

Chirality Dependence of Gas Adsorption Property of Single Wall Carbon Nanotubes

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Abstract. In this work, effect of chirality on gas adsorption property of semiconducting single-wall carbon nanotubes (SWCNTs) is reported for the first time. First principles simulation of the interaction of three different chirality SWCNTs with different gas molecules is performed maintaining equilibrium tube–molecule distance. Results are obtained employing density functional theory, using the Atomistic toolkit simulation package (ATK-DFT). Nanotube density of states is observed to vary significantly due to interaction with different types of gases as well as for same gas if chirality of SWCNTs varies. The most significant finding is, the change in DOS near Fermi level is highest in mod 2 type semiconducting SWCNT for different gas molecules irrespective of donor or acceptor. Thus, proper selection of chirality of SWCNT is important to make nanotube based gas sensor and mod 2 types semiconducting SWCNTs should get preference over mod 1 type as a sensing element so as to get better sensitivity.

Introduction

Gas sensors or chemical sensors are attracting increasing interest due to their wide range of applications in biomedicine, pharmaceutics, industry, environmental monitoring and space exploration [1]. The sensitivity of a gas sensor can be significantly enhanced by increasing the contact interfaces between the gas molecules and sensing materials. The ultimate aim of any gas sensor is to achieve such a level of sensitivity that can detect even one atom or molecule of a gas and this is so far beyond the reach of solid-state gas sensors.

Single wall carbon nanotubes (SWCNTs), with their extremely high aspect ratio, quasi one dimensional nanostructure and extraordinary electronic, mechanical and chemical properties, are ideal for gas molecules adsorption. SWCNTs bear huge potential to build highly sensitive, low cost, portable sensors with low power consumption. Electronic and optical properties of SWCNT are directly associated with their geometrical structures [2] which are uniquely specified by a pair of chiral index (n, m). A SWCNT (n, m) will be metallic if $\text{mod}(n-m, 3) = 0$ and it will be semiconducting if $\text{mod}(n-m, 3) = 1$ or 2 , giving two types of semiconducting SWCNTs, mod 1 type and mod 2 types [3]. This relation is true in general, except for tubes with too small diameters.

The change of electronic properties of CNT in gas environment is an important issue for both fundamental research and technical application of nanotubes. Considerable experimental and theoretical efforts [1] [4]-[6] have been devoted to demonstrate the potential of CNT as gas sensor. Use of CNT as chemical sensors has been reported for a number of gases e.g. hydrogen [7], oxygen [8], nitrogen [9], methane [10], ammonia [11], nitrogen dioxide [12], water vapor [13], carbon dioxide [6] as well as helium and argon [6]. Semiconducting CNTs are reported to detect small concentration of a number of gases with high sensitivity by measuring changes of the CNTs' conductance when exposed to those gases at room temperature [1].

However, previous reports ignored dependency of gas adsorption on the nanotube chirality. The objective of this work is to find if nanotube chirality has any significant dependence on its gas sensing property that may influence the performance of a SWCNT based gas sensor. First principles

simulation of the electronic structure of SWCNTs of different chirality was performed where different gas molecules interact with them maintaining equilibrium tube–molecule distance. The density of states of different SWCNTs with and without gas molecules are compared. The change in nanotube density of states due to different types of gases are investigated closely. Significant changes in nanotube density of states were observed for same gas if chirality changes from mod 1 type to mod 2 type semiconducting SWCNTs. The finding is explained based on electronic structure of SWCNT and significance of this result for nanotube based gas sensor is also discussed.

Method and Result

For first principles simulation of SWCNTs in proximity of different gas molecules, Virtual Nanolab (VNL) was used which is graphical user interface of Atomistic Toolkit (ATK). ATK is a set of atomic scale simulators, so called calculators that can calculate properties of nano scale systems [14]. ATK-DFT can model the electronic properties of closed and open quantum systems based on density functional theory (DFT). ATK-DFT can model the electronic properties of molecules, crystals and devices using both self consistence and non-self consistence tight-binding models.

