Contents lists available at ScienceDirect

Applied Surface Science

Covalent and noncovalent functionalization of pristine and defective graphene by cyclohexane and dehydrogenated derivatives

Ceren Sibel Sayin [a], Daniele Toffoli [b],*, Hande Ustunel [a],*

[a] Department of Physics, Middle East Technical University, Dumlupinar Bulvari 1, 06800 Ankara, Turkey
[b] Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Trieste, Via L. Giorgieri 1, I-34127 Trieste, Italy

ARTICLE INFO

ABSTRACT

The interaction of cyclohexane (C_6H_{12}), cyclohexyl ($C_6H_{11}^*$) and cyclohexene (C_6H_{10}) with both pristine and defective graphene (single vacancy and a carbon adatom), is systematically investigated within the density functional theory framework. C_6H_{12} physisorbs on both pristine and defective graphene while C_6H_{10} chemisorbs on graphene in the presence of an adatom. The $C_6H_{11}^*$ radical binds covalently with the graphene substrate in all adsorption geometries considered.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Advances in the fabrication and processing of graphene [1] has greatly expanded its potential applications in the last decade. In a short span of time, graphene has gone from being a novel source of fascinating physical phenomena [2,3] to having sophisticated applications in various fields including optics, catalysis and device technology [4–7]. Owing to its unique, defect-free sp^2 network structure, graphene possesses unusually high carrier mobility [8], thermal conductivity [9], and mechanical strength [10]. The distinguishing feature of its band structure is the occurrence of double cones centered at the six Fermi points in the hexagonal Brillouin zone, referred to as Dirac cones. Contributed by the delocalized π and π^* orbitals, the apices of the Dirac cones touch at a single point resulting in a linear electronic dispersion and a zero density of states at the Fermi level.

Chemical functionalization of graphene is a versatile technique with various applications in band gap engineering, gas sensing, and spintronics [11–15]. The species range from single atoms [16,17], all the way to large polymers [18]. Functionalization may be achieved

via covalent or noncovalent bonding [19]. Covalent bonding is usually accompanied by the destruction of the linear dispersion and the opening of a band gap at the Fermi points. Noncovalent functionalization, on the other hand, relies on weak dispersive forces and often leaves the band structure unchanged. A charge transfer may nonetheless occur even for noncovalent bonding. In the study by Coletti et al. [20] the Fermi level of a graphene sheet, n-doped by the SiC substrate, was restored to its original location at the Dirac point by gradually increasing the surface coverage of tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) molecules.

Defects and impurities can be introduced in the network to facilitate functionalization [13,21,22]. Point defects, such as single or double vacancies and adatoms locally alter the electronic structure and act as functionalization centers [23,24]. Due to their high formation energies, such defects are present with negligible concentration in graphene produced through standard sample growth processes. However, controlled defect creation is possible via methods such as particle irradiation and chemical treatment [25].

Cyclohexane (C_6H_{12}) is a monocyclic hydrocarbon, synthesized from hydrogenation of benzene and produced on large industrial scales primarily for use in the production of adipic acid, a nylon intermediate [26]. Interaction between C_6H_{12} (and its dehydrogenated or oxygenated derivatives) and graphene-based materials has been sporadically explored in the literature. In an experimental study by Yu *et al.* [27], N-doped carbon nanotubes (CNTs) were

shown to display catalytic activity towards the aerobic oxidation of cyclohexane. Bittner et al. [28] and Díaz et al. [29] investigated the adsorption of non-cyclic and cyclic molecules on carbon nanotubes (CNT), including C_6H_{12} and C_6H_{10}. In a density functional theory (DFT) study by Zhao et al. [30], the adsorption of C_6H_6, C_6H_{12} and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) on a single-walled CNT were explored. C_6H_{12} was found to bind slightly more strongly than benzene even though all molecule–CNT interactions were of dispersive nature. DFT was also applied by Yang et al. [31] to study the mechanism of CNT-catalyzed oxidation of C_6H_{12} by molecular oxygen.

In this work, we explore the interaction of cyclohexane (C_6H_{12}), the cyclohexyl radical ($C_6H_{11}^*$) and cyclohexene (C_6H_{10}) with both pristine and defective graphene using DFT. The graphene defects under investigation are a single vacancy and a C adatom. While in C_6H_{12}, carbon atoms are sp^3-hybridized, C_6H_{10} is characterized by a single C—C double bond. $C_6H_{11}^*$, on the other hand, is a radical with high reactivity. The aim of this study is to investigate how, and to which extent, local changes in the electronic structure of the adsorbate affect the graphene-molecule and defect-molecule interaction.

