Effect of side chain edge functionalization in pristine and defected graphene-DFT study

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ABSTRACT

The structural and electronic properties of edge-functionalized graphene sheets are systematically investigated utilizing Density Functional Theory (DFT). The functionalization includes alkyl, alkene, and seven different polyacetylene side chains as an alternative for a hydrogen atom in eight different kinds of graphene sheets. CH_3 and longer side chains functionalization have high stability and remains unaffected by increasing the size of the graphene sheet. The weak binding energy and large formation energy are observed for CH_2, C_3H_4 and C_5H_6 functionalization in all eight different kinds of the graphene sheet. The high charge transfer from graphene to side chain having high σ bonds is interpreted by Voronoi deformation density (VDD) method. The delocalization of the graphene ring decreases in side chain functionalization and gets decreased further when the size of the graphene sheet is increased. The high alteration in aromaticity is illustrated by decrease in Para Delocalization Index (PDI) value with an increase in aromatic Fluctuation Index (FLU) value in weakly binded side chains. The decrease in Highest Occupied Molecular Orbital (HOMO) along with a decrease in band gap on the substitution of nine different side chains in both pristine and defected sheet is observed. Moreover, the decrease in electron accepting ability is observed for CH_3, C_3H_5 and C_5H_7 functionalization in all kinds of graphene sheets, which is inferred from the decrease in Lowest Unoccupied Molecular Orbital (LUMO).

1. Introduction

The monolayer sp^2 hybridized graphene [1] is of much interest in the recent research due to its unique electronic structure, mechanical strength and chemical stability [2–4] which are tunable as per application. The electronic properties altered by defects due to change in hybridization intensely influence the performance of graphene based devices [5]. Among various defects, pentagon-heptagon rings forming structural distortion are a common defect [6]. In our recent studies [7,8], it is found that the adsorption enhanced by the presence of defect in the graphene. Further, this pentagon-heptagon ring is influential in forming kink structure and junctions of the carbon nanotube [9–12]. The rearrangement and 90° rotation of carbon atoms form topological defect with two pentagon-heptagon rings called Stone-Thrower-Wales defect feasible during synthesis and can also be formed by the electron irradiation [13]. Despite with unique physicochemical properties, these graphene sheets are hindered from practical applications by their insolubility and zero band gaps. Physical handling of graphene is confined by its solubility only in the solvents of 0.01 mg ml^{-1} concentration [14]. This could be overcome by different edge functionalization

resulting in favourable optical and electronic properties [15,16].

The edge functionalization of graphene is of high interest due to the high reactivity of dangling bond at the edges than the carbon atoms at basal plane [17]. These edge functionalization could overcome the band gap and solubility pitfall of graphene in practical applications [18,19]. The reactivity of graphene edges was twice higher than that of the basal region [20] and Chae et al. [21] illustrated the contribution of graphene edges for transport properties. The electronic properties of the graphene depend on the edges, which are confirmed by changes due to hydrogen termination [22]. While graphene edge with fluorination and chlorination induces p-doping along with changes in band gap [23]. The chemical functionalization of the graphene enables better solubility and control in band gap with preserved stability and intrinsic electronic properties [24–26]. Few experimental [27–31] and theoretical [32–34] works on different edge functionalization of graphene and its nano forms have been reported with modified band gap and solubility. In this aspect, the edge functionalization of the graphene inducing various chemical moieties with minimal basal plane damage can further broaden their potential applications [35]. The alkyl side chain functionalization at the edges of conjugated polymers influences the

solubility, intermolecular packing, and absorption spectra. Additionally, the difference in length of side chain plays a vital role in electronic levels such as Highest Occupied Molecular Orbital /Lowest Unoccupied Molecular Orbital (HOMO/LUMO) of the molecules [36,37]. Even though the lower length of alkyl side chain shows lower HOMO level and absorption, its length cannot be extended too long as it decreases the interchain interactions, hole mobility and the absorbance of the conjugated polymers [38,39]. The graphene sheets covalently functionalized with the alkyl azides having hexyl dodecyl, hydroxylundecanyl, and carboxy-undecanyl groups as alkyl chains are reported [40]. Moreover, in graphene nano ribbon Yang et al. [41] synthesized alkyl chain functionalization at the edges to improve the solubility and change in conduction by altering the length of alkene side chain functionalization [42]. Zhao et al. [43] reported the effect of conductivity with respect to the length of alkyl chain functionalization in nano sheet and these linear terminating groups improve the aggregation tendency in graphene nano ribbon [44]. In addition to these alkyl and alkene edge functionalization, the *trans*-polyacetylene molecule with π conjugation in the linear framework is enthralled in both experimental and theoretical investigations [45–49]. Weak interactions of polyacetylene in the basal region of nanotubes and synthesis of polyacetylene functionalized graphene with good dispersibility in various organic solvents have been reported in the literature [50,51]. From the literature reports it is inferred that the edge functionalization of graphene and its derivatives with different functional groups is useful in tailoring the electronic and optical properties and also in changing the solubility of the sheet [52–57]. Despite many works, there is a lack of insight about the effect of different side chain functionalization of varying in length with respect to the core (graphene) size and presence of defects in graphene. With these investigations as the motivation the present work deals on the structural, aromatic and electronic effect of different alkyl, alkene, and polyacetylene side chains edge functionalization in pristine (without defect) and defected graphene of a variable number of carbon atoms. The eight different kinds of graphene sheets considered are terminated with the hydrogen atoms to satisfy the dangling bonds and the side chains are substituted in the armchair edge (duo) with the placement of a hydrogen atom.

