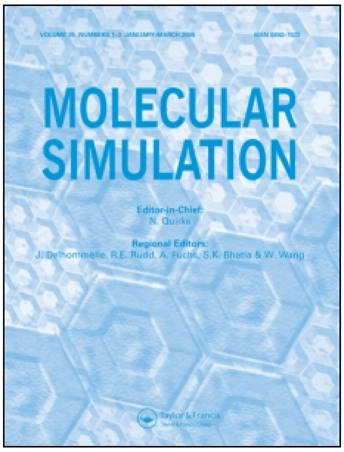

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Structural and electronic properties of diazonium functionalized (4, 4) single walled carbon nanotube: an *ab initio* study

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Structural and electronic properties of diazonium functionalized (4, 4) single walled carbon nanotube: an *ab initio* study

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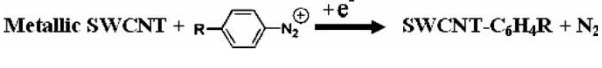
In this work, *ab initio* density functional theory (DFT) calculations are performed to study the structural and electronic properties of diazonium reagent functionalized (4, 4) single-walled carbon nanotube (SWCNT). We find the aryl group covalently bonds with SWCNT and prefers to be perpendicular to the side wall of nanotube. It has a rotational barrier of 0.35 eV around the formed aryl-tube bond axis and should be thermodynamically stable at room temperature. Additionally, new peaks appeared around the Fermi energy in the density of state (DOS) due to the weak band dispersion. Increasing of the coverage of the functional group will result in significant upshift of the Fermi level.

Keywords: *Ab initio* density functional theory calculation; Single walled carbon nanotube; Density of state; Band structure; Covalent bond

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are known to be extremely promising materials for potential applications in various fields such as material and biological sciences due to their excellent electronic, thermal and mechanical properties [1–3]. It has been shown that a variety of compounds such as small organic or inorganic molecules, biomolecules and polymers could covalently or non-covalently bond with SWCNTs to form nanotube composites [4–11]. Such modifications will strongly change the electronic properties of SWCNTs and add new functionality. Generally, SWCNTs are typically grown as mixtures of metallic and semiconducting tubes, depending on the arrangement of the hexagonal rings along tubular surface [12]. However, this actually constitutes one of the notable obstacles to the widespread application of this unique material, since metallic and semiconducting materials have very different functions in nano-devices. Hence, separating them has become a central issue in terms of effective fabrication of high performance electronic devices. Among the physical and chemical methods currently developed [7,13–17], a simple approach based on using diazonium salt reagents to react with metallic nanotubes has been shown to demonstrate high selectivity [16–17]. It is believed that the selectivity in the reaction of the diazonium salt with the SWCNT comes from the difference between the electronic band structures of metallic and semiconducting SWCNTs. In contrast to a semiconducting SWCNT, a metallic SWCNT has finite electron density of states (DOS) around the Fermi level, meaning that there are electrons available to stabilize the charge-transfer complex preceding bond formation. This process involves the diazonium reagent extracting electrons from the metallic SWCNT, evolving N_2 gas and ultimately forming a covalent aryl bond with the sidewall of the SWCNT. The reaction scheme can be described as



Here R represents a Chlorine atom. Aryl diazonium chemistry has been successfully applied for the modification of carbon surfaces of widely varying curvature. Examples include highly ordered pyrolitic graphite (HOPG) [18–19] as well as small-diameter SWCNTs [20–21].

We are not aware that there have been any previous theoretical calculations to investigate the structural and

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electronic properties of the diazonium functionalized metallic SWCNT. Understanding at the atomic level how the structural and electronic properties of the SWCNT change upon functionalization is an important first step toward an overall understanding of this chemistry. The smaller SWCNTs are more amenable to first-principle computational characterization, hence we have chosen a (4, 4) metallic SWCNT in this work. The small-diameter SWCNTs have enhanced reactivity due to the increased curvature. However, the reaction mechanism may be expected to be analogous (albeit with differing kinetics) for all the metallic SWCNTs and even HOPG. The geometry and thermodynamic stability for a single aryl functional group on the SWCNT are examined first. Then we systematically investigate the change of structural and electronic properties at the different coverages of the functional group on the SWCNT.

In Section II, we outline our computational method. Section III presents the calculated results for the structural and electronic properties of diazonium functionalized SWCNT. The last section draws relevant conclusions.

