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Structural and Mechanical Properties of Fluorinated SWCNTs: a DFT Study

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This paper presents a study on structural and mechanical properties of a series of fluorinated armchair single-walled carbon nanotubes (SWCNTs) by using density functional theory. At the PBE / SVP level, the data obtained compare well with experimental and theoretical studies. The results show that fluorination, in general, distort SWNCTs framework, but there exists the difference between 'axial' and 'circumferential' functionalization. It turns out that elastic properties diminish with increasing concentration of adsorbents, however, the fluorinated SWCNTs remain strong enough to be suitable for reinforcement of composites.

Keywords: DFT, PBE, Single-walled carbon nanotubes, Fluorination, Young's modulus.

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1. INTRODUCTION

Single-walled carbon nanotubes (SWCNTs), hollow cylinders formed by rolled graphene sheets, are novel unique material with outstanding structural, mechanical, electrical, physical and chemical properties [1-6]. Since the first Iijima's paper, SWCNTs attracted enormous attention of researchers worldwide [7]. There are two main fields of SWCNTs usage which of especial interest for scientists. First, they have unique electronic properties dependent from their structure. Semi-conducting or metallic SWCNTs can be used in the design of novel NEMS, as electron emitters and transparent electrodes [8-10]. Second, one may highlight sound mechanical properties of SWCNTs. It was established that their mean Young's modulus is *ca.* 1 TPa [11]. However, there exists difference of experimentally obtained Young's modulus values and theoretical predictions. It is caused by many reasons, such as various computational techniques used, different approaches of determination of nanotubes walls thickness and so on. Summarized data on SWCNTs strength can be found, for example, in [12].

Unfortunately, the usage of pristine SWCNTs does not always improve the mechanical properties of composites under development [13]. Pristine SWCNTs have substantial disadvantages, namely they tend to self-assemble into tangled bunches in which a lot of nanotubes are interlaced together by van der Waals forces [14]. Such a bunch can not be effectively embedded in composite matrix. Thus, for nanocomposite designers, it is crucial to separate bunches into individual tubes. To diminish SWCNTs aggregation properties non-covalent and covalent functionalization techniques are commonly used. Fluorination is a simple and effective way to improve SWCNTs assembling properties [14, 15]. It is fluorinated nanotubes (F-SWCNTs) which are often being used in the production of nanocomposites [5, 14, 15]. On the other hand, fluorination significantly distorts the framework of SWCNTs [16]. Imperfect SWNTs addition may even reduce the strength of nanocomposites. Hence, it is important to select the degree of functionalization of SWNTs carefully. Novel techniques can change it gradually and tubes with given fluorine to carbon ratio can be created [14].

In this work, we report density functional theory (DFT) study on the structure and Young's modulus of fluorinated armchair SWCNTs series in comparison with pristine SWCNTs. To the best of our knowledge, there are a few papers deal with theoretical investigations of Young's modulus of functionalized nanotubes [4, 5, 11, 17], and only two articles focus on the determination of elastic properties of fluorinated SWCNTs [5, 17]. However, in the work of Kudin et al. the 3-21G basis set is implemented. It is probably insufficient to describe accurately the structure and elastic properties of such models of SWCNTs, therefore more reliable results are needed to clarify the geometry and elasticity of fluorinated SWCNTs. In the Petrushenko's et al. work only one degree of fluorination was studied.

Thus, motivated by the above considerations, in this paper, we study the structural and elastic properties of armchair SWCNTs by techniques based on the DFT, which has been successfully applied to predict many SWCNT properties with high reliability and less computational efforts than the majority of the traditional *ab initio* methods. The emphasis of this work is on structures and Young's moduli of finite-length fluorinated SWCNTs with various degrees of functionalization.

2. COMPUTATIONAL METHODS

For all simulations, finite armchair (5,5) SWCNTs ($C_{60}H_{20}$) containing 2, 4, 6, 8, 10 fluorine atoms attached to the 'axial' or 'circumferential' positions were used as the fluorinated SWCNTs (F-SWCNT) models. The detailed description of these cases will be given below. Here, the term 'degree of functionalization' denotes the F/C ratio. Therefore, we study F-SWCNTs with the following degrees of functionalization: 3.3 %, 6.7 %, 10 %, 13.3 %, and 16.7 %. The dangling bonds at the edges of all studied tubes were saturated by the hydrogen atoms. The fluorine atom links exclusively on the tube outer wall. The places of its addition are the 'axial' and the 'circumferential' one (Fig. 1).