Using VNL builder tool, three zigzag SWCNTs having chiral index (7,0), (8,0) and (9,0) and four different gas molecules namely ammonia (NH_3), methane (CH_4), water vapor (H_2O) and Nitrogen dioxide (NO_2) were built. The reason for selecting zigzag tubes is due to their higher symmetry next to armchair tubes. Armchair tubes are always metallic and hence never a good choice as sensor despite their highest symmetry. It can be noted that, (7,0), (8,0) and (9,0) fall in three different categories of SWCNTs from electronic perspective namely mod 1 type semiconducting SWCNT, mod 2 type semiconducting SWCNT and metallic SWCNT, respectively, based on their mod $(n-m, 3)$ value. Individual gas molecule and SWCNTs of different chirality were brought in proximity maintaining equilibrium tube–molecule distance so that different gas molecules can interact with SWCNTs. The tube–molecule distance is defined as the nearest distance between atoms on the molecule and the nanotube for tube site, or the distance between the centre of the gas molecule and the centre of the carbon hexagon (carbon–carbon bond) for C site.

All three gas molecules are weakly binded to the nanotube and the tube–molecule interaction can be identified as physisorption. It has been reported earlier [6] that the conductivity of the semiconducting SWCNTs change dramatically over several orders of magnitude when exposed to NO_2 and NH_3 . These responses are due to the charge transfer between the p-type semiconducting SWCNT and the electron-donating NH_3 or electron-withdrawing NO_2 gas. Hole carriers are increased in the SWCNT as it interact with the NO_2 gas, causing an increase in conductance. The interaction with the NH_3 gas produces an opposite effect.

Fig. 1 shows the simulation result from this work representing the change in density of states of pristine SWCNT after interaction with different gas molecules. Only the region near Fermi level of the DOS is shown in each part of Fig. 1 due to the fact that change in DOS of SWCNTs was mainly noticeable around Fermi level after interaction with gas molecules. From Fig. 1, it can be noted that DOS of (7,0) and (8,0) semiconducting SWCNTs exhibit visible change for interaction with NH_3 , CH_4 and H_2O and this change is opposite for NO_2 . These results confirm that NH_3 , CH_4 and H_2O are charge donors and NO_2 is charge acceptors for SWCNTs, as reported earlier both theoretically and experimentally. To investigate the case with metallic tubes, the same process was repeated with metallic zigzag (9,0) SWCNTs and the result is

