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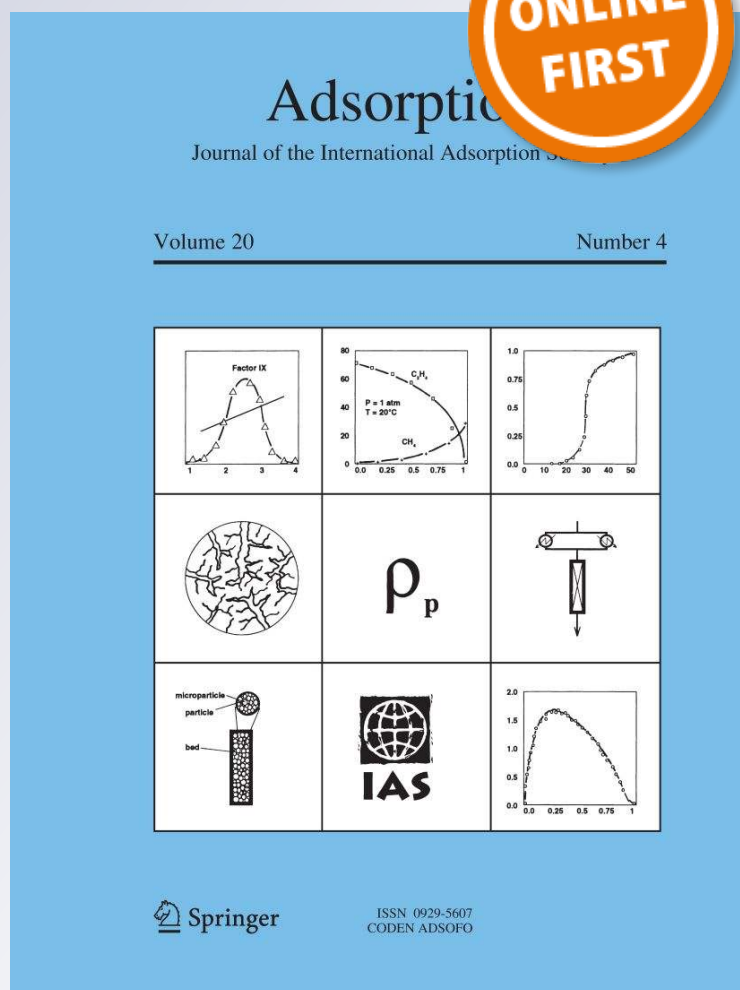
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Theoretical insights into the mechanism of CO₂ physisorption on Al–N ring doped on the carbon nanotube: a DFT study

A. S. Ghasemi¹ · F. Ashrafi¹ · H. Pezeshki¹ · M. Molla¹ · M. Rokni¹

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Abstract

Carbon nanotubes are the most important nanotechnology combinations, one of their most important applications being in the science of nano-electronic segments. In the present study, CO₂ molecule interaction with the outer surface of Zigzag (5,0) and Armchair (5,5) carbon nanotubes with specified and optimized lengths and diameters has investigated. Significance of this study is injection of insoluble carbon dioxide gas expanded in the reservoir, causing fluid movement towards the wellhead. Therefore, theoretical approaches have used to investigate the adsorption of CO₂ on single-wall carbon nanotubes, identify the adsorption structure and the attached carbon-to-gas configuration, and to calculate the parameters such as energy gap in carbon-gas nanotube structures that can help to identify carbon-gas nanotube complex stability. Results revealed that CO₂ molecule reaction with nanotube surface generates diverse adsorption structures. The best CO₂ gas adsorption has obtained on the surface of carbon nanotubes (5,5) doped with the Al–Nitride ring.

Keywords DFT · Energy gap · Carbon nanotubes · Homo–Lumo

1 Introduction

The discovery by Iijima and Ichihashi (1993) of carbon nanotubes inspired a lot of research and studies on synthesis (Jiang and Lan 2015; Shokry et al. 2015) and also identification of carbon nanotube properties and applications such as physical (Chang and Lin 2014; Reisi-Vanani and Faghih 2014) and chemical (Al-Sunaidi and Al-Saadi 2015; Zhang et al. 2012) properties. Carbon nanotubes have attracted a lot of enhanced gas and oil recovery attentions to themselves because of their interesting characteristics (Ashrafi and Ghasemi 2012) such as high permanency, density and electric resistance change in semi-conductive nanotubes as a result of CO₂ and N₂ gas molecule adsorption and also their application in the enhanced gas and oil recovery process in nano-scale (Kong and Ohadi 2010). CO₂ gas injection, which is a miscible approach, is the second-order enhanced recovery approach. Providing pressure, oil swell, miscible and immiscible displacements are among the mechanisms in gas injection. CO₂ constitutes about 64%

