The effect of humidity on the adsorption of the hydrazine on single-wall carbon nanotubes: First-principles electronic structure calculations

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Abstract

First-principles electronic structure calculations were undertaken to clarify the observed n-type behavior of the hydrazine (N₂H₄) adsorbed on zigzag carbon nanotubes (CNTs). It was found that, only in the presence of moisture, the adsorption of the hydrazine will introduce occupied impurity states near the bottom of the conduction band of the N₂H₄/CNT system, leading to the n-type behavior. To gain further insight into the role played by the moisture, an extension of this study to other gases adsorbed on CNTs was also performed. Our results suggest that humidity could affect experimental measurements of responses of CNTs to adsorbed gases.

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Single-wall carbon nanotube (CNT)-based sensors have been extensively investigated in recent years [1–7]. The advantages of CNT-based sensors over existing technologies are that these devices can be made ultra compact, low costs of fabrication, effective at room temperature, low power consumption (<1 mW), very fast response (<10 s), low recovery time (few minutes), and they exhibit good versatility. In particular, the ability of CNT-based sensors to operate in low-temperature regimes is an intrinsic safety advantage. It could reduce the risk of explosion in the presence of combustible gases. Recent experiments conducted by Desai et al. [8] have revealed that CNT networks exposed to the toxic hydrazine (N₂H₄) vapor at room temperature and various pressures exhibit considerable drop in the resistance with respect to the pristine sample. Furthermore, their gate-dependence transport measurements show an n-type nature for the CNT exposed to the N₂H₄ molecule [8], which is quite different from the p-type nature of the CNT exposed to the O₂ molecule [9]. Their experimental results indicate the potential application of the CNT network as a detector to monitor minute traces of the N₂H₄ in the environment. It is therefore of utmost importance to determine the underlying physics of the dramatic change of the electronic band structures of the CNT exposed to the N₂H₄.

To shed light on the physics behind the observed n-type behavior of the N₂H₄ adsorbed on the CNTs, we have performed first-principles electronic structure calculations and systematically studied the adsorption of the N₂H₄ molecule on the carbon nanotubes, including the effects of vacancy and humidity on the electronic structures of CNTs. In particular, we will report in this Letter the important role of the humidity on the interaction between the CNT and the N₂H₄ molecule through our calculations. We would like to provide answers to the following questions: (1) how does the pristine CNT interact with the N₂H₄, (2) how does the introduction of defects (e.g., vacancies) into the CNT affects the band structure of N₂H₄/CNT system, and (3) what is the influence of the moisture on the electronic band structure of CNTs exposed to N₂H₄? Furthermore, we will compare the results of our calculations with other relevant cases, such as N₂/CNT, O₂/CNT, CO₂/CNT, and NO₂/CNT, so that we can systematically clarify the experimental observations [8–15].

In our first-principles electronic structure calculations, we have employed the Vienna ab-initio simulation package (VASP) with generalized gradient approximation that is based on the density functional theory [16]. The interaction between ions and core electrons was described by the ultra-soft Vanderbilt pseudopotentials (US-PP) [17–19], and the exchange-correlations were described by the Perdew and Wang’s (PW1991) approximations [20]. In determining optimized structures for various systems, including the pristine tube, the tube with a vacancy, the pristine/defected tube exposed to the N₂H₄ molecule, the pristine tube with moisture, and the pristine tube exposed to the N₂H₄ with moisture, we applied the one-dimensional periodic boundary condition to the systems along the tube axis with a vacuum region (~15 Å) between tubes (or combined systems) to ensure there were no interactions between tubes (or combined systems). Several k points were taken along the tube axis according to the Monkhorst–Pack scheme [21] so as to ensure the convergence of the total energy. For the total energy calculation, the cut-off energy for the plane wave basis set was taken to be 287 eV for the bare tube, 348 eV for the tube exposed to N₂H₄ molecules, and 395 eV for the tube...
exposed to the N2H4 with water molecules, respectively. The energy convergence for the self-consistent calculation was set to 10^{-4} \text{ eV}, and the structures for all cases were relaxed using a conjugate-gradient (CG) algorithm until the atomic force was less than 10^{-1} \text{ eV/Å}.