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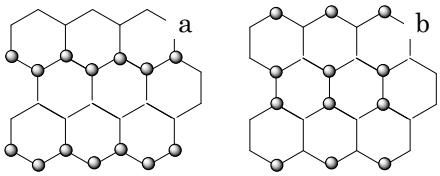

Fig. 1 – Side view of a fragment of F-SWCNTs. The balls are fluorine atoms: 1,2-fluorination ('axial') (a), 1,4-fluorination ('circumferential') (b)

The analysis of the two isomers with various sites of fluorine addition was performed owing to the uncertainty of an energetically favored type of F-SWCNT. Semi-empirical and DFT calculations in works of Kelly et al. [18] and Kudin et al. [19] gave opposite results about equilibrium structure of F-SWCNT, but calculated total energies of the two species were quite the same in both papers. It gave us the firm belief that the both structures exist.

For all calculations, we used Orca 2.9.1 program package [20] employing the DFT method with the PBE functional [21, 22]. To calculate equilibrium geometries of the studied structures, we used SVP (split valence polarization) basis set, which is equivalent to the commonly used 6-31G* basis set [23]. In SVP the inner shell atomic orbitals are described by a single basis function, and two basis functions are provided for each valence shell atomic orbital, augmented by a set of polarization functions. In order to calculate Young's modulus of every model we used the following formula:

$$Y = \sigma / \varepsilon = 2 \cdot (\Delta E / S) \cdot (L / (\Delta L)^2), \quad (1)$$

where σ is the stress, ε is the strain, E is the increment of the total energy, S is the area upon which stretching force acts, L is the length of a tube and ΔL is the elongation (1 %) upon stretching. The S area can be calculated by the formula: $S = 2\pi ar$, where r is the radius of the NT, $a = 3.4$ Å, which is equal to the graphite interlayer distance. The stability of the functionalized SWCNTs can be assessed by considering the binding energy E_b defined as:

$$E_b = 1 / N \cdot (E_{\text{SWCNT + fluorine}} - E_{\text{SWCNT}} - N \cdot E_{\text{fluorine}}), \quad (2)$$

where $E_{SWCNT + fluorine}$, E_{SWCNT}, and $E_{fluorine}$ are the total energies of the functionalized SWCNTs, pristine SWCNTs, and fluorine, respectively; N denotes number of attached molecules.

3. RESULTS AND DISCUSSIONS

3.1 Pristine SWCNTs

Before we turn to the elastic moduli of the F-SWCNTs, we would like to present our results for pristine neutral (5,5) armchair SWCNTs. This allows one to compare the results of this paper with previous works and to assess the reliability of obtained data. Young's moduli for pristine SWCNTs are summarized in Table 1.

The calculated Young's modulus of the pristine SWCNT (1.05 TPa) compare well to experimental findings (0.32-1.80 TPa) and previous theoretical works (0.8-5.5 TPa). Based on the present observations our choice of models seem to be justified.

Table 1 – Summarized Young's modulus values of SWCNTs

	This paper	Literature data
Y, TPa	1.05	0.32-1.80 [1,12] 0.8-5.5 [1, 4, 5] 1.02 [11]

3.2 Fluorinated SWCNTs

Previous papers were shown that there are two independent bond lengths in SWCNTs: axial and circumferential [4-6]. We studied the both isomers and used the following notation: 1a, 2a, 3a, 4a, and 5a for the 2F-SWCNT, 4F-SWCNT, 6F-SWCNT, 8F-SWCNT and 10F-SWCNT functionalized at the 'axial' positions; 1c, 2c, 3c, 4c, and 5c for the 2F-SWCNT, 4F-SWCNT, 6F-SWCNT, 8F-SWCNT and 10F-SWCNT functionalized at the 'circumferential positions, respectively. The 1a, c and 2a, c model are shown in Fig. 2 as an example.

The addition of fluorine atoms to the pristine SWCNTs leads to both b1 and b2 lengths changes. Thus, the optimized b1 and b2 lengths in pristine nanotubes (1.44 and 1.43 Å) are much shorter than those in F-doped nanotubes. Functionalization elongates them from 1.44 to 1.56 Å (b1), and from 1.43 to 1.65 Å (b2). We can see that in the former case we observe elongation, and one can say that the fluorination 'opens' the bond. In the latter case we can make the assumption that the bond brake occurs. Thus, the framework of F-doped SWCNTs rearranged and perfect tubular form of a pristine SWCNT became deformated. Calculated Young's moduli for studies F-doped SWCNTs are tabulated in Table 2.