of the greenhouse gas volume. The CO₂-saving project is a process to help remove it from the greenhouse gases by its injection to depleted gas and oil reservoirs (Gholamzadeh et al. 2009). Stephan et al. were the pioneers in using basic principles to calculate adsorption characteristics of various gases (NO₂, O₂, NH₃, N₂, CO₂, CH₄, H₂O, H₂, and Ar) on SWCNTs (Jauris et al. 2016; Machado et al. 2012; Molla and Behbahani 2016; Prola et al. 2013). The corroborated results of previous studies confirmed that the nanotube's structural balance and, as a result, its behavior changes in proximity of gas molecules (Machado et al. 2011). Nonetheless, only few studies have been conducted investigating gas adsorption on carbon nanotubes, including theoretical (Ansari et al. 2015; Yoosefian et al. 2015) and experimental (Shaheen et al. 2015; Yan et al. 2014) researches of CO₂ adsorption on single-wall nanotubes. Several cases, however, did not apply appropriate laboratory equipment for experiments in the nano level or running the experiments has really proved expensive. Therefore, the computations have utilized to simulate atomic and molecular processes and reactions. The present study investigated the adsorption behavior of CO₂ on single-wall zigzag (5,0) and armchair (5,5) carbon nanotubes doped with Al–Nitride ring.

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2 Computational details

The present study used electron Density Functional Theory (DFT) method (Lee et al. 1988) to investigate and interpret the CO₂ molecule interaction with (5,5) and (5,0) single wall carbon nanotubes doped with Al–Nitride ring. Considering the adsorption of the CO₂ molecule on the outer surface of the nanotubes, a study on the adsorption configuration, adsorption energy, and carbon atoms nuclei on nanotube surfaces in physisorption with the CO₂ molecules seems interesting and beneficial. Results of the computational studies reveal that the CO₂ molecule interaction with nanotube surfaces leads to diverse adsorption structures. In addition, carried out computations showed that, in some cases, CO₂ has not adsorbed by Carbon–Carbon bonds on carbon nanotube surfaces. Whereas replacing an Aluminum–Nitride ring with the carbon ring on the Zigzag (5,0) and Armchair (5,5) nanotubes increases the adsorption capability of gas on nanotubes. Moreover, the adsorption capability of gas, with more negative adsorption energy, is more on Armchair (5,5) nanotubes doped with Al–Nitride ring than on Zigzag (5,0) nanotubes. Geometric optimization, Natural bond orbital (NBO), were performed on carbon nanotubes models (5,0) and (5,5) doped with Al–Nitride ring and the Density of states (DOS) has plotted. Geometric optimizations and energy calculations were conducted using Gaussian 03 (Frisch et al. 2004) software on the DFT level with LANL2DZ (Ahmadi Peyghan et al. 2013; Mirzaei and Yousefi 2012; Soltani et al. 2014; Tournus and Charlier 2005). The adsorption energy (E_{ad}) of CO₂ on the outer surface of (5,0) and (5,5) carbon nanotubes doped with Al–Nitride ring were calculated using following formulas:

$$E_{ad} = E_{CO_2 - SWCNTs} - [E_{SWCNTs} + E_{CO_2}] \quad (1)$$

$$E_{ad} = E_{CO_2 - SWCNTs-AIN} - [E_{SWCNTs-AIN} + E_{CO_2}] \quad (2)$$

where, $E_{CO_2 - SWCNTs-AIN}$, is the interaction energy of CO₂ and carbon nanotubes doped with the Al–Nitride ring. $E_{SWCNTs-AIN}$, is the total energy of nanotubes doped with the Al–Nitride ring. Furthermore, E_{CO_2} , is the separated CO₂ energy.

μ is the electronic chemical potential of molecule and calculated by following equation:

$$\mu = -\chi = -\frac{I + A}{2} \quad (3)$$

Electron affinity χ is defined as the negative of ionization potential as $\mu = -\chi$. Moreover, chemical hardness (η) can be estimated using Koopmans' theorem (Koopmans 1934):

$$\eta = \frac{(I - A)}{2} \quad (4)$$

I ($-E_{HOMO}$) is the ionization potential and A ($-E_{LUMO}$) is the molecule's electron affinity in which E_{HOMO} is the Fermi

surface energy and E_{LUMO} is the first given value in the conduction band. Parr et al. stated the concept of electrophilicity for the first time in 1999 (Parr et al. 1999). The electrophilicity index (ω) defined by following equation:

$$\omega = \left(\frac{\mu^2}{2\eta} \right) \quad (5)$$

Also, softness (S) defined by the following equation:

$$S = \frac{1}{2\eta} \quad (6)$$

Although, errors are inevitable in computational approaches and sometimes it is hard to control for further improving, using an appropriate basic principle, the calculations can be improved. For example, replacing 6-311G** basic principles by more appropriate one such as cc-PV6Z can lead to better results. Therefore, LANL2DZ basic principle has used in the present study to improve the computations and to achieve more accurate results. Therefore, the standard LANL2DZ basis set has previously reported to study carbon nanostructures (Soltani et al. 2017, 2018).

