the most stable adsorption configuration for the toluene, ortho-mononitrotoluene (o-MNT), and 2,6-dinitrotoluene (2,6-DNT) molecules (red bars in Figure 3), whereas the initial para orientation provided the most stable adsorption configurations for the para-mononitrotoluene (p-MNT), 2,4-DNT, and TNT molecules (blue bars in Figure 3). Figure 2(c)–2(h) presents the optimized structures of the most stable adsorption configurations of the various adsorbates considered. As can be seen, the adsorption processes of all but the TNT molecule result in minor bending of the ZGNR surface, with the lithium adatom remaining atop the center of an edge hexagon of the nanoribbon surface and near the center of the molecular ring. Interestingly, the adsorption of the TNT molecule (Figure 2(h)) results in a larger bending of the ZGNR’s surface accompanied by a shift of the lithium adatom to an edge C–C bond bridge site and its binding to one of the TNT nitro groups.

In Figure 4(a), we present the dependence of the bandgap of the $(8 \times 12)$ ZGNR on the adsorption of TNT and its precursor molecules atop the lithium anchoring sites. As can be seen, the spin-polarized bandgaps are quite sensitive to the adsorption process. Upon bare lithium atom adsorption the bandgap degeneracy of the two-spin flavors is lifted, and a nearly half-metallic state is obtained with a considerable reduction of both spin channel bandgaps from 1.04 to 0.04 and 0.45 eV for the $\alpha$ and $\beta$ spin channels, respectively. Further adsorption of the toluene molecule on the lithium anchoring sites results in a large opening of the $\beta$ channel bandgap from 0.45 to 0.80 eV and a smaller increase of the corresponding $\alpha$ channel bandgap from 0.04 to 0.28 eV, thus increasing the $\alpha/\beta$ bandgap split. Upon the nitration of toluene to o-MNT and p-MNT, the $\alpha$ bandgap slightly modifies to 0.27 and 0.29 eV, respectively, and the $\beta$ bandgap increases to 0.90 eV. Further nitration of the MNT to 2,4-DNT (2,6-DNT) increases the $\alpha$ channel bandgap to up to 0.36 eV (0.31 eV) and the $\beta$ bandgap to close to 1.00 eV. Finally, full nitration to TNT increases the $\alpha$ spin bandgap to 0.80 eV and $\beta$ bandgap to 1.09 eV. In order to examine potential false positive effects, we also examine the bandgap changes as a result of the adsorption of water, carbon dioxide, and phenol molecules. As can be seen, the effects of both water and carbon dioxide are mild in comparison with TNT and its derivatives, increasing the $\alpha$ spin bandgap to 0.18 and 0.17 eV, respectively, and the $\beta$ spin bandgap to 0.62 eV. The effect of phenol adsorption on the bandgap resembles that of toluene with somewhat smaller $\beta$ gap values due to the electron-donating nature of the hydroxyl group, increasing the $\alpha$ spin bandgap to 0.28 eV and the $\beta$ spin bandgap to 0.72 eV.

In addition to the dependence of bandgap values on TNT precursor molecules, we also present the shift in Fermi level of both $\alpha$ and $\beta$ spin states, relative to that of the lithium-decorated $(8 \times 12)$ ZGNR in Figure 4(b). As can be seen, the adsorption of toluene results in an increase of 0.25 eV for the $\alpha$ spin state (top panel) and of 0.12 eV for the $\beta$ spin state.

![Figure 1](image-url) Three-step chemical synthesis of 2,4,6-trinitrotoluene via the nitration of toluene: (i) toluene is nitrated with a mixture of sulfuric acid and nitric acid to produce mononitrotoluene (MNT); (ii) the MNT is separated and then nitritated to dinitrotoluene (DNT); and (iii) in the final step, the DNT is nitritated to trinitrotoluene using an anhydrous mixture of nitric acid and oleum. Gray, white, blue, and red spheres represent carbon, hydrogen, nitrogen, and oxygen atoms, respectively. Red and blue arrows represent two possible TNT synthesis routes.
Upon nitration of toluene to o-MNT (p-MNT), the value of Fermi level decreases by $-0.03 \ (-0.04)$ eV for the $\alpha$ spin state and $-0.15 \ (-0.17)$ eV for the $\beta$ spin state relative to that of the lithium-decorated system. We attribute this to the fact that nitrated aromatic molecules are electron-withdrawing compounds. Hence, when adsorbed on the lithium-anchoring sites they serve to reduce the charge transfer from the lithium atoms to the ZGNR resulting in lower electronic doping. Accordingly, further nitration to 2,4-DNT (2,6-DNT) enhances the $\alpha$ and $\beta$ Fermi level decrease to $-0.23 \ (-0.24)$ eV and $-0.35 \ (-0.34)$ eV, respectively. Finally, upon full nitration to TNT with three electron-withdrawing groups, the Fermi level is shifted to $-0.66$ eV and $-0.55$ eV for the $\alpha$ and $\beta$ spin state, respectively. Importantly, water, carbon dioxide, and phenol molecular adsorption induces qualitatively different Fermi level shifts with respect to all TNT derivatives considered, apart from its toluene precursor. These results clearly demonstrate the selectivity of the proposed setup, where different nitrated aromatic molecules are expected to have unique fingerprints in the electronic structure and transport characteristics of the system that are distinguishable from those of background molecules abundant in the ambient environment.

