A first-principles study on the behavior of HCl inside SWCNT

Ting Liang [a], Wei-Xue Li [b], Hong Zhang [a],*

[a] School of Physical Science and Technology, Sichuan University, Chengdu 610065, China
[b] State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

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ABSTRACT

The electronic and band structure for (14, 0) single wall carbon nanotube (SWCNT) with the HCl molecule and H_2 molecule inside are investigated by using a first-principles method with the pseudopotential density functional theory (DFT). The calculated density of states and band structures can elucidate the differences for the behavior of HCl and H_2 inside SWCNT. The HCl molecule has a binding energy about -0.24 eV when it is put inside a (14, 0) SWCNT. Compared to HCl molecule, H_2 did not induce any obvious change in the band structure and electronic property. A direct band gap 0.71 eV is obtained with HCl molecule inside (14, 0) CNT, which is larger than the value for pure CNT and with H_2 molecule inside (14, 0) SWCNT.

1. Introduction

In recent years, carbon nanotubes (CNT) have been intensively studied due to their importance as building blocks in nanotechnology, the special geometry and unique properties of CNTs offer great potential applications, including nanoelectronic devices, energy storage, chemical probes and biosensors, field emission display and so on [1–4]. Many works have been done on the characterization of nanotube, for example, the modification for the properties of nanotube by adsorption atoms, molecules or clusters on the exterior walls of carbon nanotubes or by insertion of these species into their hollow interior, offer a promising way in the design of new nanomaterials [5–7]. Boron- and phosphorous-doped silicon nanowires were used as building blocks to assemble three types of semiconductor nanodevices [8]. The adsorption of transition metal atoms on carbon nanotubes is a pathway to change the electronic and mechanical properties of carbon nanotubes [9]. Moreover, recent experiments with semiconducting SWCNTs have indicated the strong role of electron–electron (e–e) interactions ignored in one-electron theories [10–15]. Based on a wide application of nanomaterials, SWNTs are produced by several methods, such as arc-discharge method in the presence of transition metal catalyst, pulsed laser vaporization, chemical vapor deposition, and catalyst-assisted decomposition. However, the SWCNTs produced by these methods still contain a larger amount of impurities such as graphite, amorphous carbon and catalytic metal particles. As these impurities can cause a serious impediment for their detailed characterization and applications, they have to be moved by further physical and chemical processing. So it is very important to prepare pure carbon nanotubes and nanomaterials. Hydrochloric acid (HCl) solution is used to purify nanomaterials [16], for example, purification of carbon nanotubes in HCl solution can dissolve residual catalyst iron particles [17]. Some reactions illustrate the particular need for hydrogen chloride in the gas-phase purification mixture [18]. Yet, the adsorption amount of supercritical H_2 at 77 K under 5 MPa pressure increased twofold as a result of the acid treatment, while the supercritical CH_4 adsorption amount at 303 K and 5 MPa pressure increased by 40%. These remarkable increases were caused by increased amount of narrow micropores as a result of the acid treatment [19]. There are many works on the acid treatment of nanotube, but the behavior of acid molecule inside CNTs is not yet clearly understood.

The purpose of this paper is to reveal the interaction between the carbon nanotube and HCl molecule by determining the band structure and electronic properties of HCl inside SWCNT. Using first-principles theoretical calculations, the band structure and electronic properties of HCl and H_2 inside SWCNT are calculated. The (14, 0) SWCNT is chosen here since there are many theoretical calculations on it [20–23], and it is a main semiconducting zigzag nanotube with 10.96 Å diameter. We discuss their electronic characteristics by analyzing the total density of state (TDOS), band structure (BS), projected density of state (PDOS) and binding energy. The different adsorption behaviors between the two kinds of gases are also shown.