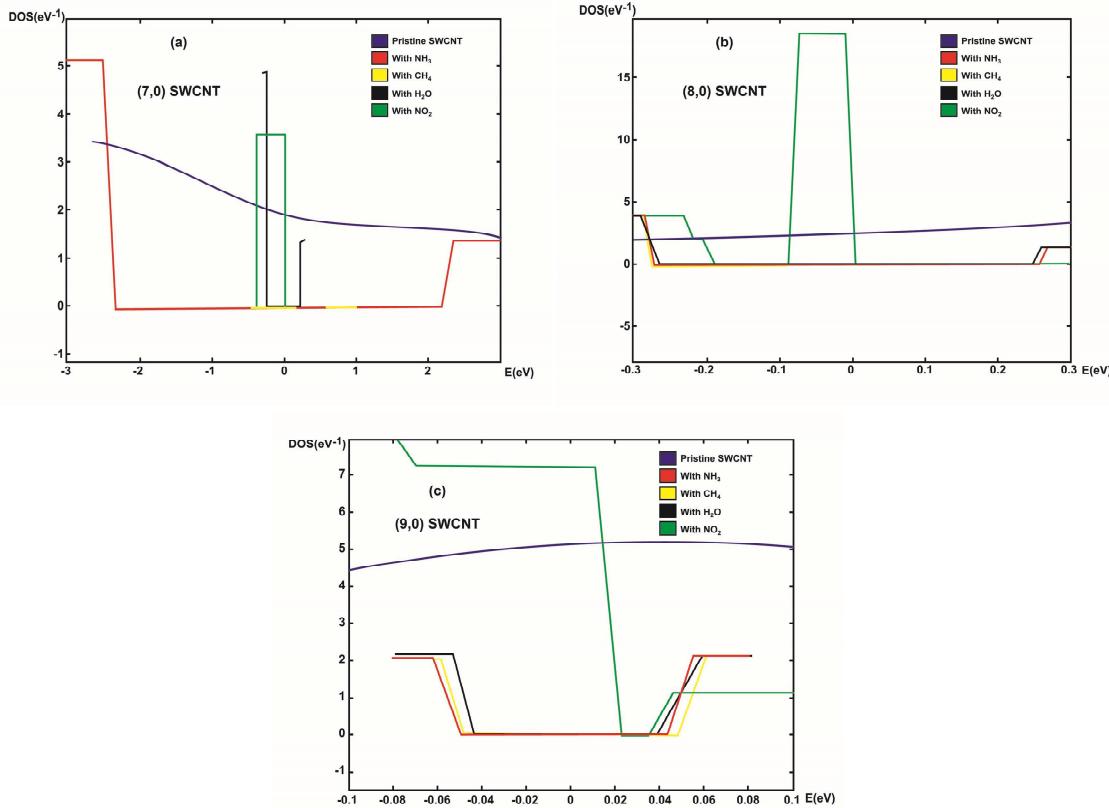


Figure 1. Density of states for (a) (7,0) (b) (8,0) and (c) (9,0) SWCNTs before and after interaction with NH_3 , CH_4 , H_2O and NO_2 , denoted in blue, red, yellow, black and green, respectively, in each figure.

shown in Fig. 1(c). It can be noted from Fig. 1(c) that interaction of metallic (9,0) tube with three different donor gas molecules remain almost unaltered unlike semiconducting (7,0) and (8,0) tubes, though opposite changes in DOS due to acceptor NO_2 molecule was observed as before. This confirms that metallic SWCNTs are not a good choice to be used as gas sensor as its carrier concentration does not change much when it interacts with various gases. In general, both mod 1 type and mod 2 types semiconducting SWCNTs are suitable as gas sensor. Now it needs to be investigated, which one of these two categories of semiconducting SWCNTs is better candidate for a gas sensor.

Effect of different gas molecules on DOS of (7,0), (8,0) and (9,0) SWCNTs, leveled as black, red and blue, respectively, are presented in Fig. 2 (a), (b), (c) and (d) for interaction with NH_3 , CH_4 , H_2O and NO_2 , respectively. Relative difference in changes in DOS due to different gas molecules and due to different chirality of SWCNTs can be readily observed and compared from these figures. Each of these figures is clear proof that interaction of same gas can create different effects not only between semiconducting and metallic tubes but also between two different semiconducting tubes. The most significant finding from these figures is, the change in DOS near Fermi level is highest in mod 2 type semiconducting (8,0) SWCNT for all four gas molecules irrespective of donor or acceptor. This means, change in electron density is maximum in mod 2 type semiconducting (8,0) SWCNT due to interaction with any of these gases.

One possible explanation for observed difference between DOS of mod 1 and mod 2 type semiconducting SWCNTs is as follows. The one-dimensionality of the SWCNTs gives rise to 1D sub-bands instead of one wide electronic energy band in nanotube density of states (DOS). Each SWCNT (n, m) has a unique set of interband transition energies E_{ii} denoting the energy differences between the i -th conduction and valence bands and optical transitions can only occur between these mirror sub-bands [2]. These

