ORIGINAL PAPER

Carbon nanotube functionalization with carboxylic derivatives: a DFT study

Javad Beheshtian · Ali Ahmadi Peyghan · Zargham Bagheri

Abstract Chemical functionalization of a single-walled carbon nanotube (CNT) with different carboxylic derivatives including –COOX (X=H, CH$_3$, CH$_2$NH$_2$, CH$_3$Ph, CH$_2$NO$_2$, and CH$_2$CN) has been theoretically investigated in terms of geometric, energetic, and electronic properties. Reaction energies have been calculated to be in the range of −0.23 to −7.07 eV. The results reveal that the reaction energy is increased by increasing the electron withdrawing character of the functional groups so that the relative magnitude order is −CH$_2$NO$_2$>−CH$_2$CN>−H>−CH$_2$Ph>−CH$_3$>−CH$_2$NH$_2$. The chemical functionalization leads to an increase in HOMO/LUMO energy gap of CNT by about 0.32 to 0.35 eV (except for −H). LUMO, HOMO, and Fermi level of the CNT are shifted to lower energies especially in the case of −CH$_2$NO$_2$ and _CH$_2$CN functional groups. Therefore, it leads to an increment in work function of the tube, impeding the field electron emission.

Keywords Adsorption · Charge transfer · DFT · Electronic structure · Nanostructures

J. Beheshtian
Department of Chemistry,
Shahid Rajaee Teacher Training University,
P.O. Box: 16875-163, Tehran, Iran

A. A. Peyghan (✉)
Young Researchers Club, Islamic Azad University,
Islamshahr Branch,
Tehran, Iran
e-mail: ahmadi.iau@gmail.com

Z. Bagheri
Physics group, Science Department, Islamic Azad University,
Islamshahr Branch, P.O. Box: 33135-369, Islamshahr Tehran, Iran

Introduction

One-dimensional nanostructures, such as nanowires and nanotubes, have numerous potential applications in science and technology [1–5] due to their unique and fascinating electrical, optical, chemical, and thermal properties, compared to the bulk materials [6–8]. As a consequence of their unusual physical properties and large potential applications, carbon nanotubes (CNTs) have attracted the interest of scientists and engineers ever since their discovery in 1991 [9]. CNTs are expected to be one of the hopeful materials of the next-generation electronic devices [10], electron source through their excellent field-emission properties and gas storage [11, 12].

Despite the exceptional electrical characteristics of CNTs, doubts have arisen concerning their real technological applicability in ultra-small electrical devices, which is mainly due to the fact that the controlled synthesis of one specific type of these tubes is hard to achieve. Furthermore, no reliable methods are currently available to produce extended ensembles of aligned nanotubes, in which each tube would be located at a desired location and is connected to its neighbors in a well-defined manner [13]. Nonetheless, recent advances in linking specific groups or molecules to the nanotubes clearly testify the strong potential of chemical functionalization not only for tuning the tubes' electronic properties, but also to enable their assembly into more-complex architectures required for integrated device operation [14–17].

Also functionalization may help to separate semiconductive tubes from metallic ones, to purify nanotubes from carbonaceous impurities or to reduce the width of diameter dispersion [18]. Theoretically, Chełmecka et al. [19] have recently investigated addition of 1 to 9 COOH group(s) to

the end of the CNTs, showing high reactivity of zigzag CNT toward carboxylation. In the present work, functionalization of a single-walled CNT with different carboxylic derivatives including −COOX (X=H, CH_3, CH_2NH_2, CH_3Ph, CH_2NO_2, and CH_2CN) has been investigated in terms of geometric, energetic, and electronic properties using density functional theory. By experimental treatment of CNTs in an oxidizing environment, for example in a mixture of concentrated nitric and sulfuric acids, the oxygen-containing groups are introduced to the ends and sidewalls of the tubes. These groups, chemically attached to the tubes, are mostly represented by −COOX groups, less by −C=O, and −OX groups [20]. These groups can serve as starting sites for further functionalization of the nanotubes [21, 22]. Our results may be useful for further studies in functionalization of CNT and construction of nanodevices.