2. Computational details

All calculations were performed by using the first-principles plane-wave pseudopotential density function theory, the ex-

* Corresponding author. Tel.: +86 28 85400158.
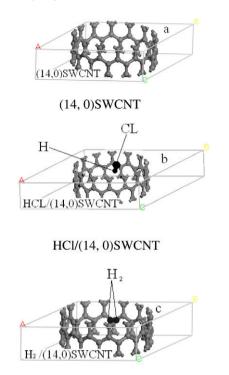E-mail address: hongzhang@scu.edu.cn (H. Zhang).

change–correlation interaction was treated by the generalized gradient approximation (GGA) with PBE functional [24–26]. It is well known that LDA does not explain the dispersion forces between molecules, which strictly acts in the limit of negligible overlap between electron densities, and thus the LDA function tends to overestimate the interaction energy between two molecules. Moreover, the LDA description tends to overbind atoms, so that the bond length and the cell volume are usually underestimated by a few percent and the bulk modulus is correspondingly overestimated. The GGA corrects these errors, and GGA functional provides a better overall description of the electronic subsystem than the LDA functional. In our calculations, ultra soft pseudopotentials are expanded by a plane-wave basis set with an energy cutoff of 350 eV. For geometry optimization, the internal coordinates for all the atoms in the unit cell are fully relaxed without any constraint. Atomic positions are determined with the energy convergence of 2.0×10^{-5} eV/atom and forces $\leqslant 0.1$ eV/Å. The Fermi level is smeared by the gaussian method [27]. Based on the optimized structures, their electronic band structure (BS), the total density of states (TDOS), the atomic orbit projected density of state (PDOS) and binding energy are evaluated, respectively.

3. Results and discussions

In order to test the accuracy of the present first-principles approach to the electronic structure of the CNT structures, we firstly optimized the structure of (14, 0) SWCNT and calculated its band structure. The optimized parameters for (14, 0) SWCNT are $a = 14.2814$ Å, $b = 14.2699$ Å, and the lattice constant is $c = 4.2221$ Å, our lattice constant is a little smaller than that of other reported result of 4.2910 Å [28]. Firstly, we performed the geometry optimization for the H_2 and HCl molecule in the inner wall of the CNT, respectively. The results show that H_2 and HCl inside the (14, 0) CNT (see Fig. 1) belong to the physisorption, and there is no C–H bond when the optimization was finished. The equilibrium structures for pure (14, 0) CNT, HCl/CNT, H_2/CNT are shown in Fig. 1a–c, respectively. The electronic band structure and the density of state near the Fermi level for a (14, 0) nanotube and with H_2 and HCl inside (14, 0) CNT are presented in Fig. 2. For pure CNT (14, 0), we can find the valence band maximum (VBM) occurs at G point and the conduction band minimum (CBM) occurs at F symmetry point, with a indirect gap (F–G) 0.39 eV. The calculated values of direct gap are 0.54 eV of F–F, 3.73 eV of Q–Q and 3.92 eV of Z–Z, near the Fermi level. Our value of 0.54 eV gap energy of F–F is in line with other reported results of 0.52 eV [28]. It is clear that the (14, 0) CNT is a semiconductor which agrees with previously reported data [5].

In order to get a better understanding for the different contributions of s and p orbital, in Fig. 3b, we illustrate the projected density of states (PDOS). For comparison, the total DOS is plotted in Fig. 3a. From Fig. 3, we know that the VBs from −9.6 eV to 0.0 eV originate mainly from the contribution of p orbital, the VBs around −17.5 eV come mainly from s orbital.

In Fig. 2(b) we present the band structure for the H_2 inside (14, 0) SWCNT, and the density of state is shown in Fig. 4, the optimized structure for H_2/(14, 0) SWCNT is performed by DFT with the GGA functional (see Fig. 1c). The H−H bond length optimized is 0.754 Å. It can be found that H_2/(14, 0) SWCNT is also a semiconductor with an energy gap of 0.394 eV. However, we find that the DOS and BS of H_2/(14, 0) are very similar with those of the pure (14, 0) SWCNT, and such similarities are also found when one uses other charge donor molecules like N_2, H_2O, and CO_2 etc. Therefore, the interaction between the nanotube and these gas molecules is very weak, and the gas molecule does not have a significant effect on the electronic structures of SWNTs [29]. This character makes CNTs act as a good hydrogen storage medium.

