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ORIGINAL RESEARCH

Carbon nanocone as an ammonia sensor: DFT studies

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Abstract Adsorption of NH_3 molecule on a carbon nanocone (CNC) was investigated using density functional theory in terms of energetic, structural, and electronic properties. It is mainly demonstrated that (i) the NH_3 molecule preferentially tends to attach to the apex of the CNC through its N atom, releasing energy of 54.28 kcal/mol, (ii) the CNC may be a promising candidate in gas sensor devices in order to detect the NH_3 molecule, and (iii) the field electron emission current may be enhanced from CNC surface upon the adsorption process.

Keywords Ammonia · Nanocone · B3LYP · Sensor · DFT

Introduction

The environmental gas monitoring is recognized as an important field and much research has been focused on the development of suitable gas-sensitive materials for continuous monitoring and setting off alarms for hazardous chemical vapors present beyond specified levels [1–7]. It is known that the NH_3 is a low boiling point compound and is volatile. Therefore, effective methods have been highly demanded to monitor and suppress the NH_3 for atmospheric environmental measurements and controls [8, 9]. Since carbon nanotube (CNT) was discovered by Iijima [10], the properties and applications of this novel material have been extensively investigated [11–14]. CNTs have been recently emerged as a promising substitute for materials of different properties and various applications in hydrogen storage, gas sensors, textiles, and many more [15–17]. Besides CNTs, carbon nanocones (CNCs) have attracted increasing scientific and technological interests due to their special electronic and mechanical features [18]. Some geometrical defects can be introduced into a graphene network to form nonplanar structures. CNCs are hollow structures exclusively made of carbon having a conical shape and may be supposed as an intermediate structure between a graphene sheet and a nanotube [19]. Their walls can be described as a stacking of conical carbon layers with a graphite-like structure. The fabrication of CNCs has attracted attention because of better mechanical stability at the interface and a reasonably sharp tip structure. The mechanically stable CNC structures usually have lower density than CNTs which makes them appropriate for field emission due to the screening effect [20].

In nanostructure research, molecular interaction (e.g., CO, NO, CH_4, and so forth) with the nanostructure surface is a subfield of considerable interest due to potential applications such as storage, chemical sensors, and electronic devices [21–23]. Their high surface area is beneficial to practical gas sensors. The fundamental sensing mechanism for these devices is the modulation of their conductivity as a result of the charge transfer between nanotube and adsorbates [1]. In this study, the interaction of NH_3 with CNC will be theoretically investigated based on analysis of structure, energies, electronic properties, etc.

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The main purpose of this study was obtaining fundamental insights of adsorbed molecules influence on electronic properties of the nanocone, and how these effects can be applied to design more sensitive gas sensing devices.

Computational methods

Geometry optimizations and frequency calculations (to find a real local minimum structure) were performed on a CNC and different NH_3/CNC complexes using X3LYP functional [24] with 6-31G (d) basis sets as implemented in GAMESS suite of the program [25]. Energy calculations and density of states (DOS) analysis were done applying the same functional with 6-311G (d,p) basis set. It has been shown that the X3LYP extended functional for DFT significantly improves the accuracy for van der Waals interactions, over the most popular and accurate method, Becke three-parameter hybrid functional combined with Lee–Yang–Parr correlation functional (B3LYP) [26]. The adsorption energy (E_{ad}) of an NH_3 molecule on the CNC is obtained using the following equation:

$$E_{ad} = E(\text{CNC/NH}_3) - E(\text{CNC}) - E(\text{NH}_3), \quad (1)$$

where $E(\text{CNC/NH}_3)$ is the energy of NH_3/CNC complex, and $E(\text{NH}_3)$ and $E(\text{CNC})$ are referred to the energies of an isolated NH_3 molecule and the pristine CNC, respectively. The negative value of E_{ad} indicates the exothermic specificity of the adsorption.