Computational methods

We have selected a zigzag (5, 0) CNT consisting of 60 carbon atoms in which open ends have been saturated by hydrogen atoms in order to avoid boundary effects. Density-functional calculations have been performed using B3LYP as exchange-correlation functional, which has been widely used and proved to be accurate enough for extensive systems including nanostructured materials [23–30]. All of the calculations have been performed using the standard basis set of 6-31G* within the GAMESS package [31]. Natural bond orbital (NBO), Mulliken charges, and density of states (DOSs) analyses have also been performed at the same level of theory. GaussSum program [32] has been used to obtain the DOS results. Finally from the optimized CNT-COOX models, quantum molecular descriptors including chemical potential (μ), global hardness (η), electrophilicity index (ω), and electronegativity (χ) have been calculated.

In an N-electron system with total energy of E and external potential of ν(r), the electronegativity (χ) is given by:

$$\chi = -\left(\frac{\delta E}{\delta N}\right)_{v(r)} = -\mu, \qquad (1)$$

where μ is the chemical potential of the species and is defined as negative value of the electronegativity. Similarly, the global hardness (η) is expressed in terms of the second derivative of energy with respect to the external potential of ν(r) and is given by:

$$\eta = \frac{1}{2}\left(\frac{\delta^2 E}{\delta N^2}\right)_{v(r)}. \qquad (2)$$

In finite difference approach, chemical potential and global hardness can be approximated as:

$$\mu = -\chi = -\frac{1}{2}(I + A) \qquad (3)$$

and

$$\eta = \frac{1}{2}(I - A), \qquad (4)$$

where I is the ionization potential and A is the electron affinity of the molecule. The Frontier orbital approach as proposed by Koopmans' theorem [33, 34] for closed shell system is very appropriate in explaining stability and chemical reactivity of the molecules based on HOMO and LUMO orbitals. The energy corresponding to HOMO represents the ionization potential of the molecule and the LUMO corresponds to electron affinity value. Using Koopmans' theorem I and A values can be correlated with the Frontier orbitals by the following relation:

$$I = -E_{HOMO} \text{ and } A = -E_{LUMO}. \qquad (5)$$

Results and discussion

Geometric optimization and electronic properties

Figure 1 shows the CNT with an average C–C bond length of about 1.42 Å and a diameter of 4.51 Å. The difference in energies between the HOMO and LUMO, E_g, was calculated from the DOS results. From the DOS plot of the bare CNT in Fig. 1, it can be concluded that it is a semiconductive material with an E_g of 0.97 eV.

In order to investigate chemical functionalization of the CNT by carboxylic derivatives, we have put all of the HCOOX molecules close to the tip of the CNT, and then it has been assumed that a reaction is occurred. Our main purpose is the study of this reaction because its feasibility has been previously reported by experimentalists [21, 22]. In this reaction, HCOOX attacks the CNT from its C atom so that one H_2 molecule releases as follows:

$$H - CNT + HCOOX \rightarrow H_2 + CNT - COOX, \qquad (6)$$
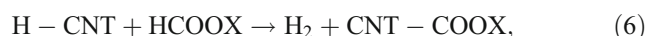
where CNT-COOX is the functionalized CNT by −COOX (X refers to −H, −CH_3, CH_2NH_2, −CH_2Ph, −CH_2NO_2, and −CH_2CN). We have defined the energy of reaction, E_r, in the usual way as follows:

$$E_r = E(CNT - COOX) + E(H_2) - E(CNT) - E(HCOOX), \qquad (7)$$

where E(CNT-COOX) corresponds to the energy of the functionalized CNT with the −COOX, E(CNT) is the energy

