

# Understanding the structure and electronic properties of N-doped graphene nanoribbons upon hydrogen saturation

MICHAEL MANANGHAYA

Department of Chemical Engineering, De La Salle University, 2401 Taft Ave, Manila 1004 Philippines  
e-mail: mikemananghaya@gmail.com

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**Abstract.** Structures and electronic properties of zigzag graphene nanoribbon (ZGNR) with pyridine (3NV-ZGNR) functionalized by Scandium (Sc) at the edge were studied through quantum chemical calculations in the formalism of density-functional theory (DFT). Pyridine-like nitrogen defects is very crucial for enhancing the Sc atom binding to the defects and is thermodynamically favoured. During Sc decoration of ZGNR there is a shift from 0.35 eV small gap semiconductor regime to that of a metal which can be used for band gap tuning by controlled saturation of Sc. ZGNR decorated with Sc can attract H<sub>2</sub>. Upon saturation of multiple H<sub>2</sub> in quasi-molecular fashion, the metallic character is converted to semiconductors of small gap of 0.10 eV, which are predicted to be interesting materials not only for hydrogen storage but also for their band gap engineered properties.

**Keywords.** Binding energy; density functional theory; pyridine defects; transition metal; zigzag graphene nanoribbon.

## 1. Introduction

The excellent mechanical strength, structural and chemical simplicity, and high conductivity of two-dimensional (2D) one-atom-thick allotrope of carbon called graphene make it an ideal system for fundamental research in nanoelectronics. When the 2D sheet is cut into rectangular slices, namely, graphene nanoribbons (GNRs), depending on crystallographic orientation of cutting edge of the nanoribbons they can become one-dimensional (1D) semiconductors. Graphene and nanoribbons due to its unique and unusual electronic properties<sup>1–8</sup> opens up new perspectives and research. In particular, problems of fossil-fuel reduction and greenhouse effect arising from the combustion of non-renewable fuels have led to search for materials such as GNRs suitable for the applications for hydrogen storage technologies<sup>9–26</sup> that can be used not only to produce energy from hydrogen but also provide a feasible solution for storage. Pure zigzag graphene nanoribbon (ZGNR) are not proper for hydrogen storage but remarkably large amount of hydrogen can be stored in functionalized ZGNR. Transition-metal (TM) atoms or clusters can be used to modify the band structure of graphene and nanoribbons. ZGNRs decorated by Sc atoms can be functional materials for hydrogen storage. This paper presents a systematic study of electronic structures of ZGNR with pyridine (3NV) whose edges are decorated with Sc. The fascinating properties of

graphene for potential applications were explored using the formalism of first-principle spin-unrestricted density-functional theory (DFT) to study how the N doping and Sc functionalization in ZGNRs affect the binding energy of H<sub>2</sub> and the largest number of H<sub>2</sub> adsorption on Sc-doped ZGNRs with 3NV defect by gradually increasing the number of H<sub>2</sub> molecules. An efficient and low cost storage material for hydrogen is a challenge for this area of active research in the current scientific community. The U.S. Department of Energy (DOE) hydrogen storage system targeted a 6.5 weight percent gravimetric capacity and a volumetric capacity of 0.045 kg/L.

## 2. Computational

The electronic properties were studied using first-principles. DFT calculations are carried out via *Dmol*<sup>3</sup> package.<sup>27–29</sup> 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 computation<sup>30</sup> with atomic cut-off set at 5.5 Å. In the 10-ZGNRs, a cuboid supercell was used with a wall-to-wall distance of at least 20 Å sufficient enough to avoid in-plane interactions between adjacent cells. For geometric optimization, the Brillouin zone was sampled by 3 k points using the Monkhorst-

pack scheme,<sup>31</sup> the forces on all atoms were optimized using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm to be less than 0.005 eV/Å. Modified 10-ZGNRs were constructed by removing a single C atom among three hexagons and replacing the three surrounding C atoms with 3 N atoms (3NV-10-ZGNR, substitution of nitrogen dopants with vacancy formation) and afterwards chemical decoration of Sc on the edge of 10-ZGNR with 3NV (figure 1b). The Fermi levels of the band structures and density of states (DOS) were reset at the 0 eV position.