Fig. 1. Optimized structures (a) for a (14, 0) single-walled zigzag nanotube (b) for a HCl molecule adsorbed onto the inner of the carbon nanotube (c) for a H_2 molecule adsorbed onto the inner of the carbon nanotube. Larger and small black ball represents the Cl and H atom, respectively.

The optimized geometry for the HCl molecule inside the (14, 0) CNT is shown in Fig. 1b. The optimized bond length of H–Cl is 1.281 Å, which is only a little smaller than 1.284 Å of the experimental value at gas state. For the HCl/(14, 0) CNT, the calculated band structure and DOS are shown in Fig. 2c and Fig. 5, respectively. The valence band maximum (VBM) and the conduction band minimum (CBM) occur at G and F symmetry points with a direct gap of 0.71 eV. Clearly, the (14, 0) CNT is still semiconductor when the HCl is put inside it. We concentrate on the Fig. 2c near the fermi level, the band in HCl case turns out to be 0.71 eV at G point which is larger than that of the pure CNT and the H_2/SWCNT. More interestingly, from the TDOS and PDOS plots of Cl and H shown in Fig. 5, three bonding peaks of HCl/(14, 0) SWCNT nearby the Fermi level are located at three energy rang between −8 eV and −7 eV, −4.5 eV, and −3 eV, 3.05 eV and 3.94 eV. The bonding peaks between −8 eV and −7 eV are valence band (VB), which are contributed by the C 2p, H 1s, and Cl 3p. The states of Cl 3p contribute greatly to the valence band ranging from −4.5 eV to −3 eV. The peaks between 3.05 eV and 3.94 eV are formed mainly by the H 1s states, and a few from Cl 3p. From the total DOS and projected DOS of HCl/(14, 0) SWCNT, we notice some overlap of atomic orbital among Cl 3p, H 1s and C 2p states. There is a overlap of atomic orbital between Cl 3p and C 2p ranging from −16.4 eV to −17.3 eV, also another overlap between C 2p and H 1s ranging from −7.9 eV to −7 eV. Meanwhile, the PDOS shows that there is overlap between H 1s and C 2p states in the energy range of 2.5 eV to 4 eV. It can be seen that there is a small change in the valence and conduction band between HCl/(14, 0) SWCNT and pure CNT. In HCl case, the bottom of conduction band moves up by 0.32 eV, meanwhile, the top of valence band moves down by 0.005 eV. To our best knowledge, there are no available experimental data on the
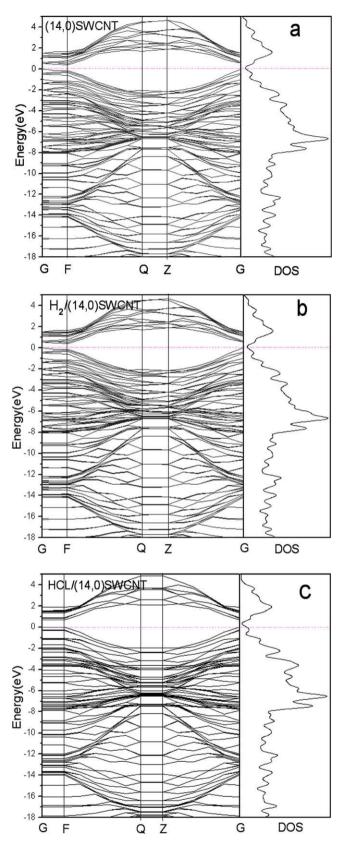
Fig. 2. Band structures of the calculations (a) for pure (14, 0) SWCNT (b) for H_2 inside (14, 0) SWCNT (c) for HCl inside (14.0) SWCNT. The horizontal dash line is the Fermi energy level.

