

A computational study of atomic oxygen-doped silicon carbide nanotubes

Maryam Mirzaei · Mahmoud Mirzaei

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Abstract We investigated the properties of atomic oxygen-doped (O-doped) models of representative (6,0) and (4,4) silicon carbide nanotubes (SiCNTs) by density functional theory (DFT) calculations of isotropic and anisotropic chemical shielding (CS) parameters of Si-29, O-17 and C-13 atoms for the optimized structures. The calculated parameters indicated the effects of O-doping on the electronic environments of the first neighboring atoms of the doped sites. Comparing the results of the zigzag and armchair models also indicated that the latter model detects more effects of the O-doping than the former one.

Keywords Chemical shielding · Electronic structure · Oxygen doping · Silicon carbide nanotube

Introduction

The discovery of carbon nanotubes (CNTs) by Iijima [1] has stimulated numerous studies on investigation of the properties of this novel material [2, 3]. Many studies have also been devoted to characterize other kinds of nanotubes rather than the CNTs. Among the CNT-like structures, the stable tubular structures of boron nitride (BN) and silicon carbide (SiC) were initially predicted by calculations and

were then successfully synthesized [4–7]. The BNNT and SiCNT are always semiconductors in contrast with the CNTs, which are metal or semiconductor depending on the tubular diameter and chirality [8–11]. Moreover, due to the different values of electronegativities of C and Si atoms, the SiCNTs are polar materials whereas the CNTs are non-polar. In addition, longer Si-C bond (1.80 Å) than B-N (1.44 Å) and C-C (1.42 Å) ones makes the SiCNTs as a proper candidate for applications in materials storage better than the BNNTs and CNTs [12]. More stability have also been recognized for the structures of counterparts of Si and C atoms than the structures which only consist of C or Si atoms [13]. To this time, theoretical and experimental researchers have investigated the properties of SiCNTs [14–18]. Very recently, Cao *et al.* [19] and Szabó and Gali [20] investigated the chemical and physical adsorptions of oxygen (O) atoms on the SiCNTs and showed that this process deserves further investigations.

In this work, we have studied the electronic and structural properties of O-doped models of representative (6,0) zigzag and (4,4) armchair single-walled SiCNTs (Figs. 1 and 2) by means of computed NMR parameters (Tables 1 and 2). Nuclear magnetic resonance (NMR) spectroscopy is a versatile technique to study the electronic structures of matters [21]. Any changes to the electronic environments of dipolar atoms, *e.g.*, ^{29}Si , ^{17}O and ^{13}C could be detected by chemical shielding (CS) tensors. Density functional theory (DFT) calculations have been performed to optimize the models and to calculate the CS tensors of ^{29}Si , ^{17}O and ^{13}C atoms for the optimized structures. The properties of two O-doped models for each of zigzag and armchair SiCNTs have been investigated; O (Si) and O(C) models. One Si atom is doped by one O atom in the O(Si) model and one C atom is doped by one O atom in the O(C) model. The obtained results of O-doped models

M. Mirzaei
Department of Electrical Engineering, Islamic Azad University,
South Tehran Branch,
Tehran, Iran

M. Mirzaei (✉)
Department of Chemistry, Islamic Azad University,
Shahr-e-Rey Branch,
Shahr-e-Rey, Iran
e-mail: mdmirzaei@yahoo.com

have been compared with the perfect SiCNTs. Our results indicated that the properties of O-doped SiCNTs could well be investigated by the computed NMR parameters.