3 Results and discussion

The initial structure of the nanotube, in an optimized length and diameter, was prepared with nanotube modeler software (30). By choosing a certain length for nanotube, carbon atoms at the both ends of the nanotube would negatively charged due to the break in the carbon bonds.

Hydrogen atoms have added to the both ends of the nanotube rings to saturate the bonding on the end carbon atoms in the nanotube string and create a model close to a real nanotube string. In the nanotube model (5,5), twenty hydrogen atoms and in the nanotube model (5,0), ten hydrogen atoms were added to the original structure. The difference is due to the different geometric structures of these two types of nanotubes. The minimum length required for the calculations for the armchair nanotube (5,5) were set to 17 Å in length and 7 Å in diameter, and for the Zigzag model (5,0) was set to 15 Å in length and 4 Å in diameter. The lengths for these nanotubes have chosen considering the length of unit cells in each nanotube.

The nanotubes have optimized at the end after being make. Optimizations of these two structures have performed using LANL2DZ. Fig. 1 shows the initial structure of the carbon nanotubes doped with the Al–Nitride ring: (A) armchair (5,5) and (B) Zigzag (5,0).

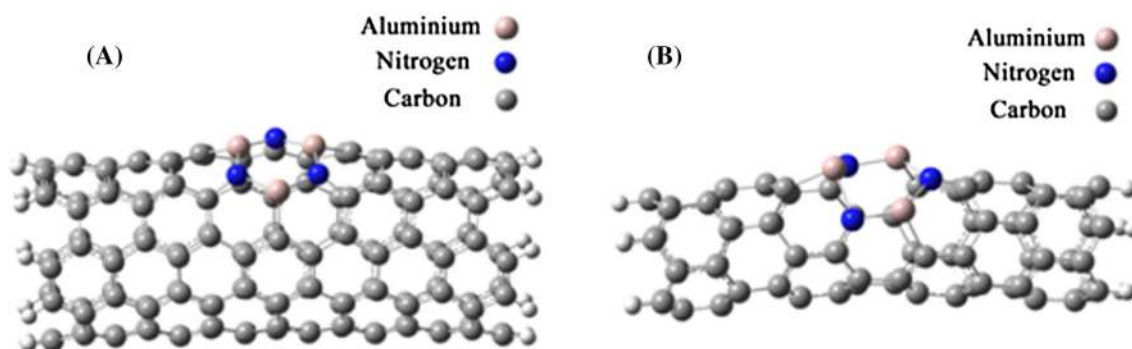
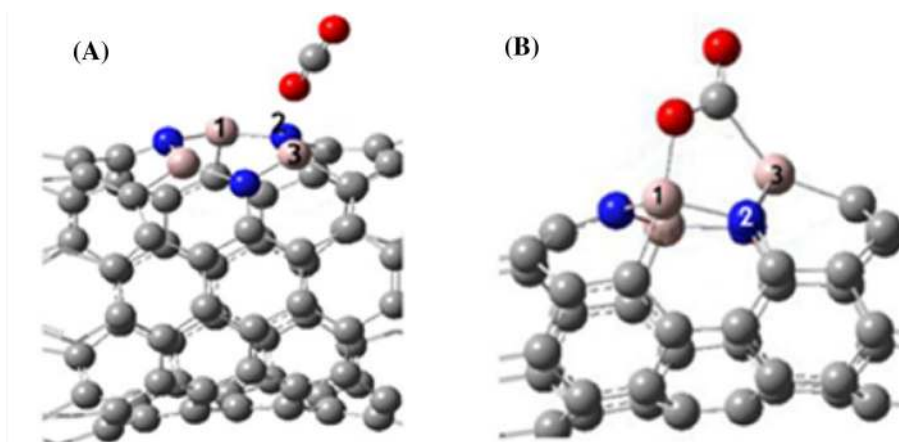


Fig. 1 Initial structures of carbon nanotubes doped with the Al–Nitride ring: **a** armchair (5,5) and **b** Zigzag (5,0)

Fig. 2 The optimized structures of carbon nanotubes doped with the Al–Nitride ring, **a** armchair (5,5) and **b** Zigzag (5,0). In addition, the CO₂ molecules adsorbed on the surfaces have shown



3.1 The optimized structure of the nanotubes (5,0) and (5,5) and the adsorbed CO₂ molecule

Due to the geometric structure of the single-walled carbon nanotube, gas adsorption on the surface of carbon atoms is not possible (Ghasemi et al. 2016). Therefore, on the surface of the single-walled carbon nanotubes (5,5) and (5,0) in the range of the CO₂ molecule adsorption, Al and N atoms were doped. In the gaseous phase, a selective site was determined for the CO₂ molecule adsorption on the surfaces of the single-walled carbon nanotubes (5,5) and (5,0) models. Figure 2 shows the adsorption of CO₂ molecules on the surface of the single-walled carbon nanotubes (5,5) and (5,0).

