Ab initio study of chemical bond interactions between covalently functionalized carbon nanotubes via amide, ester and anhydride linkages

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ABSTRACT

In this paper, we have investigated the chemical bond interactions between covalently functionalized zigzag (5,0) and (8,0) SWCNT—SWCNT via various covalent linkages. Side-to-side junctions connected via amide, ester and anhydride linkages were particularly studied. The geometries and energy of the forming reaction were investigated using first-principles density functional theory. Furthermore, the band structures and the total density of states (DOS) of the junctions have also been analyzed. Our results show that several promising structures could be obtained by using chemical connection strategy and particularly the junctions formed by coupling amino functionalized SWCNT and carboxylic acid functionalized SWCNT was more favorable.

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1. Introduction

Nanoscale carbon-based materials including carbon nanotubes (CNTs), graphene oxide (GO) and carbon nanofibers (CNFs) among others, have unique and tunable properties enabling applications in various fields such as electronic applications [1], composites [2], energy storage devices [3,4], medical applications [5] and water treatment technologies [6,7]. Single-walled carbon nanotubes (SWCNTs) have been one of the most popular nanomaterials that have interesting physical properties and the potential to be incorporated into a wide variety of technological applications [8—11].

In recent years, an important part of the research is focused on the intramolecular junctions of CNTs because of their fascinating applications in nanodevices [12—18]. In particular, junctions obtained from SWCNTs are of interest for nanoscale electronic devices because of the nanoscale diameter of the tubes and their room temperature transport properties. These intramolecular carbon nanotubes junctions which can be formed in single-walled carbon nanotubes by introducing a pentagon and/or heptagon into the hexagonal carbon lattice can serve as functional components in the circuit such as photovoltaic devices, amplifiers, rectifiers, switches, etc. [19]. Many studies have been performed to investigate methods of joining single-walled carbon nanotubes [20—28]. Intramolecular junctions in single-walled carbon nanotubes are potentially ideal structures for building robust, molecular-scale electronics but the realization of these carbon-based molecular electronics is still quite challenging [29].

Besides the CNT intramolecular junctions, the interconnection of carbon nanotubes via chemical functionalization has been also reported in literature [30—35]. In fact, integrating other functional groups in a controlled manner onto CNT surfaces allows the possibility to form intermolecular CNT junctions via covalent linkages. This approach could enable the linking of individual carbon nanotubes to form complex networks and opens the possibility to realize carbon based devices and circuits for potential nanoelectronic applications [31].

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It was reported that covalent interconnected semiconducting carbon nanotubes can be used as field-effect active channels [36,37], nanorectifiers [38], or even nanoinverters [39,40]. Metallic counterparts can function as interconnects in electronic devices for local tuning on an active component or for probing local electronic states. Chiu et al. reported that the attached chemical functional groups can behave as either an electron donor or an acceptor, and attributed the charge transfer to molecular linker at the junctions, which show diode-like behavior [32]. Moreover, due to the superior mechanical properties of CNTs, intermolecular CNT junctions may potentially be used as reinforcing components in polymer composites [41]. These promising applications enhance the importance of studying the properties of CNT intermolecular junctions.

An end-to-end intermolecular carbon nanotube junctions by coupling chemically functionalized nanotubes with molecular linkers were widely reported in literature. However, a side-to-side intermolecular carbon nanotube junctions remain very little studied and the theoretical works are not numerous. This can be explained by the fact that it is generally believed that any chemical linking reaction would be most favorable at the open ends of each tube than at the exterior sidewalls.

In this work, several junction models built from (5,0) and (8,0) covalently functionalized single-walled carbon nanotubes via covalent linkages have been studied by using first-principles density functional theory calculations. In particular, we focus our study on side-to-side junction connected via amide, ester and anhydride linkages. The geometries and energy of the forming reaction for intermolecular SWCNT junctions are investigated. Furthermore, the electronic properties of the junctions are analyzed and compared with those of pristine SWCNTs.

