

Theoretical Investigation of Edge-modified Zigzag Graphene Nanoribbons by Scandium Metal with Pyridine-like Defects: A Potential Hydrogen Storage Material

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Received May 30, 2013, Accepted October 30, 2013

Functionalization of zigzag graphene nanoribbon (ZGNR) segment containing 120 C atoms with pyridine (3NV-ZGNR) defects was investigated on the basis of density-functional theory (DFT) calculations, results show that edge-modified ZGNRs by Sc can adsorb multiple hydrogen molecules in a quasi-molecular fashion, thereby can be a potential candidate for hydrogen storage. The stability of Sc functionalization is dictated by a strong binding energy, suggesting a reduction of clustering of metal atoms over the metal-decorated ZGNR.

Key Words : Binding energy, Density functional theory, Pyridine defects, Transition metal, Zigzag graphene nanoribbon

Introduction

Graphene which is a single layer of graphite has attracted considerable research interests owing to its novel properties¹⁻⁸ opening up new perspectives and future research. In particular, graphene is suitable for the applications in semiconductor devices and for hydrogen storage.⁹⁻²⁶ The two-dimensional (2D) graphene sheet itself is a semi-metal. However, when the 2D sheet is cut into rectangle slices, namely, graphene nanoribbons (GNRs), they can become one-dimensional (1-D) semiconductors with their energy band gap depending on the width and crystallographic orientation of cutting edge of the nanoribbons. Nitrogen (N) and/or Transition-metal (TM) atoms or clusters can also be used to modify the band structure of graphene and nanoribbons. Here a systematic study of electronic structures of zigzag graphene nanoribbon (ZGNR) whose edges are decorated with N dopants with vacancy formation and Scandium (Sc) is presented. Pure ZGNR are not proper for hydrogen storage. Remarkably large amount of hydrogen can be stored in functionalized ZGNR. ZGNRs decorated by N and Sc atoms can be functional materials that can be applied for hydrogen storage. In order to find how the N doping with defects and TM functionalization in ZGNRs affects the binding energy of H₂, in this paper, we used first-principle spin-unrestricted density-functional theory (DFT) to study the largest number of H₂ adsorption on Sc-doped ZGNRs with pyridine defects (3NV) by gradually increasing the number of H₂ molecules to these Sc-doped ZGNRs with pyridine deficiencies (3NV-ZGNR).

Methodology

The electronic properties were studied using first-principles DFT calculations are carried out *via* Dmol³ package,²⁷⁻²⁹ The generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form and an all-electron (AE) double numerical basis set with polarized function (DNP basis set)

were chosen for the spin-unrestricted DFT computation³⁰ with atomic cutoff set at 5.5 Å. A triclinic supercell of 84 × 84 × 14 Å³ was used simulate the 10-ZGNRs, with a wall-to-wall distance of at least 20 Å sufficient enough to avoid in-plane interactions between adjacent cells. The lattice parameters *a* and *b* were large enough to ignore the effect of neighboring nanoribbons. The Monkhorst-pack scheme³¹ was used in the Brillouin zone with 1 × 1 × 3 special k-points for all geometric optimization, the forces on all atoms were optimized to be less than 0.005 eV/Å using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm. The number of k-points was verified using energy optimization.

Two types of modified 10-ZGNRs were considered: Substitution of nitrogen dopants with vacancy formation, by removing a single C atom among three hexagons and replacing the three surrounding C atoms with 3 N atoms (3NV-10-ZGNR) (see Fig. 1(b)) and edge decorated ZGNR by Sc with 3NV defects (see Fig. 1(c)). The Fermi levels of the band structures and density of states (DOS) were reset at the 0 eV position.

