Characterization of graphene–fullerene interactions: Insights from density functional theory


Abstract

Using density functional theory (DFT) based approaches that utilize appropriate semi-empirical and non-local van der Waals corrections, we rigorously examine the interactions between fullerene (C_{60}) molecules and pristine single layer graphene (SLG) sheets as well as SLG containing isolated mono-vacancy, divacancy and Stone–Wales defect-sites respectively. Our results show that chemical bonding between the C_{60} molecule and SLG at mono-vacancy defect-sites demonstrate predominantly sp^2-like hybridization, in contrast to weaker π–π interactions that characterize C_{60}–SLG systems containing divacancies and Stone–Wales defects.

1. Introduction

The remarkable structure property relations exhibited by low-dimensional carbon nanostructures such as single-sheet graphene (SLG), fullerenes (C_{60}) and carbon nanotubes (CNT), has spurred a growing interest in fabricating corresponding hybrid nanostructures for a wide range of applications including electronics, spintronics, energy harvesting, and energy storage applications. Theory-based and experimental investigations have demonstrated the feasibility of SLG–CNT based hybrid structures [1,2], while robust CNT–C_{60} structures are yet to be realized. Since pristine SLG is known to interact with C_{60} via weak van der Waals (vdW) forces, methods that promote strong chemical bonding between C_{60} and SLG need to be explored in order to pave way for fabricating hybrid C_{60}–SLG nanostructures. Two possible routes for facilitating strong C_{60}–SLG interactions include (i) chemical functionalization of SLG and/or C_{60} leading to chemical-bond formation and (ii) defect-mediated chemistry, where the higher reactivity of the defect sites induce chemisorption of C_{60} on SLG. While Yu et al. [3] have already examined the usage of chemical functionalization groups to ensure chemical attachment of C_{60} on SLG, there is not much available information on quantifying the role of defects in enabling strong chemical interactions between SLG and C_{60} molecules. Towards this end, as an important first step, using density functional theory (DFT) we examine energy-minimized C_{60}–SLG hybrid-structures, and quantify the effect of various intrinsic SLG defects (mono-vacancy, di-vacancies and Stone–Wales defect) that are stable at room temperature [28], on the binding energetics and geometries of the hybrid structures.

DFT has become the electronic-structure method of choice for providing a first-principles understanding of molecular-adsorption mechanisms on surfaces and extended systems [4–6]. Nevertheless, the popular descriptions for the exchange–correlation functionals in DFT, namely local density approximation (LDA) and the generalized gradient approximation (GGA) do not define weak noncovalent dispersive vdW interactions with sufficient precision and hence corrections to the energy functionals are required to account for these shortcomings, especially for graphitic systems, as discussed by Dappe et al. [7].

Building on the work of Dappe et al. [7], in the present study, we employ GGA functionals with semi-empirical and non-local vdW corrections, within the framework of computationally efficient plane-wave DFT, to model the interactions between C_{60} and pristine and defected SLG sheets. A hierarchy of intrinsic defects within SLG is considered namely mono-vacancy, Stone–Wales, pentagon–octagon–pentagon (5–8–5) divacancy, and a tri-pentagon–tri-heptagon (555–777) reconstructed divacancy [8–13]. For each C_{60}–SLG hybrid-nanostructure, the binding energetics, the corresponding minimum-energy configuration as well as changes in electronic-structure that underlie the nature of binding are characterized.

2. Methodology

The DFT calculations were carried out using the Vienna \textit{ab initio} Simulation Package VASP 5.2 [14]. The projected augmented wave formalism (PAW) was employed to model the electron–ion interactions [15]. The exchange–correlation functionals followed the standard generalized gradient approximation of Perdew–
Burke–Ernzerhof (GGA–PBE) [16], and in addition, two modified PBE functionals incorporating different flavors of vdW corrections were also utilized. Specifically, the (i) vdW semi-empirical PBE-D2 correction as established by Grimme [17–18], and the (ii) non-local method of Klimeš et al. (optB86b) [19] were employed in our studies. The two dimensional single layer graphene (SLG) sheets were represented by an 8 x 8 periodic supercell consisting of 128 atoms; the different defects were created at the center of the supercell. A vacuum region of 24 Å was introduced perpendicular to the SLG sheet to prevent unphysical periodic effects. This strategy was also employed for the case of examining C₆₀ adsorption on SLG.