In this study, using density functional method (DFT), the interaction of carbon dioxide molecules on the surface of both armchair (5,5) and zigzag (5,0) single-walled carbon nanotubes doped with Al–Nitride ring is compared (Table 1) and the energy of molecular carbon dioxide adsorption in both armchair (5,5) and zigzag (5,0) models is studied (Table 2).

Table 1 Calculated bond lengths (Å) and dipole moment ($\mu_{\text{D/Debye}}$) of the CO₂ adsorbed on the surface of zigzag (5,0) and armchair (5,5) single-walled carbon nanotubes

Property	(5,5) SWCNT– AlN–CO ₂	(5,0) SWCNT– AlN–CO ₂	(5,5) SWCNT– AlN	(5,0) SWCNT–AlN
R(Al(1)– N(2))	1.57	1.45	1.82	1.88
R(N(2)– Al(3))	1.58	1.40	1.85	1.91
R(Al(1)– CO ₂)	–	–	2.12	1.84
R(Al(3)– CO ₂)	–	–	–	2.05
μ_{Debye}	5.93	3.85	8.31	5.94

According to the investigations carried out on the adsorption of small molecules and atoms on the single-walled carbon nanotubes doped with Al–Nitride ring, it was found that the most probable site for adsorption is placed on a nitrogen-bound aluminum bond (Fig. 2).

Table 2 Calculated E_{LUMO} and E_{HOMO} , energy gap (E_g), energy adsorption (E_{ad}), chemical potential (μ), hardness (η), softness (S), and electrophilicity (ω) before and after CO_2 adsorption on (5,5) SWCNT–AlN and (5,0) SWCNT–AlN

Property	(5,5) SWCNT–AlN	(5,0) SWCNT–AlN	(5,5) SWCNT–AlN– CO_2	(5,0) SWCNT–AlN– CO_2
$E_{HOMO}/a.u.$	–0.173	–0.165	–0.172	–0.167
$E_{LUMO}/a.u.$	–0.047	–0.129	–0.104	–0.129
$E_g/a.u.$	0.126	–.036	0.068	0.038
$E_{ad}/a.u.$	–	–	–1.905	–2.204
$I/a.u.$	0.173	0.165	0.172	0.167
$A/a.u.$	0.047	0.129	0.104	0.129
$\eta/a.u.$	0.063	0.018	0.034	0.019
$\mu/a.u.$	–0.110	–0.147	–0.138	–0.148
$S/(a.u.)^{-1}$	7.94	27.77	14.70	26.32
$\omega/a.u.$	0.096	0.600	0.280	0.576

The values of energies, E_g , I , A , η , μ and ω are on a.u. and to convert to eV, it must multiply by 27.211396

The optimized structure of the single-walled carbon nanotubes (5,0) and (5,5) and the CO_2 molecule adsorbed on the carbon nanotubes doped by the Al–Nitride ring in the gaseous phase are investigated and shown in the Fig. 2.

3.2 A comparison between the CO_2 adsorption bond lengths and identification of the dipole moments of (5,5) and (5,0) models

Table 1 shows the computational details of the length of the N–Al bond forming the ring doped on the single-walled carbon nanotube in the proximity of the Al–O bond in the optimized structure (Fig. 1). The computations for SWCNT–AlN– CO_2 zigzag (5,0) structure indicates that the bond length of Al(1)–N(2) is 1.88 Å and the bond length of N(2)–Al(3) is 1.92 Å. While in the armchair (5,5) configuration the length of bonds are 1.82 and 1.85 Å for Al(1)–N(2) and N(2)–Al(3) respectively. Jiao et al. (2010) reported a length of O– CO_2 bond of 3.80 Å in their study on CO_2 molecule adsorption on single-wall Boron Nitride (6,6) nanotube using the PW91 basic principles. They proposed that this is a physisorption (Jiao et al. 2010).

The results of calculation using LANL2DZ basic principles, show that by placing an Al–Nitride ring on the single-walled carbon nanotube, carbon dioxide has adsorbed and the length of Al(1)– CO_2 bond and Al(3)– CO_2 bond in (5,0) configuration is about 1.84 and 2.05 Å respectively. By the same calculation for (5,5) configuration, the length of Al(1)– CO_2 bond was obtained 2.12 Å but the calculation did not show any binding of Al(3)– CO_2 . The results of the calculations conducted for adsorption of CO_2 on the SWCNT (5,0) surface leads to the bond lengths C(1)–C'(1)=1.52 Å and C(1)–O(1)=2.62 Å (Ghasemi et al. 2016). This reveals that carbon dioxide has better adsorption on doped Al–N ring. Moreover, the bond lengths of Al(1)– CO_2 after adsorption of CO_2 were 1.84 and 2.12 Å for SWCNT (5,0) and for SWCNT (5,5) in the gaseous