Fig. 1 Geometrical parameters of the optimized CNT and its density of state. Distances are in Å
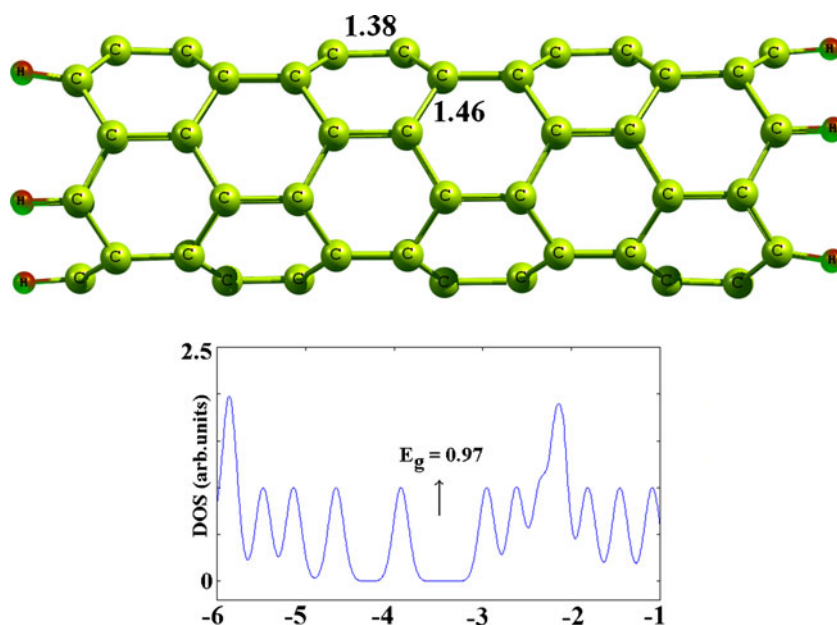
of the isolated nanotube, and $E(H_2)$ and E(HCOOX) are the energies of the released H_2 and HCOOX molecules, respectively.

At first we have focused on −COOH addition to the CNT. As shown in panel (a) of Fig. 2, carbon atom of the −COOH is bonded to a carbon atom of the CNT tip so that the length of the newly formed C-C bond is about 1.43 Å. The E_r value for this process is approximately −1.07 kcal mol^{-1} with a charge transfer from the CNT to the adsorbate. Furthermore, the reaction induces a locally structural deformation to the CNT. For example, C−C*−C angle (C* is referred to COOH-attached carbon of the CNT) in the hexagonal ring is significantly decreased from 116.3° to 107.2°.

Subsequently, hydrogen atom of the −COOH has been replaced by five other functional groups including −CH$_3$, −CH$_2$NH$_2$, −CH$_2$Ph, −CF$_3$, −CH$_2$NO$_2$, and −CH$_2$CN, and then the molecule has been subjected to the reaction of Eq. 6, to investigate the effect of functional groups on the functionalization. All of the optimized structures of the products are shown in Fig. 2. Relative magnitude order of the E_r for different functional groups is as follows:

$$-CH_2NO_2 > -CH_2CN > -H > -CH_2Ph > -CH_3 > -CH_2NH_2.$$
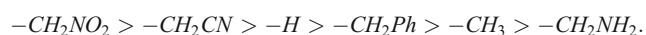
The most negative E_r belongs to the −CH$_2$NO$_2$ group with the value of −7.07 kcal mol^{-1} and the smallest one to −CH$_2$NH$_2$ (−0.23 kcal mol^{-1}, Table 1). A question that immediately arises is why the E_r values in the case of −CH$_2$NO$_2$ and −CH$_2$CN functionals are more negative than those of −CH$_2$NH$_2$, −CH$_3$, −CH$_2$Ph. In order to answer this question it is noteworthy to say that high electron density is localized on the surface of CNT, resulting in no tendency to achieve more electrons from the adsorbates. Thus, electron

donating groups which tend to give negative charges to the CNT lead to a weaker reaction as seen here. The charge transfer between the adsorbates and CNT has been estimated based on the popular Mulliken analysis (Table 1), showing that charges are transferred from the CNT to the adsorbates. The charge transfer to the −COOX groups containing electron withdrawing group including −CH$_2$NO$_2$ (0.228 e) and −CH$_2$CN (0.211 e) is significant.

DOS plots of the CNT-COOX structures have been shown in Fig. 3 and corresponding data have been summarized in Table 1. Upon the functionalization of CNT with −COOH a charge of 0.201 e is transferred from the tube to this functional. As a result, the LUMO, HOMO, and Fermi level slightly shift to lower energies and the E_g of the tube is decreased from 0.97 to 0.88 eV (Fig. 3). Canonical assumption for the Fermi level is that in a molecule (at T=0 K) it lies approximately in the middle of the E_g. It is noteworthy to mention that, in fact, what lies in the middle of the E_g is the chemical potential, and since the chemical potential of a free gas of electrons, as traditionally defined, is equal to its Fermi level, herein, the Fermi level of the considered systems is at the center of the E_g.