2. Methodology

The density functional calculations in the present work were performed within the generalized gradient approximation GGA [42] using the first-principles code SIESTA [43]. In all calculations, the double-zeta plus polarization (DZP) numerical atomic orbital basis set was used. Norm-conservative Pseudopotentials were constructed using Troullier–Martins schemes [44]. A cut-off of 300 Ry for the grid integration was utilized to represent the charge density. A Monkhorst-Pack k-point grid of dimension (1, 1, m) has been used where m was determined to ensure convergence of the total energy with acceptable numerical precision [45]. We found that total energy converges for m equal to 14 which corresponds to $1 \times 1 \times 14$ Monkhorst-Pack. Our calculations were performed using two zigzag (5,0) and (8,0) single-walled carbon nanotubes having respectively a diameter equal to 3.978 Å and 6.263 Å. Periodic boundary conditions and a supercell approximation are used to ensure that the junction models constructed from different SWCNTs via covalent linkage do not interact with their periodic images. The supercell used has three periods, with a total length of 1.286 nm. To avoid the basis set superposition error (BSSE), we have adopted the counterpoise correction suggested by Boys et al. [46] for correcting the binding energies. The atomic positions of the structure are relaxed until all the residual forces are smaller than 0.02 eV/Å.

3. Results and discussion

Fig. 1 depicts the adsorption of hydroxyl (−OH), carboxylic acid (−COOH) and amine (−NH$_2$) functional groups on the (5,0) SWCNT.

This clearly shows that the covalent bond between the carbon atom and a functional group pulls out the carbon atom radially resulting in the distortion of the tube at the functional site. This phenomenon is also observed for all sidewall functionalized (8,0) SWCNTs. This distortion can be understood by the local sp^3 rehybridization within a functionalized site. Indeed, the C−C bond length between the C atom connected to the functional groups and its three nearest neighbors on the carbon nanotube are around 1.52−1.56 Å which are close to the C−C distance in the diamond phase with sp^3 hybridization and significantly larger than the C−C bond length of 1.42 Å in the pristine nanotube with sp^2 hybridization. The C−C bond lengths in the carbon nanotube beyond the first neighbors are found to be little affected by the functionalization. Table 1 summarizes the bond angle variation for pristine and functionalized (5,0) and (8,0) SWCNTs. As shown in Table 1, we can observe that the covalent attachment of functional groups to nanotube leads to the formation of a local sp^3 defect on the tube sidewall.

The chemical interactions between these functional groups and the nanotubes were evaluated by calculating the binding energies using the following equation:

$$E_b = E(fSWCNT) - E(SWCNT) - E(\text{functional group})$$

where E(fSWCNT) is the total energy of the functionalized SWCNT (tube with the functional group), E(SWCNT) is the total energy of the pristine SWCNT and E(functional group) is the total energy of the isolated functional group. All the analyzed systems have the atomic positions totally relaxed.

The results of the binding energies and the corresponding charge transfers between the functional groups and the nanotube are summarized in Table 2. We can observe that all the studied systems have a very stable interaction with the nanotubes ($E_b < 0$).
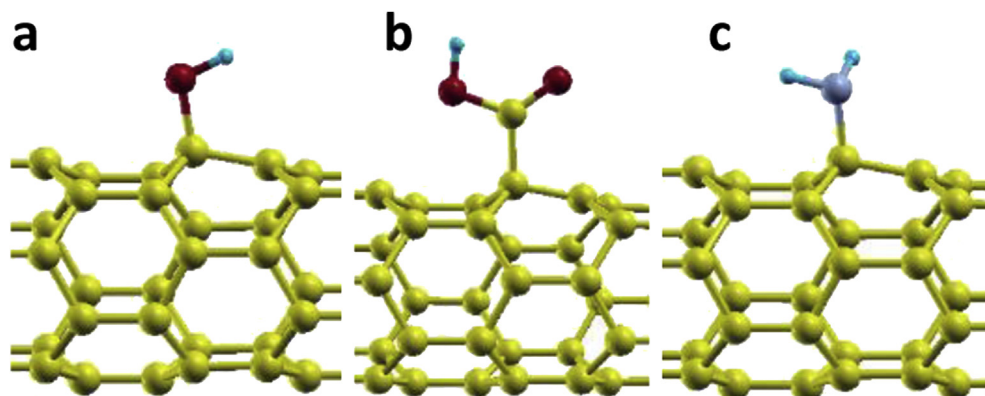

Fig. 1. Adsorption of (a) hydroxyl, (b) carboxylic acid and (c) amine functional groups on the (5,0) SWCNT.