Adsorption of Small Gas Molecules onto Ni–Doped Carbon Nanocap

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Abstract. *Adsorption of various small molecule gases including H_2, O_2, H_2O, CO, CO_2, and NH_3 on Ni–doped carbon nanocap (CNC) was studied. The geometrical and electronic properties of these gases adsorbed on Ni–doped CNC were calculated using the density functional theory (DFT) method at B3LYP/LANL2DZ level of the theory. Natural bond orbital (NBO) was performed to estimate the partial charge transfer (QT) and total density of states (DOSs) of all systems were also computed and reported. Based on the results, it was found that CNC bind strongly to Ni atom forming Ni–CNC complex with –154 kcal/mol binding energy. For gas adsorption study, the Ni–doped CNC absorb all small gases more preferential to those of undoped CNC. The O_2/Ni–doped CNC is the most stable complex while the H_2/Ni–doped CNC is in the reverse in comparison to those of the others.*

Keywords:

Adsorption, Carbon nanocap, Density functional theory, Ni–doped, Small molecule gases

1. Introduction

Carbon–based nanostructure materials are considered to be one of the promising materials because of both large specific surface and low weight [1]. Carbon nanotubes were discovered since 1991 by Iijima then later single–walled carbon nanotubes (SWCNTs) were found [2]. Especially, capped single–walled carbon nanotubes were fabricated by with controlled structures via chemical vapor deposition reported by Yu and co–workers [3]. Cap formation engineering and SWCNT growth using fragmented C_{60} as a cap have been produced. They show that the diameter distribution of capped SWCNT with such C_{60} fragments is related to the temperature of the thermal oxidation. The above reports demonstrate that cap formation engineering using opened C_{60} has potential applications.

It is well-known that the electronic structures of SWCNTs can be either metallic or semiconductor depending on their tube diameter and chirality [4]. SWCNTs have excellent chemical and physical properties and potential applications in molecular electronics [5], optics [6], nanomechanics [7], and sensors [8] were widely studied. Many researches focused on SWCNTs with experimental investigations. However, the high dispersion of experimental results concerning gas adsorption by SWCNTs. This is a field in which experiments are very difficult, thus giving great chances for modeling studies. Therefore, the closely related theoretical studies are reported.

One promising concept, modification of sidewall of the tubes with chemical species by functionalization [9] or doping [10,11], is changed significantly in electronic structures. In the similar way, decoration on tip of nanotubes is one of the key factors enhancing the performance of the nanotube chemical reactivities. Thus, it is essential to understand the electronic properties of the nanotubes [12]. The reactivities and stabilities of capped and open–ended SWCNTs were studied using the density functional theory (DFT) calculations. Theoretical studies reported that doping systems of SWCNTs with transition metals such as Fe, Co, Ni, Cu, Pd, Os, Pt can be changed significantly the electronic properties and making highly chemical reactivities [10,11].

Recently, adsorptions of small gas molecules by pure and metal–doped SWCNTs were therefore widely studied for their gas sensing properties. The adsorptions of H_2, O_2, N_2, H_2O, NH_3, NO, NO_2, CO, CO_2, CH_4, C_2H_2, and C_2H_4 gases on their metal–doped SWCNTs were studied using the DFT calculations [13]. Han and co–workers [14] reported the investigation of physisorption and chemisorption properties of hydrogen on the surface reactivity of SWCNT using the DFT calculations. The energy barriers and thermodynamic properties of these process reactions were investigated and reported. In addition, Pt–doped SWCNTs for small gas molecule adsorption studies were investigated using DFT calculations reported by Yeung and co–workers [15]. They found that the adsorptions of CO, NO, NH_3, N_2, H_2, C_2H_4, and C_2H_2 gases studied were found to be exothermic process and the affinity strongly depended on the orientation of the molecule. Moreover, the geometric and electronic properties of these complexes were studied and reported.

However, gas adsorption on capped SWCNTs is needy studied, thus modeling study is fully helped to understand several properties listed below. According to our previous work [16], carbon nanocap (CNC) was modeled and selected to be the prototype for doping with VIIIB transition metal (TM) such as Fe, Ru, Os, Co, Rh, Ir, Ni, Pd, and Pt atoms. The geometrical structures and electronic properties of TM–doped CNCs were investigated. The results showed that TM atoms can interact with CNC to form TM–CNC complexes. Due to a Ni atom showed a good catalyst atoms [17]. Then, in the present work, Ni–doped on CNCs were investigated for small molecule gas adsorption studies. The geometrical stabilities and electronic properties of Ni–doped on CNCs and their gas adsorptions have been investigated by density functional theory calculations.