Results and Discussions

Structure of 10-ZGNR and 3NV-10-ZGNR. Figure 1(a) shows the relaxed geometries of the nanoribbon, which was chosen as a typical semiconducting model for investigation. The width of the pure ZGNR was defined with the width parameter *n* of zigzag graphene nanoribbons as the number of zigzag lines across the ribbon width, as exemplified by 10-ZGNR was chosen in the present work. Hereafter, we label a GNR with *n* zig-zag chains as *n*-ZGNR. The edge carbon atoms of the nanoribbon are all saturated with H atoms to avoid the dangling bond states. The total energies for different magnetic phases of 10-ZGNR were calculated to determine the ground state and it was found out that the antiferromagnetic (AFM) phase is the most favorable for 10-ZGNR. The results are in agreement with literature, indicating that the methods in this work are reliable to describe

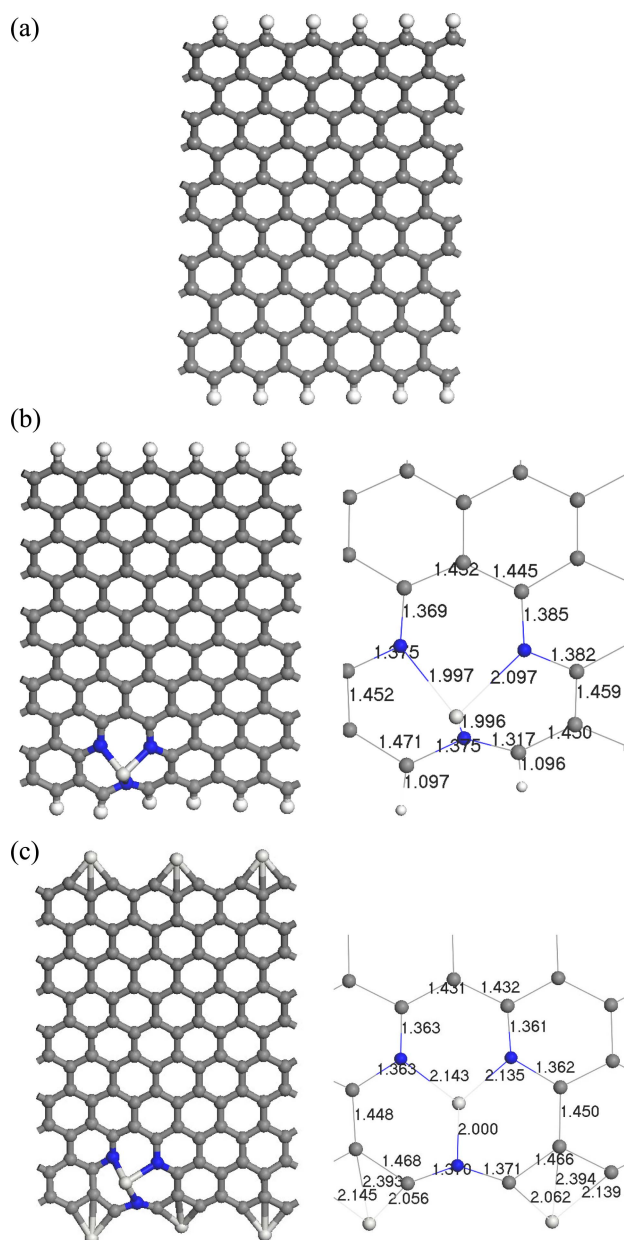


Figure 1. Optimized geometry of (a) the infinite ZGNR, (b) ZGNR with pyridine defects (c) edge-decorated ZGNR by Scandium with pyridine defects. Gray color depicts carbon atoms, blue is Nitrogen, white is Hydrogen and Scandium.

fully the electronic properties of ZGNRs.

There are limitless possibilities with respect to configurations since the pyridine defect can exist in different locations but computation shows that the configuration with defects close to the edge is favored energetically. The C–C bonds for the pure 10-ZGNR ranges from 1.407–1.443 Å. The C–N bond lengths of 10-ZGNR with pyridine-like defect is determined to be ~1.317–1.385 Å (see Fig. 1(b)). Edge-decorated 10-ZGNR by Sc with pyridine defects can be observed as shown in Figure 1(c) wherein the C–N bond length is ~1.361–1.371 Å; this is attributed in part to the functionalized Sc atom. Thus TM impurities in ZGNRs produce local strains and deformation.

Electronic Properties of 3NV-ZGNR Doped with Sc.