Replacing the H atom of −COOH by different functional groups, the shift of LUMO, HOMO, and Fermi level is increased. The results of Table 1 show that this increment is more significant in the case of substituting the −H group by electron withdrawing groups of −CH$_2$CN and −CH$_2$NO$_2$ ascribed to more charge transfer from the tube to the functional groups. Also, E_g of the tube is dramatically increased by replacing the −H atom by all of the other functional groups. This occurrence may bring about a change in the corresponding electrical conductivity since it is well known that the E_g (or band gap in the bulk materials)

Fig. 2 Models for (**a**) −COOH,
(**b**) −COOCH$_2$Ph, (**c**)
−COOCH$_3$, (**d**) −COOCH$_2$NO$_2$,
(**e**) −COOCH$_2$CN and
(**f**) −COOCH$_2$NH$_2$ molecule
attached on the CNT
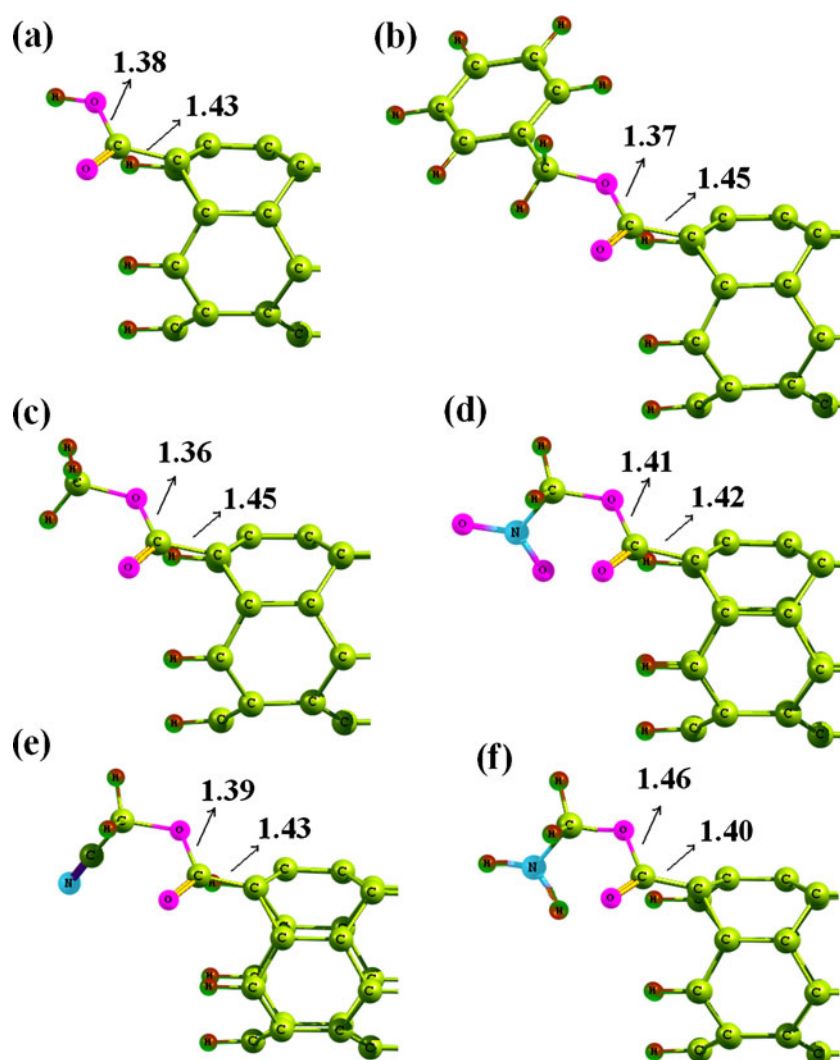
is a major factor determining the electrical conductivity of the material and a classic relation between them is as follows [35]:

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right), \tag{8}$$

where σ is the electrical conductance and k is the Boltzmann's constant. According to the equation, smaller E_g values lead to higher conductance at a given temperature. Therefore, the observed substantial increment of E_g of CNT upon the reaction process leads to the decrease in electrical conductivity of the nanotube.

