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Functionalization of carbon nanotubes by covalently bonded graphite nanoplatelets: a theoretical study

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Atomic models of carbon nanotubes functionalised by the covalently bonded graphite nanoplatelets are proposed and stability and electronic properties of these new ($sp + sp^2 + sp^3$) adducts are studied using the density functional tight-binding theory (DFTB) method.

Carbon nanotubes have attracted considerable attention due to their unique structural, mechanical, chemical and electronic properties.[1] Functionalization of carbon nanotubes, namely, the modification of their properties by the adsorption of atoms, molecules or clusters on the exterior walls of carbon nanotubes or by insertion of these species into their hollow interior, offers a promising way in the design of new nanomaterials.[1–3]

For example, the incapsulation of Fe_n clusters inside carbon nanotubes leads[4] to the formation of composites with interesting conductive and magnetic properties. Chemical attachment of the phenyl rings is a reason of the rapid drop in thermal conductivity of carbon nanotubes.[5] The adsorption of transition metal atoms on carbon nanotubes is a pathway in the engineering of electronic and mechanical properties of carbon nanotubes.[6] Moreover, the hybrids of biomolecules (such as DNA or protein) and carbon nanotubes are of importance for nanotechnological and biochemical applications.[7]

Among various applications, carbon nanotubes have been regarded as attractive substrates for hydrogen storage.[8,9] As hydrogen condenses on the surface of a nanotube (or in the cavity of a tube),[9] the obvious way for an enhancement of the hydrogen adsorption capacity of carbon-based materials is the creation of new tubular nanostructures with greater surface areas, as compared with ‘classical’ cylinder-like carbon nanotubes (among other offered approaches, for example, a decoration of carbon nanotubes with titanium atoms that is favourable for dissociative adsorption of hydrogen molecules[10]). This way can be performed[11] by the deposition of an ensemble of graphite nanoplatelets on the side walls of carbon nanotubes. Chen *et al.*[11] have prepared successfully the petal-like graphitic ‘nanoflakes’ on the side wall of carbon nanotubes using bias assisted microwave plasma-enhanced chemical vapor deposition (MWPECVD). In result, the specific surface area of carbon nanotubes about 90 $m^2\,g^{-1}$ was increased up to 131 $m^2\,g^{-1}$ for the material prepared, graphite ‘nanoflakes’/carbon nanotubes. This tubular-like carbon material with an increased surface area could be used for catalysts with higher activity or for electrodes in fuel cell applications.[11]

In addition, it is well known that the chemical and physical properties of carbon nanomaterials are closely related to their atomic and electronic structures.

Here we propose the atomic models of the single-walled carbon nanotubes functionalised by graphite nanoplatelets and report the results of quantum-chemical investigations of the stability and electronic properties of such adducts depending on the types of (i) carbon nanotubes (chiral or nonchiral); (ii) graphite platelets and (iii) possible variants of adsorption of a platelete on the side walls of tubes.

The initial atomistic models of carbon nanotubes were constructed in a conventional way[1–3] by rolling graphite fragments into cylinders. These carbon nanotubes are characterised by two integers (n, m) determining the rolling (or chiral) vector $\mathbf{C} = n\mathbf{a}_1 + m\mathbf{a}_2$ in terms of the two-dimensional (2D) hexagonal Bravais lattice vectors of graphite sheet, $\mathbf{a}_1$ and $\mathbf{a}_2$. Thus, the radius of a tube is given in terms of (n, m) by the relation $R = a_0(n^2 + m^2 + nm)^{1/2}/2\pi$, where $a_0 = |\mathbf{a}_1| = |\mathbf{a}_2|$. As single-walled carbon tubes demonstrate different electronic structures (metallic or semiconducting[1]) depending on n and m (*i.e.*, on their chiralities and radii), we have examined three typical carbon nanotubes: non-chiral zigzag-like (14,0), armchair-like (8,8) and chiral (12,4) with comparable radii of 0.554, 0.547 and 0.570 nm, respectively. Note that, according to our calculations, (8,8) carbon nanotube is metallic-like, and (14,0) and (12,4) carbon nanotubes belong to the semiconducting tubes in agreement with previously reported data.[1]