2. Models, methods and theoretical background

2.1. Modeling

We study the structural, aromaticity, and electronic properties of pristine and defected modelled graphene with one alkyl/alkene and seven different polyacetylene side chain. Hydrogen capped graphenes as shown in Fig. 1 consisting of $C_{32}H_{14}$, $C_{42}H_{16}$, $C_{66}H_{20}$ and $C_{80}H_{22}$ molecular formula are considered and these graphenes are of a pristine and defective kind. The two kinds of pristine graphene sheets with a diverse number of carbon atoms are considered in order to replace with two different kinds of defects such as single pentagon-heptagon defect (PH) and Stone-Wales defect (SW) in the center of the sheet. For the convenience the pristine and defected graphene sheets with smaller size are termed as Pr1, Pr2, PH and SW, and further these graphene sheets with increased size are termed as Pr1ex, Pr2ex, PHex and SWex respectively. The one alkyl, alkene and seven different polyacetylene side chains as illustrated in Fig. 2 are considered in the form of C_nH_{n+1} and C_nH_{n+2} where n as an integer number (n = 1,2,3…).

2.2. Methodology

In this work, the electronic structural calculations are performed by Gaussian 09 software package [58] using B3LYP/6-31G* level of theory of DFT method. The changes in the structures on functionalization are explained with the assistance of atomic partial charges obtained by means of VDD method. The VDD method avoids the problems built in the basis set based schemes and provides meaningful charges that

confirm the chemical experience [59]. Moreover, Mayer's bond order has been discussed to illustrate the bond length alteration by side chains. Energy gap (E_g) is the difference of the frontier molecular orbitals HOMO and LUMO that are used to investigate the electronic properties of the modified graphene sheet. The ionization potential (IP) of the graphene sheet is investigated since it is affected by graphene size [60] and the side chain functionalization which cause π extension in graphene. Further, the influence of side chain in bare sheets is investigated using Total Density of the states (TDOS) using GaussSum 3.0 [61].

The semi finite graphene structures have high aromaticity in the armchair edges than zig-zag edges [62] hence the set of theoretical aromaticity descriptors for side chain functionalized graphene sheets was calculated. The brief description of all techniques and their results are discussed below.

2.3. Theoretical background

2.3.1. Harmonic oscillator model of aromaticity (HOMA)

The HOMA approach works on the normalized deviation of a given bond length (R_i) from the optimal aromatic value (R_{opt} = 1.388 Å for benzene) and this generalized HOMA is defined as

$$HOMA = 1 - \frac{\alpha}{n} \sum_{i=1}^{n} (R_{opt} - R_i)^2$$

where n is the number of bonds considered and α is the normalization coefficient. Here HOMA is 0 for the non-aromatic system and 1 for a system having all bonds equal to the bond of a given optimal aromatic system.

2.3.2. Para-delocalization index (PDI) and aromatic fluctuation index (FLU).

PDI [63] and FLU [64] descriptors are based on the topological Quantum Theory of Atoms in Molecules (QTAIM) [65,66] approach. The PDI is a specific measure of aromaticity of six-membered rings, in which it is defined using three *para*-related positions as

$$PDI = \frac{\delta(1, 4) + \delta(2, 5) + \delta(3, 6)}{3}$$

where δ(1,4), δ(2,5) and δ(3,6) are the delocalization indices of para site atom pairs. The greater PDI value indicates the higher strength of the delocalization of electrons around a ring relating to greater aromaticity. The FLU index constructed by following the HOMA philosophy measures the divergence of a given molecule to an optimal aromatic molecule (here benzene) using the delocalization index of each bond and the localization index of atoms in the bond pair. The lower FLU value corresponds to stronger aromaticity and the formula was given as

$$FLU = \frac{1}{n} \sum_{A-B}^{ring} \left[\left(\frac{V(B)}{V(A)} \right)^{\alpha} \left(\frac{\delta(A, B) - \delta_{ref}(A, B)}{\delta_{ref}(A, B)} \right) \right]^2$$

where the summation is considered for all adjacent pairs of atoms around the ring, n is the number of atoms in the ring. V(A) and V(B) are the global delocalization of atoms A and B or the so-called valence electrons are defined as

$$V(A) = \sum_{B \neq A} \delta(A, B)$$

whereas δ(A,B) and δ_{ref}(A,B) are the delocalization indices of atoms A and B and their pre-calculated reference values respectively. The α is the simple function to ensure the ratio of atomic valences to be greater or equal to 1 and it is defined as

$$\alpha = \begin{cases} 1, & V(B) > V(A) \\ -1, & V(B) \leq V(A) \end{cases}$$