### 3. Results and Discussions

#### 3.1 Structure

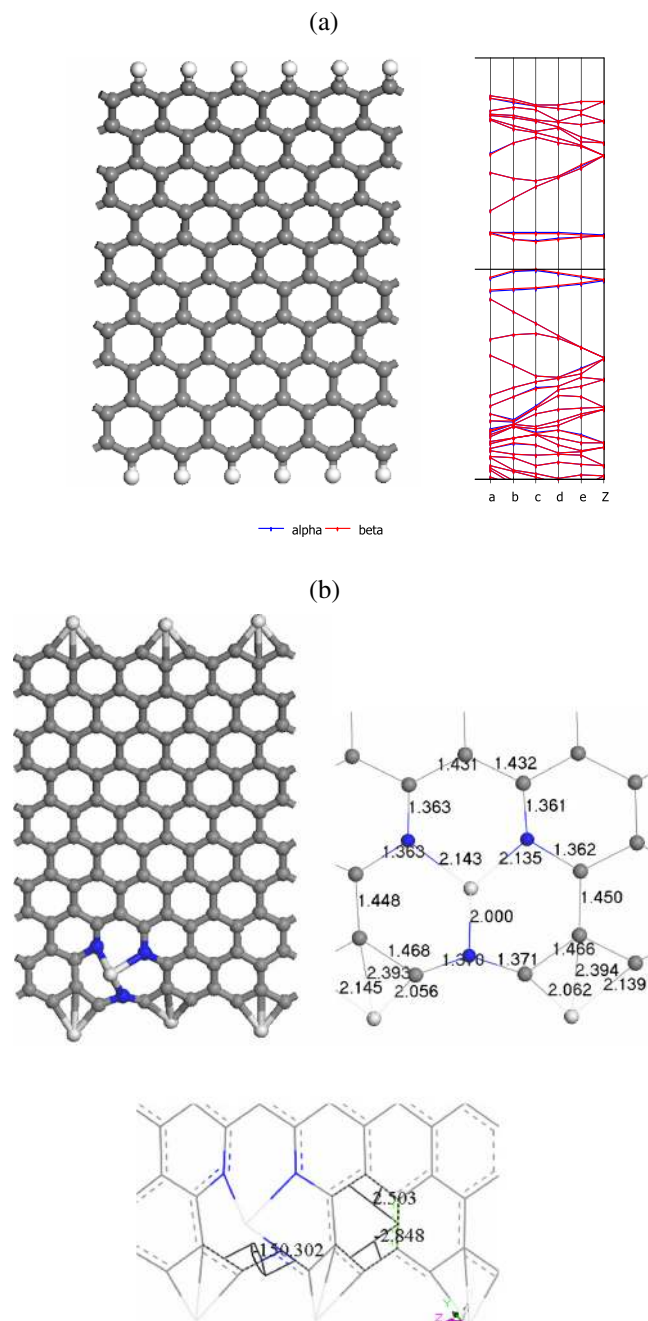
Figure 1a shows the relaxed geometries of the 10-ZGNR, which was chosen as a model in the present work. The edge carbon atoms of the nanoribbon are all saturated with H atoms to avoid the dangling bond states. The total energies for different magnetic phases of 10-ZGNR were calculated to determine the ground state and it was found out that the anti-ferromagnetic (AFM) phase is the most favourable for 10-ZGNR. The pyridine defect can exist in different locations but computation shows that the configuration with defects close to the edge is favoured energetically. The C–C bonds for the pure 10-ZGNR ranges from 1.407–1.443 Å. Edge-decorated 10-ZGNR by Sc with pyridine defects can be observed as shown in figure 1b wherein the C–N bond length is ~1.361–1.371 Å; this is attributed in part to the functionalized Sc atom.