As the models for graphite platelets we have chosen three carbon clusters, which consist of one (*b*), two (*n*) and three (*f*) C_6 hexagons (Figure 1). These graphite platelets were considered as bidentate molecules, which are covalently bonded perpendicularly to the outer walls of tubes; the possible variants (I–IX) of these connections are depicted in Figure 1.

Our calculations were performed by the density-functional-based tight-binding (DFTB) method[12,13] with full geometry optimization. This method gives reliable data for structural, energetic and electronic characteristics of carbon nanostructures in agreement with other experimental and theoretical *ab initio* results.[9,14,15]

The results related to the effects of binding of the above graphite platelets on carbon nanotubes and the geometric and electronic properties of final adducts are summarised in Online Supplementary Materials and Figures 2 and 3.

First, our calculations for optimised atomic geometries of constructed nanostructures (platelets/carbon nanotubes) reveal that these adducts preserve the common structure (*i.e.*, are not divided up to the initial particles: platelets and carbon nanotubes) due to the formation of strong covalent C–C bonds. It indicates a possibility of their existence. Second, we calculated the energies of formation of these adducts as $E_\mathrm{f} = E_\mathrm{comp} - \{E_\mathrm{plat} + E_\mathrm{CNT}\}$; where E_comp, E_plat and E_CNT are the total energies of the product and reactants (nanoplatelete and carbon nanotube), respectively, as obtained from our DFTB calculations. The data collected in Online Supplementary Materials demonstrate that the preferred