Table 1 Calculated reaction energy (E_r, kcal mol^{-1}), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), and HOMO-LUMO energy gap (E_g) of systems in eV

System	E_r	Q_T (e)[a]	E_{HOMO}	E_{FL}	E_{LUMO}	E_g	ΔE_g(%)[b]
CNT	−	−	−3.92	−3.43	−2.95	0.97	−
−COOCH$_2$NH$_2$	−0.23	−0.113	−4.48	−3.82	−3.16	1.32	+36.0
−COOCH$_3$	−0.34	−0.123	−4.49	−3.83	−3.18	1.31	+35.0
−COOCH$_2$Ph	−0.52	−0.127	−4.50	−3.84	−3.19	1.31	+35.0
−COOH	−1.07	−0.201	−4.02	−3.58	−3.14	0.88	−9.2
−COOCH$_2$CN	−3.77	−0.211	−4.66	−4.01	−3.36	1.30	+34.0
−COOCH$_2$NO$_2$	−7.07	−0.228	−4.68	−4.03	−3.39	1.29	+33.0

[a] Q is defined as the average of total Mulliken charge on the molecule

[b] The change of HOMO-LUMO gap of CNT after functionalization

Fig. 3 Calculated density of states (DOS) for different models of CNT-COOX complexes
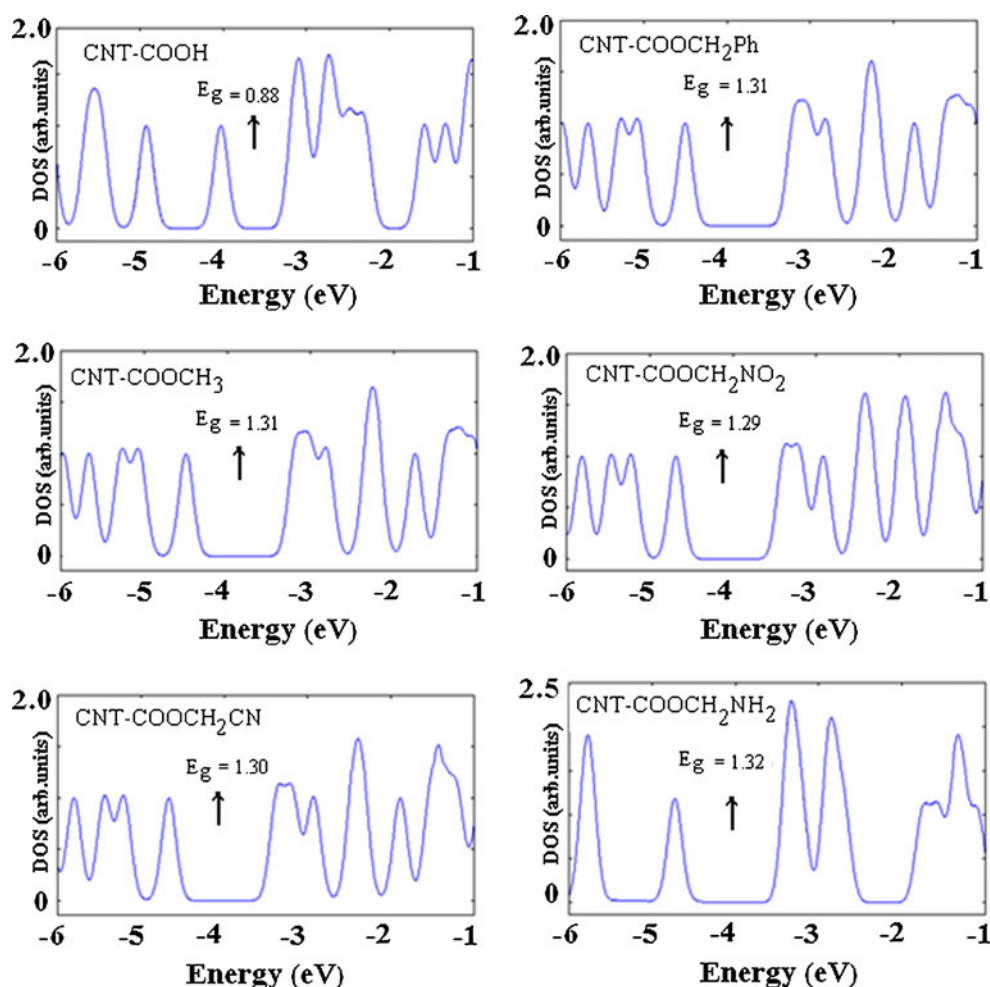
Recently, field emission properties of CNTs have attracted great interest [36]. As shown in Table 1, the E_{FL} is decreased after $-$COOX functionalization which indicates that the E_{FL} shifts toward the valence level. For instance, the E_{FL} is decreased from -3.43 to -4.03 eV in CNT-COOCH$_2$NO$_2$ structure. However, these phenomena lead to an increment in the work function that is important in field emission applications. The work function can be found using the standard procedure by calculating the potential energy difference between the vacuum level and the Fermi level, which is the minimum energy required for one electron to be removed from the Fermi level to the vacuum. The increment in the work function indicates that the field emission properties of the tube are impeded upon the $-$COOX functionalization. Furthermore, this will raise the potential barrier of the electron emission for the tube, and makes the field emission difficult.