phase, respectively. Taking into account the obtained results it seems that practically SWCNT(5,0)–AlN maybe more useful than SWCNT(5,5)–AlN for carbon dioxide injection to oil wells in order to increase oil recovery. Considering SWCNTs structures doped by Al–N ring and shown in Fig. 2 and the results of calculations, high electronegativity of oxygen atom causes the electrons moving out of p_x and p_y anti-hybrid orbitals when Al–O bond would formed and this phenomenon expands the bond length of doped Al–N ring. As a result, the distance between nanotubes and the Oxygen in CO_2 increases and the gas may be desorbs from the surface of nanotube. Nevertheless, when Al–N ring has doped on SWCNT's surface due to the unoccupied orbitals of Al the adsorption capacity increases. In the gaseous phase, the bond lengths of Al–N in both configurations, (5,5) and (5,0), have increased after CO_2 adsorption (Table 1). Considering CO_2 interaction with doped nanotube electron charge transfers from oxygen to two molecular orbitals σ^* Al–N bond that leads to an increase of electron density in these anti-hybrid orbitals and consequently a decrease in the electron density of σ hybrid orbitals that leads to a weaker and longer Al–N bond. The bond lengths in SWCNT–AlN before and after CO_2 adsorption on (5,0) and (5,5) configurations and also the dipole have shown in Table 1. It may be conclude that, the larger is the dipole moment the absolute value of the binding energy will be larger. This will be expecting because a larger dipole moment applies more transfer of the electron charge that leads to the larger absolute value of the binding energy. Lower electrophilicity index (ω) reveals lower electrophilicity of a complex. For two complexes, the values of ω are changed to 0.280 a.u. in SWCNT(5,5)–AlN and 0.576 a.u. in SWCNT(5,0)–AlN (see Table 2). When CO_2 interacting with SWCNT(5,5)–AlN and SWCNT(5,0)–AlN, the softness (S) values increased to 14.70 (a.u.)^{–1} and 26.32 (a.u.)^{–1}, respectively.

3.3 A comparison of the adsorption energy of CO₂ on (5,0) and (5,5) doped nanotubes

The adsorption energy E_{ad} has calculated using the following formula (Table 2):

$$E_{ad} = E_{tot}(SWCNT - AlN - CO_2) - [E_{tot}(SWCNT - AlN) + E_{tot}(CO_2)]$$

where, E_{tot} is the total energy of system, E_{ad} is the energy of SWCNT(5,0)–AlN–CO₂ and SWCNT(5,5)–AlN–CO₂ complexes that is – 2.204 and – 1.905 a.u., respectively. The amount of negative adsorption energy obtained in both structures shows that the reactions are exothermic. Upon the adsorption of CO₂ on the surface of SWCNT(5,0)–AlN, this semiconductor will turned to conductor, however, no such behavior was observed in SWCNT(5,5)–AlN. This can explain more negative and stable adsorption energy of SWCNT(5,0)–AlN–CO₂ complex (see Table 2).

3.4 The analysis of the molecular orbitals (MO)

Quantum effects appear, as the semi-conductive nanoparticles achieve a small size. Electrons have energy ranges in quantum dots but energy levels are not consistent because of infinitesimal size of these nanoparticles. Therefore, the formation of these quantized energy levels reduces the recombination time (Chukwuocha et al. 2012). A decrease or increase in the number of atoms in quantum dots changes the energy gap that will reproduces because of the very small size of these dots. In this case, the electron density in Al–N ring on nanotubes doped with Al–N has investigated. In the carbon dioxide molecule an oxygen atom, has a 2 s energy level less than that in the atomic carbon energy level and it remains as anti-hybrid form σ^n . The two molecular orbitals σ and σ^* are formed by two sp orbitals of carbon and two P_z ones of oxygen. The main electronic arrangement of CO₂ is $(\sigma_g^n)^2 (\sigma_u^n)^2 (\sigma_g^n)^2 (\pi_u^n)^4 (\pi_g^n)^4 (\pi_g^*)^2 (\sigma_g^*)^2 (\sigma_u^*)^2$. Considering the single arrangement, $(\pi_u^n)^4$ is $(\pi_u(x))^2 (\pi_u(y))^2$ and $(\pi_g^n)^4$ is $(\pi_g^n(x))^2 (\pi_g^n(y))^2$. This occurs when the π bond due to the