The energetically preferred location and orientation, as well as the equilibrium distance of the N2H4 molecule adsorbed on the surface of the CNT were first optimized. Figure 1a illustrates schematically various locations of a N2H4 on the hexagonal surface unit cell of a pristine tube. The circles indicate the locations of the center of the N–N bond of the N2H4 on the irreducible zone of the hexagonal surface unit cell. We have optimized all the marked locations with the N–N bond either parallel or perpendicular to the CNT axis (the zigzag (14, 0)), respectively. We found that adsorption energies of the N2H4 on the tube at different locations and orientations were not significantly different (energy differences being \sim 10^{-4} \text{ eV}). This then indicates that the N2H4 does not favor any specific adsorption site or orientation on the surface of the CNT. Figure 1b shows, as an example, the optimized geometry of the N2H4 with the center of its N–N bond directly above the center of the hexagonal surface unit cell and with the N–N bond perpendicular to the (14, 0) tube axis. The corresponding adsorption energy per N2H4, defined as \( E_{\text{adsorption}} = E_{\text{N2H4/CNT}} - E_{\text{CNT}} - E_{\text{N2H4}} \), vs. the distance between the center of the N–N bond and the tube surface is presented in Figure 1c. It can be seen that a very shallow minimum exists at a vertical distance of \sim 3.25 \text{ Å}, indicating a weak interaction (\sim 10^{-3} \text{ eV}) between the N2H4 and the CNT and hence a physisorption-like interaction.

To obtain a comprehensive understanding of the interactions between carbon nanotubes and the N2H4 under various situations, we have performed electronic structure calculations for the pristine tube interacting with the N2H4, the tube having a vacancy interacting with the N2H4, and the tube with moisture interacting with the N2H4, respectively. The electronic structures of the pristine zigzag (8, 0) tube interacting with N2H4 for different coverage are shown in Figure 2. The corresponding optimized conformations of the tube interacting with N2H4 molecules are presented in the inset of each band structure. The pristine tube considered was a zigzag (8, 0) semiconductor with the calculated band gap of \sim 0.56 \text{ eV} (see Figure 2a). Choosing smaller CNT (8, 0) is due to the consideration of computational efficiency and the physics of gas adsorption on CNT (8, 0) would be the same. When a N2H4 molecule was adsorbed on the tube surface, a localized (occupied) state associated with the N2H4 was introduced on the top of the valence band (see Figure 2b). The band gap was narrowed by about 0.1 \text{ eV}. In addition, some electronic states associated with the N2H4 appear in the conduction band. But, there were no occupied localized states appearing near the bottom of the conduction band to generate an n-type behavior. When two N2H4 molecules were adsorbed on the tube surface (see Figure 2c), in addition to localized states associated with the two N2H4 molecules appearing on the top of the valence band, impurity states associated with N2H4 molecules also appeared in the valence and conduction bands. As in the case shown in Figure 2b, no occupied impurity state was found near the bottom of the conduction band. When more N2H4 molecules were introduced to the surface of the pristine tube (e.g., four N2H4 molecules adsorbed on the tube surface (see Figure 2d) or eight N2H4 molecules adsorbed on the tube surface (see Figure 2e), the occupied impurity states associated with N2H4 are no longer found near the top of the valence band, but have moved deeper into the valence band. This phenomenon demonstrates the role played by the interaction between the N2H4 molecules and the CNT in the band structures of the combined system of the N2H4/CNT as the coverage of the N2H4 molecules increased. It should be noted that, although the coverage of N2H4 molecules was increased, no occupied impurity states appeared near the bottom of the conduction band to generate an n-type behavior. Therefore, our studies indicate that neither the orientation nor the coverage of the N2H4 adsorbed on the surface of the tube could lead to an impurity state near the bottom of the conduction band of the CNTs. Thus, the n-type nature observed in the experiments [8,12,13] could not be interpreted in terms of the bare pristine tube interacting with the N2H4 molecules.

We next focused our attention on the possible role of the vacancy on the band structure of the combined system of the N2H4/CNT. Because the defective CNT has more chemically reactive

Figure 1. (a) The surface unit cell (hexagon) of a pristine CNT, its irreducible zone (triangular region), and locations of the center of N–N bond of a N2H4 projected on to the CNT surface corresponding to different initial adsorption locations of N2H4 above the surface unit cell (open circles). (b) The optimized geometry of a N2H4 adsorbed on the surface of (14, 0) tube with its N–N bond oriented perpendicular to the tube axis. The location of the center of its N–N bond is above the center of the hexagonal surface unit cell. The blue atoms denote the N atoms, and the small gray atoms the H atoms, respectively. (c) The adsorption energy \( E_{\text{adsorption}} \) per N2H4 molecule corresponding to the case (b) vs. the distance between the center of the N–N bond of the N2H4 molecule and the surface of the pristine (14, 0) CNT. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
locations to attract foreign molecules, it is anticipated that foreign molecules would easily bond to the CNT at the defect sites. Figure 3a shows the band structure and the geometry of the (8, 0) CNT with a vacancy. We found that dangling bonds associated with the vacancy introduced empty localized defect states between the valence band and the conduction band (see the flat energy level located above the Fermi energy in Figure 3a). Furthermore, the degeneracy associated with top energy levels in the valence band of the pristine CNT was lifted and the dispersion of these levels was also reduced. The reduction of the dispersion indicates that these states are becoming more localized. The energy gap was narrowed by 0.15 eV compared to the case of the pristine tube. When the N$_2$H$_4$ was introduced to the tube surface near the vacancy, one of the N atoms of the N$_2$H$_4$ molecule was found to bond to the carbon atom near the vacancy, indicating that the N$_2$H$_4$ molecule was chemisorbed to the CNT at the vacancy site (see Figure 3b). By comparing the calculated band structure of the tube/vacancy system (Figure 3a) with that of the N$_2$H$_4$/vacancy/CNT system (Figure 3b), it can be seen that the defect states introduced by the vacancy were removed with the introduction of the N$_2$H$_4$ molecule near the vacancy. This is not surprising because the N$_2$H$_4$ molecule has a lone electron pair that passivates the dangling bonds.
bonds. We have also repeated this calculation using the spin-polarized version of VASP and found almost identical results. Thus, the presence of a vacancy in the CNT also does not answer the question posed in this work, namely: ‘why does the CNT exposed to N$_2$H$_4$ exhibit an n-type behavior’?