In order to better understand the above-mentioned bandgap dependence on the chemical identity of the contaminant, we provide in Figure 5 a comparison of the spin-resolved total density of states (DOS) and its projection (PDOS) on the various chemisorbed (8 × 12) ZGNRs considered. Focusing first on the two upper rows, the adsorption of a bare lithium atom on the surface of the pristine ZGNR influences the low-energy DOS of both spin channels, significantly reducing the corresponding bandgaps as discussed above.

Figure 2. HSE/6-31G** optimized structures of the various adsorption schemes on the (8 × 12) ZGNR unit-cell used to study the electronic structure response of the ribbon: (a) the pristine nanoribbon; (b) lithium adatom adsorption; (c) toluene adsorption; (d) o-MNT adsorption; (e) p-MNT adsorption; (f) 2,4-DNT adsorption; (g) 2,6-DNT adsorption; and (h) TNT adsorption on the lithium anchoring site. For each adsorbate the most energetically stable structure obtained is presented. Gray, white, blue, red, and magenta spheres represent carbon, hydrogen, nitrogen, oxygen, and lithium atoms, respectively. The carbon atoms of the various molecules have been marked in turquoise for clarity of the representation. Red arrows in panel (a) represent the initial orientation of the methyl group in the various molecular positions studied. Black arrows represent the translational vector along the ribbon’s axis.

Figure 3. Relative stability of different adsorption orientations for the various molecules studied obtained at the HSE/6-31G** level of theory. For each molecule, the most stable fully relaxed orientation was used as reference. Coordinates of the various systems after geometry optimization are provided in the Supporting Information.
indicating the distinct electronic structure of each molecule. Clearly, these can be divided into subgroups of toluene, o/p-MNT, 2,4/2,6-DNT, and TNT, where each subgroup induces characteristic signatures in the low-energy electronic structure of the ribbon that allows for their selective detection.

Having studied the influence of individual contaminants on the electronic properties of the ZGNR, we now turn to examine the selective detection of molecular mixtures. To this end, we define the TNT molecule as the target molecule to be detected and study the effect of adsorption of a second contaminant molecule on the ZGNR’s surface. A single TNT molecule is positioned atop a lithium adatom on one side of the surface in the optimal geometry shown in Figure 2(b), and the second molecule is located atop a laterally shifted lithium atom on the other side of the surface in the geometry shown in Figures 2(c)−2(g) (see, for example, the optimized geometry for the mutual adsorption of TNT and o-MNT on the surface of an (8 × 24) ZGNR unit-cell shown in Figure 6). In this configuration the interaction between the two partially charged lithium atoms as well as the steric repulsions between the two adsorbed molecules are minimized. The geometry of the whole system is then reoptimized, and its electronic properties are investigated. We note that for all systems studied the triplet energy is in the range of −3.50 eV and −3.64 eV, respectively.

Figure 4. Effect of molecular adsorption on the electronic properties of lithium-decorated (8 × 12) ZGNR. (a) The influence of chemisorption of various individual TNT molecular derivatives and some common background molecules on the α (full black triangles) and β (open red circles) spin channel bandgaps of lithium-doped ZGNRs. (b) The corresponding Fermi level shifts of the α (top) and β (bottom) spin channels. All shifts are calculated with respect to the corresponding bare lithium-decorated (8 × 12) ZGNR α and β spin channel Fermi energies of −3.50 eV and −3.64 eV, respectively.

Figure 5. Comparison of the spin-resolved total DOS (black line) and its projection on the various adsorbates (red line) for the different chemisorbed (8 × 12) ZGNRs considered with single contaminant per unit-cell, as calculated at the HSE/6-31G** level of theory. In each panel the origin of the energy axis is set to the Fermi energy of the relevant system. All DOSs are given in arbitrary units.

Figure 6. Optimized geometry of TNT/o-MNT mixed adsorption scheme on the duplicated (8 × 24) ZGNR unit-cell. Gray, white, blue, red, and magenta spheres represent carbon, hydrogen, nitrogen, oxygen, and lithium atoms, respectively. The carbon atoms of the adsorbate molecules have been colored in turquoise for clarity of the representation.
spin state was found to be favorable with triplet/singlet differences reaching ~0.5 eV/supercell. In Figure 7(a) we present the dependence of the bandgap of a lithium-decorated (8 × 24) ZGNRs on the simultaneous adsorption of TNT and a second precursor molecule on the lithium anchoring sites. As can be seen, the bandgap of the TNT adsorbed system generally reduces upon the adsorption of a second molecule. Furthermore, the mixed adsorption schemes can be divided into two main groups: (i) TNT with the second molecule being toluene/p-MNT/2,4-DNT that presents both α and β gaps in the range of 0.15–0.4 eV and (ii) TNT with o-MNT/2,6-DNT adsorbates showing similar α spin channel bandgaps and considerably higher β spin bandgap values of ~0.9 eV. As shown in Figure 7(b), the shift in Fermi energies of the mixed adsorptions with respect to the lithium-decorated system can also be divided into two main groups: (i) TNT with the second molecule being p-MNT/2,4-DNT having relatively large α spin Fermi level shift of ~0.59 and ~0.67 eV, respectively (see red bars); and (ii) TNT with o-MNT/2,6-DNT adsorbates showing smaller α spin Fermi level shifts of ~0.28 and ~0.30 eV, respectively (see blue bars). Importantly, these two subgroups correspond to the intermediates of the two synthesis routes depicted in Figure 1. These results thus suggest that measuring the electronic properties of the two synthesis routes depicted in Figure 1. These results thus suggest that lithium-decorated GNRs may serve as sensitive and selective chemical detectors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b07540.

- Assessment of the effects of dispersion correction and ground state spin multiplicity analysis (PDF)
- Optimized coordinates of the various model systems studied (XLSX)

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