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ORIGINAL PAPER

Adsorption properties of N_2O on (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag single-walled carbon nanotubes: a density functional study

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Abstract The behavior of N_2O adsorbed on the external surface of H-capped (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag single-walled carbon nanotubes was studied by using density functional calculations. Geometry optimizations were carried out at the B3LYP/6-31G* level of theory using the Gaussian 03 suite of programs. We present the nature of the N_2O interaction in selected sites of the nanotubes. Binding energies corresponding to adsorption of the N_2O are calculated to be in the range 4–21 kJ mol^{-1}. More efficient binding energies cannot be achieved by increasing the nanotube diameter. We also provide the effects of N_2O adsorption on the electronic properties of the nanotubes.

Keywords Nanotube · Adsorption · Binding energy · DFT

Introduction

Since the discovery of carbon nanotubes (CNTs) [1], single-walled carbon nanotubes (SWCNTs) have attracted great interest owing to their physical and chemical properties [1–3] and applications as a fascinating novel material [4, 5]. SWCNTs have a wide range of applications in nanoelectronics, nanoscaling biotechnology, and biosensors [3, 6–9]. Because of their size, large surface area, and hollow geometry, SWCNTs are being considered as prime materials for gas adsorption [10–14]; biological, chemical, and electromechanical sensors; and nanoelectronic devices [15–17]. For example, CNTs have been experimentally investigated for use in the detection of gas molecules [18–20], organic vapors [21, 22], biomolecules, and different ions [23–25]. The doped or defective CNTs improved the sensitivity in detecting molecules like CO, H_2O, 1,2-dichlorobenzene, or gaseous cyanide and formaldehyde [26–28]. The possibilities of using chemically doped CNTs as highly sensitive gas sensors are also under intensive investigation [18, 29]. Moreover, electronic conductance of a CNT semiconductor can be changed upon exposure to gas molecules, serving as a basis for nanotube molecular sensors.

Sensitivity of CNTs to N_2O has been indicated by means of quantum mechanics calculations. The determination of the structure of adsorbed N_2O on CNT surfaces is also important for understanding its bonding and reactivity in catalysis and other surface phenomena. Nitrous oxide (N_2O) has been generated as a by-product in nitric and adipic acids, and its decomposition into N_2 and O_2 is a topic of biotic interest for environmental chemistry [30–32]. The study of the chemical reactions of N_2O on CNT surfaces is of scientific importance because N_2O has been recognized as an environmental pollutant and a relatively strong greenhouse gas [30, 31, 33, 34]; N_2O is also a significant contributor to the destruction of the ozone layer in the stratosphere. At present, the N_2O concentration in the aerosphere is rising almost 0.25% every year [35]. It is very desirable to find efficient and economical methods to convert harmful N_2O

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into unharmful gases such as N_2 through catalytic surface reactions, e.g., $N_2O \rightarrow N_2 + O(s)$ (O(s) denotes an O atom adsorbed on the surface). There is increasing interest in using CNTs instead of noble metals in the environmental catalysis field.

The reactions of N_2O with alkaline earth oxides [36–42], TiO_2 [43], molecular zeolite [44–50], metals [51], and isolated Cu^+ [52, 53] have been largely studied in many fields. However, to our knowledge, no experiments and theoretical investigation have been reported on the adsorption of N_2O on CNT surfaces. The understanding of the physisorption of N_2O on CNT surfaces is important for N_2O storage. In this study, we report the results of density functional theory (DFT) calculations on the physisorption of N_2O on (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag SWCNTs with two molecular orientations, N- and O-down, at four distinct sites.

