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Electronic structures and transport properties of sulfurized carbon nanotubes

B. Xu [a,b], Y.P. Feng [a,*]

[a] Department of Physics, National University of Singapore, 2 Science Drive 3, 117542, Singapore

[b] College of Physics and Communication Electronics, Jiangxi Normal University, Nanchang, Jiangxi 330022, PR China

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ABSTRACT

The electronic and transport properties of side-walled sulfurized (8, 0) zigzag carbon nanotube were investigated by using density functional theory coupled with a non-equilibrium Green function approach. It is found that the adsorption of the sulfur chains largely reduces the bandgap of the semiconducting (8, 0) carbon nanotube, even changing it into a metallic one. More importantly, the transmission eigenstates around the Fermi level are contributed by not only the sulfur chains but also the complex system made of the sulfur chains and the single-walled carbon nanotube. Our results provide a method to improve the conductivity and utilization rate of the surface in the electrodes of supercapacitor which are made of the carbon nanotubes.

1. Introduction

Due to their excellent electrical [1,2], thermal [3] and mechanical [4,5] properties, carbon nanotubes (CNTs) are potential candidates for application in electronic devices [6–8]. In addition, the peculiar property, a high surface area, makes CNTs suitable electrode materials in the energy-storage supercapacitor. However, macroscopic forms of CNTs usually lose the intrinsic properties of individual CNTs. For example, not all single-walled carbon nanotubes (SWCNTs) inevitably exhibit metallic high conductivity, because the conductivity is determined by the chirality of the tubes. As we know, the as-synthesized SWCNTs are a mixture of semiconducting and metallic tubes. Therefore, it is difficult to retain the fundamental SWCNT conductivity on a macroscopic scale. The severe drawback hinders the application of SWCNTs in the electrodes of supercapacitors, where high conductivity of the electrodes is essential. To solve this problem, one approach is to have a posttreatment to choose selectively an appropriate chirality. Unfortunately, this method is neither controllable nor scalable.

An alternative approach is to modify the electronic properties of SWCNT through chemical functionalization. For instance, functionalization of the SWCNTs by atomic hydrogen leads to a transformation in electronic structures from metallic to semiconducting by removing π states near the Fermi level [9]. Seifert et al. showed that side-walled functionalization with one-dimension (1D) fluorine chains can close the bandgap of a semiconducting CNT, consequently increasing the conductivity of the SWCNT [10,11]. Recently, Wang et al. [12] selected thionyl bromide ($SOBr_2$) to modify SWCNTs and found the electrical conductivity of the SWCNTs were highly enhanced. Through X-ray photoemission spectroscopy (XPS) analysis, they proposed the existence of C–S bonds, suggesting that the SWCNTs are sulfurized. Similar results were presented in the work reported by Urszula et al. [13], where $SOCl_2$ were chosen as the chemical modification. Theoretical calculations revealed that the sulfur atom preferentially adsorbed on the carbon atom when the $SOCl_2$ molecule interacted with a pyrene molecule was considered [13]. Therefore, the formation of C–S bonds in $SOBr_2$ modified CNTs can be well understood because the pyrene molecule represented a nanotube fragment and similar properties existed between $SOCl_2$ and $SOBr_2$. Although the sulfurization probably results in the increase of the conductivity of the SWCNT, no further results can be used to confirm it. If the conductivity of the semiconducting SWCNT is increased by sulfurization, the method will be useful to enhance the conductivity of the CNT electrodes of supercapacitors, as well as improving the performance of supercapacitors.

Motivated by the results reported by Wang et al., herein we studied the electronic properties of a semiconducting SWCNT with side-walled functionalization of sulfur. As the density of the adsorbed sulfur increases, the carbon nanotubes are probably modified by continual sulfur species. As a general and simple model, we considered the adsorption of sulfur chains, similar to the case of the CNT functionalized by the 1D fluorine chains [10, 11]. Our results reveal that the sulfurization would largely decrease the bandgap of semiconducting SWCNT, even convert the SWCNT from semiconducting to metallic.

* Corresponding author. Tel.: +65 65164335.
E-mail address: phyfyp@nus.edu.sg (Y.P. Feng).

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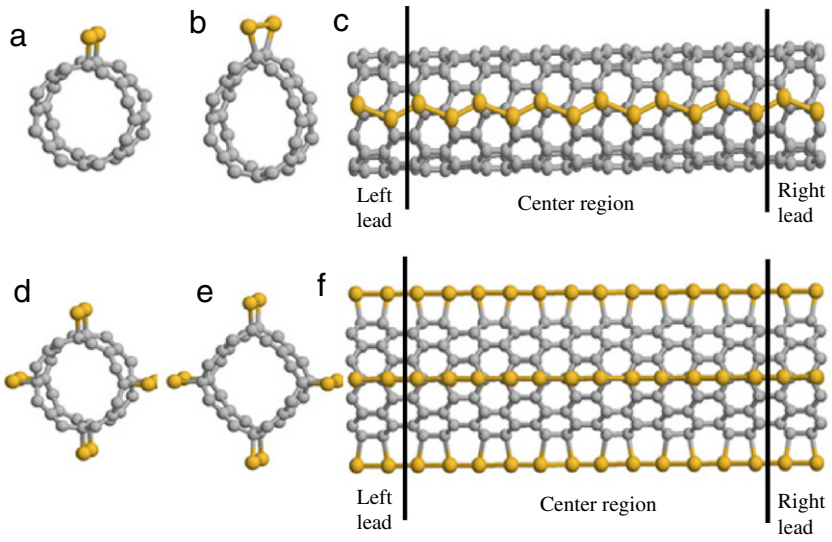