Computational aspects

Within the current research, the electronic and structural properties of O-doped models of representative (6,0) zigzag and (4,4) armchair single-walled SiCNTs were investigated by DFT calculations using the Gaussian 98 package [22]. The first O-doped models of both zigzag and armchair SiCNTs, designated by O(Si), consist of 35 Si, one O and 36 C atoms (Figs. 1a and 2a). The second O-doped models, designated by O(C), consist of 36 Si, 35 C and one O atoms (Figs. 1b and 2b). The perfect models consist of 36 Si and 36 C atoms. The tips of all models of nanotubes are saturated by hydrogen (H) atoms to avoid the dangling effects. In the initial step, the all-atomic geometries of the structures have been allowed to relax by optimization at the level of the B3LYP method and 6–31G* standard basis set. In the last step, the CS tensors were calculated for the optimized structures at the same level of theory based on the gauge included atomic orbital approach (GIAO) [23]. The quantum chemical calculations yield the CS tensors in the principal axis system (PAS) with the order of $\sigma_{33} > \sigma_{22} > \sigma_{11}$; therefore, Eqs. 1 and 2 are used to convert the calculated CS tensors to the absolute isotropic (σ_{iso}) and anisotropic ($\Delta\sigma$) CS parameters [21]. The computed absolute NMR parameters of ^{29}Si , ^{17}O and ^{13}C atoms for the investigated models of the (6,0) and (4,4) SiCNTs are listed in Tables 1 and 2. It is worth noting that the size of model considered and the level of theory employed for the study of the properties of electronic structures of nanotubes have been validated by results from previous works [24, 25].

$$\sigma_{iso}(\text{ppm}) = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33}), \quad (1)$$

$$\Delta\sigma(\text{ppm}) = \sigma_{33} - \frac{1}{2}(\sigma_{11} + \sigma_{22}). \quad (2)$$

Results and discussion

Investigated models

The structures of perfect and O-doped models of (6,0) zigzag and (4,4) armchair SiCNTs are optimized and then the NMR parameters are calculated for the optimized structures. Average value of 1.80 Å was calculated for Si-C bond distance in the perfect models whereas these

values are changed in the O-doped models which are exhibited in Figs. 1 and 2. Comparing the values of bond distances in the O-doped models and the averaged value of perfect model indicates that the Si-C bonds detect the effects of O-doping in which these effects are more significant in the O(C) models. Parallel to different detected effects by Si-C bond distances due to O-doping, different effects are also observed for the calculated values of NMR parameters. The following text discusses the calculated NMR parameters in the optimized structures of perfect and O-doped models of zigzag and armchair SiCNTs.

NMR parameters of the zigzag SiCNTs

Table 1 presents the calculated NMR parameters consisting of the absolute isotropic and anisotropic chemical shieldings (σ_{iso} and $\Delta\sigma$) of ^{29}Si , ^{13}C and ^{17}O atoms for O(Si), O(C) and perfect models of the (6,0) zigzag SiCNT (Fig. 1). The perfect model consists of 36 Si and 36 C atoms in which both tips of nanotube are saturated by the H atoms to avoid the dangling effects. In the O(Si) and O(C) models, one Si and one C atom is respectively doped by one O atom. A quick look at the results indicates that the NMR parameters of the O-doped models detect notable changes in comparison with the perfect model. To ease of discussion, the atoms of nanotube are divided into layers based on the similarities of NMR parameters for atoms of each layer. This trend means that the atoms which detect similar electronic environment are categorized in an atomic layer.

In the O(Si) model (Fig. 1a) where one Si atom is doped by one O atom, although some changes are observed for the NMR parameters of the Si atoms but there are not any notable changes. This trend means that the electronic environments of the ^{29}Si atoms are kept almost unchanged. In contrast with the ^{29}Si atoms, notable changes are observed for the ^{13}C atoms in this model of the O-doped zigzag SiCNT. The most notable change is observed for the eighth layer of C atoms where two C atoms of this layer are in direct chemical bonding with the O atom. In comparison with the perfect model, the value of σ_{iso} is reduced by a magnitude of 34 ppm. It is known that the value of σ_{iso} is proportional to the electronic density at the sites of atoms and could be influenced by the contribution of atom to the bonds with different strengths. The electronegativity of O atom is more than C atom; therefore, it could be expected that the bonding electrons of C-O bonds would orient to the O site; therefore, the value of σ_{iso} would be reduced for C atom but would be increased for O atom, as could be seen by the calculated results. In the sixth layer of C atoms, there is also a C-O bond in which the value of σ_{iso} of the ^{13}C atoms of this layer detects changes due to this bond but less