Given the large size of the supercell, the numerical integration was carried out over the Brillouin zone using a 1 x 1 x 1 Monkhorst–Pack k-point grid [20]. The pseudo-wave functions were expanded in a plane-wave basis set with an energy cut-off of 400 eV, and accuracy was ensured by adopting an energy-convergence criteria of 10⁻⁵ eV. Simultaneously, structural relaxation was carried out using the conjugate gradient technique, until the force on each atom was below 0.02 eV/Å.

The binding energy (E_{bind}) of the various C₆₀–SLG systems was estimated by evaluating the energy of the structurally optimized (i) C₆₀–SLG system (E_{tot}), SLG with and without defects (E_{Gr}), and an isolated C₆₀ molecule (E_{C60}). In each case, E_{bind} = (E_{tot} - E_{Gr} - E_{C60}).

3. Results and discussion

3.1. C₆₀–pristine SLG interactions

Four energetically favorable physisorption geometries of C₆₀ on pristine SLG were identified as shown in Figure 1. Specifically, they are denoted as (i) BRI: where a C–C dimer shared by neighboring hexagons in the C₆₀ molecule is aligned with a C–C bond in SLG, leading to an alignment of two hexagonal rings within the SLG and C₆₀ respectively; (ii) C-RING: a C₆₀ hexagon ring is aligned with another hexagon ring in SLG; (iii) C-ATP: a single carbon atom of the C₆₀ molecule is directly atop a carbon atom of SLG; (iv) C-RING2: the center of a hexagon ring of C₆₀ is aligned with a carbon atom of SLG.

Table 1 lists the corresponding binding energies as evaluated using PBE, PBE-D2 and optB86 for the identified adsorption geometries. Interestingly, all methods predict the C-ATP geometry to be the most stable (i.e. the highest binding energy). Further, all methods predict similar variations in binding energies for the different geometries. PBE severely underestimates the binding energies due to the lack of dispersion corrections, while the vdW-incorporated methods predict the binding energy to be of the order of 1 eV, consistent with the observation of Dappe et al. [7]. Further, for a given adsorption geometry, optB86 predicts higher binding energies relative to PBE-D2. This can be attributed to the method of implementation of the adopted vdW approximations; specifically, for the case of the semi-empirical corrections, neither repulsion that arises from the overlap of electronic densities nor multipole effects are accounted for. For the non-local method, the corrections to the long-range correlations are incomplete due to restrictions imposed by using double-space integrals to express the non-local correlation energy [21].

The choice of including dispersion effects also affects the predicted equilibrium C₆₀ adsorption distances (see Table 2). PBE consistently overestimates the adsorption distance with respect to vdW-incorporated methods; when vdW corrections are included, however, the predicted adsorption distance for the C-ATP configuration (i.e. the most stable geometry) is in good agreement with the previously reported theoretical and experimental results [7,22–24]. A more detailed analysis relating the interplay between the choice of the vdW correction and the binding energy characteristics will be presented in a follow-up Letter.

It should be noted that energetically favorable adsorption geometries have also been identified by Švec et al., who used localized-orbitals (LCAO–S² + vdW) based DFT calculations to characterize C₆₀–SLG interactions [24]. A notable difference between the two studies is the fact that the size of the supercell is much larger in our Letter, hence we restrict our investigations to

Figure 1. The adsorption geometries of C₆₀ on pristine (top) and defected (below) SLG. The C₆₀ atoms close to the SLG surface are brown in color, for ease of viewing. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
molecule interactions. Further, we allow for unre-
bond forming respective covalent
system is the least stable,
atom, they represent chemically reactive sites.
and SLG, with a pair of
is characterized by the for-
or C3
on SLG containing a single vacancy. This is also re-
chemisorption.
and either of C2
Figure 2.
important dis-
work as evaluated by the three different methods. For comparison, available literature data
as evaluated by the three different methods. For comparison, available literature data
(both theory-based and experimental estimations) are provided below.