2. Computational Method

Geometrical optimizations of studied systems were taken under the density functional theory (DFT) calculations. The calculations were performed with hybrid density functional B3LYP, Becke's three parameter exchange functional with the Lee–Yang–Parr correlation functional (B3LYP) [18–20] and the Los Alamos LanL2DZ split–valence basis set [21, 22]. All calculations were carried out with GAUSSIAN 09 program [23]. The molecular graphics of all related species were generated with the MOLEKEL 4.3 program [24]. The electronic densities of states (DOSs) of all systems were plotted by the GaussSum 2.2 program [25].

According to experimental study [3], cap formation engineering of the structures of thermally opened C_{60} using thermal oxidation techniques were studied and reported. The opened C_{60} can be applied as caps to grow SWNTs with controlled diameters. As our previous works [10,11,16], terminated nanotubes were purposely studied, hydrogen–terminated nanocaps were therefore selected for this study. So one–sided capped (5,5) carbon nanotube ($C_{60}H_{10}$) [16] was modeled with ended of CNC which was terminated by hydrogen atom to saturate the carbon atoms with dangling bonds as displayed in Fig. 1. The one of carbon atom (point C4 in Fig. 1b) of pentagon ring located on top of CNC was substituted with Ni metal atom. Therefore, the binding interaction of a CNC with Ni atom was considered. Thus, binding energy was defined with respect to the reaction Ni + CNC → Ni−CNC which refers to the replacement of one Ni atom on a C atom of intact CNC. The Ni/C−exchange at a CNC which corresponds to Ni + CNC_{VAC} → Ni−CNC, here CNC_{VAC} is refer to atomic C vacancy on a CNC. The binding energies (ΔE_b) and gas adsorption energies (ΔE_{ads}) of studied systems were calculated according to equations:

$$\Delta E_b = E(\text{Ni−CNC}) - E(\text{CNC}_{VAC}) - E(\text{Ni}) \quad (1)$$

$$\Delta E_{ads} = E(\text{gas/CNC}) - E(\text{CNC}) - E(\text{gas}) \quad (2)$$

$$\Delta E_{ads} = E(\text{gas/Ni–CNC}) - E(\text{Ni−CNC}) - E(\text{gas}) \quad (3)$$

where E(Ni−CNC) is a total energy for Ni–doped CNC, in which one carbon atom of a CNC is removed and replaced by Ni atom. Whereas $E(CNC_{VAC})$, E(CNC) and E(Ni) are the total energies of CNC with one C atom vacancy ($C_{59}H_{10}$), of CNC ($C_{60}H_{10}$), and of Ni atom respectively, while E(gas/CNC) and E(gas/Ni–CNC) are the total energies of each gas adsorption on pristine CNC and Ni−CNC structures, respectively. A negative binding energy (adsorption energy) indicates that the system is an exothermic interaction.

Considering the electronic properties, the single point calculations of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO), and the energy gaps (ΔE_{gap}) refer to the energy difference between HOMO and LUMO orbitals were studied at the same level. Natural bond orbital (NBO) analysis of all complexes was carried out to estimate the partial charge transfer (Q_T) [26]. The total DOSs [27] of all systems were also studied and reported. In addition, basis set superposition error (BSSE) corrections for the adsorption energies were realized at the same level of theory using Boys–Bernardi counterpoise (CP) calculations [28–31]. Here, the adsorption energy corrected for the BSSE correction is denoted ΔE_{ads}^{BSSE} .

3. Results and Discussions

3.1 Undoped and Ni–doped CNC

The B3LYP/LanL2DZ–optimized structures of pristine CNC and metal doped configuration are displayed in Fig. 1. The C1, C2, C3, and C4 are considered for enhancing perturbation with metal atom, in which C4 is substituted by one of free Ni atom, because of C1, C2, and C4 are actually symmetry equivalent.