2. Computational methods

Our DFT based computations were partially performed using a plane wave pseudo potential CPMD code [22] and implementing the PBE exchange correlation functional [23]. The ultrasoft pseudopotentials were employed to describe the core-valence interaction for C, H and Chlorine (Cl) atoms. A (4, 4) nanotube containing 12 units along tube axis (96 C atoms) is put in a periodically repeating hexagonal supercell. The lateral dimension is 26 × 26 Å, which is large enough to ensure the negligible interaction between the tube and its periodic images. Only the gamma point [24] is used for the integration of the Brillouin zone (BZ) and the Kohn-Sham electronic wave functions are expanded in a plane wave basis with a kinetic energy cutoff of 25 Ry. Geometry optimization was performed by a Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [25].

To obtain accurate band structure and DOS, additional calculations were performed by using VASP code [26–27]. Different from the former calculation, here we use the projector augmented wave method [28–29] instead of the pseudo potential approach and the typical supercell is reduced to four units in the direction of the tube axis (containing 32 atoms). Totally sixty K-points were employed for sampling the one dimensional BZ and cutoff energy for plane waves is chosen up to 500 eV.

Additionally, the lattice constant (i.e. the value of c) for the supercells mentioned above were first optimized to minimize the strain effect along the tube axis. Different values of c along the tube axis are chosen and then we perform geometry optimization independently by either BFGS or conjugated gradient methods. The variation of energy as a function of lattice constant (c) was thus obtained and the configuration corresponding to the lowest energy will be used in the following calculations.

3. Results and discussion

To obtain the equilibrium configuration for the diazonium reagent functionalized SWCNT, we first put a single aryl functional group (i.e. a C_6H_4Cl radical) at a distance of 2 Å from the side wall of nanotube and perform geometry optimization. Figure 1(a) presents the final configuration containing a single aryl group and a (4, 4) SWCNT. A covalent aryl-tube bond is formed, with the functional group preferring a perpendicular orientation with respect to the surface of the SWCNT. The structural distortion of the nanotube is limited to the nearest neighbors of the bonding site. The C—C bond angles about the bonding site vary from 106.5 to 112.8°. The computed aryl-tube bond length is 1.545 Å, while the C—C bond lengths on the nanotube around the bonding site are 1.535 Å—both are close to the typical C—C distance in the sp^3 hybridized diamond phase and significantly larger than the C—C bond length of 1.44 Å in a perfect nanotube with sp^2 hybridization. A contour plot of the valence charge density in a slice passing through the plane of the aryl group is shown in figure 1(b). It clearly demonstrates the formation of a covalent bond between the functional group and the SWCNT as well as the local distortion along the radial direction on the tube sidewall due to the sp^3 re-hybridization of C—C bond. Here we should emphasize that spin-polarization has not been systematically included since we found that once the aryl chlorine group is covalently attached onto the SWCNT, the system will

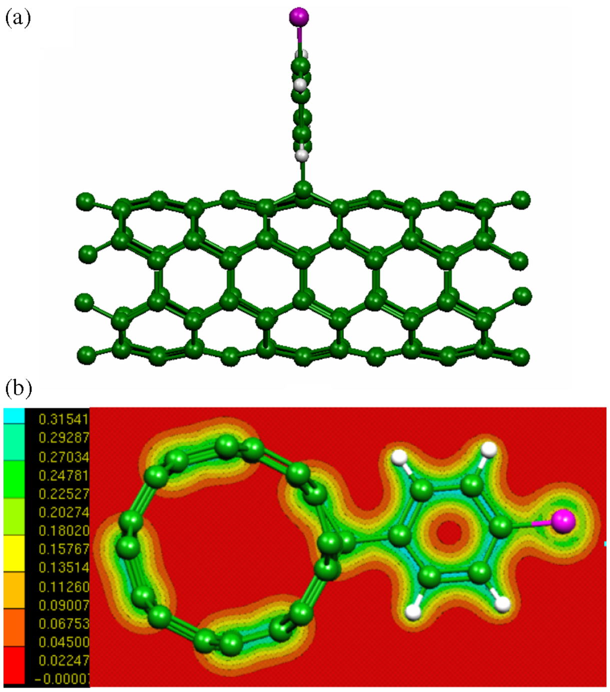

Figure 1. (a) The energy preferred configuration for the diazonium functionalized SWCNT in a hexagonal supercell containing 12 units in the direction of nanotube axis. The blue, white and red balls represent carbon, hydrogen and Chlorine atoms, respectively; (b) projection of valence charge density of the diazonium reagent functionalized SWCNT on a plane passing through the functional group.