Results and discussion

Geometric optimization

At first, the accuracy of the method used in this study has been tested initially to describe the properties of NH_3 molecule in gas phase. The bond length of individual N–H and bond angle of free NH_3 from our approach are 1.01 Å and 108°, which are in good consistency with the experimental values of 1.01 Å and 107° [27], respectively. In Fig. 1, we have shown top and side views of the optimized structure of the CNC. The proposed pristine CNC consists of 46 carbon atoms and the dangling bonds of CNC are saturated with hydrogen atoms. The length and height of the optimized pure CNC have been computed to be about 6.97 and 9.06 Å, respectively. Several types of C–C bond are observed in CNC with different lengths.

In order to determine minimum energy adsorption structures, NH_3 molecule was initially placed at different positions above the cone surface with different orientations and then relax optimizations have been done. Simplifying, we have considered four most stable ones (Fig. 2) in which

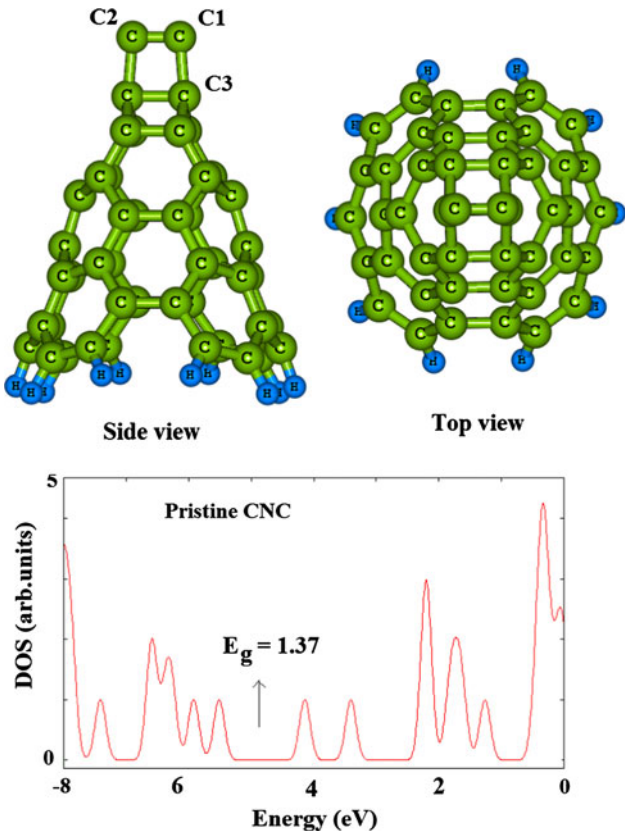

Fig. 1 *Top* and *side* views of the optimized CNC. Distances are in Å

the NH_3 molecule is as near as possible to the head of CNC including: (**P**) the NH_3 molecule is bonded via nitrogen atom to a C1 atom in top of CNC, (**Q**) the NH_3 molecule is bonded via hydrogen atom to C1 atom in top of CNC, (**R**) three hydrogen atoms of NH_3 adsorbed on cone surface, and (**S**) nitrogen atom of NH_3 adsorbed on cone surface. More detailed information including values of E_{ad} and the charge transfer (Q_T) are listed in Table 1.

As shown in Table 1, the E_{ad} values corresponding to various adsorption configurations are in the range of −44.17 to −54.28 kcal/mol. The **P** configuration gives rise to an E_{ad} of −54.28 kcal/mol, which is higher than that of **Q** (−46.46 kcal/mol), **R** (−44.17 kcal/mol), and **S** configurations (−46.87 kcal/mol). Meanwhile, a large charge transfer (0.736*e*) from NH_3 molecule to the nanocone was predicted. The highest E_{ad} of the **P** configuration may be rationalized by the fact that, in the CNC, the lowest unoccupied molecular orbital (LUMO) is mainly located on the apex of the CNC (Fig. 3). As a result, the HOMO of NH_3, locating on the N atom, donates electrons preferably to the LUMO centered on the apex of the CNC. It has also been found that the CNC undergoes an obvious distortion upon NH_3 adsorption via **P** configuration (Fig. 2), so that the C1–C2 and C1–C3 bonds of CNC in adsorption area were changed from 1.25 and 1.58 Å in pristine form to 1.35