TheB3LYP/LanL2DZ–optimized geometry of Ni metal–doped CNC is also displayed in Fig. 1c. When a carbon atom on the top of the capped tube was successfully replaced, the geometrical structures of the CNC present dramatic changes due to the doping effect. In comparison to the undoped CNC, the bonds pointing inward in the doped CNC create an even larger curvature, the deformation of the six–membered ring in the doping area away from the energetically favored. To verify this understanding, the chemical bonds between the Ni atom and its three nearest carbon atoms are almost perpendicular to the other bonds of these carbon atoms [13]. This is in particular important for the Ni–doped CNC structure. Therefore, studied systems are energetically structures consistent with calculated binding energy of Ni atom doped on CNC that ΔE_b is –154.80 kcal/mol [16]. The large ΔE_b exhibitly strong interaction between Ni and CNC to form stable complex, corresponding to large charge transfers (0.773e). To obtain partial charge transfers (Q_T), the Q_T is defined as a change of free metallic Ni atom and Ni charge during adsorption. Therefore the positive Q_T of Ni, implied that charge of Ni metal is transferred to the cap.

In addition, plots of molecular orbitals and density of states (DOSs) of undoped and Ni–doped CNC are displayed in Fig. 2. The plots show that the HOMOs and LUMOs of pristine CNC are vicinity around the cap. Moreover, the LUMO of Ni–doped CNC is located on the Ni metal. It is confirmed that electron transfer between metal and cap is occurred. On the basic concept, the gaps between HOMO and LUMO are important tools to study the stabilities of these complexes. According to our previous work [16], the pristine CNC structure which has the energy gap (ΔE_{gap}= 2.468 eV) is generated the semiconductive. The DOSs of the Ni–doped CNC are exhibited the difference patterns and band gaps. Introducing the filling electronic states of the dopant Ni atom into the undoped CNC induces narrower band gaps (ΔE_{gap} = 1.551 eV). Considering the energy gaps, the filling electronic states of the dopant TM atoms into the undoped CNC can narrow the E_{gap}, which suggests that the CNC changes nearly to a conductor [16].

3.2 Adsorption of Various Small Molecule Gases on Undoped CNC

B3LYP/LanL2DZ–optimized structures of adsorption of gaseous H_2, O_2, H_2O, CO, CO_2, and NH_3 on Ni–doped CNC are displayed in Fig. 3. Adsorption energies (ΔE_{ads}), partial charge transfers, and BSSE corrections of small gaseous on undoped, computed at the B3LYP/LanL2DZ level are listed in Table 1.

Based on calculation, the results show that the adsorption of gases on top of the undoped CNC has hardly ever affected the bond length C1–C4, C2–C4, C3–C4 (see Fig. 3). The weak interaction with gas molecules shows that the elongate binding distance is observed, suggesting that these interactions are van der Waals distances. According to adsorption reactivity, small adsorption energies are exothermically carried out via physisorption process. The reacted outstanding of O_2 on undoped CNC is obtained. The pristine CNC shows the highest interaction with O_2 (ΔE_{ads} = –14.17 kcal/mol), indicating that the oxygen appeared the stronger electronegativity than of other species. However, except for NH_3–CNC configuration the NH_3 molecule appears to be almost planar (see Fig. 3d).

NBO charge transfers (Q_T) of all various CNC doped with small gases tabulated in Table 1 show that partial charges of small gases slightly transfer to CNC. Nearly values of charge transfers of small gases to CNC are positive because during gases adsorb on CNC, its electron transfers to the cap. There is, however, one exception to this rule: the configuration O_2/Ni–CNC, for which the partial charge transfer values are negative.

Table 1 Adsorption energies (ΔE_{ads}), partial charge transfers (Q_T), and BSSE corrections of small gaseous on undoped and Ni–doped CNC, computed at the B3LYP/LanL2DZ level