#### 3.2 Electronic properties

The spin resolved band for the AFM structures of 10-ZGNR is shown. The spin-up and spin-down bands are fully degenerated. The net magnetic moment of the AFM phase is zero and a 0.35 eV energy gap is observed. 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 that the Sc-adsorption on the hollow site is energetically favourable verified by calculating the formation energy ( $E_f$ ) defined as:

$$E_f = E_{\text{tot}} - n_C (\mu_C - n_H \mu_H) / 120 - n_N \mu_N - n_H \mu_H, \quad (1)$$

where  $E_{\text{tot}}$  is the total energy of the 10-ZGNR with 3NV,  $n_C$ ,  $n_N$  and  $n_H$  are the number of C, N and H atoms, respectively.  $\mu_C$  is the chemical potential of C obtained



**Figure 1.** Geometry optimized structure of (a) the infinite 10-ZGNR and (b) edge-decorated 10-ZGNR by Scandium with pyridine defects. Gray colour depicts carbon atoms, blue is Nitrogen, white is Hydrogen and Scandium.

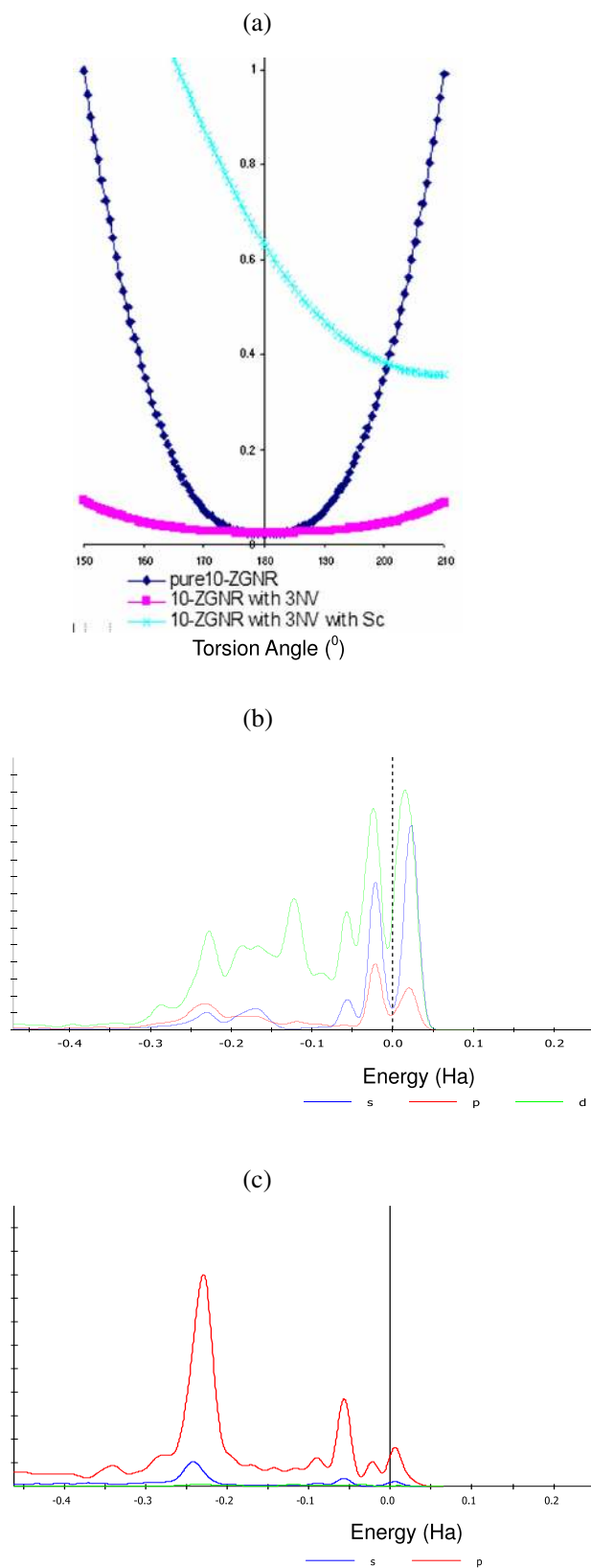
from the corresponding pure 10-ZGNR, and  $\mu_N$  with  $\mu_H$  is the chemical potential of N, H obtained from nitrogen and hydrogen in gas phase. The formation energy of the 3NV-ZGNR is on the average of 2.78 eV. Sc-adsorption on the hollow site leads to the formation of Sc-porphyrin-like structure in which the adsorbed Sc is protruded from the 10-ZGNR with an average Sc-TM bond length of 2.093 Å. Also, edge of the 10-ZGNR was modified by the lightest transition metal Sc. The