Results and discussion

An N_2O molecule can approach the nanotube walls from outside (out), which is the most common case, and from the inside (in). Zigzag configurations of (6,0), (7,0), and (8,0) SWCNTs have two different C–C bonds (C1–C2 and C2–C3) (see Fig. 1a, b; Table 1). For the adsorption of the N_2O (N-down and O-down) on the CNTs, we considered four possible sites [i.e., the C site (center site) above the hexagon, the C2 and C3 sites above the carbon atoms, and the Z site above the zigzag and axial C–C bond] as described in Fig. 1a and b. The notation N-down and O-down denotes an N_2O perpendicular to the surface via N and O. Al-doped (6,0) SWCNTs have two different Al–C bonds (Al–C2 and Al–C6) (see Fig. 1c, d; Table 1). For the adsorption of N_2O (N-down and O-down) on the CNTs, we considered three possible sites (i.e., the Al site above the aluminum atom, and the C2 and C6 sites above the carbon atoms) as described in Fig. 1c and d.

We limited our analysis to the interaction of N_2O with the nanotubes' outer walls. Considering each site and configuration, we ended up with sixteen different approaches of N_2O to the CNTs walls. For each of these cases we investigated the CNT–N_2O potential energy surface (PES). The binding energies of the N_2O (N-down and O-down) at the four sites on the zigzag configurations of (6,0), (7,0), and (8,0), and at the three sites on the Al-doped (6,0)

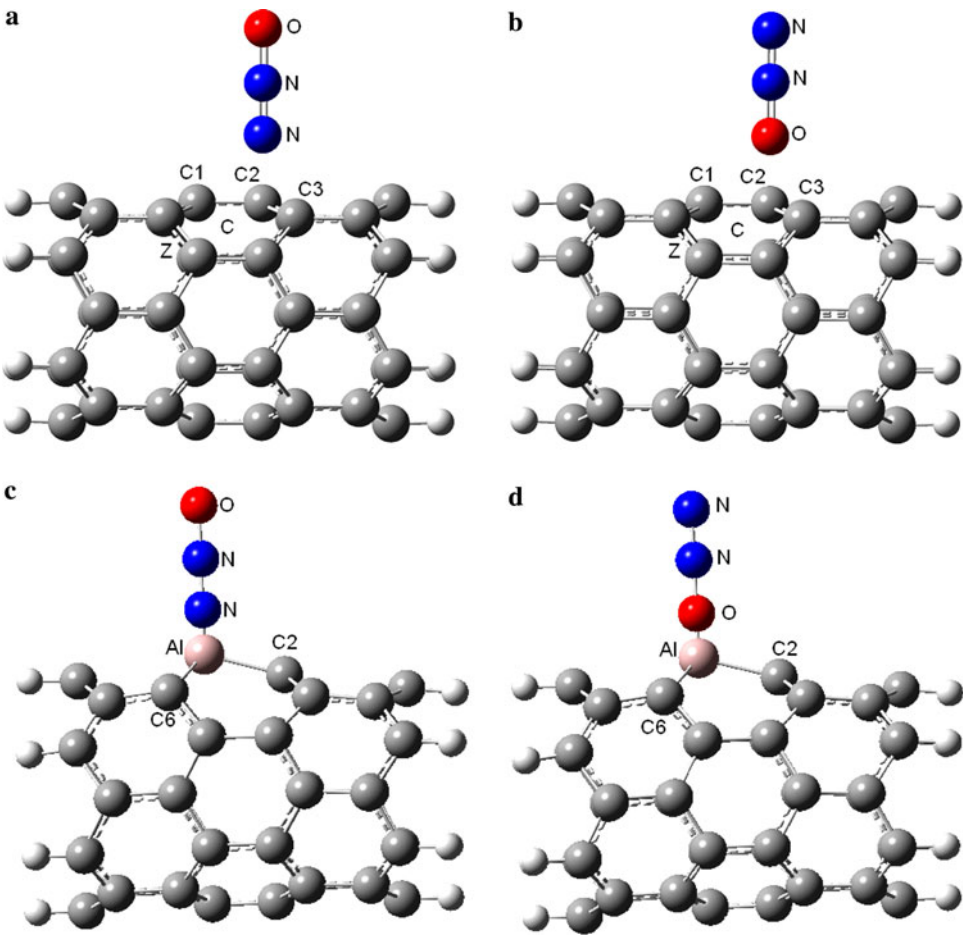

Fig. 1 Adsorption configurations of N_2O (**a** N-down and **b** O-down) on CNTs. Adsorption configurations of N_2O (**c** N-down and **d** O-down) on the Al-doped (6,0) SWCNTs