Recently, Sumanasekera’s group has systematically investigated the response of CNTs exposed to different types of gaseous molecules through resistance and thermoelectric power measurements [8,12,13,22–24]. They reported that the humidity effect indeed plays an important role in the interaction between the CNTs and gaseous molecules. They also pointed out that humidity could not be avoided when the CNTs are exposed to foreign species (e.g., the N$_2$H$_4$ vapor) at room temperatures [25].

Taking the cue from the experimental finding and the fact that traces of moisture are inherent in experimental observations, we decided to investigate theoretically the effect of a single layer of the water film on the electronic structure of the CNT (the (8, 0) tube), in particular, if humidity is responsible for the n-type behavior of the N$_2$H$_4$/CNT system. The monolayer of the water film was set up as follows. We first constructed the unit cell for the combined system using two primitive cells of the (8, 0) CNT (64 C atoms) and a vacuum region of ~15 Å. We then added water

![Figure 4](image1)

**Figure 4.** Band structures corresponding to: (a) CNT (8, 0) covered with a water film and (b) N$_2$H$_4$H$_2$O/CNT (8, 0). The insets show the corresponding optimized structures, where the red circles represent O atoms, gray circles the H atoms, blue circles the N atoms, and the thin red-dashed lines the hydrogen bonding among N, O, and H atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

![Figure 5](image2)

**Figure 5.** Band structures of N$_2$H$_4$/CNT (8, 0) covered with: (a) three H$_2$O molecules, (b) 10 H$_2$O molecules, (c) one-half layer of a water film, and (d) two-thirds layer of a water film. The inset shown in each panel is the optimized structure corresponding to the above cases.
molecules one-by-one on the tube surface in the chosen unit cell. During this process, we arranged the distance and the orientation of water molecules such that hydrogen bonding nature could always be maintained. The process continued until the onset of a new water layer as signaled by a water molecule popping up to a higher location. This happened when the 36th water molecule was added to the system. Hence the monolayer was determined to consist of 35 water molecules on the surface of the (8, 0) CNT. We had also left an open space on the water film to allow the addition of a N$_2$H$_4$ for the study of the adsorption of the N$_2$H$_4$ molecule on the (8, 0) CNT with the inclusion of the water film.

The optimized conformation for the combined H$_2$O-film/CNT system is shown in the inset of Figure 4a. At this coverage, we found that the average H–O distance (i.e., the hydrogen bond) between H$_2$O molecules in the water film is $\sim$1.65 Å (as shown by the red dashed lines between H and O atoms). The nearest neighbor distances between atoms in H$_2$O and those in CNT range from 2.15 to 3.15 Å, showing a weak interaction between the H$_2$O film and the CNT. The inset of Figure 4b shows the optimized conformation for a N$_2$H$_4$ molecule that is added to the H$_2$O-film/CNT system. The distance between the center of the N–N bond of the N$_2$H$_4$ and the surface of the tube is $\sim$3.4 Å, showing a weak interaction between the N$_2$H$_4$ and the CNT.

Electronic structures corresponding to the tube covered with the H$_2$O film and those corresponding to the combined N$_2$H$_4$/H$_2$O-film/CNT system are shown in Figure 4a and b, respectively. The band gap for the case when a layer of H$_2$O film covers the CNT is $\sim$0.3 eV and is substantially smaller compared to that of a pristine CNT (Figure 2a). The most interesting and telling finding is that when the N$_2$H$_4$ molecule is added to the CNT near the H$_2$O film, there are now new occupied states associated with the N$_2$H$_4$ appearing near the bottom of the conduction band with

![Figure 6](image-url)

**Figure 6.** (a) Band structures corresponding to CNT (8, 0) exposed to N$_2$, O$_2$, CO$_2$, NO$_2$, and N$_2$H$_4$ molecules, respectively. (b) Band structures of the pristine CNT (8, 0) covered with a water film and exposed to different types of molecules (N$_2$, O$_2$, CO$_2$, NO$_2$, and N$_2$H$_4$, respectively). The p-type behavior corresponding to an empty state (black solid line) above the Fermi-level (red-dashed line) and the n-type behavior corresponding to a filled state (black solid line) below the Fermi-level (red-dashed line) are indicated. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
the Fermi level pinned to the bottom of the conduction band. This results in an n-type behavior for the N_2H_4/H_2O-film/CNT system which elucidates the experimental observations [8,12,13].