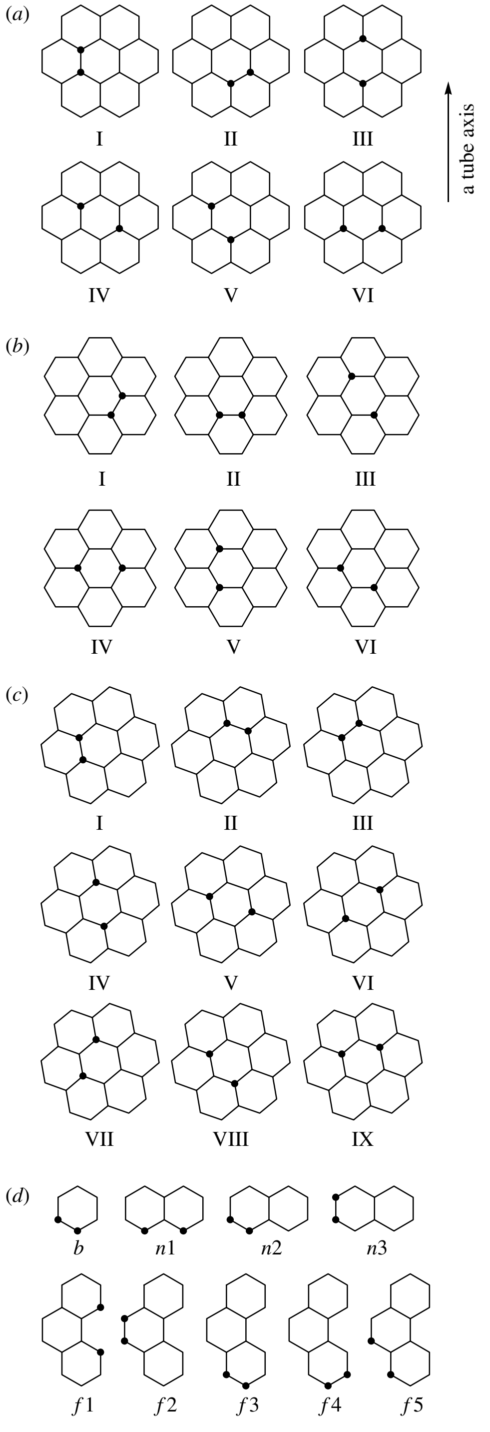

Figure 1 Possible variants (I–IX) of connection for a bidentate particle on a side-wall of (*a*) zigzag (14,0) tube, (*b*) armchair (8,8) tube and (*c*) chiral (12,4) tube (the fragments of tubes are shown); (*d*) graphite platelets (*b*–*f*) considered as mentioned bidentate molecules and possible variants (*b*, *n*1–*n*3, *f*1–*f*5) of their connections with carbon nanotubes.

configurations of connection for various platelets and tubes exist. For example, the simplest 'platelets', C_6 hexagons, will be preferentially connected to a zigzag (14,0) carbon nanotube along, while to an armchair (8,8) carbon nanotube across the tube axis; whereas for a chiral (12,4) nanotube the most favourite configuration has the intermediate type V (Figure 1). For larger platelets, the type of their connection to a tube becomes important. For example, among $\{C_6\}_2$ particles the most stable adducts are formed with the platelets connected by *n*3 type, among $\{C_6\}_3$ – with the platelets by *f*2 type (Figure 1). These platelets will be connected in different positions of the side walls of various tubes.

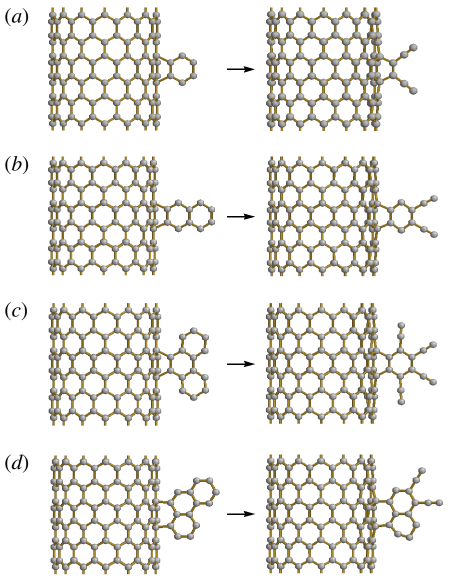

Figure 2 Side views of initial (left) and optimised (right) structures of (14,0) carbon nanotube functionalised by graphitic platelets: (*a*) *b*, (*b*) *n*3, (*c*) *f*2 and (*d*) *f*5.

Thus, our calculations predict the preferences in formation of periodically decorated nanostructures. Note that the type of periodic ordering of platelets on the side walls of carbon tubes depends on (i) the type (size and geometry) of graphite platelets and (ii) the type (chirality) of the carbon nanotube. Hence, varying the above factors for initial nanostructures (platelets and tubes) offers an efficient pathway for the engineering of the decoration ordering of carbon nanotubes and for the regulation of properties of these adducts.

Let us analyse in more detail the atomic structures of the adducts (platelets/carbon nanotubes). We found that, after structural relaxation, the atomic structure of the tubes remains practically unchanged, whereas the structures of bonded platelets differ considerably from their initial models. Namely, a set of the C–C bonds in the hexagonal rings of platelets was broken, and the corresponding atoms formed new carbon chains, as illustrated in Figure 2. For example, the connection of an individual C_6 ring to a tube transforms it into two fragments of carbyne-like chains. For larger platelets ($\{C_6\}_2$ and $\{C_6\}_3$), as can be seen in Figure 2, the nearest (to a tube) hexagons are kept, whereas outer C_6 rings are destroyed with the formation of carbyne-like chain fragments. Thus, in comparison to the initial carbon nanotubes and graphite platelets comprising exclusively hexagons (with three-fold coordinated carbon atoms) the proposed adducts (platelets/carbon nanotubes) contain three kinds of carbon atoms: four-, three- and two-fold coordinated. The majority of carbon atoms (in C_6 hexagons forming tube walls and platelets) is three-fold coordinated (*i.e.*, these atoms are in an sp^2 hybridization state). Additionally, four-fold coordinated (sp^3 hybridized) are atoms of the tube walls, which are responsible for bonding with platelets. Finally, two-fold coordinated (*sp* hybridized) are atoms of carbyne-like chains.