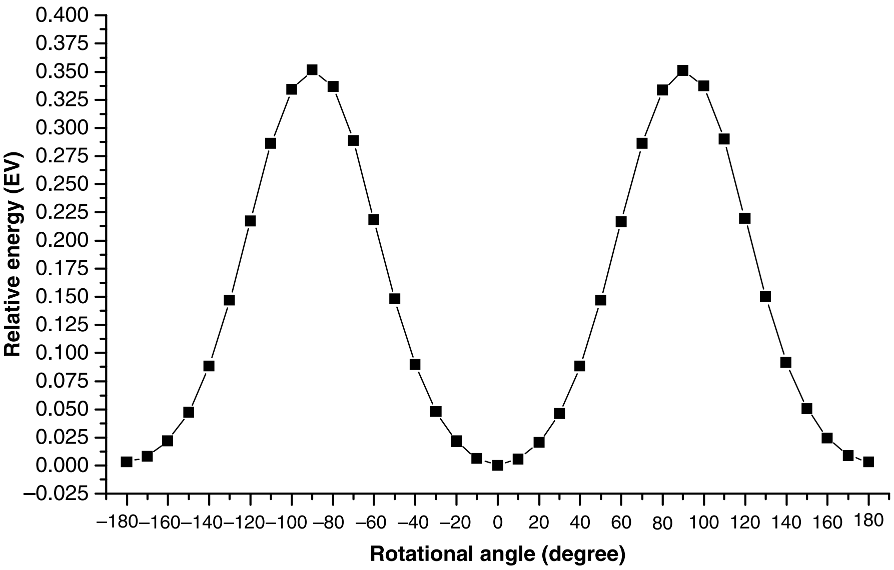

Figure 2. The variation of the relative energy to the lowest energy structure shown in figure 1(a) as a function of the rotational angles around the formed aryl-tube bond axis.

converge to non-magnetic ground state (this was verified with inclusion of spin polarization).

Experimentally, it has been shown that the functional group is stable at room temperature [17]. Starting from the equilibrium configuration, we let the diazonium group rotate about the formed aryl-tube bond axis. Geometry optimizations were then performed by relaxing other structural degrees of freedom except for the fixed rotation angle. The energies relative to the lowest energy structure were thus obtained as a function of rotational angle and are plotted in figure 2. The deepest minimum (i.e. the rotational angle equal to zero) represents the starting position. Two maxima could be recognized as the configuration corresponding to the aryl plane is along tube axis. The effective rotational barrier is about 0.35 eV, which is much bigger than the thermal energy (0.025 eV) at 300 K. This indicates the functional aryl group should be dynamically stable at room temperature but may be thermally activated at the elevated temperatures.

Having established the energetically preferred configuration for a single diazonium functional group on a (4, 4) SWCNT, we now turn to study its electronic structure. The pristine (4, 4) SWCNT (containing four units in the direction of tube axis) was firstly studied for comparison with other earlier theoretical studies. Utilizing 60 k-points along the tube axis is sufficient to obtain accurate band structure. Figure 3(a) presents the band structure of a pristine (4, 4) carbon nanotube, which clearly reveals the metallic behavior. The $\pi - \pi^*$ band crossing can be seen near the BZ boundary (Z-Point) and gives rise to a constant DOS at the Fermi level as shown in figure 3(b). This is in full agreement with the band structure calculated by Rubio *et al.* [30] except for the different point for the Fermi energy crossing in the BZ due to the smaller simulation box of the supercell in Ref. [30] (only two units are used in the direction of tube axis). Figure 4a presents the final configuration obtained following geometry optimization of a single functional group on the SWCNT. Clearly, the orientation is very similar to the one obtained in the former calculation based on the supercell containing 12 units in the direction of