Table 1 Binding energy value (kJ mol^{-1}) and equilibrium distance (rd, Å) of N_2O on zigzag of (6,0), (7,0), (8,0), and Al-doped (6,0) CNTs

Model	Length (Å)	Site		C2	C3	Z	Center
(6,0)	C1–C2 = 1.435	N-down	Binding energy	−4.82	0.36	−3.11	−5.29
	C2–C3 = 1.431		rd	4.0	4.0	4.0	3.0
		O-down	Binding energy	−3.89	0.77	−2.11	−0.26
			rd	4.0	3.5	4.5	3.5
(7,0)	C1–C2 = 1.431	N-down	Binding energy	−4.64	−8.10	−7.37	−3.02
	C2–C3 = 1.430		rd	3.5	4.0	4.5	4.5
		O-down	Binding energy	−3.15	−4.78	−1.23	−5.42
			rd	4.0	3.5	3.5	3.5
(8,0)	C1–C2 = 1.438	N-down	Binding energy	−6.36	−7.99	−4.26	−9.26
	C2–C3 = 1.424		rd	4.0	4.0	4.5	4.5
		O-down	Binding energy	−2.14	−2.24	0.78	−2.25
			rd	5.0	4.5	4.5	4.5
Al-doped (6,0)	Al–C2 = 1.853	N-down		C2	C6	Al	–
	Al–C6 = 1.896		Binding energy	−3.63	−1.56	−1.78	–
			rd	3.5	4.0	3.5	–
		O-down	Binding energy	−3.92	−2.87	−20.99	–
			rd	3.5	4	2.5	–

SWCNTs are plotted in Fig. 2, and the binding energy with the equilibrium distance in each case is summarized in Table 1.

In all pathways for the zigzag of (6,0), (7,0), and (8,0) the potential is not attractive, presenting a well of maximum −10 kJ mol^{-1}, which does not characterize a chemisorption process. The binding energies obtained from these calculations are slightly dependent on orientations and locations of the N_2O, and the interaction becomes rapidly repulsive as the molecule approaches the CNT wall. The calculated BE (binding energy) of the CNTs indicated that N_2O cannot be absorbed on the sites; the BEs for the different sites have very small differences in total energy (<4 kJ mol^{-1}); and the calculated BE for N_2O in N-down is more than that in O-down. The most stable configuration of N_2O for N-down in the (6,0) CNT is the C site (center site), the perpendicular approach of the N_2O (N-down) molecule to the (6,0) CNT wall on the upper hexagon, and the current calculation shows that the adsorption energy for this site is −5.29 kJ mol^{-1} with an equilibrium distance (rd) of 3.0 Å.

The most stable configurations of N_2O for N-down in the (7,0) and (8,0) CNTs are the C3 and center site, respectively. The current calculation showed that the adsorption energies for these sites are −8.10 and −9.26 kJ mol^{-1} with an equilibrium distance (rd) of 4.0 Å for both of them. We observed that when the CNT diameter increases, the BE of the N_2O also increases at each particular site of the interaction but only very slightly (<3 kJ mol^{-1}). For example, N_2O (N-down) binds on the center site of a (6,0) CNT with −5.29 kJ mol^{-1}, whereas it binds on the C3 site of a (7,0) CNT with −8.10 kJ mol^{-1} or on the center site of a (8,0) CNT with −9.26 kJ mol^{-1}. Therefore, the BE of the N_2O from (6,0) to (7,0) and from (7,0) to (8,0) CNTs increases very slightly. An interesting conclusion that can be drawn from these pathways is that only the type of the tube (CNT) plays an important role in determining the BE of the N_2O and not the diameter of the tube as observed in previous cases [54]. All the results are clearly summarized in Table 1. The results show that absolute CNTs cannot detect the N_2O molecule, because it cannot be adsorbed on the pure CNT surface. Therefore to solve this problems, we used Al-doped (6,0) SWCNTs for the adsorption of the N_2O molecule, because the sensitivity of SWCNTs can be increased substantially through either doping technology or surface engineering [26, 55, 56]. But the calculated BE of the Al-doped (6,0) SWCNTs indicated that N_2O cannot be absorbed on the sites, and the calculated BE for N_2O in O-down is more than that in N-down. The most stable configuration of N_2O for O-down in the Al-doped (6,0) CNT is the Al site, the perpendicular approach of N_2O (O-down) molecule on the Al-doped (6,0) CNT wall, and the current calculation shows that the adsorption energy for this site is −20.99 kJ mol^{-1} with an equilibrium distance (rd) of 2.5 Å.