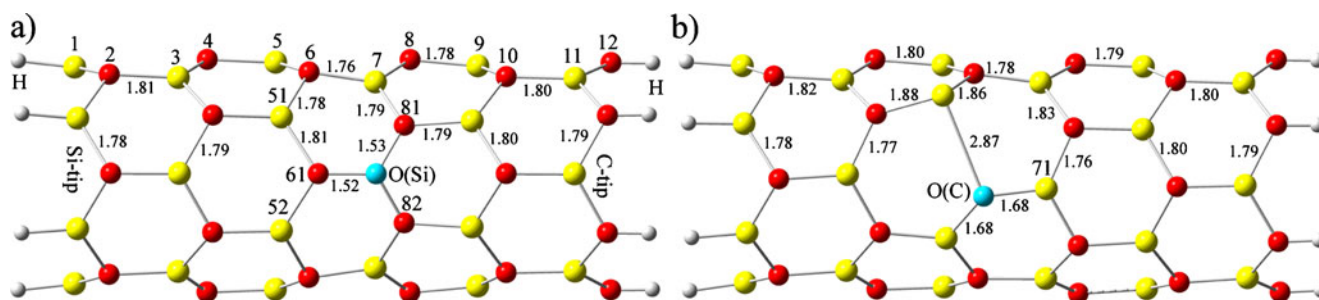


Fig. 1 2D views of O(Si) model (a) and O(C) model (b) of the zigzag SiCNT. Selected bond distances (Å) are exhibited for interested readers. Si, C and O atoms are indicated by yellow, red and cyan

colors, respectively. Si atoms are labeled by odd numbers and C atoms are labeled by even numbers

significant than the eighth layer. The changes of the values of σ_{iso} are due to the effects of changes of electronic environments at the sites of atoms but the values of $\Delta\sigma$ indicate the orientations of the CS tensors in the molecular frame. Our results indicated that the orientations of the CS tensors are also changed by the changes of the electronic environments at the sites of different atoms. It is important to note that the atoms of the tips of nanotube do not detect the changes of O-doping; therefore, the model size of study could be validated for the purpose. One C atom is doped by one O atom in the O(C) model (Fig. 1b) which results Si-O bonds in addition to the initial Si-C bonds to this model of SiCNT. In contrast with the O(Si) model, the NMR parameters of the ^{29}Si atoms detect notable changes in this model. In the fifth layer, it was expected that two Si atoms could be in chemical bonding with the O atom but just one Si atom, Si-52, contributes to this bond and Si-51 is kept in the bonding with two neighboring C atoms. In the seventh layer, Si-71 is also in chemical bonding with the O atom. These trends could well be indicated by the results of σ_{iso} of these atoms. Due to these bonds, the value of σ_{iso} of the fifth layer, especially Si-51 which is in chemical bonding with the two neighboring C atoms, detects the most significant changes among other layers of Si atoms. The other Si-layers of the O(C) model do not show any notable

changes in comparison with the perfect model. Due to the overall effects of O-doping, the values of NMR parameters of C atoms also exhibit some small changes but less notable than those of the O(Si) model.

NMR parameters of the armchair SiCNTs

Figure 2 exhibits the investigated O(Si) and O(C) models of the (4,4) armchair SiCNT. The values of σ_{iso} and $\Delta\sigma$ of ^{29}Si , ^{13}C and ^{17}O atoms for the optimized structures of these models and also the perfect model are listed in Table 2. A quick look at the results indicates that the NMR parameters of these models also detect the effects of O-doping.

Figure 2a exhibits the O(Si) model in which one Si atom is doped by one O atom and there are C-O bonds in addition to the initial Si-C ones in this structure. Comparing the NMR parameters of Si atoms of this model and the perfect model indicates that the seventh layer detects the most significant change of the parameters. In this layer, Si-71 causes the most significant changes of the NMR parameters of the seventh layer. As could be seen in Fig. 2a, C-81 and C-101 are in direct chemical bonding with the O atom and the values of their σ_{iso} are significantly changed in comparison with the perfect model. Since the electronegativity of O is larger than C, it seems that all the