Table 2 shows that the fluorination generally leads to the decrease in Young's modulus. One can highlight the comparatively high value for the 1c model. It is not strange as such a functionalization leaves the perfect framework of the SWCNT practically undisturbed (Fig. 2). In turn, the 1a counterpart loses the perfect shape upon functionalization (Fig. 2). This leads to the smaller Young' modulus in comparison with 1c. The further fluorination leads to the moderate decrease in Young's modulus for all studied models. It should be noted, however, that the decrease is not very high, and the F-SWCNTs remain elastic enough. Although 'axially' and 'circumferentially' doped F-SWCNTs show the same trend in Young's modulus diminishing, their elastic moduli are not equal. Young's moduli of 1a, 2a, 3a, 4a, and 5a are equal to 0.96 (9.5 % drop in comparison with the pristine SWCNT), 0.95 (10.0 %), 0.93 (12.1 %), 0.88 (15.9 %), and 0.86 (18.3 %) TPa, respectively. The F-SWCNTs models 1c, 2c, 3c, 4c, and 5c have the following Young's modulus values: 1.01 (4.0 %), 0.93 (11.7 %), 0.90 (14.5 %), 0.87 (17.8 %), and 0.85 (19.8 %) TPa, respectively. It is very likely that in all cases sp2 hybridization of pristine SWCNT being changed to sp3 one in the neighborhood of the fluorine attachment. The framework of F-SWCNTs rearranged and perfect tubular form of a pristine SWCNT became strongly deformated. The effect is more pronounced for the larger number of attached fluorine atoms. However, even in the case of the highest degree of functionalization, the Young's modulus drop is only 18.3 % (5a) and 19.8 % (5c). In order to identify the fluorination effect in detail,

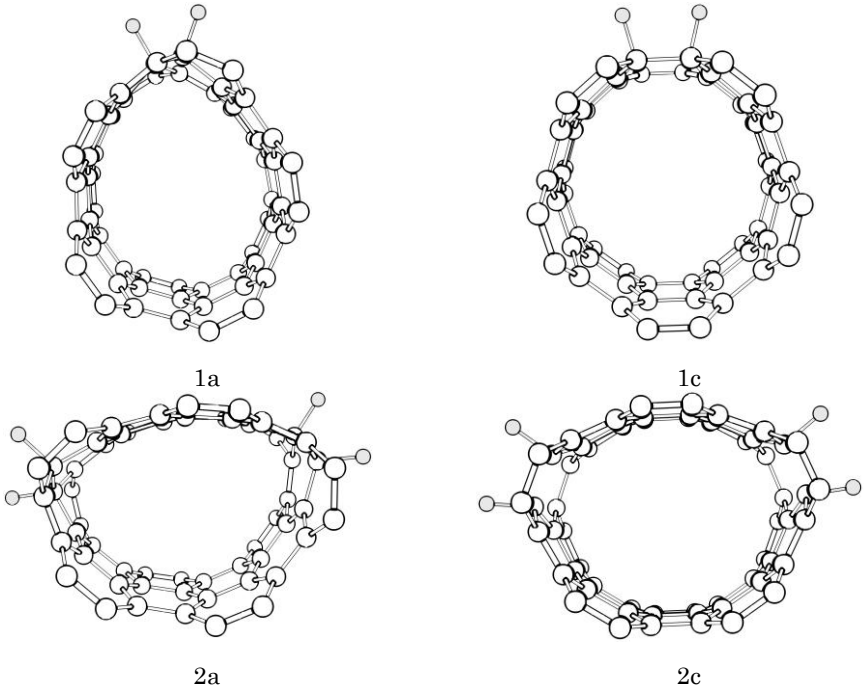

Fig. 2 – Cross-sections of 1a, c and 2a, c models. White balls denote carbon, grey balls – fluorine. Hydrogen atoms omitted for clarity

Table 2 – Young's moduli of the F-doped (5,5) SWCNT. The studied degrees of functionalization: 1a, c – 3.3 %, 2a, c – 6.7 %, 3a, c – 10 %, 4a, c – 13.3 %, 5a, c – 16.7 %.