Electronic properties

Finally, we studied the influence of N_2O adsorptions on the electronic properties of the CNTs. The calculated band gaps of the clean perfect (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag SWCNTs are about 0.59, 0.65, 0.72, and 0.83 eV, respectively. The effects of the N_2O on adsorption

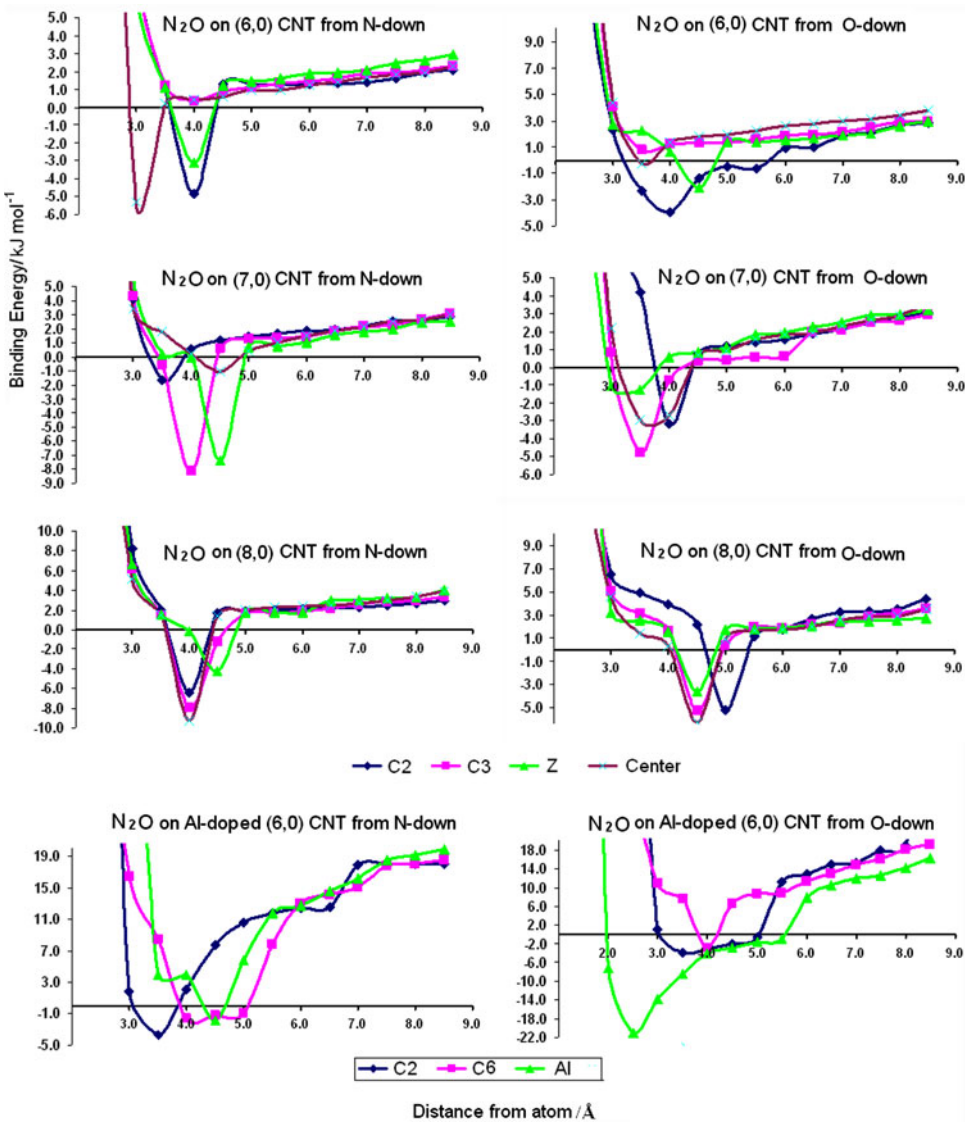

Fig. 2 Binding energy curves of N_2O (O-down and N-down) adsorption at C2, C3, Z, and center sites on zigzag of (6,0), (7,0), and (8,0) CNTs and at C2, C6, and center sites on the Al-doped (6,0) SWCNTs

energies in the CNTs relate to their electronic structure. When the N_2O is adsorbed on the CNTs, the interaction between them being very weak, the electronic properties of these tubes are not changed obviously and the band gaps are calculated to be about 0.59, 0.66, and 0.84 eV, respectively. But for the Al-doped (6,0) zigzag SWCNTs, the interaction between them being further from the CNTs, the band gap is calculated to be about 0.96 eV. However, the adsorption of N_2O on the Al-doped SWCNTs slightly increases the energy gap of the pristine CNTs, and reduces their electrical conductance.

Conclusions

We have studied the adsorptions of N_2O on zigzag configurations of (6,0), (7,0), (8,0), and Al-doped (6,0) SWCNTs by means of DFT calculations. On the basis of our calculations, comparing all the BE curves of N_2O interacting with all possible sites of adsorption on nanotube walls and in several structural configurations, it seems that the pristine CNTs and the Al-doped (6,0) SWCNTs cannot be used as an N_2O storage medium. For the CNTs, the calculated BE for N_2O in N-down is a little more than that in O-down, but for the