Complexes	ΔE_{ads} [a]	Q_T [b]	BSSE [a]	ΔE_{ads}^{BSSE} [a]
Undoped system:				
H_2/CNC	0.04	0.000	0.19	0.23
O_2/CNC	–14.17	–0.055	2.86	–11.32
H_2O/CNC	–2.33	0.002	1.61	–0.72
NH_3/CNC	–0.18	0.008	0.73	0.54
CO/CNC	–1.19	0.002	1.77	0.58
CO_2/CNC	–0.26	0.004	0.48	0.22
Ni–doped system:				
H_2/Ni–CNC	–4.53	0.026	1.57	–2.96
O_2/Ni–CNC	–59.22	–0.544	5.83	–53.40
H_2O/Ni–CNC	–25.38	0.096	4.66	–20.72
NH_3/Ni–CNC	–31.78	0.150	4.31	–27.47
$\underline{C}O$/Ni–CNC [c]	–26.92	–0.016	7.42	–19.50
$C\underline{O}$/Ni–CNC [c]	–9.37	0.022	5.10	–4.26
CO_2/Ni–CNC	–10.34	0.011	4.15	–6.18

[a] In kcal/mol. [b] In e. [c] Pointing either its C or its O atom toward the top of Ni metal of Ni–doped CNC, we denote these orientations by $\underline{C}O$ and $C\underline{O}$, respectively.

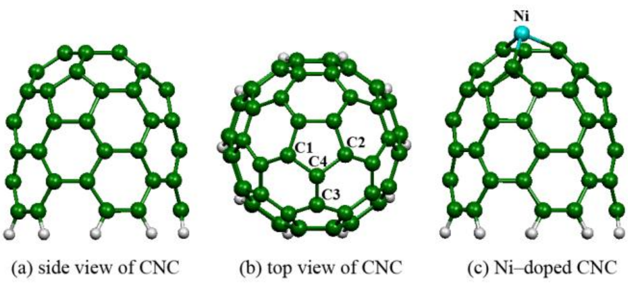

Fig. 1 Optimized structures of CNC with doping site and doping configuration. The dopant, labeled by “C4”, is surrounded by three neighboring carbon atoms (C1, C2, and C3). (a) Side and (b) top views of CNC, and (c) Ni metal doped on CNC

3.3 Adsorption of Various Gases on Ni–Doped CNC

B3LYP/LanL2DZ–optimized structures of adsorption of gaseous H_2, O_2, H_2O, CO, CO_2, and NH_3 on Ni–doped CNC are displayed in Fig. 4. In case of CO, when the CO is adsorbed onto Ni–doped CNC, it should be noted that pointing either its C or its O atom toward the side–wall atoms of the Ni–doped CNC; these orientations denoted by $\underline{C}O$ and $C\underline{O}$, respectively. Therefore, the adsorption configurations in which CO points its C or O atom toward the side–wall atoms of Ni–doped CNC are denoted $\underline{C}O$/Ni–CNC and $C\underline{O}$/Ni–CNC, respectively.

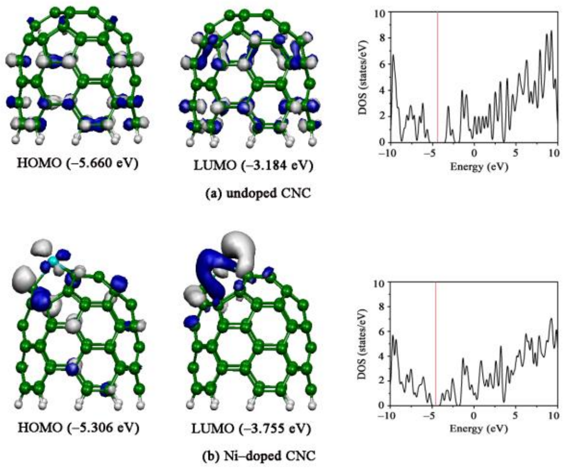

Fig. 2 Frontier molecular orbitals of HOMOs and LUMOs and density of states (DOSs) of (a) undoped and (b) Ni–doped CNC, computed at the B3LYP/LanL2DZ level. The red vertical line in plotted DOSs is referred to Fermi energy level.