adsorbed Sc on the edge has an average bond length of 2.198 Å. The increased interatomic distance, compared to C–C bonds for pure 10-ZGNR, further weakens the  $\pi$ -bonding resulting in a buckled structure. Unstable planar structure due to weak  $\pi$ -bond regains the stability by puckering and it is quite interesting to partially understand the puckering in the edge of 10-ZGNR with 3NV deficiency in terms of the torsion angle as seen in figure 1b. It can be observed from the plots of the torsion angle versus relative optimized energy for the 10-ZGNR, ZGNR with 3NV and ZGNR with 3NV decorated with Sc in figure 2a that the pure 10-ZGNR and 10-ZGNR with 3NV deficiency systems are both destabilized. As a result, the system becomes unstable with puckering and the optimized structure structure is planar with a  $180^\circ$  (flat) torsion angle. However, in Sc edge decorated 10-ZGNR with 3NV defects, the puckered structure becomes more stable than the planar one with an optimized torsion angle of  $209.7^\circ$  ( $-150.3^\circ$  as seen in figure 1b due to  $+360^\circ$  shift incorporated in the plot). This agrees well with an analogous calculation results previously reported<sup>32–34</sup> wherein delocalization of the electrons in silicenes (through aromaticity) is not adequate enough to overcome the puckering. The energy difference between the planar and the puckered structures, the frequency mode which results in the puckering, and the Gibbs free energy order of stability of planar and puckered structures for various silicenes species at B3PW91/TZVP level suggests that puckering is favoured in silicenes. Also, values of 1.43 kcal/mol at B3LYP/cc-pVTZ+1 and 1.29 kcal/mol using CCSD(T)/ccpVTZ electron correlation as the energy difference between the buckled and planar form of hexasilabenzene were reported.

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 10-ZGNR>Sc/2), the calculated binding energy of each Sc atom is  $-5.79$  eV calculated according to the formula

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

where  $E_{\text{tot}}$  denotes the total energy of the optimized system in the bracket.  $E_b < 0$  corresponds to a stable optimized configuration and indicates bonding. The interactions between Sc and the ZGNR with pyridine-like nitrogen defects can be explained through partial densities of states (PDOS) as shown in figures 2b and 2c. The  $d$  electrons of Sc and the  $p$  electrons of N atoms mainly contribute to the electronic states near Fermi level. The hybridization contributes to the strong