Hence, in terms of the classification[16] based on the electronic configurations (hybridization type) of the carbon atoms in a carbon allotrope, the above adducts (platelets/carbon nanotubes) may be described as a new 'hybrid' carbon allotrope with mixed electronic configurations ($sp + sp^2 + sp^3$). Note that other variants of ($sp + sp^2 + sp^3$) carbon nanohybrides, which are composed by the nanotubes with encapsulated carbon chains, rings or 'hybrid' fullerene-carbyne structures are known.[17,18]

Finally, let us analyse the electronic structure of the platelets/carbon nanotubes adducts. For this purpose, we calculated the

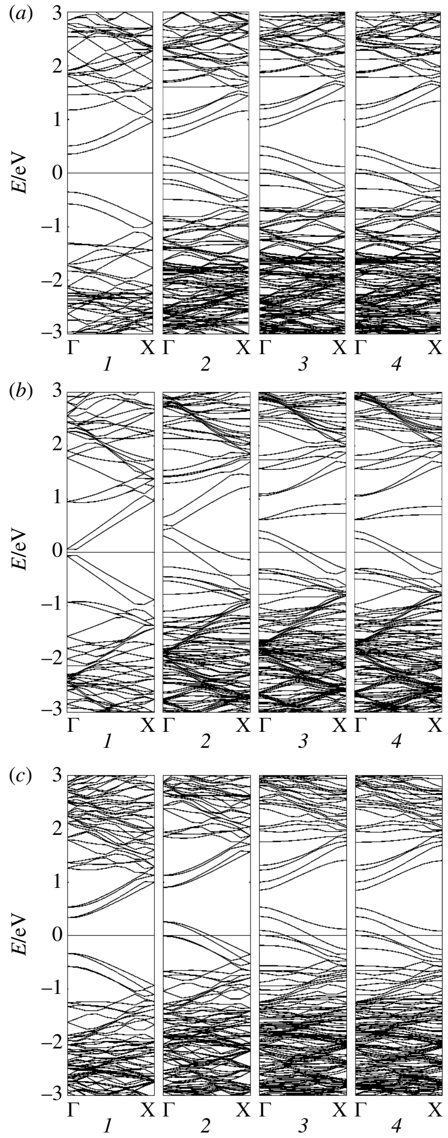

Figure 3 Band structures of (*a*) (*1*) a free (14,0) tube, and one with platelets adsorbed: (*2*) *b*, (*3*) *n*3, (*4*) *f*2; (*b*) (*1*) a free (8,8) tube, and one with platelets adsorbed: (*2*) *b*, (*3*) *n*3, (*4*) *f*2; (*c*) (*1*) a free (12,4) tube, and one with platelets adsorbed: (*2*) *b*, (*3*) *n*3, (*4*) *f*2. The types of platelets and the types of connections between platelets and tubes see in Figure 1. Fermi level – 0.0 eV.

band structures of the free carbon nanotubes and the same tubes functionalised by C_6, $\{C_6\}_2$ and $\{C_6\}_3$ platelets in the most favourite positions. As mentioned above, free (14,0) and (12,4) tubes are semiconductors with distinct band gaps of about 0.71 and 0.66 eV, respectively, whereas (8,8) tube has a metallic-like electronic spectrum. Figure 3 shows that, after the decoration, the band structures near the Fermi level of free tubes are drastically changed and for all adducts (platelets/carbon nanotubes) the partially occupied bands appear around the Fermi level and cross over it. The near-Fermi (non-bonding) bands with small *k*-dispersion appear from the most weakly bonded two-fold coordinated carbon atoms within one-dimensional carbyne-like chains. As a result all adducts become metallic-like.