The results show that binding distances between each species of gases and dopant Ni atom are found in the ranges of 1.705 to 2.187 Å, which are shorter than when compared to those of undoped CNC complexes. It is possible that interactions of all gases on Ni–doped CNC are approached to chemisorption distances. This can be confirmed here by using adsorption energies and partial charge transfers. The energies associated with the adsorption of gases onto the Ni–doped CNC, computed at the B3LYP/LanL2DZ level with and without the BSSE correction are presented in Table 1. These adsorption energies indicate that gas adsorptions by the Ni–doped CNC are always an exothermic process. The adsorption energies of gases on Ni–doped CNC are remarkably increased in comparison to the undoped CNC. The Ni–CNC shows the highest interaction in O_2 binding indicated by ΔE_{ads} and ΔE_{ads}^{BSSE} values are –59.22 and –53.39 kcal/mol, respectively. According to NBO partial charge transfers of these complexes, the Q_T for all adsorbed gases on Ni–doped CNC are positive, except for the adsorption of O_2 and $\underline{C}O$ configurations on Ni–doped CNC being negative Q_T values, which is implied that the direction of Q_T found in O_2 and $\underline{C}O$ is different from the other gas adsorptions. The highest charge transfer (Q_T = –0.544e) for O_2 on Ni–doped CNC is obtained, suggesting that the charge on Ni atom transfers to the O_2 molecule due to strong electronegativity of O atom.

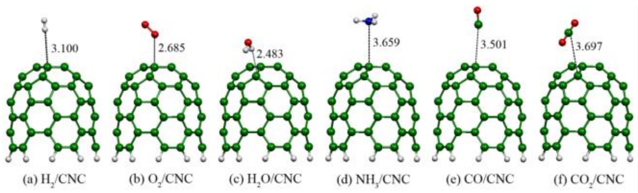

Fig. 3 Optimized structures of various gases adsorbed on the pristine CNC. Bond distances are in Å.

In the case of CO adsorption, the Ni–doped CNC show strong binding with CO molecule; the $\underline{C}O$/Ni−CNC configuration possesses the highest values of ΔE_{ads} and ΔE_{ads}^{BSSE} values (−26.92 and −19.50 kcal/mol, respectively). In this case, the adsorption is accompanied by −0.016e of Q_T from Ni−CNC to CO, occurs due to the strong electronegativity of the O atom of the CO molecule. On the other hand, for $C\underline{O}$/Ni−CNC configuration, the binding of CO to the Ni–doped CNC is weaker which ΔE_{ads} and ΔE_{ads}^{BSSE} values are −9.37 and −4.26 kcal/mol, respectively. This indicates that CO adsorption onto Ni–doped CNC using C atom toward Ni atom is not very favorable. The BSSE values for all gas adsorptions onto the studied Ni–doped surface are rather low: 1.57–7.42 kcal/mol.

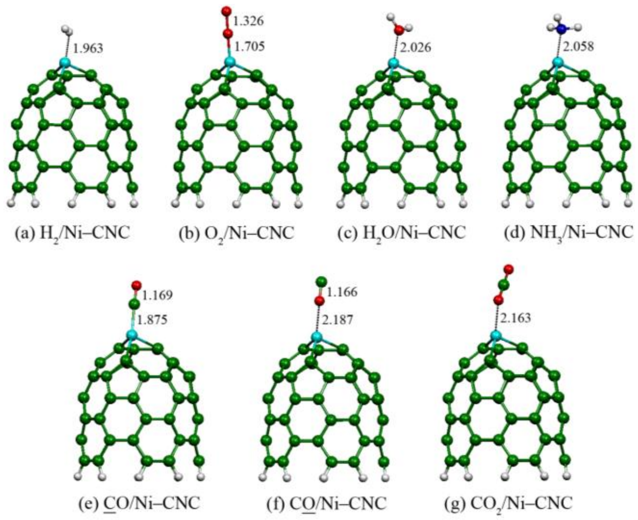

Fig. 4 Optimized structures of various gases adsorbed on the Ni–doped CNC. Bond distances are in Å.

4. Conclusions

The geometrical and electronic properties of small molecule gases adsorbed on Ni–doped CNC were calculated using DFT/LanL2DZ level of the theory. It was found that CNC showed strongly binding (ΔE_b = –154.80 kcal/mol) to Ni atom to form stable Ni–CNC complex. Doping of Ni atom on CNC induces narrower of energy gaps, suggesting that the CNC changes from semiconductor to nearly conductor. For gas adsorption behavior, the adsorption energies of various gases on Ni–doped CNC are surprisingly increased in comparison to those of the undoped CNC. The highest and lowest interactions are found in O_2/Ni–CNC and CO/Ni–CNC, respectively.

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