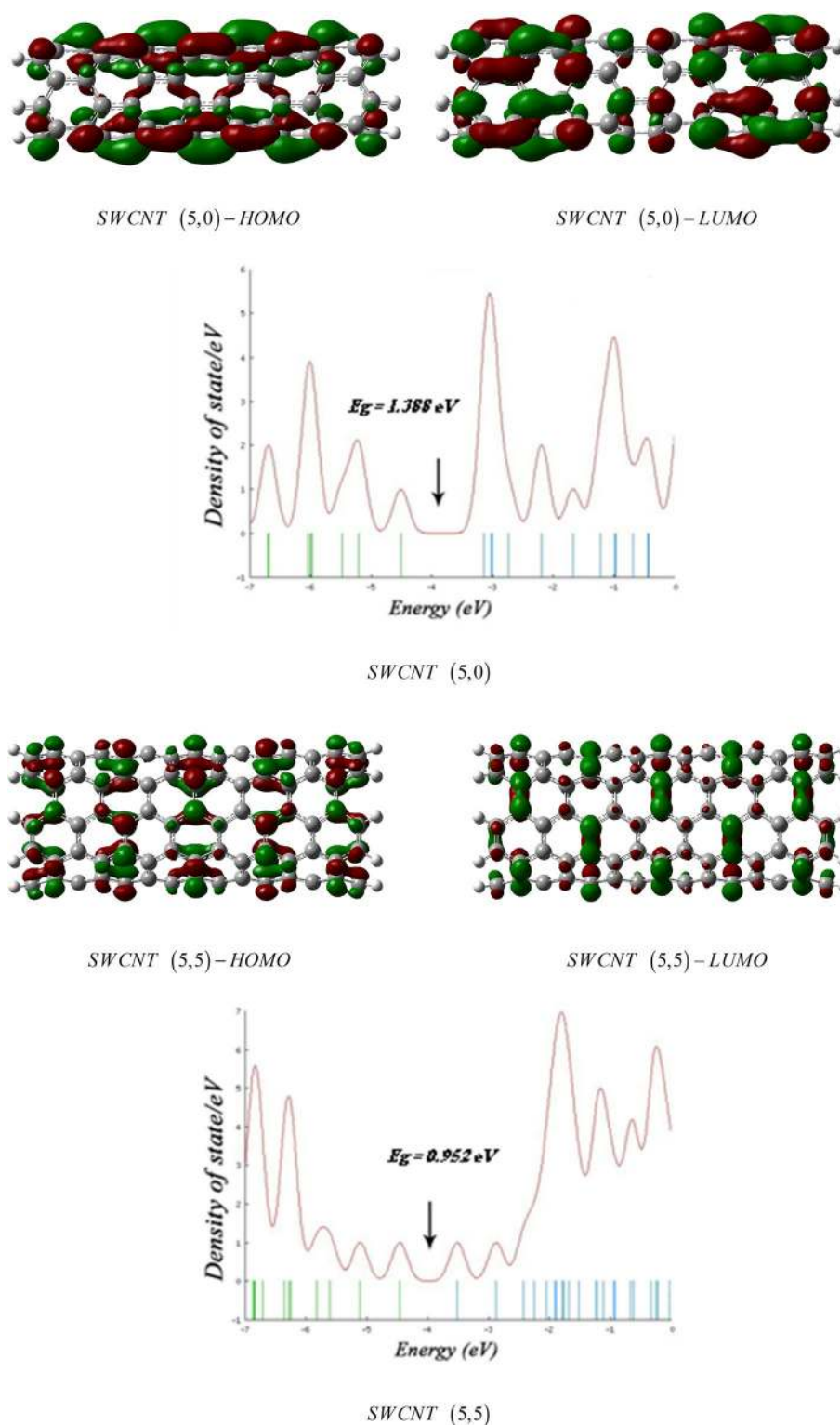
d orbitals of Al returns to the π^* MO bonds in the carbon dioxide (Baei et al. 2016; Javan et al. 2017) Another reason for the SWCNTs–N–Al–CO₂ bond formation is the interaction between the highest occupied molecular orbital (HOMO) known as π^n and the unoccupied d orbitals of Al-

minum. In the present study, the calculations have performed by density functional theory method using Gaussian 03 software applying LANL2DZ level. The geometry of carbon nanotubes has optimized at the LANL2DZ level. The electron arrangement in a single CO₂ bonded to the Al–N ring on SWCNT has considered. The energies of HOMO orbitals of SWCNT–AlN and SWCNT–AlN–CO₂ for (5,0) and (5,5) configurations in the gaseous phase are – 0.167, – 0.165, – 0.172 and – 0.173 a.u., respectively (Table 3). The energies of LUMO orbitals of SWCNT–AlN and SWCNT–AlN–CO₂ for (5,0) and (5,5) configurations in the gaseous phase are – 0.129, – 0.129, – 0.104 and – 0.047 a.u., respectively (Table 3). HOMO (positive electron density) and LUMO (negative electron density) electron density distributions of SWCNT (5,0) and (5,5), SWCNT–AlN (5,0) and (5,5) and SWCNT–AlN–CO₂ (5,0) and (5,5) and their DOS plots are shown in Fig. 3. The small HOMO–LUMO bond gap indicates effortless electron transfer between occupied and unoccupied molecular orbitals that increases the sensor behavior of electrical conductivity. Electron density distributions in HOMO and LUMO orbitals of SWCNT (5,0) and (5,5) are nearly uniform (Fig. 3). Whereas, in SWCNT–AlN (5,0) and (5,5) and SWCNT–AlN–CO₂ (5,0) and (5,5) electron density distributions in HOMO and LUMO orbitals are no more uniform. This event occurs because of electron acceptor feature of Al in AlN ring and high electronegativity of oxygen in CO₂ Molecule. The energy gap of HOMO and LUMO orbitals can evaluate the rate of adsorption of CO₂ on AlN ring of SWCNT–AlN (5,0) and (5,5). The energy gaps of SWCNT, SWCNT–AlN and SWCNT–AlN–CO₂ in (5,0) and (5,5) configurations in the gaseous phase obtained by calculations are 1.388, 0.952, 1.034, 1.850, 0.980 and 3.428 eV, respectively (Fig. 3; Table 3).

