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Adsorption of Si@C60 Endofullerenes on Graphene: A ReaxFF Molecular Dynamics Study

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Abstract: Graphene–fullerene nanohybrids are promising building blocks for nanoelectronics, sensing and energy storage, yet the way an encapsulated atom controls the fullerene–graphene interface is still poorly understood. In this work, the adsorption of silicon-doped endohedral fullerenes (Si@C60) on pristine graphene was studied by reactive molecular dynamics (MD) simulations using the ReaxFF force field implemented in LAMMPS. Three scenarios were considered: (i) a single Si@C60 molecule approaching graphene from vacuum; (ii) four Si@C60 molecules adsorbing simultaneously on one graphene sheet at 300 K in the NVT ensemble; and (iii) a comparison of Si@C60 with Cu@C60 during heating from 0.1 K to 300 K. A single Si@C60 molecule forms a stable adsorbed configuration with an adsorption energy of −1.70 eV. In the multi-molecule system, the interaction energy of individual molecules ranges from −4.14 to −6.21 eV, and each molecule forms 4–6 interfacial C–C bonds with the surface. Remarkably, the interaction energy per bond is nearly constant (−1.034 to −1.035 eV) for all molecules, which shows that the interfacial bonds are energetically equivalent and the total binding strength scales with the number of bonds. Si@C60 binds to graphene through strong covalent bonding, whereas Cu@C60 is held mainly by weaker van der Waals forces. These results demonstrate that the chemical nature of the encapsulated atom governs the interaction mechanism and provide a basis for the computer-aided design of endofullerene–graphene nanohybrids.

Keywords: endohedral fullerene; Si@C60; Cu@C60; graphene; adsorption energy; molecular dynamics; ReaxFF; nanohybrid materials

1. Introduction

Since the discovery of buckminsterfullerene C60 [1] and the isolation of single-layer graphene [2, 3], carbon nanostructures have become central to modern materials science. Graphene combines very high carrier mobility, mechanical strength and a large specific surface area. Fullerenes, in turn, are well-defined zero-dimensional molecules with a closed cage that can accept electrons and act as molecular spacers or active sites. Combining the two in graphene–fullerene nanohybrids opens a route to materials whose electronic, mechanical and adsorption properties differ from those of either component [6, 13].

The hollow interior of the C60 cage can host foreign atoms, giving endohedral fullerenes, written M@C60 [4, 5]. The encapsulated atom changes the charge distribution of the cage, its reactivity and its frontier orbitals while the carbon shell protects it from the environment. For this reason, endohedral fullerenes are considered for molecular electronics, spintronics, quantum information and contrast agents [4, 5]. When such molecules are placed on graphene, the encapsulated atom may also change how strongly and in what manner the cage binds to the

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surface. This makes M@C60/graphene systems attractive for designing functional nanohybrids for sensors and nanoelectronic devices.

Despite this interest, the interface between metal- or semimetal-doped endohedral fullerenes and graphene is not well characterised. Most previous studies have dealt with pristine C60 on graphene or on metal surfaces, or with the adsorption of lithium on graphene–fullerene hybrids [6, 13]. In our related work, the adsorption of C60 on an Fe(110) surface was simulated with a second-generation Tersoff/ZBL potential [12], because such adsorption and the accompanying charge transfer can change the physical, chemical and magnetic properties of a surface. However, the adsorption energy, equilibrium configuration and orientation of Si@C60 on graphene, and the collective behaviour of several such molecules on one surface, have not been reported. It is also unclear whether a different encapsulated atom, for example Cu, leads to the same type of bonding.

In this work, we use reactive molecular dynamics with the ReaxFF force field [7, 8] to address three questions. First, how stable is a single Si@C60 molecule adsorbed on graphene? Second, how do several Si@C60 molecules organise on one graphene sheet, and how many interfacial bonds does each molecule form? Third, how does the interaction of Si@C60 with graphene differ from that of Cu@C60? The answers clarify the role of the encapsulated atom in fullerene–graphene bonding at the molecular level.