Quantum molecular description

The quantum molecular descriptors for the pristine and functionalized CNTs are summarized in Table 2. Localization

of electron density in HOMO advocates that the particular site is nucleophilic whereas the site for LUMO is electrophilic in nature. A high E_g indicates greater stability and low reactivity of the chemical system [37]. As mentioned in Computational methods, using the HOMO and LUMO energies, parameters

Table 2 Quantum molecular descriptors (in eV) for the pristine CNT and CNT-COOX model in the stable configurations

System	χ^a	μ^b	η^c	ω^d
CNT	3.43	-3.43	0.48	12.1
$-$COOCH$_2$NH$_2$	3.82	-3.82	0.66	11.05
$-$COOCH$_3$	3.83	-3.83	0.65	11.2
$-$COOCH$_2$Ph	3.84	-3.84	0.65	11.2
$-$COOH	3.58	-3.58	0.44	14.5
$-$COOCH$_2$CN	4.01	-4.01	0.65	12.3
$-$COOCH$_2$NO$_2$	4.03	-4.03	0.64	12.6

[a] electronegativity

[b] chemical potential

[c] global hardness

[d] electrophilicity index

such as hardness, electronegativity, chemical potential, and electrophilicity index can be computed. The decrease of E_g by the −COOH functionalization may be able to increase the reactivity of the CNT. The global hardness is decreased with decreasing the E_g. The decrement in global hardness and E_g because of the −COOH group proposes the decrease of stability and increase in reactivity of the CNT. Whereas, for functionalization of other −COOXs, the E_g and global hardness of the CNT increase which can enhances the stability of CNT.

The electrophilicity index is a measure of the electrophilic power of a molecule. The electrophilicity index as defined by Parr et al. [38] is given by the expression ($\omega = \frac{\mu^2}{2\eta}$). When two molecules react with each other one molecule behaves as a nucleophile while the other one acts as an electrophile. Higher electrophilicity index shows higher electrophilic nature of a molecule. In the −COOH attached CNT the electrophilicity of the complex (14.5) is higher than that of the pristine model (about 12.1). Therefore, −COOH adsorption on the CNT can obviously increase the electrophilicity of the tube about 20%. In summary, we believe that the present work may help researchers to design new CNT-based materials with different properties.

Conclusions

We have studied the chemical functionalization of a CNT with different carboxylic derivatives including −COOX (X=H, CH_3, CH_2NH_2, CH_3Ph, CH_2NO_2, and CH_2CN) using DFT calculations. The reaction energies have been calculated to be in the range of −0.23 to −7.07 eV, so that the relative magnitude order follows −CH_2NO_2> −CH_2CN> −H> −CH_2Ph> −CH_3> −CH_2NH_2. The chemical functionalization leads to an E_g opening of CNT by about 0.32 to 0.35 eV (except −H) which stabilize the nanotube. The LUMO, HOMO, and Fermi level of the CNT are shifted to lower energies especially in the case of −CH_2NO_2 and −CH_2CN functional groups. Therefore, it leads to an increment in work function of the tube, impeding the field electron emission. The present work may help researchers to design new CNT-based materials with different properties.