Table 3 Calculated E_{LUMO} and E_{HOMO} , energy gap (eV) Of (5,0) and (5,5) SWCNTs, SWCNTs–AlN and SWCNTs–AlN–CO₂

Molecule	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	Energy gap (a.u.)
SWCNT (5,0)	– 0.166	– 0.115	0.051 [13]
SWCNT (5,5)	– 0.164	– 0.129	0.035 [13]
SWCNT (5,0) – AlN	– 0.167	– 0.129	0.038
SWCNT (5,5) – AlN	– 0.172	– 0.104	0.068
SWCNT(5,0) – AlN – CO ₂	– 0.165	– 0.129	0.036
SWCNT(5,5) – AlN – CO ₂	– 0.173	– 0.047	0.126

Fig. 3 Adsorption configurations of the SWCNTs, SWCNTs–AlN and SWCNTs–AlN–CO₂ structures of (5,0) and (5,5) configurations and their corresponding density of state (DOS) plots in eV

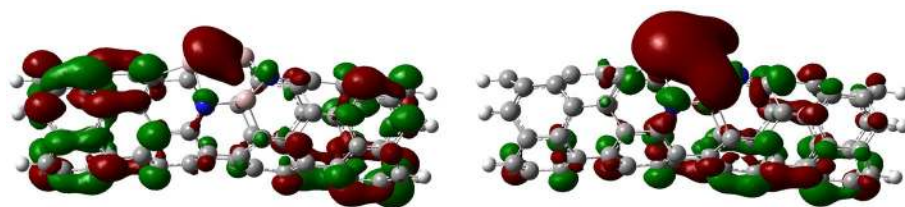


4 Conclusion

The adsorption energy, the dipole moment, the energy gap, and the energies of HOMO and LUMO orbitals in SWCNT, SWCNT–AlN and SWCNT–AlN–CO₂ of (5,0)

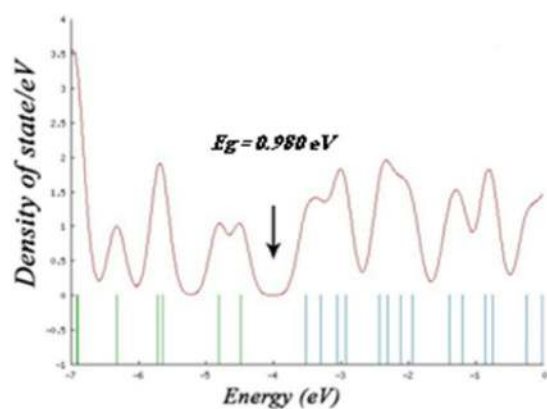
and (5,5) configurations were calculated using the Gaussian 03 software. The computational results suggested the physisorption of CO₂ on the outer surface of the nanotubes doped with the Al–N ring. Furthermore, the adsorption structures of the CO₂ molecule on the SWCNTs armchair

Fig. 3 (continued)

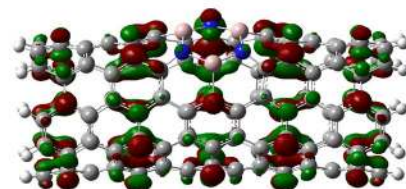
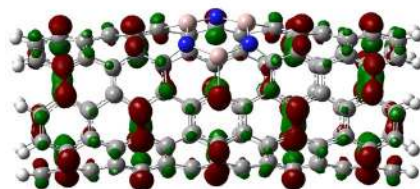