Type of F-doped SWCNT	Young's modulus, TPa	Young's modulus drop, %	Type of F-doped SWCNT	Young's modulus, TPa	Young's modulus drop, %
1a	0.96	9.5	1c	1.01	4.0
2a	0.95	10.0	2c	0.93	11.7
3a	0.93	12.1	3c	0.90	14.5
4a	0.88	15.9	4c	0.87	17.8
5a	0.86	18.3	5c	0.85	19.8

we examine SWCNT functionalization by a series of fluorine atoms. The computed binding energies are shown in Fig. 3. To eliminate mutual interaction between fluorine molecules they being step-by-step linked as far as possible around the circumference of the tube. It can be seen that the molecules bind to the surface of the (5,5) nanotube (i.e. the adsorption energy is negative). However, the strength of the bonding differs depending on the site of addition. For 'circumferential' functionalization, the adsorption energies decrease with increasing number of attached molecules (Fig. 3). In terms of the thermal stability, the more negative values demonstrate the ease of functionalization with fluorine.

It is natural that the fluorine attack of the sidewall of the SWCNT is accompanied by the distortion of the ideal SWCNT framework. Such a deformation is followed by the easier adsorption of other fluorine molecules. The opposite is in the case of 'axial' functionalization. One can see the clear minimum when two molecules attached that reflects the strong binding. Further, the adsorption energy per molecule gets less negative (indicating that the bonding weakens) with increasing number of attached molecules. In this case, the reaction energies differ little, except the minimum value. The difference between 'axial' and 'circumferential' values

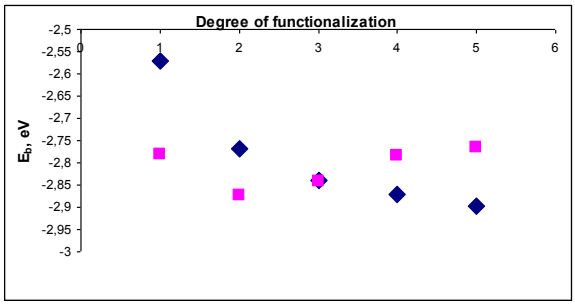

Fig. 3 – Binding energies (E_b) of the (5,5) SWCNT functionalized with fluorine as a function of the number of adsorbed molecules. The studied degrees of functionalization: 1 – 3.3 %, 2 – 6.7 %, 3 – 10 %, 4 – 13.3 %, 5 – 16.7 %; ■ – 'axial' functionalization, ♦ – 'circumferential' functionalization

confirms the difference between induced changes in geometry and elastic moduli of SWCNTs.

We can set the connection between Young's modulus and binding energies in studied tubes. As it has been shown above, in general, 'circumferentially' functionalized SWCNTs exhibit lower Young's modulus than their counterparts. Their binding energies get more negative on going from low to high degree of functionalization. It confirms the tendency that the mole-

cules with stronger binding to the SWCNTs surface modify the properties in a stronger manner.

To sum up, fluorination of SWCNTs is exothermic. All studied reactions are spontaneous, although the binding energies on 'circumferential' and 'axial' functionalization are different. Young's modulus gradually diminishes when the number of adsorbed species increases. Our future works will review various types of nanotubes functionalized with a wide range of attached molecules.

4. CONCLUSION

We have presented the DFT study of the structural and mechanical properties of fluorinated SWCNTs. When functionalized, the SWCNT model acquires a distorted structure. Any fluorine reaction on SWCNTs is exothermic. At low concentrations of attached fluorine, the structural properties of nanotubes are moderately modified. We observe, however, that these properties are dependent on the site of fluorine addition. The larger degree of fluorination leads to the significant structural changes. The local deformations include rehybridization of the C-C bonds that leads to the diminishing of strength of studied systems.

For 'axially' modified SWCNTs, Young's modulus decreases from 0.96 (the degree of functionalization is 3.3 %,) to 0.86 (16.7 %) TPa. For 'circumferentially' modified SWCNTs, Young's modulus decreases from 1.01 (3.3 %) to 0.85 (16.7 %) TPa. Despite the fact, that the fluorination leads to the gradual drop of the elastic moduli of SWCNTs and this effect cannot be generally neglected, the Young's moduli remain high enough to guarantee successful involvement of fluorinated SWCNTs in reinforcement of composite materials.

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