References

1. Lakhlifi A, Dahoo PR (2011) Chem Phys 386:73–80
2. Ahmadi A, Hadipour NL, Kamfiroozi M, Bagheri Z (2012) Sens Actuators B Chem 161:1025–1029
3. Dinadayalane TC, Murray JS, Concha MC, Politzer P, Leszczynski J (2010) J Chem Theor Comp 6:1351–1357
4. Beheshtian J, Baei MT, Peyghan AA (2012) Surf Sci 606:981–985
5. Politzer P, Murray J, Lane P, Concha M, Jin P, Peralta-Inga Z (2006) J Mol Model 12:528–528
6. Baei MT, Peyghan AA, Bagheri Z (2012) Chin Chem Lett 23:965–968
7. Contreras C, Cocoletzi H, Anota E (2011) J Mol Model 17:2093–2097
8. Beheshtian J, Peyghan AA, Bagheri Z (2012) Sens Actuators B Chem 171–172:846–852
9. Iijima S (1991) Nature 354:56–58
10. Dekker C (1999) Phys Today 52:22–28
11. Bonard JM, Salvetat JP, Stockli T, Forro L, Chatelain A (1999) Appl Phys A 69:245–254
12. Vaseashta A, Dimova-Malinovska D (2005) Sci Technol Adv Mater 6:312–318
13. Keren K, Berman RS, Buchstab E, Sivan U, Braun E (2003) Science 302:1380–1382
14. Niyogi S, Hamon MA, Hu H, Zhao B, Bhowmik P, Sen R, Itkis ME, Haddon RC (2002) Acc Chem Res 35:1105–1113
15. Kaczmarek A, Dinadayalane TC, Łukaszewicz J, Leszczynski J (2007) Int J Quantum Chem 107:2211–2219
16. Dinadayalane TC, Kaczmarek A, Łukaszewicz J, Leszczynski J (2007) J Phys Chem C 111:7376–7383
17. Turabekova MA, Dinadayalane TC, Leszczynska D, Leszczynski J (2012) J Phys Chem C 116:6012–6021
18. Burghard M (2005) Surf Sci Rep 58:1–109
19. Chełmecka E, Pasterny K, Kupka T, Stobiński L (2012) J Mol Model 18:2241-2246
20. Kuznetsova A, Popova I, Yates JT, Bronikowski MJ, Huffman CB, Liu J, Smalley RE, Hwu HH, Chen JGG (2001) J Am Chem Soc 123:10699–10704
21. Klumpp C, Kostarelos K, Prato M, Bianco A (2006) Biochim Biophys Acta 1758:404–412
22. Ramanathan T, Fisher FT, Ruoff RS, Brinson LC (2005) Chem Mater 17:1290–1295
23. Contreras M, Avila D, Alvarez J, Rozas R (2010) Struct Chem 21:573–581
24. Beheshtian J, Kamfiroozi M, Bagheri Z, Ahmadi A (2011) Physica E 44:546–549
25. Breza M (2006) Chem Phys 330:224–230
26. Beheshtian J, Soleymanabadi H, Kamfiroozi M, Ahmadi A (2012) J Mol Model 18:2343–2348
27. Ahmadi A, Beheshtian J, Kamfiroozi M (2012) J Mol Model 18:1729–1734
28. Beheshtian J, Peyghan AA, Bagheri Z (2012) Comput Theor Chem 992:164–167
29. Beheshtian J, Ahmadi Peyghan A, Bagheri Z (2012) Physica E 44:1963–1968
30. Beheshtian J, Baei MT, Bagheri Z, Peyghan AA (2012) Microelectron J 43:452–455
31. Schmidt M et al (1993) J Comput Chem 14:1347–1363
32. O'Boyle N, Tenderholt A, Langner K (2008) J Comput Chem 29:839–845
33. Koopmans T (1933) Physica 1:104–113
34. Phillips JC (1961) Phys Rev 123:420–424
35. Li S (2006) Semiconductor physical electronics, 2nd edn. Springer, Berlin
36. Grujicic M, Cao G, Gersten B (2003) Appl Surf Sci 206:167–177
37. Saikia N, Deka RC (2011) Comput Theor Chem 964:257–261
38. Parr RG, Szentpaly L, Liu S (1999) J Am Chem Soc 121:1922–1924