When Sc metal is adsorbed on the 10-ZGNR with 3NV deficiency, as initial guesses, we consider the TM is directly bound to the hollow site of 3NV and the TM is attached to the sites near 3NV and after full structural optimization it is found out that the Sc-adsorption on the hollow site is energetically favorable. Sc-adsorption on the hollow site leads to the formation of Sc-porphyrin-like structure in which the adsorbed Sc is protruded from the 3NV-10-ZGNR with an average Sc-TM bond length of 2.093 Å. Also edge of the 3NV-10-ZGNR was modified by the lightest transition metal Sc. If a modest level of edge decoration is realized on the edge such that every two-carbon atom on the edge is bonded with one Sc atom (such a model system is named as 3NV-10-ZGNR-Sc/2, where Sc decorates both edges.), the calculated binding energy of each Sc atom is -5.79 eV. Here, the binding energy of Sc at the 10-ZGNR edges is calculated according to the formula

$$E_b = [E_{\text{tot}}(3\text{NV-10-ZGNR-Sc/2}) - E_{\text{tot}}(3\text{NV-10-ZGNR with bare edge}) - E_{\text{tot}}(\text{Sc})]/n_{\text{Sc}} \quad (2)$$

where E_{tot} denotes the total energy of the optimized system in the bracket and $E_{\text{tot}}(\text{Sc})$ is the energy of free Sc atoms. $E_b < 0$ corresponds to a stable optimized configuration and indicates bonding. Notably, this Sc binding energy is greater than that of a fully Sc-decorated 3NV-10-ZGNR (where every carbon atom on the edge is bonded with a Sc atom). More importantly, Sc binding energy is lower than the cohesive energy (-4.4 eV) of bulk Sc, suggesting that Sc will not form clusters once bonded with carbon atoms at the 3NV-10-ZGNR edges. The cohesive energy is calculated according to the formula: cohesive energy of Sc = crystal energy of Sc - energy of free Sc atoms. A hexagonal crystal structure was employed in calculating crystal energy of Sc. Do Sc atoms also prefer to bind with carbon atoms on the surface of GNR? Our calculation indicates that if Sc atoms are uniformly dispersed on the surface of graphene, with each Sc atom located at the center of a carbon hexagon, binding energy is much less than the cohesive energy of bulk Sc, it is more likely that Sc atoms will form clusters on the surface of GNR rather than disperse uniformly. In other words, edge-decorated GNR by Sc is energetically robust. Graphene ribbons with open side bonds are known to be very reactive and unstable energetically, and therefore it is quite natural that the edges are saturated with other atoms. The most common edge species is hydrogen, a modified version of the binding energy wherein the bare edge term was replaced by hydrogenated edge. $E_b = [E_{\text{tot}}(10\text{-ZGNR-Sc/2}) - E_{\text{tot}}(\text{hydrogenated 10-ZGNR}) - E_{\text{tot}}(\text{Sc})]/n_{\text{Sc}}$. E_b is positive around 0.23 eV, suggesting a competition between hydrogen and Sc atoms, the small positive value indicates that the edge will eventually remain hydrogenated rather than functionalized with Sc atoms but hydrogen is certainly unstable under electron bombardment³²; Sulphur atoms are difficult to remove with an electron beam and lend themselves as a more stable side termination. These sulphur-terminated