Fig. 1. The unit cells of the (8, 0) zigzag carbon nanotube with sulfur adsorption and the two-probe models constructed by the optimized unit cell. (a), (b) are structures of ZZ8-2S before and after relaxation, respectively. (c) is the two-probe model of ZZ8-2S. (d), (e) are structures of ZZ8-8S before and after relaxation, respectively. (f) is the two-probe model of ZZ8-8S.

2. Theory

We used the *ab initio* pseudopotential density functional theory (DFT) as implemented in the SIESTA code [14] to obtain the electronic structures and relaxed atomic positions. We employed the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [15]. The mesh cutoff value defining the real-space grid used for relaxation for the considered system is 150 Ry and a double-ζ plus polarization (DZP) basis set for all of the atoms. A Monkhorst–Pack grid of $1\times1\times30$ was used for structure optimization and electronic structure calculations. All the structures were fully relaxed using the conjugate gradient method until the maximum absolute force was less than 0.04 eV Å^{-1}.

Semiconducting (8, 0) zigzag SWCNT was chosen as an example for the sulfurized nanotube. For DFT calculations, we chose a unit cell with periodic boundary conditions along the tube axis. The period along the tube axis is 4.26 Å and the lateral separation between tube centers is beyond 40 Å in order to prevent the interaction of SWCNTs plus sulfur chains with their periodic images. For the adsorption of sulfur, two cases were considered. The unit cell consists of two (Fig. 1(a)) or eight (Fig. 1(d)) sulfur atoms and the primitive tube cell, thus forming one or four sulfur chains along the axial direction of SWCNT within periodic boundary conditions. For convenience, we denoted the former case as ZZ8-2S, and the latter case as ZZ8-8S.

The transport calculations were performed by using the ATOMISTIX TOOLKIT (ATK) [16], which is based on the combination of density functional theory (DFT) with the non-equilibrium Green function (NEGF) technique. The most unique feature of ATK is the ability to calculate the electrical properties of two-probe systems. The transmission coefficient T as a function of the electron energy E is given by

$$T(E) = 4Tr\left[Im(\Sigma^l G^R \Sigma^r G^A)\right]. \quad (1)$$

Σ^l (Σ^r) represents the self-energies of the left (right) electrode, G^R (G^A) is retard (advanced) Green's function.

Using the relaxed geometries, we constructed the two-probe system model in which the central region consists of six unit cells, and both the left and the right electrodes are composed of one unit cell, as seen in Fig. 1(c) and (f). The left (right) electrode extends to $z = -\infty$ ($z = +\infty$) with periodic boundary condition. During transport calculations, the exchange–correlation, basis sets and mesh cutoff are the same as the geometric optimization in SIESTA calculations. Obviously, the results from the ATK are entirely comparable with that from the SIESTA due to the same computational level.

3. Results and discussion

3.1. Adsorption geometries

We started to look for the stable geometry for the initial configuration of ZZ8-2S in Fig. 1(a). At first, two sulfur atoms were respectively placed 1.8 Å away from the top sites of the carbon atoms in the tube wall and arranged along the axial direction. Fig. 1(b) shows the fully relaxed geometry. After optimization, the sulfur atoms are chemisorbed on the carbon atoms with bond length of 1.92 Å. But the arrangement of the two sulfur atoms deviates from the tube axis, consequently the sulfur chain adsorbed on the sidewall of the SWCNT is not linear but in a zigzag configuration, as seen in Fig. 1(c). The S–S bond lengths are alternatively 2.05 and 2.47 Å. In addition, the sulfur adsorption causes a severe distortion of the tube wall, particularly near the adsorption sites. As seen in Fig. 1(b), the circular tube seems elliptical after sulfur adsorption. In the case of ZZ8-8S, eight sulfur atoms are divided into four groups, with two atoms in each group. The two sulfur atoms in each group adsorb on the SWCNT along axial direction. By applying the periodic boundary condition, hence, four sulfur chains are formed. Similarly, we placed these atoms 1.8 Å away from the top site of the carbon atoms in the tube wall. After relaxation, we obtained the structure shown in Fig. 1(e). The sulfur atoms are chemisorbed on the carbon atoms of the CNT with bond length of 1.92 Å. Interestingly, unlike the case of ZZ8-2S, sulfur atoms in ZZ8-8S are still arranged along the tube axis. As a result, four parallel linear sulfur chains are formed on the sidewall of the SWCNT, as shown in Fig. 1(f). The S–S bond lengths are alternatively 2.00 and 2.26 Å, both shorter than that in ZZ8-2S. In addition, the tube wall is also distorted in ZZ8-8S. The cross section of the SWCNT is close to a square.

The structure changes of the sulfur chains may be understood based on charge transfer. From the Mulliken population analysis, we found that each sulfur atom in ZZ8-2S accepts about 0.074e, larger than that in ZZ8-8S where the charge transfer is about 0.054e