<table>
<thead>
<tr>
<th>Adsorption</th>
<th>PBE</th>
<th>PBE-D2</th>
<th>optB86b</th>
</tr>
</thead>
<tbody>
<tr>
<td>BRI</td>
<td>0.13</td>
<td>0.84</td>
<td>1.20</td>
</tr>
<tr>
<td>C-RING</td>
<td>0.13</td>
<td>0.83</td>
<td>1.17</td>
</tr>
<tr>
<td>C-ATP</td>
<td>0.15</td>
<td>0.91</td>
<td>1.28</td>
</tr>
<tr>
<td>C-RING2</td>
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<td>1.23</td>
</tr>
<tr>
<td>VAC</td>
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<td>3.19</td>
</tr>
<tr>
<td>dVAC</td>
<td>0.09</td>
<td>0.82</td>
<td>1.14</td>
</tr>
<tr>
<td>SW</td>
<td>0.10</td>
<td>0.48</td>
<td>1.05</td>
</tr>
<tr>
<td>H3p3h</td>
<td>0.09</td>
<td>0.82</td>
<td>1.13</td>
</tr>
</tbody>
</table>

$E_{\text{Bind}}(\text{Exp.}) = 0.85 \text{ eV} \ (\text{Ref.}[22])$.
$E_{\text{Bind}}(\text{Theo.}) = 1 \text{ eV} \ (\text{Refs.}[5,24])$.

<table>
<thead>
<tr>
<th>Adsorption</th>
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<th>PBE</th>
<th>PBE-D2</th>
<th>optB86b</th>
</tr>
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<tbody>
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<td>BRI</td>
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<td>3.14</td>
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<tr>
<td>C-RING</td>
<td>3.79</td>
<td>3.32</td>
<td>3.35</td>
<td></td>
</tr>
<tr>
<td>C-ATP</td>
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<td>2.82</td>
<td>2.81</td>
<td></td>
</tr>
<tr>
<td>C-RING2</td>
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<td>3.15</td>
<td>3.16</td>
<td></td>
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<tr>
<td>VAC</td>
<td>1.56</td>
<td>1.55</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>dVAC</td>
<td>3.54</td>
<td>2.93</td>
<td>2.90</td>
<td></td>
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<tr>
<td>SW</td>
<td>4.11</td>
<td>4.08</td>
<td>3.40</td>
<td></td>
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<tr>
<td>H3p3h</td>
<td>3.52</td>
<td>2.83</td>
<td>2.83</td>
<td></td>
</tr>
</tbody>
</table>

C–C distance (Theo.) = 2.9 Å (Ref. [7]).
C–C distance (Exp.) = 2.9 Å (Ref. [22]).

SLG-isolated C60 molecule interactions. Further, we allow for unre-
stricted geometry-optimization to identify the energy-minimized
adsorbed structures in our studies.

3.2. C60-defected SLG interactions

SLG sheets containing (i) a mono-vacancy (VAC), (ii) a 5–8–5
divacancy (dVAC), (iii) the Stone–Wales defect (SW), and (iv) a
555–777 reconstructed divacancy (H3p3h) were geometrically
optimized. The corresponding defect-formation energies ($E_f$) are
given in Table 3, and the predicted trends agree well with literature-
data [25–29]. Nevertheless, it is worth noting that the predicted $E_f$
value for the 5–8–5 divacancy is lower than that reported in Ref.
[30], a consequence of the fact that Ref [30] examines hydrogen
terminated graphene clusters within the LDA–DFT framework that
utilize a Gaussian basis.