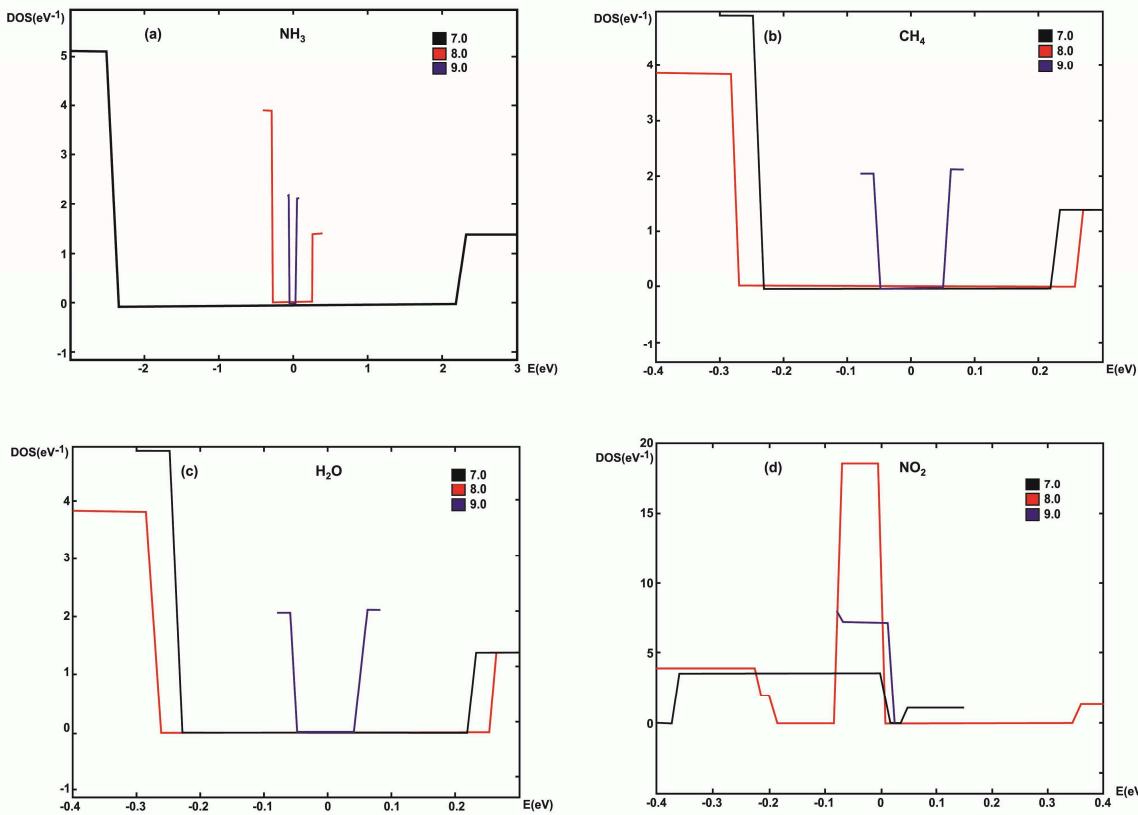


Figure 2. Density of states of (7,0), (8,0) and (9,0) SWCNTs, leveled as black, red and blue, respectively, in (a), (b), (c) and (d) for interaction with NH₃, CH₄, H₂O and NO₂, respectively.

singularities are unique feature of nanotubes and also primarily responsible for many distinguished electronic and optical properties of SWCNTs. As the first optical transition energy, which represents the band gap of a SWCNT, occurs near the Fermi level of SWCNT, so, this implies that change in DOS due to interaction with different gas molecules is mainly realized around this energy level. Now, it has been established both theoretically and experimentally that band gap of mod 2 semiconducting SWCNT is always found higher than that of mod 1 type with similar or comparable diameter [3]. This can be the cause due to which the change in DOS near Fermi level is more for mod 2 type semiconducting SWCNT than its mod 1 counterpart with comparable diameter.

As simulation result of this work shows that the change in electron density due to interaction with any of these gases is higher in mod 2 type semiconducting SWCNTs than mod 1 type, so, mod 2 type is expected to create higher sensitivity in external circuit when used as gas sensor. This result shows that selection of SWCNT with appropriate chirality is important before using it in gas sensor so as to get better sensitivity.

Conclusions

In this work, first principles simulation of the electronic structure of SWCNTs of different chirality was performed where different gas molecules interact with them maintaining equilibrium tube-molecule distance. Four different gas molecules namely ammonia (NH₃), methane (CH₄), water vapor (H₂O) and Nitrogen dioxide (NO₂) were used in this work to interact with three zigzag SWCNTs having chiral index (7,0), (8,0), and (9,0) comprising metallic and two types of semiconducting tubes. Clear changes in SWCNT DOS were observed due to adsorption of different type of gas molecules. These changes in DOS are opposite for donor and acceptor type gases. It was also observed that DOS does not change significantly in metallic SWCNT while interacting with same set of gas molecules. The most significant finding is, the change in DOS near Fermi level is highest in mod 2 type semiconducting SWCNT for all four gas molecules irrespective of donor or

acceptor. The finding was explained based on SWCNT electronic structure. Thus, proper selection of chirality is important to make nanotube based gas sensor and mod 2 type semiconducting SWCNTs is preferred over mod 1 type so as to get better sensitivity.

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