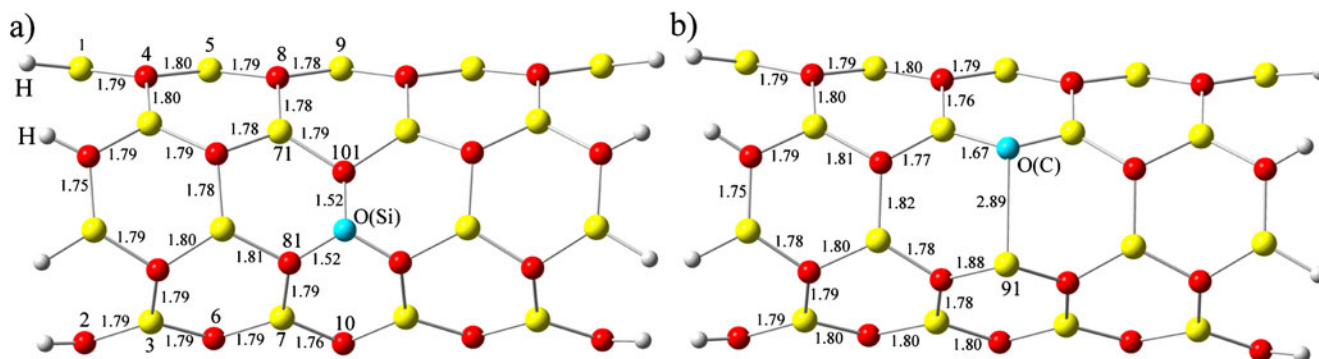


Fig. 2 X 2D views of O(Si) model (a) and O(C) model (b) of armchair SiCNT. Selected bond distances (Å) are exhibited for interested readers. Si, C and O atoms are indicated by yellow, red and cyan

and cyan colors, respectively. Si atoms are labeled by odd numbers and C atoms are labeled by even numbers

Table 1 The NMR parameters of the zigzag model^a

Si-29 Atoms	O(Si) Model	O(C) Model	Perfect Model	C-13 Atoms	O(Si) Model	O(C) Model	Perfect Model
1	359 [87]	355 [90]	356 [93]	2	131 [108]	123 [109]	131 [109]
3	384 [110]	374 [92]	378 [104]	4	131 [84]	121 [84]	128 [88]
5	324 [108]	275 [177]	325 [105]	6	108 [90]	112 [87]	120 [87]
51	337 [112]	90 [431]	325 [105]	61	30 [83]	– [–]	120 [87]
52	336 [113]	343 [180]	325 [105]	8	81 [95]	118 [85]	115 [93]
7	300 [128]	298 [148]	293 [137]	81	6 [113]	119 [71]	115 [93]
71	– [–]	333 [188]	293 [137]	82	5 [106]	123 [64]	115 [93]
9	297 [134]	288 [144]	289 [145]	10	131 [82]	124 [99]	126 [101]
11	275 [138]	276 [135]	275 [132]	12	107 [155]	109 [148]	103 [160]
¹⁷ O(Si)	230 [91]	– [–]	– [–]	¹⁷ O(C)	– [–]	163 [59]	– [–]

^a See Fig. 1. The isotropic CS values are out of brackets and the anisotropic CS values are in the brackets. The values are in ppm.

electron densities of the C-O bonds are oriented to the site of O atom; therefore, the values of σ_{iso} of C-81 and C-101 atoms are significantly reduced in comparison with the perfect model. Looking again at the value of σ_{iso} of Si-71 indicates that due to major contribution of C-81 and C-101 atoms to the C-O bond, Si-71 recovers its electron density which was initially shared with C-101 atom. The changes of the NMR parameters of other atoms of this model in comparison with the perfect model are not notable. Figure 2b exhibits the O(C) model where one C atom is doped by one O atom resulting Si-O bonds in addition to the initial Si-C bonds in this model. In this structure, the doped O atom is in chemical bonding only with two Si atoms whereas Si-91 contributes to only two neighboring C atoms, C-81 and the mirror one. The trend could well be indicated by the changes of the values of σ_{iso} of Si-71, Si-91 and C-81 atoms.

Concluding remarks

We have performed a DFT study to investigate the electronic and structural properties of the O-doped models of representative zigzag and armchair SiCNTs by calculations of NMR parameters. The computed NMR parameters indicated that the electronic environments of the atoms of the nanotubes could be divided into layers based on similarities of the parameters of the atoms in each layer. Comparing the results of the O-doped models with the perfect models indicated that the most significant effects of the O-doping on the properties of nanotubes could be detected only by the first neighbors of the doped site. Comparing the results of the zigzag and armchair models indicated that the effects of the O-doping on the properties of nanotubes are more obvious for the latter model.