2. Computational details

All simulations were performed with the open-source molecular dynamics package LAMMPS [9]. Interatomic interactions (C–C, C–Si and C–Cu) were described by the ReaxFF reactive force field [7, 8]. ReaxFF is a bond-order-based potential: bond orders are computed from interatomic distances at every step, so chemical bonds can form and break during the simulation. Charges are equilibrated dynamically, and van der Waals and Coulomb terms are included for all atom pairs. This makes ReaxFF suitable for distinguishing covalent bonding from physical (van der Waals) adsorption at the fullerene–graphene interface.

The model systems consisted of a pristine single-layer graphene sheet and one or more endohedral fullerenes placed above it in vacuum (Fig. 1). In Si@C60 and Cu@C60, the guest atom was initially placed at the centre of the C60 cage. Three simulation scenarios were considered:

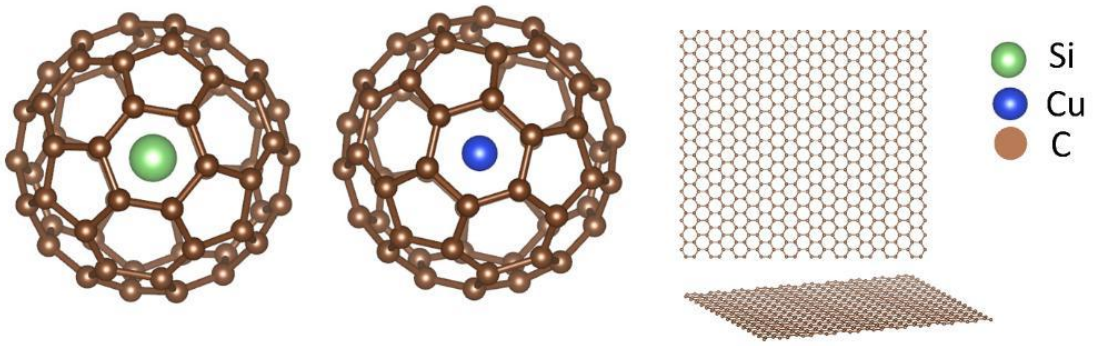

Fig. 1. Initial models of the Si@C60 and Cu@C60 endohedral fullerenes and the graphene sheet (top and side views). Si, Cu and C atoms are shown in green, blue and brown, respectively.

1. **Single Si@C60 on graphene.** The initial structure was relaxed by energy minimisation. The approach of the molecule to the surface, its spatial position and the change of the total potential energy were then followed until a stable adsorbed configuration formed.

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2. **Four Si@C60 molecules on graphene.** Four Si@C60 molecules were placed above one graphene sheet. After energy minimisation, the system was equilibrated in the NVT (canonical) ensemble at 300 K, with the temperature controlled by a Nosé–Hoover thermostat [10, 11], with a time step of 1 fs. The approach of each molecule to the surface, their relative arrangement, the molecule–surface distances and the time evolution of the potential energy were analysed.

3. **Si@C60 versus Cu@C60.** Each endofullerene–graphene system was first energy-minimised and then heated in the NVT ensemble from 0.1 K to 300 K, which allowed the bonding of the two molecules to the surface to be compared under identical conditions.

The adsorption energy of a single molecule was calculated as

E_{ads} = E_{Si@C_{60}/graphene} - \left(E_{graphene} + E_{Si@C_{60}} \right)

where E(Si@C60/graphene) is the total energy of the adsorbed system, and E(graphene) and E(Si@C60) are the energies of the isolated graphene sheet and the isolated endofullerene, respectively. A negative value means that adsorption is energetically favourable. For the multi-molecule system, the interaction energy E(int) of each molecule with graphene was evaluated in the same way, and the number of interfacial C–C bonds N(b) formed between that molecule and surface atoms was counted. The average energy per bond was then obtained as

\varepsilon_{b} = \frac{E_{int}}{N_{b}}

This quantity shows whether the interfacial bonds formed by different molecules are energetically equivalent.

3. Results and discussion

3.1. Adsorption of a single Si@C60 molecule

A single Si@C60 molecule adsorbs on graphene spontaneously and forms a stable configuration with E(ads) = −1.70 eV. As the molecule approaches the surface, the total potential energy of the system decreases steadily until it reaches a minimum, where the cage rests on the graphene sheet (Fig. 2). In this equilibrium configuration, the Si atom remains inside the cage, and the C60 shell keeps its nearly spherical shape. Only the cage atoms facing the surface are slightly displaced towards the graphene plane.