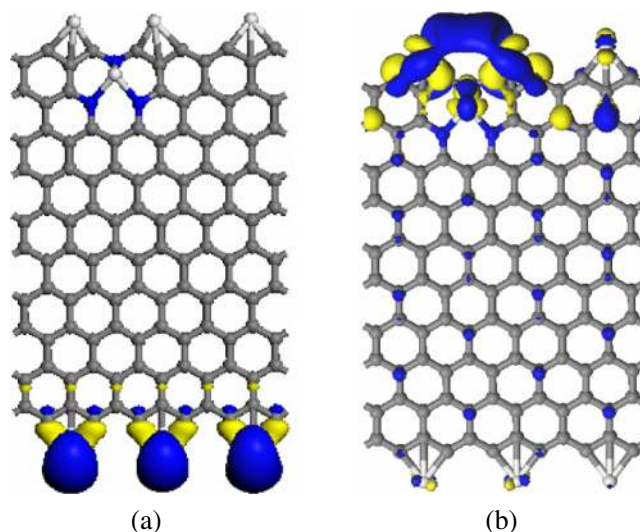


**Figure 2.** (a) Torsion angle versus relative optimized energy for the 10-ZGNR, ZGNR with 3NV and ZGNR with 3NV decorated with Sc; PDOS of (b) Sc, (c) N in the adsorption system for the 10-ZGNR, blue, red and green plots denote s, p and d orbitals, respectively. The vertical axis is set at arbitrary units.

interaction. The 3NV-10-ZGNR is a half-metallic material after the adsorption of Sc atom due to the charge transfer of 0.46e from the Sc atom to the 10-ZGNR with 3NV using the Hirshfeld population analysis. Partially cationic Sc can attract  $H_2$  as discussed next.

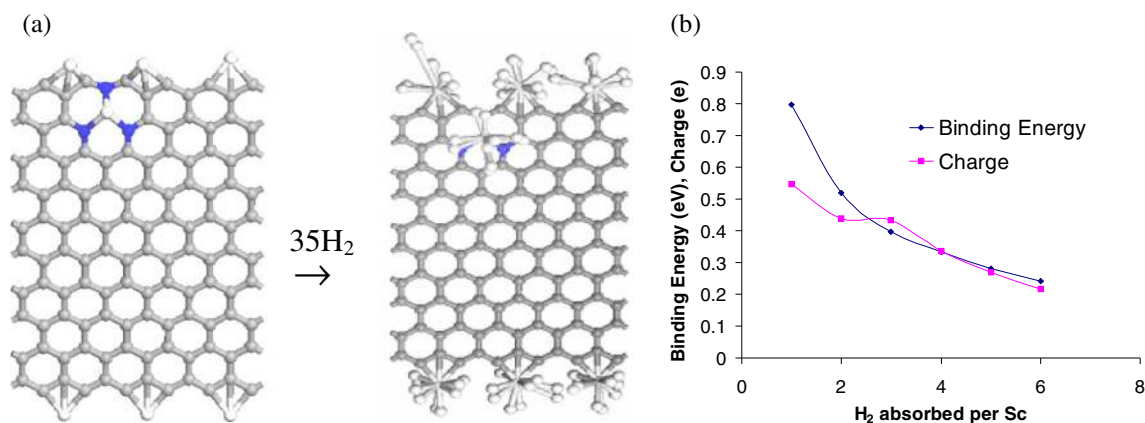
### 3.3 Sc decorated 3NV-ZGNR as hydrogen storage media

For the 10-ZGNR>Sc/2 system, the number of  $H_2$  was gradually increased to address the maximum number of  $H_2$  molecules that can be bound to the system and after full relaxation for every  $H_2$  adsorption configuration, the GGA predicted 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 3. 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/ $H_2$ .<sup>26,35</sup> Under this condition, the highest hydrogen storage gravimetric capacity for this system is 2.5 wt%. The  $-0.285$  eV falls within the physical adsorption range of about 6 kcal/mol.<sup>36–40</sup> Quantum chemical calculations have been performed by Datta<sup>41</sup> on a series of cyclic rings ( $S_2N_2$  and  $S_3N_3^-$ ) with and without doping of TM (Ni, Pd and Pt) to study their ability to store hydrogen. Calculations show that  $S_2N_2$  is planar while  $S_3N_3^-$  is puckered to  $C_{3v}$  symmetry and undoped SN rings and chains are predicted to have dispersive interactions with  $H_2$  with endothermic binding energies and significant contributions from entropy at room temperature. The HOMO and LUMO is shown in figure 4a and 4b, the distributions are polarized at the

