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SiC nanotubes: DFT calculations of ^{29}Si and ^{13}C NMR properties

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Abstract We performed density functional theory (DFT) calculations to investigate the properties of electronic structures of representative armchair and zigzag silicon carbide nanotubes (SiCNTs). The model structures were optimized and the NMR parameters were calculated at the sites of silicon-29 and carbon-13 atoms in these structures. Our results indicated that different electronic environments could be detected by using the atoms of nanotubes in which the atoms of tips, especially for zigzag SiCNT, exhibit distinctive properties among other atoms.

Keywords Silicon carbide · Nanotube · Density functional theory · Electronic structure · NMR

Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima [1], some researchers have focused on the characterization of other kinds of nanotubes. Among these investigations, the theoretically predicted CNT-like tubular structures of boron nitride (BN) and silicon carbide (SiC) have been successfully synthesized [2–5]. In contrast to CNTs, which are metal or semiconductor depending on the tubular diameter and chirality, both BNNTs and SiCNTs have always been viewed as semiconductors [6–8]. In addition, the difference between the electronegativities of C and Si atoms induces polarities in the SiCNTs in contrast to the non-polar CNTs. The structural counterparts comprising Si and C atoms have been viewed as being more stable than the structures consisting of only C or Si atoms [9]. Moreover, the larger length of the Si–C bond (1.80 Å) versus B–N (1.44 Å) and C–C (1.42 Å) bonds makes the SiCNTs a more suitable candidate than BNNTs and CNTs for applications in storage materials [10]. Although theoretical and experimental researchers have investigated the properties of SiCNTs [11–15], none of them have yet reported the NMR properties of these structures.

Nuclear magnetic resonance (NMR) spectroscopy is among the most important and versatile techniques to investigate the properties of the electronic structure of matter [16]. Chemical shielding (CS) tensors are very sensitive to the electronic environment at the sites of dipolar atoms such as ^{29}Si and ^{13}C and could be used to detect any changes of this environment.

We therefore investigated the properties of electronic structures of representative (4,4) armchair and (6,0) zigzag single-walled SiCNTs (Fig. 1) by density functional theory (DFT) calculations of their NMR properties (Table 1). The representative structures were firstly optimized and then the CS tensors were calculated for these structures. Our results indicated that the Si and C atoms can be used to detect different electronic environments in the structures of SiCNTs, which could be detected by using the calculated NMR properties.

Results and discussion

Table 1 presents the absolute values of isotropic (σ_{iso}) and anisotropic ($\Delta\sigma$) CS properties of the investigated (4,4) and

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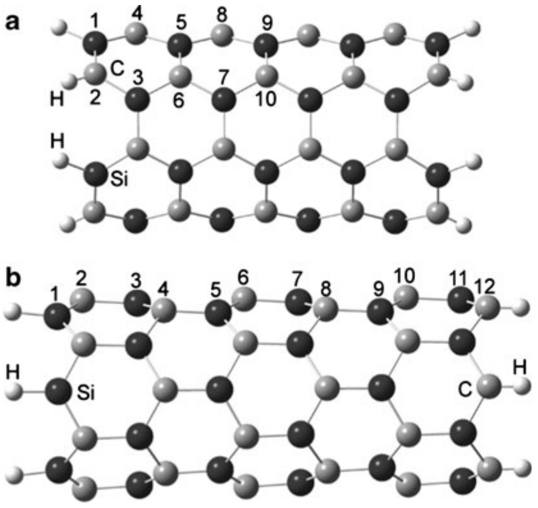

Fig. 1 Armchair (**a**) and zigzag (**b**) models of SiCNTs. For clarity, only the 2D views are shown. The *odd numbers* designate the Si atomic layers and the *even numbers* designate the C atomic layers