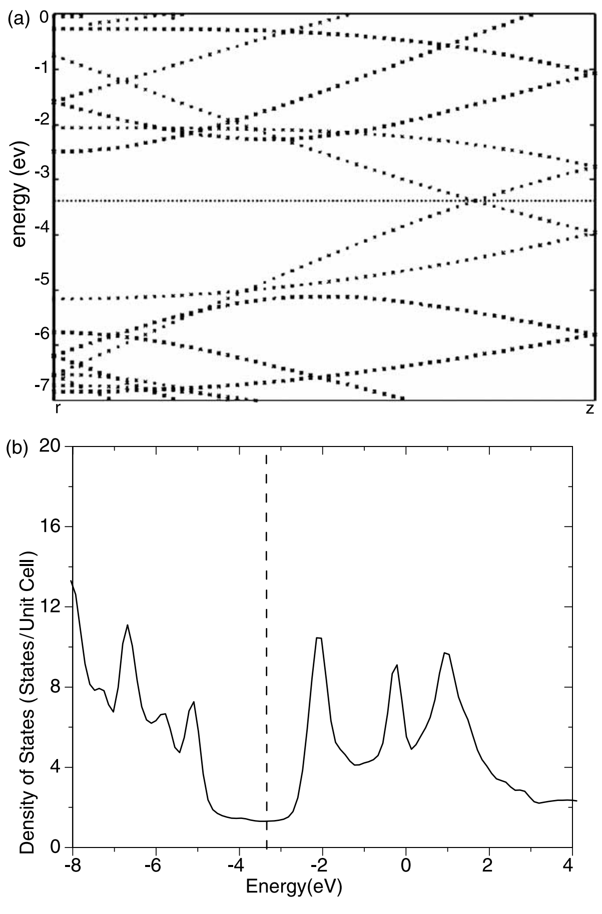

Figure 3. The calculated (a) Band structure (b) DOS for a pristine (4, 4) SWCNT with four units along tube axis in a hexagonal cell. The dashed line represents the Fermi level.

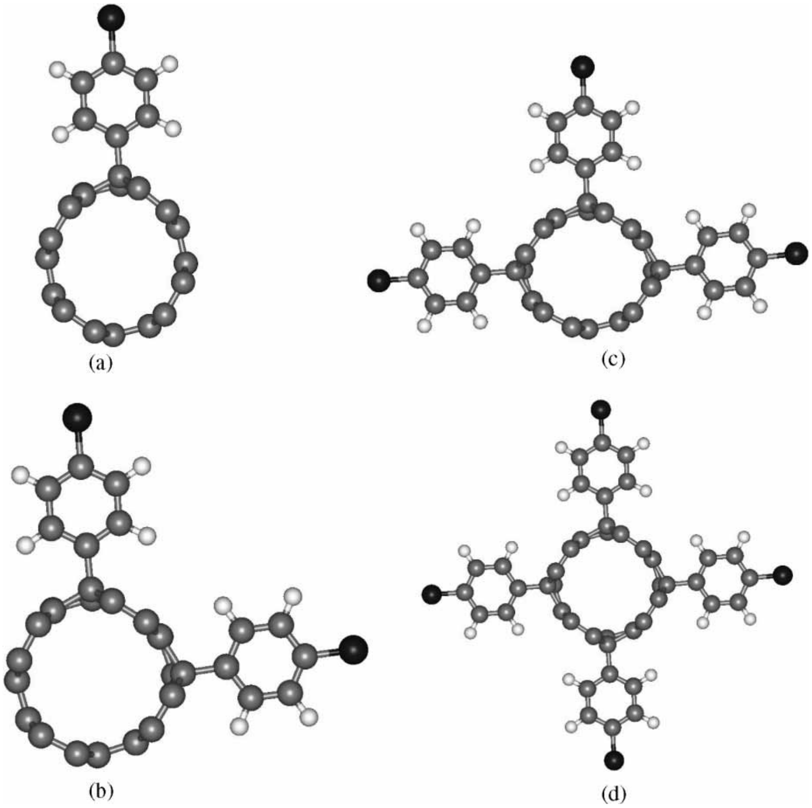

Figure 4. Geometry obtained from fully optimization of the diazonium functionalized SWCNT at different coverages of the functional groups. The grey, black and white balls represent C, Cl and H atoms, respectively.