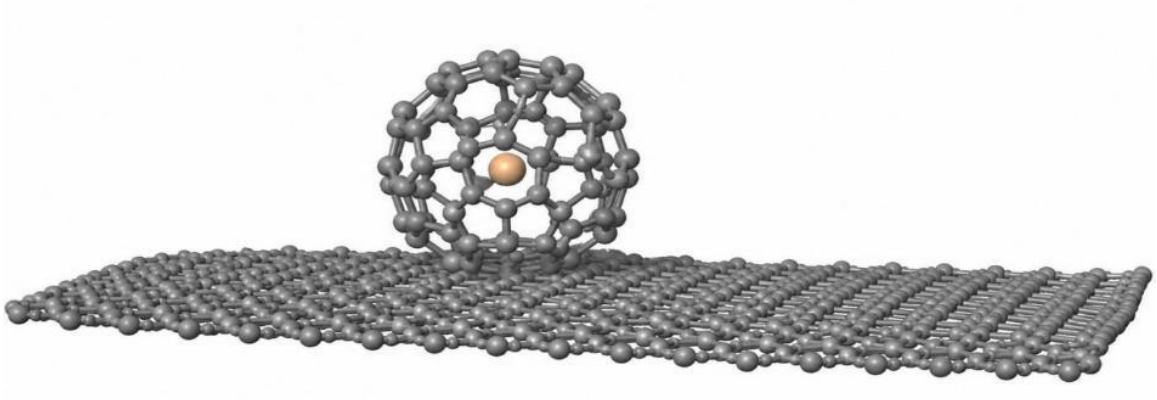

Fig. 2. Equilibrium adsorption configuration of a single Si@C60 endofullerene on graphene. C and Si atoms are shown in grey and orange, respectively.

The negative adsorption energy shows that the Si@C60/graphene system is energetically more favourable than its separated components. Its magnitude, about 1.7 eV, is clearly larger than the thermal energy at room temperature (kT ≈ 0.026 eV), so the adsorbed molecule will not desorb spontaneously under ambient conditions. The encapsulated Si atom changes the electron density of the cage and makes the facing carbon atoms more reactive towards the π-system of graphene, which favours a strong cage–surface interaction.

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3.2. Collective adsorption of four Si@C60 molecules

When four Si@C60 molecules adsorb on one graphene sheet at 300 K, every molecule binds covalently to the surface, with interaction energies of −4.14 to −6.21 eV. Fig. 3 shows a snapshot of the system as the molecules approach and attach to the surface. The time dependence of the molecule–surface distances showed that all four molecules move towards graphene and settle into adsorbed positions, while the potential energy of the system decreases and then fluctuates around a constant value. During this process, the graphene sheet develops a slight local corrugation under the molecules.

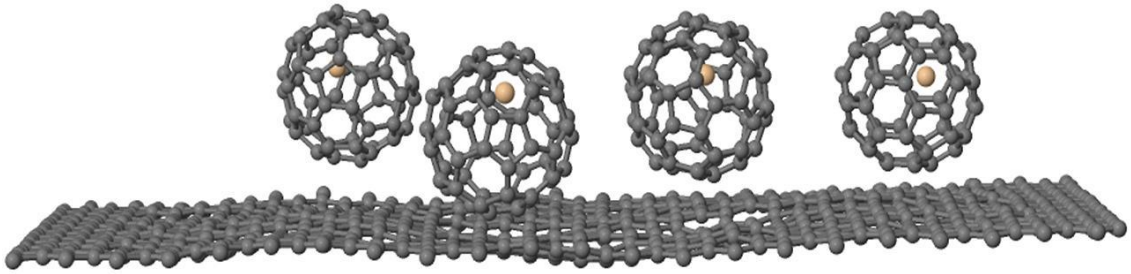

Fig. 3. Snapshot of four Si@C60 endofullerenes adsorbing on graphene during the MD simulation at 300 K. C and Si atoms are shown in grey and orange, respectively.