Table 1 NMR properties (ppm) of the models of SiCNTs

^{29}Si atoms	Armchair model[a]	Zigzag model[a]	^{13}C atoms	Armchair model[a]	Zigzag model[a]
1	289; 142	347; 104	2	116; 102	132; 106
3	284; 140	363; 108	4	127; 88	131; 84
5	275; 158	310; 116	6	115; 96	121; 84
7	288; 135	281; 142	8	124; 84	119; 88
9	278; 150	278; 142	10	120; 92	125; 95
11	–	272; 131	12	–	104; 145

Atom labels are shown in Fig. 1

[a] The first number is the isotropic (σ_{iso}) and the second number is the anisotropic ($\Delta\sigma$) chemical shielding parameter

(6,0) SiCNTs (Fig. 1). The numbers in Fig. 1 indicate that the atoms of nanotubes could be divided into layers in which the atoms of each layer are used to detect similar electronic environments. The Si atoms are designated by odd numbers and the C atoms are designated by even numbers. As a result of the similarities between the tips of armchair nanotube (Fig. 1a), this structure could be divided into two similar parts; hence, we have only designated the layers of one part of this model. In contrast, the zigzag nanotube (Fig. 1b) has two different tips, the Si- and C-tip.

The atoms of armchair SiCNT are divided into five layers for Si atoms and five layers for C atoms based on the similarities of NMR properties of atoms of each layer. The results indicated that the atoms of different layers have different values of NMR properties which means that these atoms can be used to detect different electronic environments in the structure of armchair SiCNT. As can be seen from Eq. 1, the value of σ_{iso} is directly proportional to the electronic density at the atomic sites. For Si atoms, the largest value of σ_{iso} belongs to the Si-1 layer which is part of the nanotube tip incorporating the C-2 layer; however, for C atoms, the value of σ_{iso} for the C-2 layer is not the largest one among the C layers. The major contribution to $\Delta\sigma$ stems from the orientation of the CS tensors in the z-axis of the molecular frame, which can be seen from Eq. 2, and this value is the largest for the C-2 layer among the C layers but not for the Si-1 layer among the Si layers. The atoms of the tips are very important in determining the electronic properties of nanotubes in which we could see that the Si and C atoms of the tip of armchair SiCNT behave differently. The results indicated that similar electronic environments are detected for some layers in which the electronic environments for Si-3 and Si-7 layers and also for Si-5 and Si-9 layers are almost similar. Interestingly, the corresponding C layers of the mentioned Si layers are also used to detect similar electronic environments in which similarities could be seen between the properties of C-4 and C-8 layers and also for C-6 and C-10 layers. It is worth noting that the electronic densities at the atomic sites of nanotubes are very important for interactions occurring between nanotube and other molecules or atoms. Here, by means of the values of σ_{iso} we could conclude that similar electronic densities could be detected for Si and C atoms in the side wall of the armchair SiCNT.

The calculated NMR properties of zigzag SiCNT (Fig. 1b) are divided into six layers for Si atoms and also six layers for C atoms based on the similarities of the properties of atoms of each layer. The structure of zigzag nanotube due to having two different tips is completely different from armchair nanotube which has similar tips. Si-tip and C-tip are completely distinguished in the investigated zigzag SiCNT by their typical NMR properties among the Si and C layers of zigzag nanotube. For the Si layers, with the exception of Si-3 layer, the value of σ_{iso} for the Si-1 layer (Si-tip) is the largest one and that of $\Delta\sigma$ is the smallest one among other Si layers. Interestingly, reversed results are observed for the C layers in which the value of σ_{iso} for the C-12 layer (C-tip) is the smallest one and that of $\Delta\sigma$ is the largest one among other C layers. The NMR properties of atomic layers are used to detect several changes along the nanotube which means that the atoms of different layers highlight different electronic environments. From Si-1 to Si-9, the values of $\Delta\sigma$ are increased but this value is decreased for the Si-11 layer, which is involved in chemical bonding with the atoms of C-tip. In the same direction, the value of σ_{iso} is increased from Si-1 to Si-2 but this value is deceased from the Si-2 to Si-11 layer. For C layers, the value of σ_{iso} is increased from C-12 to C-2 which means that the changes of values of σ_{iso} follow opposite directions for Si and C layers. Interestingly, a similar trend could be concluded for the changes of the values of $\Delta\sigma$ in which this value is decreased from C-12 to C-4. The increasing of $\Delta\sigma$ for C-2 is due to chemical bonding of the atoms of this layer with the atoms of the Si-tip.