The geometrically optimized defected SLG systems were probed
by a C60 molecule, and the most-stable geometries of the different
defected SLG–C60 systems are shown in Figure 1. An important dis-
tinguishing feature characterizing the interaction of VAC with C60
is the large binding energy (see Table 1) indicating strong chemi-
sorption of C60 on SLG containing a single vacancy. This is also re-
lected by the corresponding adsorption distance of 1.55/1.56 Å
(depending on the method used) as given in Table 2. PBE underes-
timates the binding energy, while the predicted adsorption dis-
tances are consistent with PBE-D2 and optB86b results, pointing
out the need for vdW corrections, despite the fact that PBE is able
to accurately represent bond-formation between VAC and C60. For
the other defected systems, the most stable geometries as pre-
bided by all methods correspond to physisorbed orientations of
C60 as evident from the binding energies (see Table 1) and cor-
responding adsorption distances (see Table 2). Also, while we do
observe energetically stable chemisorption of C60 on dVAC systems,
the physisorbed geometry is energetically more favorable by
around 0.1 eV and hence we do not consider the chemisorbed
dVAC systems further in our discussion. Further, based on the ener-
getics, it can be inferred that the SW–C60 system is the least stable,
as also seen by the corresponding larger adsorption distance. Inter-
estingly, the trends in the binding energies of the different C60-de-
defected-SLG systems correlate well with the observed trends in
the respective defect-formation energies, represented in Table 3.
These observations can be analyzed based on the defect-site geometry. The VAC system is characterized by significant recon-
struction around the mono-vacancy, with the local-structure con-
ists of a nine-membered ring that contains an under-
coordinated carbon atom (C1), and an adjoining pentagon ring that
shares a common high-strain C–C bond (C2 and C3) with the nine-
membered ring (see Figure 2). This C–C bond-distance equals 2.02
Å as compared to the equilibrium 1.42 Å, and together with the un-
der-coordinated C1 atom, they represent chemically reactive sites.
Consequently, the chemisorption of C60 is characterized by the for-
mation of two chemical bonds between C60 and SLG, with a pair of
adjacent carbon atoms of the C60 forming respective covalent
bonds with C1 and either of C2 or C3. In this process, the C2–C3 bond
is further weakened and extends to 2.54 Å. In contrast, the other
defected-SLG structures reconstruct to ensure the absence of dang-
gling bonds, which impedes C60 chemisorption.

Supporting electron density plots reveal the formation of direc-
tional covalent bonds between the C60 and VAC–SLG as seen in
Figure 3. Specifically, Figure 3a illustrates the spatial 3-D electronic
charge difference profile ($\Delta \rho(r)$) of VAC–SLG, where $r$ is a spatial
coordinate. $\Delta \rho(r)$ is defined in terms of the electron density of
the VAC–SLG system ($\rho_{\text{VAC–SLG}}(r)$), the corresponding isolated C60

Table 3

<table>
<thead>
<tr>
<th>Adsorption</th>
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<th>PBE-D2</th>
<th>optB86b</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAC</td>
<td>7.90, 7.78, 7.50</td>
<td>7.61</td>
<td>7.63</td>
</tr>
<tr>
<td>dVAC</td>
<td>7.60, 8.5, 30</td>
<td>7.33</td>
<td>7.34</td>
</tr>
<tr>
<td>SW</td>
<td>3.80, 4.75, 4.80</td>
<td>4.54</td>
<td>4.66</td>
</tr>
<tr>
<td>H3p3h</td>
<td>6.58</td>
<td>6.59</td>
<td>6.64</td>
</tr>
</tbody>
</table>

Figure 2. Minimum energy configuration of SLG containing an isolated monovacancy.
and SLG boundaries are on pristine SLG were examined and SLG boundaries in the presence of a mono-vacancy was attributed to the physisorbed on SLG containing either on VAC–SLG. In contrast, the physisorbed systems are characterized by electron-localization at the C₆₀ and SLG boundaries respectively and do not exhibit covalent bond-formation as seen in Figure 3c, which depicts the 1-D averaged electron–density difference plots for the C-ATP system.

4. Conclusions

By explicitly including vdW corrections within the DFT framework, interactions between an isolated C₆₀ molecule and pristine and defected SLG were accurately characterized. Energetically stable adsorption geometries of C₆₀ on pristine SLG were examined and identified to be typical of physisorption. Further, C₆₀ interactions with SLG containing different intrinsic point-defects were studied. SLG containing an isolated mono-vacancy chemically bonded with the C₆₀ molecule via the formation of two covalent C–C bonds. In contrast, C₆₀ physisorbed on SLG containing either isolated Stone–Wales defects or divacancies. The chemisorption of C₆₀ in the presence of a mono-vacancy was attributed to the presence of an undercoordinated carbon atom at the defect-site. These observations, while not unexpected, have profound implications for the fabrication of hybrid C₆₀–SLG nanostructures; specifically, appropriate defect-engineering could enable the formation of robust, thermally and mechanically stable C₆₀–SLG lattices with interesting structure–property relations.

Acknowledgement

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References