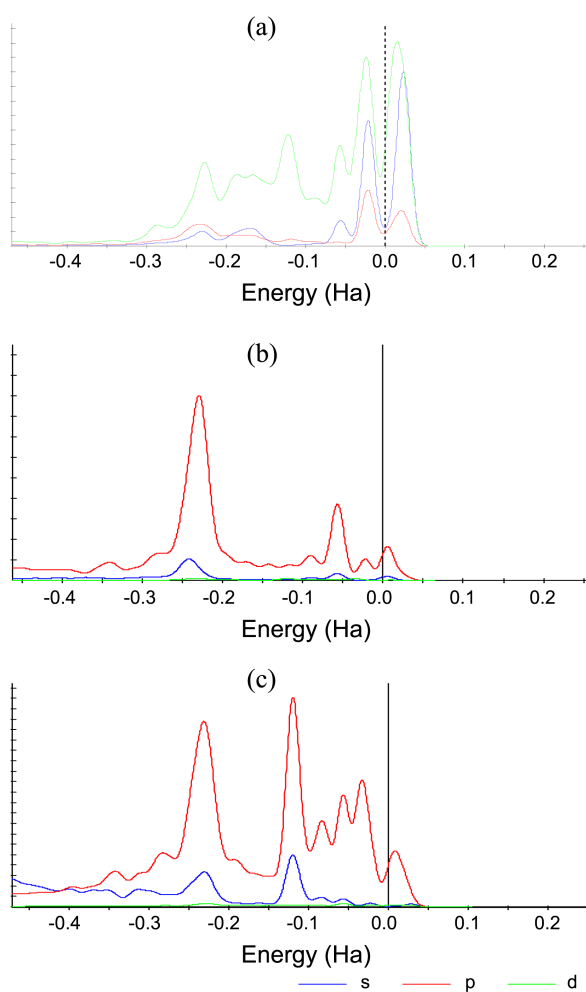


Figure 2. PDOS of (a) Sc, (b) N and (c) C in the adsorption system for the 10-ZGNR, blue, red and green plots denote s, p and d orbitals, respectively.

carbon strips might be the narrowest graphene ribbons that have ever been made and perhaps even the narrowest possible graphene ribbons that are stable.³² In light of that controlled synthesis of narrow GNRs, it is expected that edge-decorated GNR by Sc can be realized in the laboratory as well.

The formation of pyridine-like nitrogen defects is very crucial for enhancing the metal binding to the defects. The strong interactions between these TMs and the ZGNR with defects can be explained through partial densities of states (PDOS), that is, Sc adsorption on the 3NV-10-ZGNR as shown in Figures 2(a)–2(c). It is found that the *d* electrons of Sc and the *p* electrons of C and N atoms mainly contribute to the electronic states near Fermi level. Strong interaction exists between the *d* orbitals of Sc and the *p* orbitals of N atoms due to their hybridization with each other. This is reasonable, because the ZGNR with 3NV defects uses two valence electrons to form a lone pair. The non-bonding lone pair of the 3NV-ZGNR is greatly enhanced compared with the pure ZGNR.

In Figure 3(a) the spin resolved band structures of 10-

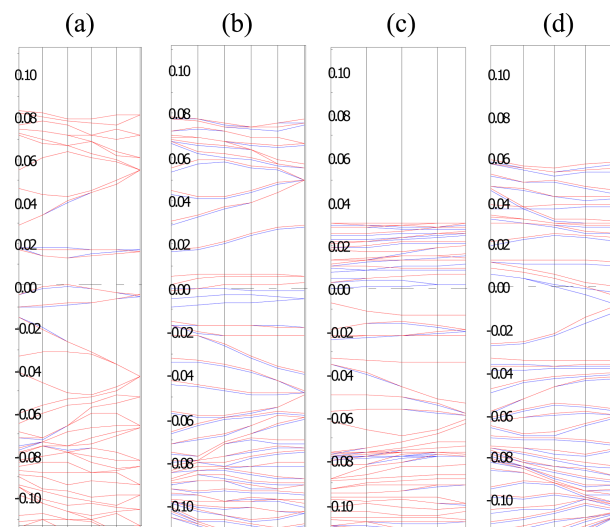


Figure 3. The band structures of (a) pure 10-ZGNR, (b) 10-ZGNR with pyridine-like defect, (c) edge decorated 3NV-10-ZGNR by Sc, and (d) a 3NV-10-ZGNR bilayer with an adjacent layer. Fermi level is set as zero and plotted with a broken line.