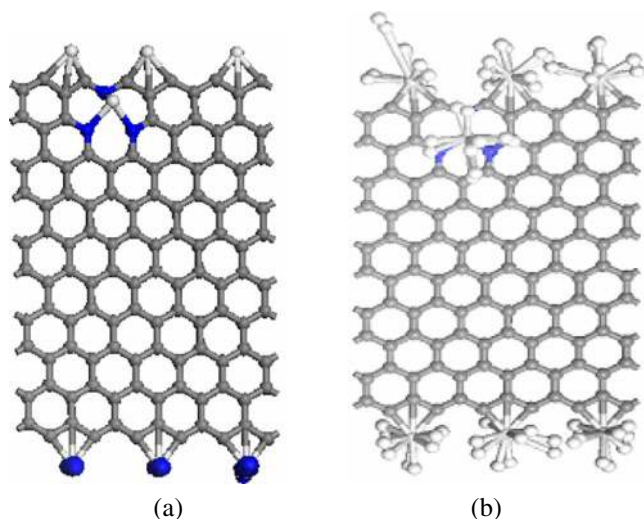


**Figure 4.** (a) HOMO and (b) LUMO of the optimized geometry of Sc-decorated ZGNR containing a pyridine defect.

Sc dopants. Under the study, the HOMO–LUMO gap is zero, indicating a shift from the 0.35 eV gap semiconductor realms to that of a metal. The decrease of the band gap during Sc saturation of ZGNR with 3NV can be used for band gap tuning by controlled saturation of Sc. The storage capacities of these periodic systems, coupled with their band engineering properties can be seen as promising materials. Also, the AFM phase is modified as seen in the spin density plot in figure 5a that is at the bottom end with a net magnetic moment of around 0.3  $\mu_B$ . Upon saturation with  $H_2$ , the metallic character is converted to small gap semiconductor of 0.1 eV value and the net magnetic moment is reduced to almost 0.0  $\mu_B$  as shown in figure 5b.



**Figure 3.** (a) 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 colour depicts carbon atoms, blue is nitrogen, white is hydrogen and Sc. (b) Plot of binding energy and charge transferred from Sc atom to the 10-ZGNR with 3NV versus the hydrogen molecule absorbed per functionalized Sc. The optimal adsorption energy range for hydrogen storage at room temperature of 0.20–0.70 eV/ $H_2$ .<sup>26</sup>



**Figure 5.** Spin density of the optimized geometry of (a) Sc-decorated ZGNR containing a pyridine defect and (b) Sc-ZGNR with 3NV saturated with H<sub>2</sub>.

Modelling materials for the storage of hydrogen is very challenging as it is the lightest element in the periodic table and thus requires the confinement of a large number of H<sub>2</sub> molecules. To achieve high H<sub>2</sub> adsorption capacity, the narrowest GNR system was considered, namely, 2-ZGNR>Sc/2. Although Sc is a heavy metal, it is the lightest transition metal known and it decorates both edges. Under this condition, a 9.7 wt% hydrogen storage gravimetric capacity is possible, within the standards set by the U.S. DOE. Most importantly, the H-H distances are increased slightly due to the charge transfer from the H<sub>2</sub> molecules to the Sc/4ND-CN<sub>x</sub> NT. Yet all the adsorbed H<sub>2</sub> remain molecular.

#### 4. Conclusions

On the basis of quantum chemical calculations, edge-modified GNR by Sc is a potential candidate for hydrogen storage. For the GNR with Sc-decorated zigzag edges, the average binding energy of H<sub>2</sub> is thermodynamically favourable. The predicted weight percentage of H<sub>2</sub> is greater than 9 wt% for narrowest GNR, meeting the DOE target. In view of controlled synthesis of narrow GNRs, it is expected that edge-decorated GNR by Sc can be realized in the laboratory as well.

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