Table 2 The NMR parameters of the armchair model^a

Si-29 Atoms	O(Si) Model	O(C) Model	Perfect Model	C-13 Atoms	O(Si) Model	O(C) Model	Perfect Model
1	292 [145]	294 [145]	293 [145]	2	114 [105]	114 [105]	113 [106]
3	295 [145]	291 [149]	291 [148]	4	125 [90]	122 [94]	123 [94]
5	288 [149]	287 [156]	288 [150]	6	118 [90]	115 [88]	115 [97]
7	299 [144]	308 [146]	291 [140]	8	103 [78]	114 [88]	121 [91]
71	324 [125]	333 [173]	291 [140]	81	29 [58]	84 [108]	121 [91]
9	289 [144]	244 [229]	288 [145]	10	98 [98]	120 [95]	121 [92]
91	– [–]	104 [500]	288 [145]	101	22 [99]	– [–]	121 [92]
¹⁷ O(Si)	256 [85]	– [–]	– [–]	¹⁷ O(C)	– [–]	169 [85]	– [–]

^a See Fig. 2. The isotropic CS values are out of brackets and the anisotropic CS values are in the brackets. The values are in ppm.

References

1. Iijima S (1991) *Nature* 354:56–58
2. Mykhailenko O, Matsui D, Prylutsky Y, Le Normand F, Eklund P, Scharff P (2007) *J Mol Model* 13:283–287
3. Lal B (2007) *J Mol Model* 13:531–536
4. Blasé X, Rubio A, Louie SG, Cohen ML (1994) *Europhys Lett* 28:335–340
5. Miyamoto Y, Yu BD (2002) *Appl Phys Lett* 80:586–588
6. Chopra NG, Luyken RJ, Cherrey K, Crespi VH, Cohen ML, Louie SG, Zettl A (1995) *Science* 269:966–967
7. Sun XH, Li CP, Wong WK, Wong NB, Lee CS, Lee ST, Teo BK (2002) *J Am Chem Soc* 124:14464–14471
8. Peralta-Inga Z, Lane P, Murray JS, Boyd S, Grice ME, O'Connor CJ, Politzer P (2003) *Nano Lett* 3:21–28
9. Zhao M, Xia Y, Li F, Zhang RQ, Lee ST (2005) *Phys Rev B* 71:085312
10. Gali A (18) *Phys Rev B* 73:245415
11. Zhang SL (2001) *Phys Lett A* 285:207–211
12. Zhang JM, Chen LY, Wang SF, Xu KW (2010) *Eur Phys J B*. doi:10.1140/epjb/e2010-00020-y
13. Menon M, Richter E, Mavrandonakis A, Froudakis G, Andriotis AN (2004) *Phys Rev B* 36:115322
14. Taguchi T, Igawa N, Yamamoto H, Jitsukawa S (2005) *J Am Ceram Soc* 88:459–461
15. Baumeier B, Krüger P, Pollmann J (2007) *Phys Rev B* 76:085407
16. Moradian R, Nehzad S, Chegel R (2008) *Physica B* 403:3623–3626
17. Moradian R, Nehzad S, Chegel R (2008) *J Phys Condens Matter* 20:465214
18. Gao G, Park SH (2009) kang HS. *Chem Phys* 355:50–54
19. Cao F, Xu X, Ren W, Zhao C (2010) *J Phys Chem C* 114:970–976
20. Szabó Á, Gali A (2009) *Phys Rev B* 80:075425
21. Bovey FA (1988) *Nuclear Magnetic Resonance Spectroscopy*. Academic, San Diego
22. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (1998) *GAUSSIAN 98*. Gaussian Inc, Pittsburgh
23. Wolinski K, Hinton JF, Pulay P (1990) *J Am Chem Soc* 112:8251–8260
24. Mirzaei M, Nouri A (2010) *J Mol Struct Theochem* 942:83–87
25. Mirzaei M (2010) *J Mol Model*. doi:10.1007/s00894-010-0702-z