Al-doped (6,0) SWCNTs, the BE in O-down is a little more than that in N-down. We showed that more efficient binding could not be achieved by increasing the nanotube diameter. Furthermore, in this study the presence of the N_2O on the Al-doped SWCNTs slightly increases the energy gap of pristine CNTs and reduces their electrical conductance.

Methods

In the present work, adsorption behaviors of the N_2O on the SWCNTs were studied by using the representative models

of (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag SWCNTs in which the ends of the nanotubes are saturated by hydrogen atoms. The hydrogenated (6,0), (7,0), (8,0), and Al-doped (6,0) zigzag SWCNTs have 60 ($C_{48}H_{12}$), 70 ($C_{56}H_{14}$), 80 ($C_{64}H_{16}$), and 60 ($C_{47}H_{12}Al$) atoms. In the first step, the structures were allowed to relax by all atomic geometrical optimization at the DFT level of B3LYP exchange-functional and 6-31G* standard basis set. The optimized structures have diameters of $\sim$4.80, 5.63, and 6.33 Å. The BE of an N_2O on the CNTs wall was calculated as follows:

$$\mathrm{BE} = E_{\mathrm{CNT}-\mathrm{N_2O}} - (E_{\mathrm{CNT}} + E_{\mathrm{N_2O}}) \quad (1)$$

or

$$\mathrm{BE} = E_{\mathrm{Al}-\mathrm{CNT}-\mathrm{N_2O}} - (E_{\mathrm{Al}-\mathrm{CNT}} + E_{\mathrm{N_2O}}) \quad (2)$$

where $E_{\mathrm{CNT}-\mathrm{N_2O}}$ was obtained from the scan of the potential energy of the CNT–molecular nitrous oxide structure, E_{CNT} is the energy of the optimized CNT structure, and $E_{\mathrm{N_2O}}$ is the energy of an optimized N_2O. All the calculations were carried out by using the Gaussian 03 suite of programs [57].

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