Conclusions

We investigated the properties of the electronic structures of representative armchair ad zigzag SiCNTs by DFT calculations of NMR parameters. Our results indicate that the atoms of nanotubes could be divided into atomic layers based on the similarities of the calculated NMR properties of atoms of each layer. This trend is due to the detection of similar electronic environments by using the atoms of each layer. However, the atoms of different layers are used to detect different electronic environments as could be seen by their different NMR properties. In both the armchair and zigzag SiCNTs, the atoms of the tips of nanotubes exhibit distinctive properties among other atoms in the structure of nanotubes and this trend is much more significant for zigzag SiCNT, which has two different tips.

Computational details

In this research, representative (4,4) armchair and (6,0) zigzag single-walled SiCNTs were investigated by DFT calculations using the Gaussian 98 package [17]. Both models (Fig. 1) consist of 36 Si and 36 C atoms, in which the tips of the nanotubes are saturated by hydrogen (H) atoms to avoid the dangling effects (since periodic boundary conditions are not considered in molecular calculations, the tips of nanotubes should be saturated by H atoms to remove the effects of dangling bonds on the properties of nanotubes [18]). In the initial step, the all-atomic geometries of the structures were allowed to relax by optimization at the level of the B3LYP method and 6-31G* standard basis set. In the last step, the chemical shielding (CS) properties were calculated for the optimized structures at the same method level but 6-31+G* standard basis set to include diffusion effects in the calculations. The NMR properties were calculated by employing the gauge included atomic orbital approach (GIAO) [19]. 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 the nanotubes have been validated by results from previous work [20, 21]. 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 properties [16]. The NMR properties evaluated for the investigated models of the (4,4) and (6,0) SiCNTs are listed in Table 1.

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

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

References

1. Iijima S (1991) Nature 354:56
2. Blasé X, Rubio A, Louie SG, Cohen ML (1994) Europhys Lett 28:335
3. Miyamoto Y, Yu BD (2002) Appl Phys Lett 80:586
4. Chopra NG, Luyken RJ, Cherrey K, Crespi VH, Cohen ML, Louie SG, Zettl A (1995) Science 269:966
5. Sun XH, Li CP, Wong WK, Wong NB, Lee CS, Lee ST, Teo BK (2002) J Am Chem Soc 124:14464
6. Zhao M, Xia Y, Li F, Zhang RQ, Lee ST (2005) Phys Rev B 71:085312
7. Gali A (2006) Phys Rev B 73:245415
8. Zhang SL (2001) Phys Lett A 285:207
9. Menon M, Richter E, Mavrandonakis A, Froudakis G, Andriotis AN (2004) Phys Rev B 36:115322
10. Zhang JM, Chen LY, Wang SF, Xu KW (2010) Eur Phys J B. doi: 10.1140/epjb/e2010-00020-y
11. Gao G, Park SH, Kang HS (2009) Chem Phys 355:50
12. Moradian R, Nehzad S, Chegel R (2008) Physica B 403:3623
13. Moradian R, Nehzad S, Chegel R (2008) J Phys Condens Matter 20:465214
14. Baumeier B, Krüger P, Pollmann J (2007) Phys Rev B 76:085407
15. Taguchi T, Igawa N, Yamamoto H, Jitsukawa S (2005) J Am Ceram Soc 88:459
16. Bovey FA (1988) Nuclear magnetic resonance spectroscopy. Academic, San Diego
17. 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
18. Bodaghi A, Mirzaei M, Seif A, Giahi M (2008) Physica E 41:209
19. Wolinski K, Hinton JF, Pulay P (1990) J Am Chem Soc 112:8251
20. Mirzaei M, Nouri A (2010) J Mol Struct (Theochem) 942:83
21. Mirzaei M (2009) Monatsh Chem 140:1275