In summary, we have performed the detailed theoretical study of carbon tubes functionalised by covalently bonded graphite nanoplatelets. After the decoration, all carbon nanotubes include the mixed electronic configurations and may be described as a new ‘hybrid’ ($sp + sp^2 + sp^3$) carbon allotrope. The decoration of both semiconducting and metallic carbon nanotubes significantly changes their electronic states and conducting properties and, as a result, all ‘platelets/carbon nanotubes’ adducts become metallic-like.

The most intriguing is a periodic ordering predicted for the binding of the platelets on the carbon nanotube walls, which depends on two factors: the type (size and geometry) of a graphite platelet and the chirality of a carbon nanotube. Thus, one can obtain carbon tubular nanomaterials with larger specific surface areas and with the beforehand determined decoration type that may be important for selective physical and chemical adsorption of atoms and molecules and will be interesting for future applications of these materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2007.06.003.

References

1 P. J. F. Harris, *Carbon Nanotubes and Related Structures: New Materials for the Twenty-First Century*, University of Ontario Press, Cambridge, 1999.
2 S. Ciraci, S. Dag, T. Yildirim, O. Gulseren and R. T. Senger, *J. Phys.: Condens. Matter*, 2004, **16**, R901.
3 G. S. Zakharova, V. L. Volkov, V. V. Ivanovskaya and A. L. Ivanovskii, *Usp. Khim.*, 2005, **74**, 651 (*Russ. Chem. Rev.*, 2005, **74**, 587).
4 V. V. Ivanovskaya and A. L. Ivanovskii, *Theor. Exp. Chem.*, 2006, **42**, 231.
5 C. W. Padgett and D. W. Brenner, *NANO Letters*, 2004, **4**, 1051.
6 E. Durgun, S. Dag, V. M. K. Bagci, O. Gulseren, T. Yildirim and S. Ciraci, *Phys. Rev.*, 2003, **B67**, R201401.
7 E. Katz and I. Willner, *Chem. Phys. Chem.*, 2004, **5**, 1084.
8 E. David, *J. Mater. Proc. Technol.*, 2005, **162–163**, 169.
9 S. Patchkovskii, J. S. Tse, S. Yurchenko, L. Zhechkov, Th. Heine and G. Seifert, *Proc. Nat. Acad. Sci. USA (PNAS)*, 2005, **102**, 10439.
10 T. Yildirim and S. Ciraci, *Phys. Rev. Lett.*, 2005, **94**, 175501.
11 C.-C. Chen, C.-F. Chen, I.-H. Lee and C.-L. Lin, *Diamond Relat. Mater.*, 2005, **14**, 1897.
12 D. Porezag, T. Frauenheim, T. Köhler, G. Seifert and R. Kashner, *Phys. Rev. B*, 1995, **51**, 12947.
13 G. Seifert, D. Porezag and T. Frauenheim, *Int. J. Quantum Chem.*, 1996, **58**, 185.
14 G. Seifert, *Solid State Ionics*, 2004, **168**, 265.
15 G. Seifert, A. N. Enyashin and Th. Heine, *Phys. Rev. B*, 2005, **72**, 012102.
16 R. B. Heimann, S. E. Evsykov and Y. Koga, *Carbon*, 1997, **35**, 1654.
17 A. L. Ivanovskii, *Zh. Neorg. Khim.*, 2005, **50**, 1480 (*Russ. J. Inorg. Chem.*, 2005, **50**, 1408).
18 E. A. Belenkov, A. L. Ivanovskii, S. N. Ul’yanov and F. K. Shabiev, *Zh. Strukt. Khim.*, 2005, **46**, 1001 [*J. Struct. Chem.* (*Engl. Transl.*), 2005, **46**, 961].

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