band gap of HCl/(14, 0) SWCNT. So our calculated results are useful for further investigations of HCl/CNT electronic properties.
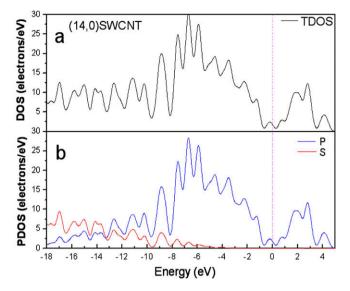

Fig. 3. (a) Density of states (DOS) of the (14, 0) SWCNT. (b) Projected local density of states (PDOS) onto the s, p orbital, respectively. The horizontal dash line is the Fermi energy level.
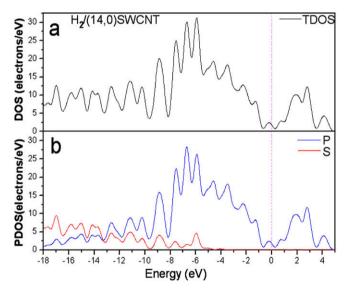

Fig. 4. (a) Density of states (DOS) for the H_2/SWCNT. (b) The projected density of states (PDOS) for the H_2/SWCNT onto the s, p orbital, respectively.

We also calculated the binding energy for H_2 adsorption onto nanotube and it was found to be −0.0009 eV, which is close to the binding energy of H_2 molecules at the top of the nanotube tip (0.0 kcal/mol) [30]. In the HCl case, the binding energy was −0.24 eV. The large difference in the binding energy between HCl/(14, 0)SWCNT and H2/(14, 0)SWCNT can be understood from the polarity for H_2 and HCl molecules. We know that HCl is strongly dipolar molecule and H_2 is non-polar with complete symmetry. In accord with our calculation, the electron transfer does not exist as H_2 inside (14, 0) SWCNT. The phenomenon is in agreement with that of O_2/SWNT, which has no charge transfer between the O_2 molecule and the semiconducting SWNT [31] in air, and the adsorption of O_2 has the characteristics of physisorption [32]. However, the binding energy is less than 0.5 eV in all case, which supports the hypothesis that the adsorption of both molecules, (H_2/CNT) and (HCl/CNT), is physisorption.
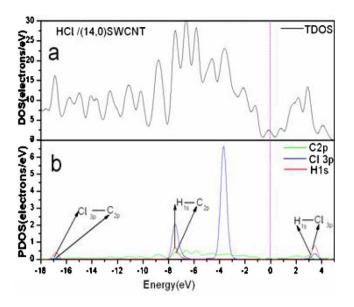
Fig. 5. (a) Density of states (DOS) of HCl/(14, 0) CNT. (b) The PDOS of C 2p, H 1s, and Cl 3p atomic orbital.

4. Conclusions

As for the continuous research of our previous work [33], in this paper, we obtain the electronic properties of HCl/(14, 0) CNT by DFT calculations, and the comparison with that of pure CNT and H_2/(14, 0)SWCNT is made. The band structure and DOS for H_2/(14, 0) SWCNT are very similar as that of pure CNT. The energy gap for H_2/(14, 0) SWCNT is about 0.4 eV, which is smaller than the energy gap of HCl/(14, 0) SWCNT. Compared to the pure (14, 0) CNT system, there is not any noticeable change in the PDOS when H_2 is put into the nanotube because of zero charge transfer and the small binding energy between the H_2 molecule and the nanotube. In HCl case, the band gap increases to 0.71 eV. Our computed binding energy of HCl inside CNT(14, 0) is smaller than that of HCl dimer inside CNT (14, 0) [34]. Simultaneously, our calculations prove that the interaction between HCl and CNT is rather weak, and HCl belongs to physical adsorption on CNT (14, 0). Our results make sure of that HCl is effective in reducing the amount of metal particles and amorphous carbon and will not change the property of CNT evidently [35,36]. HCl will continuously provide us with potential applications in the modification of CNT through acid treatment. Future work might be addressed towards the interaction between polar molecule and nanotube with different diameter and various nanomaterial.

Acknowledgements

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