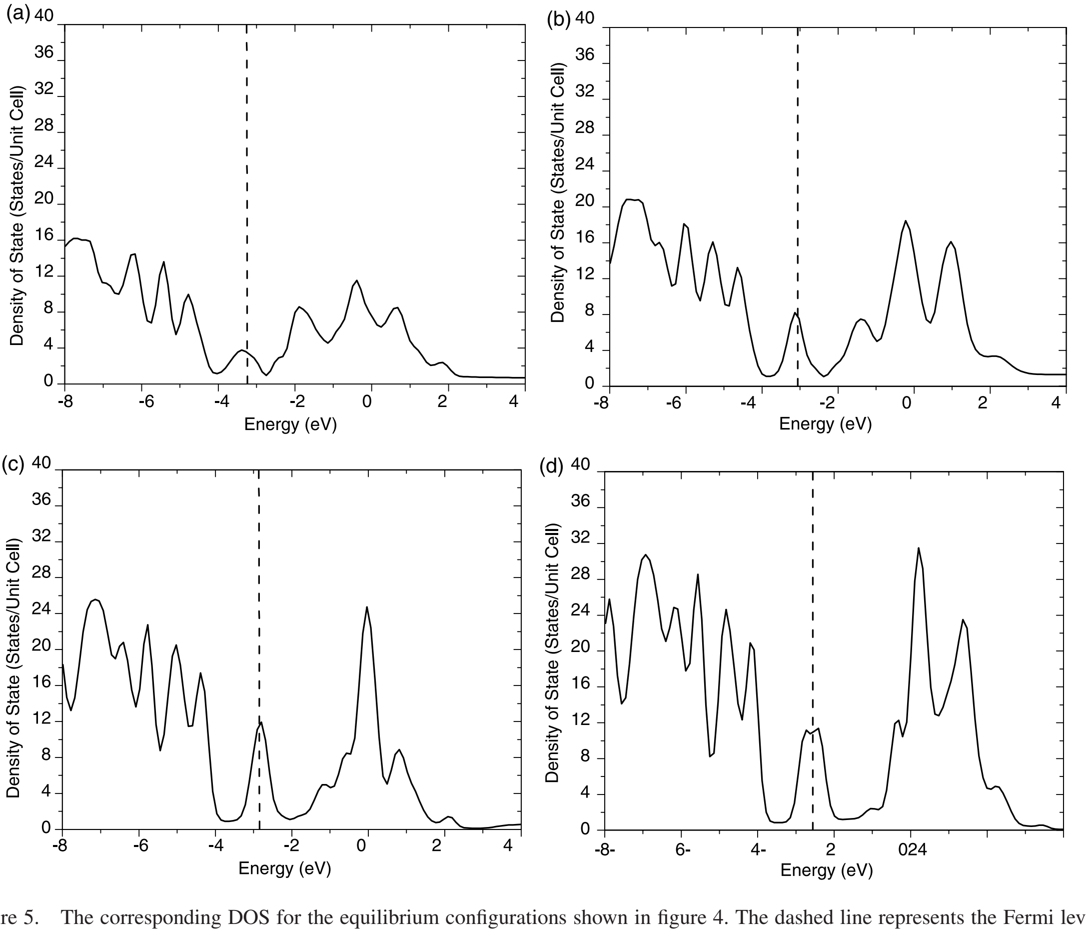

Figure 5. The corresponding DOS for the equilibrium configurations shown in figure 4. The dashed line represents the Fermi level.

tube axis. However, the local distortion around the bonding site is much stronger. Subsequently, two, three and four diazonium groups are arranged on the sidewall of SWCNT in equidistance within the plane perpendicular to the tube axis. Figure 4(b)–(d) present their equilibrium configurations, respectively. The changes of geometry are minor and limited to the vicinity of the bonding sites. Based on the equilibrium configurations at different coverage of the functional groups on the SWCNT, DOSs are then calculated as shown in figure 5. In contrast to the pristine SWCNT, new peaks appeared at the Fermi energy for the diazonium functionalized SWCNT. This is attributed to the local sp^3 defects on the side wall of tubes alluded to above, which induces a half-occupied band having a weak dispersion across the Fermi level. Apparently, the intensity of DOS at the Fermi energy is also increased as more functional groups are added on SWCNT surface. Additionally, increasing the coverage of the functional groups also appears to result in significant upshifting of the Fermi level.

4. Conclusions

In summary, *ab initio* density functional theory (DFT) calculations have been performed to study the structural and electronic properties of diazonium reagent functionalized (4, 4) SWCNT. We found that the aryl group binds covalently with SWCNT and prefers an orientation perpendicular to the side wall of SWCNT. A barrier of 0.35 eV was computed with respect to rotation about the axis of the aryl-tube bond, consistent with thermodynamic stability of the equilibrium structure at room temperature. Analysis of the electronic structure of the functionalized SWCNT shows there is a peak in the DOS, which represents a weak dispersion around the Fermi energy. Increasing of the coverage of the functional groups also results in a noticeable upshift in the Fermi level.

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