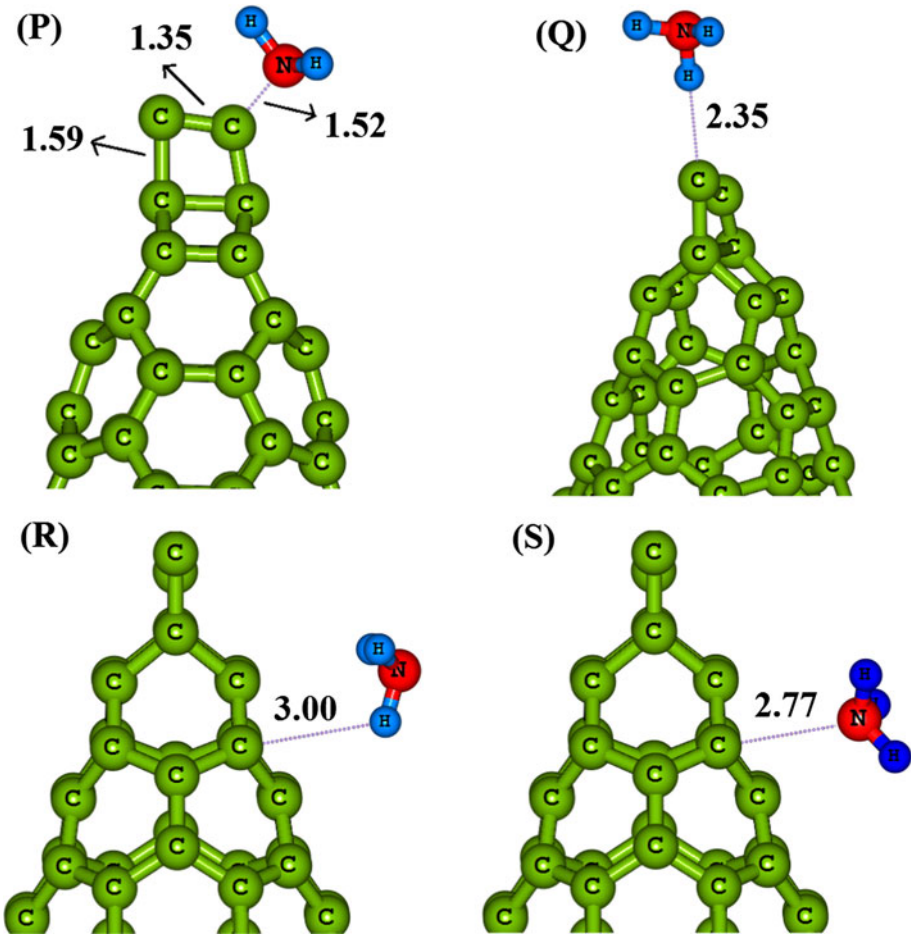

Fig. 2 Optimized structures of different NH_3/CNC complexes. Distances are in Å

Table 1 Calculated adsorption energies of NH_3 on the CNC (E_{ad}, kcal/mol), and also HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), Fermi level energies (E_{FL}), and HOMO–LUMO energy gap (E_g) of pristine and NH_3-adsorbed CNCs (Fig. 2) in eV

System	E_{ad}	Q_T[a] (e)	E_{HOMO}	E_{FL}	E_{LUMO}	E_g	ΔE_g[b] (%)
CNC	–	–	−5.51	−4.82	−4.14	1.37	–
P	−54.28	0.736	−4.94	−4.00	−3.07	1.87	36.5
Q	−46.46	0.062	−5.69	−4.80	−3.91	1.78	30.0
R	−44.17	0.054	−5.70	−4.81	−3.93	1.77	29.2
S	−46.87	0.123	−5.37	−4.12	−3.52	1.85	35.0

[a] Q is defined as the average of total Mulliken charge on the adsorbed NH_3 molecule

[b] The change of E_g of the CNC after NH_3 adsorption

and 1.47 Å, respectively. Also molecular angle of NH_3 was increased from 108° in the free molecule to 111° in the adsorbed state. Three other possible stable configurations are **Q**, **R**, and **S** in which the NH_3 molecule was adsorbed forming the H–C bond with gas–cone distances of 2.35, 3.00, and 2.77 Å, respectively (see Fig. 2Q–S). Based on the Mulliken population charge analysis, net charge transfers of 0.062e, 0.154e, and 0.023e from the molecule to the cone were occurred in the **Q**, **R**, and **S**, configurations, respectively. For these configurations, especially in the **Q** case, a locally structural deformation at the adsorption site can be observed, where the adsorbing C atom was pulled out of the surface.