Table 1 lists, for each molecule, the interaction energy, the number of interfacial bonds and the average energy per bond.

Table 1. Interaction energy (E(int)), number of interfacial bonds (N(b)) and average energy per bond (E(int)/N(b)) for four Si@C60 molecules adsorbed on graphene at 300 K.

Si@C60 molecule	E(int), eV	N(b)	E(int)/N(b), eV
1	−4.14	4	−1.035
2	−4.14	4	−1.035
3	−6.21	6	−1.035
4	−5.17	5	−1.034

The number of bonds varies from molecule to molecule (4, 4, 6 and 5), and so does the total interaction energy. The energy per bond, however, is almost the same for all molecules: −1.034 to −1.035 eV. This means that each interfacial C–C bond contributes about 1.03 eV, regardless of where the molecule lands on the surface. In other words, the binding strength of a molecule is controlled by how many bonds it forms, and all these bonds are of the same type and similarly stable.

The larger interaction energies in the four-molecule system, compared with the single-molecule value of −1.70 eV, reflect the difference in conditions. The single-molecule configuration was obtained by energy minimisation, whereas the four-molecule system was equilibrated at 300 K. Thermal motion at 300 K appears to help the cage atoms overcome the barrier to covalent bond formation, so several bonds per molecule are formed. This suggests that the adsorption state of Si@C60 on graphene can be tuned by temperature, from a weakly bound state to a chemisorbed state with 4–6 bonds.

3.3. Comparison of Si@C60 and Cu@C60

The type of bonding to graphene depends on the encapsulated atom: Si@C60 chemisorbs, while Cu@C60 physisorbs. Fig. 1 shows the initial models of both molecules and the graphene sheet. During heating from 0.1 K to 300 K, Si@C60 formed strong covalent bonds with graphene

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and showed a high adsorption energy. Cu@C60, in contrast, was held to the surface mainly by van der Waals forces and showed noticeably weaker adsorption.

This difference can be explained by the electronic nature of the guest atoms. Silicon is a group-14 element, like carbon, and readily forms directional covalent bonds. Inside the cage, it perturbs the charge distribution of the C60 shell and activates the carbon atoms facing the surface. Copper is a transition metal with a filled 3d shell, which interacts with the cage mainly through charge transfer and has a weaker effect on the reactivity of the outer surface. As a result, the Cu@C60 shell behaves more like pristine C60, which is known to physisorb on graphene [13].

Taken together, the three scenarios show that the chemical nature of the encapsulated atom is a key parameter of endofullerene–graphene interfaces. Choosing the guest atom therefore allows the interface to be tuned from weak, reversible van der Waals adsorption to strong covalent anchoring. Strong anchoring is useful where mechanical and thermal stability is needed, for example in electrodes and sensors. Weak adsorption is preferable where the electronic structure of graphene should be preserved or the molecules should remain mobile.

4. Conclusions

The adsorption of Si@C60 endohedral fullerenes on graphene was studied by ReaxFF molecular dynamics, and the following conclusions can be drawn:

1. A single Si@C60 molecule forms a stable adsorbed configuration on graphene with an adsorption energy of −1.70 eV, so the Si@C60/graphene hybrid is energetically favourable compared with its separated components.

2. When four Si@C60 molecules adsorb on graphene at 300 K, each molecule forms 4–6 interfacial bonds, and the interaction energies range from −4.14 to −6.21 eV.

3. The interaction energy per bond is nearly identical for all molecules (−1.034 to −1.035 eV). The interfacial bonds are therefore energetically equivalent, and the total binding strength of a molecule scales with the number of bonds it forms.

4. Si@C60 binds to graphene through strong covalent bonds, whereas Cu@C60 is held mainly by weaker van der Waals forces. The interaction mechanism thus depends strongly on the chemical nature of the encapsulated atom.

These findings provide a molecular-level picture of endofullerene–graphene interfaces and can guide the computer-aided design of carbon-based nanohybrids for nanoelectronics, sensors and energy storage. Future work will combine these MD results with first-principles calculations of charge transfer and electronic structure, and extend the study to other guest atoms and to metallic substrates.

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