2. Computational details

The calculations were performed using plane wave-based density functional theory as implemented in the Quantum Espresso code suite [32]. Vanderbilt ultrasoft pseudopotentials [33] within GGA(PBE [34]) were used to describe the ion-electron interaction. Van der Waals dispersion forces were included to treat the molecule-graphene interaction for physisorbed species. For spin-unpolarized configurations, a van der Waals correction to the exchange-correlation functional was included in a fully self-consistent scheme through the Soler algorithm [35]. In particular, a vdW-DF2 type van der Waals functional was used with the C09 exchange (vdW-DF2^{C09x}) [36,37] along with a kinetic energy cut-off of 30 Ryd. Due to the lack of a spin-polarized implementation for self-consistent van der Waals functionals, the PBE-D2 method of Grimme [38] was used for those cases where spin polarization is important. Covalently bonded species instead were handled using conventional GGA. Marzari–Vanderbilt cold smearing with a broadening of 0.02 Ryd was adopted for Brillouin zone integration [39] with Monkhorst-Pack meshes of $6 \times 6 \times 1$ and $3 \times 3 \times 1$ respectively for the 3×3 and 6×6 simulation cells used in our calculations. A separation between periodic images of at least 12 Å was allowed in all calculations. Using these parameters, the lattice constant of graphene was calculated to be 2.46 Å at the GGA, vdW-DF2^{C09x} and PBE-D2 levels of theory, in agreement with previously reported values [40]. Geometry optimization was performed with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm with a force convergence threshold of 0.025 eV/Å per atom. Figures were generated using the open source visualization program XCrySDen [41]. The geometry optimization for isolated molecules was carried out in a large cubic unit cell at the Γ point. The optimized geometries are shown in Fig. 1 and calculated structural parameters agree well with values reported in the literature [42,43].

In order to understand coverage effects, molecular adsorption on pristine graphene was explored using coverages $\Theta = 1/36$ and $\Theta = 1/9$ monolayer (ML), which correspond to surface densities of one molecule per 6×6 and 3×3 simulation cells respectively. In the terminology adopted in this study, coverage refers to the number of molecules per primitive unit cell. The 1/36 ML coverage corresponds to a center-to-center intermolecular distance of about 14.7 Å, while $\Theta = 1/9$ ML corresponds to full coverage for flat geometries. Fig. 2 illustrates a representative flat adsorption geometry for C_6H_{12} for the two coverages.

Calculations involving defective graphene were performed only in the 6×6 supercell. The defect formation energies are calculated from:

$$E_f = E_{def-gr} - n\mu_C - E_{gr}, \qquad (1)$$

where E_{gr} is the total energy of the pristine graphene sheet, E_{def-gr} is the total energy of defective graphene and $\mu_C = E_{gr}/N$ is the chemical potential of carbon. Here N is the number of C atoms in the simulation cell, $n = -1$ for the vacancy and $n = +1$ for an adatom. The GGA formation energies for the single vacancy and the adatom are calculated to be 7.56 eV and 6.41 eV respectively, both in good agreement with previous results [44,45].

The molecular adsorption energies are calculated using:

$$E_{ads} = E_{gr} + E_{mol} - E_{mol+gr} \qquad (2)$$

where E_{mol+gr} is the total energy of the combined system, E_{gr} is the energy of the pristine or defective graphene sheet and E_{mol} is the energy of an isolated neutral C_6H_{12}, $C_6H_{11}^*$ or C_6H_{10} molecule, all calculated with the same computational parameters. With this definition, positive adsorption energies correspond to stable adsorption geometries. For physisorbed species, E_{mol} and E_{gr} were both calculated using the relevant vdW-based exchange-correlation functionals while for chemisorption, traditional GGA was used. Spin polarization was employed as needed.

Charge density differences for chemisorbed species were calculated by using the formula:

$$\Delta\rho(\vec{r}) = \rho_{mol+gr}(\vec{r}) - \rho_{gr}(\vec{r}) - \rho_{mol}(\vec{r}) \qquad (3)$$

where $\rho_{mol+gr}(\vec{r})$ is the electronic charge density of the pristine or defective graphene substrate interacting with the adsorbate, $\rho_{gr}(\vec{r})$ is the charge density of either pristine or defective graphene alone and $\rho_{mol}(\vec{r})$ is the charge density of the isolated molecule.

Charge transfer between the graphene network and the adsorbates upon adsorption was investigated using the Bader charge analysis as implemented by the Henkelman group [46]. The charge on $C_6H_{11}^*$ due to adsorption was determined taking as reference the neutral C_6H_{11} radical.

3. Results and discussion

3.1. Electronic properties of pristine and defective graphene

As a basis for our discussion on molecular adsorption, we briefly review the electronic properties of pristine graphene and graphene with point defects. Fig. 3 displays the band structures of pristine graphene as well as graphene with a single vacancy and a C adatom calculated using the GGA exchange-correlation potential. Due to zone folding, the Fermi level now appears at the Γ point. In the case of the single vacancy, spin polarization lifts the degeneracies while the Fermi level is depressed below the original location. The adatom introduces a flat state lying along the Fermi level throughout the Brillouin zone while degeneracies around the Fermi level are lifted. For the single vacancy, spin-unpolarized GGA and vdW-DF2^{C09x} calculations both yield a ground state where one of the three atoms surrounding the vacancy undergoes an out-of-plane displacement of about 0.6 Å. The remaining two atoms approach each other to a distance of 2.0 Å. Spin polarized GGA and PBE-D2 calculations, on the other hand, both converge to a flat geometry with a magnetization of about 1.40 μ_B per simulation cell. The GGA spin-polarized ground state is energetically more favorable by 0.19 eV per vacancy with respect to the GGA spin zero state, in good agreement with past investigations [47–49].

The most stable geometry for the carbon adatom is the bridge position where the adatom resides on top of the mid-point of a C—C