Electronic properties

In the following, we have studied the influence of the NH_3 adsorption on the electronic properties of the nanocone.

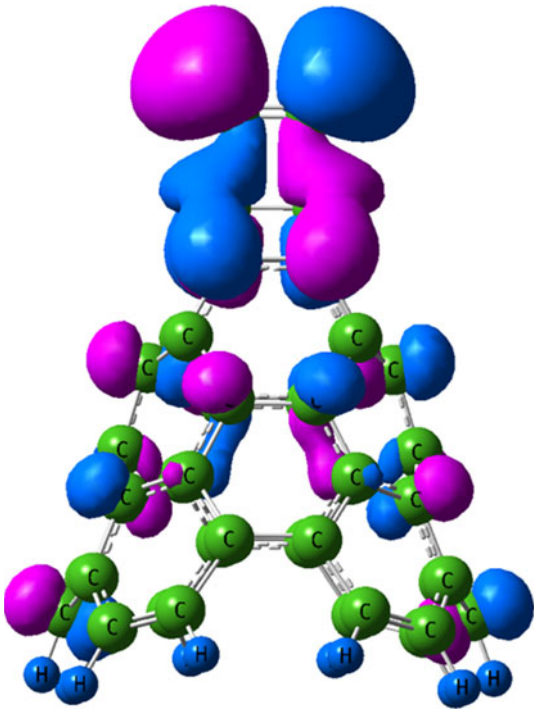

Fig. 3 Profile of the LUMO of the CNC

The difference in energies between HOMO and LUMO, E_g, was calculated via DOS plots. For the bare CNC (Fig. 1), it can be concluded that it is a semiconductor material with an E_g of 1.37 eV. Referring to Fig. 4, it can be seen that the NH_3/CNC complexes attain E_g value ranging from 1.77 to 1.87 eV. It is well known that the E_g (or band gap in bulk materials) is a major factor determining the electrical conductivity of a material and there is a classic relation between them as follows [28]

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right), \tag{2}$$

where σ is the electrical conductivity and k is the Boltzmann constant.

According to the equation, larger E_g, at a given temperature, leads to smaller electrical conductivity. For example, in **P** configuration (as the most stable), the DOS near the conduction and valence levels have a distinct change compared to that of the pristine CNC and the E_g increases from 1.37 to 1.87 eV upon the adsorption of NH_3 molecule. The considerable change of about 0.50 eV in the E_g value demonstrates the high sensitivity of the electronic properties of CNCs towards the presence of NH_3 molecule. Therefore, the presences of the NH_3 molecules may be detected by calculating the conductivity change of CNC before and after the adsorption process. The results suggest that the CNCs may be promising candidates for serving as effective sensors to detect the NH_3.

We think that the proposed sensor may benefit from some advantages including *high sensitivity*: the E_g of CNC is appreciably sensitive towards the presence of NH_3 so that it increases by about 36.5 % upon the adsorption of NH_3, *pristine application:* this nanocone can detect the NH_3 molecule in its *pristine type* without manipulating its structure through doping, chemical functionalization, making defect, etc., *short recovery time*: the adsorption energy of NH_3 molecule is not so large to hinder the recovery of CNCs and therefore the sensor will possess