To further delineate the role of water film and how its interaction with N_2H_4 alters the band structure of the CNT, we have compared the results for the tube exposed to a N_2H_4 with different coverage of water molecules. The optimized conformations corresponding to different coverage of water molecules and their electronic structures are shown in Figure 5a-d. It was found that those cases with lower water coverage on CNT (covered with three (Figure 5a) or 10 H_2O molecules (Figure 5b) did not yield defect states near the bottom of the conduction band. When over half of the surface of the CNT is covered by water molecules, occupied defect states appear near the bottom of the conduction band (see Figure 5c and d), similar to the result shown in Figure 4b. These studies confirm that humidity is the cause of the n-type behavior of the CNT system exposed to N_2H_4 [26–28].

The physics responsible for the appearance of occupied impurity states near the bottom of the conduction band can be understood as follows. Figure 2b shows that the adsorption of a hydrazine molecule on the surface of the (8, 0) CNT gives rise to an occupied localized impurity state with the characteristics of hydrazine molecule on the surface of the (8, 0) CNT. As the amount of water molecules near the N_2H_4 increases to about half coverage (Figure 5b), it is the combination of the substantial reduction of the interaction between N_2H_4 and neighboring water molecules (indicated by most of the N–H and O–H distances between N_2H_4 and neighboring water molecules being in the range of 1.8–2.5 Å) remove that localized impurity state and give rise to resonance modes within the valence band. As the amount of water molecules near the N_2H_4 increases to about half coverage (Figure 5b), our analysis of the equilibrium structure of the hydrazine molecule indicates that, although the bond lengths in the hydrazine molecule remain about the same, the bond angles are noticeably smaller (e.g., an angle of H–N–H = 104° for N_2H_4 in half water coverage vs. ~108° for a lone N_2H_4 and an angle of H–N–N ~ 106° for N_2H_4 in half water coverage vs. ~113° for the lone N_2H_4). It then suggests that the hydrazine molecule is now more compact. In the mean time, there is only one N–H pair and one O–H pair between N_2H_4 and water molecules with separations still about 1.9 Å while the rest with separations far greater than 2.5 Å. Thus it is the combination of the substantial reduction of the interactions between N_2H_4 and water molecules and the more compact structure of N_2H_4 for more than half water coverage that is responsible for the appearance of occupied impurity states beneath the bottom of the conduction band. The substantially weakened interactions restore the impurity state associated with N_2H_4 in the energy gap while the quantum confinement due to the more compact structure of N_2H_4 raises the impurity state to the bottom of the conduction band.

We have also expanded our studies of the humidity effect to the electronic structures of CNTs exposed to various gaseous species with and without the presence of the H_2O film. The calculations followed the same procedure as that used for the case of N_2H_4. The band structure results of a (8, 0) CNT exposed to N_2, O_2, CO_2, NO_2, and N_2H_4 are shown in Figure 6a in the absence of the water film. We found that for N_2 and CO_2 adsorptions on CNTs, no defect states were introduced between the valence band and the conduction band, and the band gaps in these cases were almost independent of the type of adsorbed species. In the case of the adsorption of N_2H_4 on the CNT, although occupied states associated with the N_2H_4 appeared on the top of the valence band, they did not generate either n- or p-type behavior. Exceptions were found for CNTs exposed to O_2 and NO_2 gases that exhibited p-type behaviors due to the presence of unoccupied impurity states close to the top of the valence band. When the CNT was covered with the H_2O film and then exposed to different types of foreign molecules, the band structure calculations revealed that, with the exception of N_2H_4/H_2O/CNT system, the semiconducting behaviors (e.g., p-, intrinsic, etc.) of other systems studied (e.g., N_2H_4/H_2O/CNT, O_2/H_2O/CNT, NO_2/H_2O/CNT) remained the same as those of the original systems without the water film (see Figure 6b).

In conclusion, our calculations have clarified that humidity is the cause of the observed n-type behavior for N_2H_4 molecules adsorbed on CNTs [12,13]. However, the effect of humidity is not pronounced for other systems studied, namely, both O_2/CNT [9] and NO_2/CNT [2,15] systems behave as p-type with and without the water film, and both N_2/CNT [10] and CO_2/CNT [14] systems behave like intrinsic semiconductors with and without the water film.

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