SWCNT (5,0)-AlN -HOMO

SWCNT (5,0)-AlN -LUMO

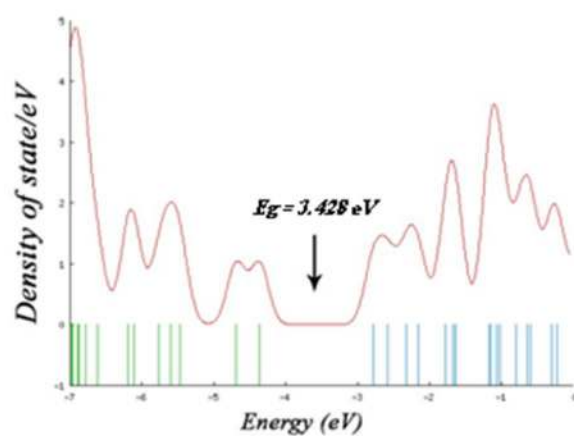


SWCNT (5,0)-AlN



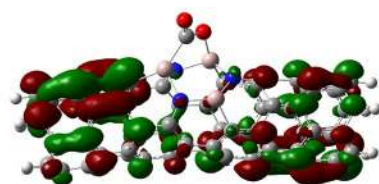
SWCNT (5,5)-AlN -HOMO

SWCNT (5,5)-AlN -LUMO

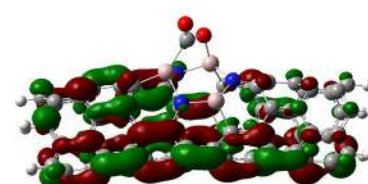


SWCNT (5,5)-AlN

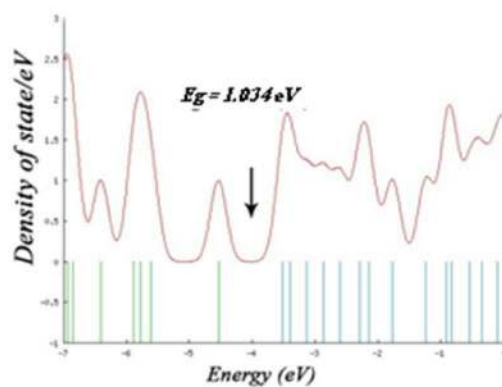
Fig. 3 (continued)



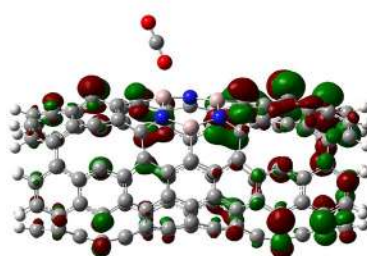
SWCNT (5,0)-AlN-CO₂ - HOMO



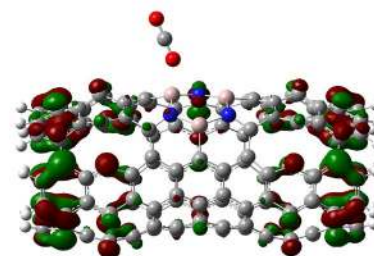
SWCNT (5,0)-AlN-CO₂ - LUMO



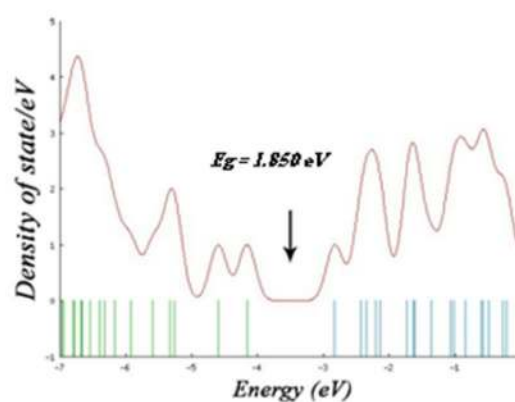
SWCNT (5,0)-AlN-CO₂



SWCNT (5,5)-AlN-CO₂ - HOMO



SWCNT (5,5)-AlN-CO₂ - LUMO



SWCNT (5,5)-AlN-CO₂

(5,5) and zigzag (5,0) doped with the Al–N ring were studied using the density functional theory (DFT). The obtained results of calculations have shown that adsorption of CO₂ molecule on AlN ring doped on nanotube is a physical reaction where the amount of energy changes with adsorption position of CO₂ and the type of SWCNT. Considering the geometric structure of the carbon nanotubes armchair (5,5) and the zigzag (5,0) models and adsorption of CO₂ molecule on the outer surface of these carbon nanotubes showed that the semi-conductor carbon nanotube (5,0) doped with an Al–N ring gave the best results that was closer to the real value (Table 3). The structural changes in the CO₂ gas adsorption on the surface of the SWCNTs–AlN included a small increase in the bond length of the Al–N due to the high electronegativity of oxygen. Moreover, when π bond due to the d orbitals of Al returns to the π^* MO bonds in the carbon dioxide, this may be in the origin of an increase of gas adsorption on carbon nanotubes in some cases. The results also shown that the amount of adsorption energy of the CO₂ molecule on the zigzag (5,0) and armchair (5,5) carbon calculating by DFT method have shown the significant difference. The adsorption energies obtained from CO₂ gas adsorption on the surface of the SWCNT–AlN in both configurations of carbon nanotubes prove the possibility of this reaction. The obtained results of this study reveal that the doped rings on the carbon nanotubes increases the CO₂ gas adsorption capability. This will considered and applied to study the adsorption of other gases on doped SWCNTs. The results of this study will be useful in application of these types of sensors to increase oil recovery.

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