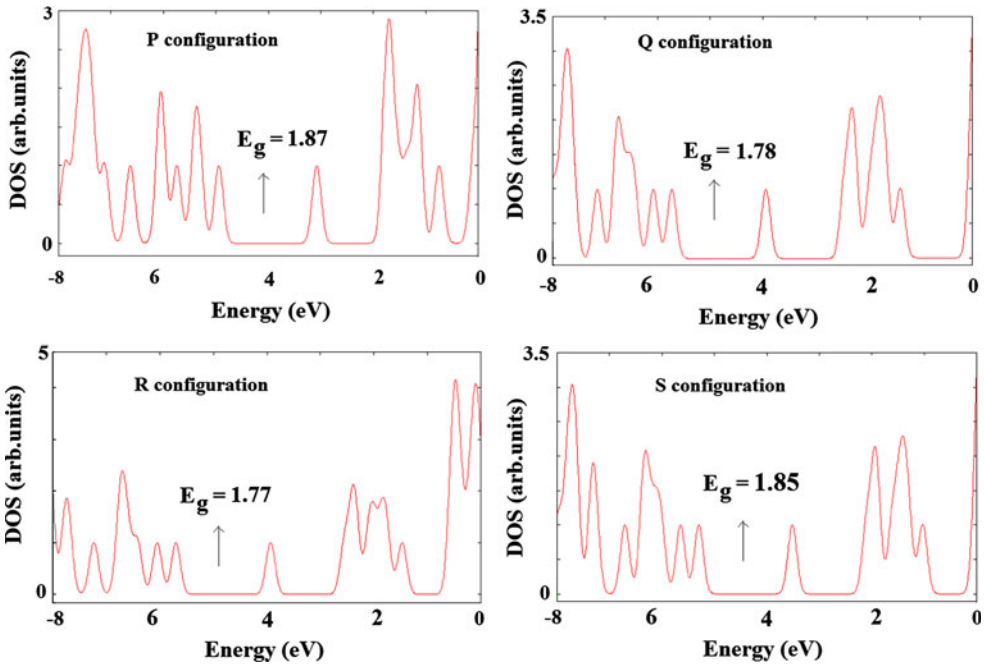

Fig. 4 Calculated DOS for different NH_3-adsorbed CNCs

short recovery times since, the recovery time can be expressed as (3) based on the conventional transition state theory

$$\tau = v_0^{-1} \exp(-E_{ad}/kT), \quad (3)$$

where T is the temperature, k is the Boltzmann constant, and v_0 is the attempt frequency. According to this equation, more negative E_{ad} values will prolong the recovery time in an exponential manner.

There has been great interest in field emission properties of nanocones recently [29]. As shown in Table 1, the E_{FL} is significantly shifted to higher energies when the NH_3 is adsorbed on the CNC via its N atom (in configurations **P** and **S**). For instance, in **P** configuration, the E_{FL} is increased from −4.82 eV in pristine CNC to −4.00 eV in the NH_3/CNC complex. However, these phenomena lead to a decrement in the work function which is important in field emission applications. The canonical assumption for Fermi level is that in a molecule (at $T = 0$ K) it lies approximately in the middle of the E_g. In fact, what lies in the middle of the E_g is the chemical potential, and since the chemical potential of a free gas of electrons is equal to its Fermi level as traditionally defined, herein, the Fermi level of the considered systems is at the center of the E_g. The Fermi level change of a semiconductor upon the NH_3 alters its field emission currents. The work function can be found using the standard procedure by calculating the potential energy difference between the vacuum level and Fermi level, which is the minimum energy required for one electron to be removed from the Fermi level to the vacuum. The decrement in the work function indicates that the field emission properties of the CNC are improved upon the NH_3 adsorption. Furthermore, this results in reduced potential barrier of the electron emission for the nanocone, facilitating the electron emission from the CNC surface. All of the above calculations suggest that the NH_3 adsorption has an advantageous effect on the field emission properties of CNC and also the CNC may function as a work function-based sensor for NH_3 detection.

Conclusions

The interaction between a CNC and NH_3 molecule has been explored by DFT calculations in terms of energetic, geometric, and electronic properties. The results indicate that NH_3 molecule prefers to be adsorbed on the apex of CNC with appreciable adsorption energy and charge transfer, which would lead to the significant changes of CNC conductance. Thus, the CNC may be a promising candidate for NH_3 detection. Furthermore, the NH_3 adsorption may reduce the work function of the CNC, thereby, enhancing the field electron emission current from its head.

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