ZGNR is shown. The spin-up and spin-down bands are fully degenerate, the net magnetic moment of the AFM phase is zero and a 0.35 eV energy gap is observed. After the introduction of a 3NV defect Figure 3(b), the energy bands near the Fermi level become asymmetric for different spin channels: in the spin-up channel, metallicity is obtained, while the spin-down channel is semiconducting. Therefore, the 10-ZGNR containing a 3NV defect is half-metallic and is in agreement with the results obtained by H. Park *et al.*³³ wherein the semiconducting ZGNRs became half-metallic or remained semiconducting depending on the configuration of N–C covalent bonds between pyridine and the outermost C atom of the ZGNRs; the 3NV-10-ZGNR is a semiconductor nanocomposite material after the adsorption of Sc atom Figure 3(c). In addition, 10-ZGNR containing a 3NV defect which is half-metallic may form a bilayer with an adjacent layer, this was calculated and after optimization the resulting band structure is presented in Figure 3(d) wherein a metallic behavior is observed. Hirshfeld charge analysis indicates that about 0.46 e are transferred from the Sc atom to the as 3NV-10-ZGNR-Sc/2 structure, partially cationic Sc atom results due to the charge transfer from the Sc atom to the GNR. Partially cationic specie can attract H₂ as discussed in the next section 3.3, in comparison anionic specie was investigated by S. Yan and J.Y. Lee³⁴ wherein hydrogen interactions with nearby atoms of the anionic LiAlH₄ (LAH) clusters and their hydrogenated species was presented. The anionic LAH cluster size and the coupling mode between Li⁺ and the AlH₄ fragment are important factors influencing the hydrogen storage capacity.

Hydrogen Storage of Sc Decorated 3NV-ZGNR. For the 3NV-10-ZGNR-Sc/2 system, the number of H₂ was gradually increased to address the maximum number of H₂ molecules that can be bound to the system and after full relaxation for every H₂ adsorption configuration, the GGA pre-

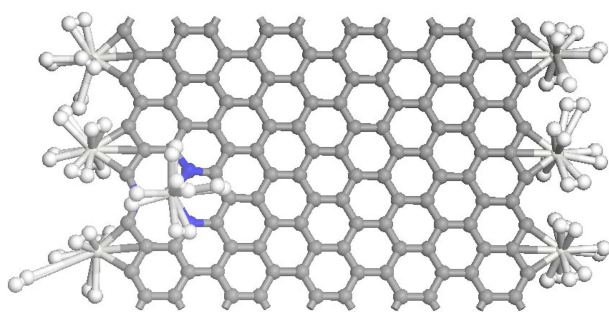


Figure 4. Optimized geometry of Sc-decorated ZGNR containing a pyridine defect with thirty-five hydrogen molecules absorbed. Seven Sc atoms were used to decorate the ZGNR. Gray color depicts carbon atoms, blue is nitrogen, white is hydrogen and Sc.

dicted that the maximum number of hydrogen molecules that can be adsorbed on each Sc atom is five for which the average adsorption energy of H_2 is -0.285 eV as seen in Figure 4. Under this condition, the highest hydrogen storage gravimetric capacity for this system is 2.5 wt %. To achieve high H_2 adsorption capacity, the system should have high ratio of number of adsorption sites to the weight of adsorbate material, besides quasi-molecular H_2 binding capability for the adsorption sites. To achieve highest ratio, we consider a narrowest GNR system, namely, 3NV-2-ZGNR-Sc/2, where Sc decorates both edges. Under this condition, the highest hydrogen storage gravimetric capacity for this system is 9.7 wt %, which is within the standards set by the U.S. Department of Energy (DOE) target with respect to gravimetric density. Most importantly, the H-H distances are increased slightly due to the charge transfer from the H_2 molecules to the Sc yet all the adsorbed H_2 remain molecular. A calculation using LDA-PWC was also carried out and average hydrogen adsorption energy is within the optimal adsorption energy range for hydrogen storage at room temperature of 0.20-0.70 eV/ H_2 .²⁶

Conclusions

Edge-modified GNRs by Sc can adsorb multiple hydrogen molecules in a quasi-molecular fashion based on the formalism of density-functional theory calculations, thereby can be a potential candidate for hydrogen storage. For the GNR with Sc-decorated zigzag edges, the average binding energy of H_2 is within optimal range suitable for hydrogen storage at room temperature. The predicted weight percentage of H_2 for narrowest GNR, meets the DOE target.

Acknowledgments. This work was supported in part by the Department of Science and Technology, Philippine Council for Industry, Energy and Emerging Technology Research and Development (PCIEERD) formerly Philippine Council for Advanced Science and Technology Research and Development (DOST, PCASTRD) for the acquisition of the *Dmol*³ v6.0 software.

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