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Atom-decorated nanotubes

V V Ivanovskaya, A L Ivanovskii

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Abstract. Quantum chemical and molecular dynamics studies of nanotubes decorated with atoms of various elements are surveyed. The effect of adsorption of hydrogen, oxygen, alkali metal, alkaline earth metal, d-metal, halogen, and inert gas atoms on external walls of carbon nanotubes on the structure and electronic or other physicochemical properties of nanotubes is considered. The results of simulation of the properties of some atom-decorated non-carbon nanotubes (BN, BC_x, $B_xC_yN_z$) are briefly discussed.
The bibliography includes 332 references.

I. Introduction

The discovery of carbon nanotubes (CNTs) [1] is a landmark in the modern development of concepts of quasi-one-dimensional (quasi-1D) nanomaterials. Carbon nanotubes represent extended, hollow cylindrical structures from one to a few tens of nanometres in diameter. They are formed by rolling one (single-walled CNTs) or more (multi-walled CNTs) graphene sheets comprised of C_6 hexagons in a seamless fashion. This unique atomic structure predetermines interesting physicochemical properties of CNTs, such as large specific surface area, low density, high stability, strength and thermal conductivity, as well as unusual electronic and emission properties.[2 – 22]

A combination of these properties of CNTs makes them attractive for various technological applications, *e.g.*, as containers for storage of gases, salts or metals, as materials for production of biosensors, chemical or electromechanical sensors, nanomechanical devices, *etc.*[19 – 34] Currently, there has been a large-scale search for novel materials, and new inorganic tubular nanostructures with a more complex chemical composition and atomic structures are synthesized.[23 – 34]

Of course, soon after the discovery and determination of the key properties of CNTs the attention of researchers was focused on the development of methods for control of their properties. One of the most efficient approaches consists in chemical functionalization of nanotubes.

It should be noted that the term 'functionalized nanotubes' is used to specify a wide range of products of targeted variation of the chemical composition and structure of the initial (unmodified) nanotubes using various chemical or physical methods. There are three main methods for nanotube functionalization (Fig. 1):

— partial replacement of carbon atoms in nanotubes by other types of atoms ('doping' of nanotubes) or introduction of various defects into nanotube walls;

— encapsulation of atoms or molecules within the nanotube, within the space between the neighbouring walls of multi-walled nanotubes or in the intertubular space within nanotube 'bundles';

— attachment of atoms or molecules to outer nanotube walls (adsorption on the nanotube surface), to 'terminal' atomic rings of the open nanotubes or to 'caps' (terminal units) of the capped nanotubes.

The last-named technique makes it possible to obtain a vast variety of quasi-1D nanomaterials and attracts considerable attention of researchers. At the same time, it is assumed that the synthesis of surface-decorated tubular structures resulting from the interaction of nanotubes with various gaseous media, solutions or melts will help solving a lot of interrelated physicochemical problems. These are

— the determination of specific features and establishment of optimum conditions for adsorption of atoms (molecules, clusters, complexes or other species) on nanotubes,

— determination of the character of the adsorbate – nanotube interactions;

V V Ivanovskaya Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, ul. Pervomaiskaya 91, 620990 Ekaterinburg, Russian Federation. Fax (7-343) 374 44 95, tel. (7-343) 362 31 15, e-mail: v.ivanovskaya@gmail.com
Institute des Matériaux J Rouxel, Université de Nantes (UMR 66502 CNRS-IMN), Rue de la Houssinière, BP 32229, 44322 Nantes, France. Fax (33-0956) 97 24 96
A L Ivanovskii Institute of Solid State Chemistry, Ural Branch of the Russian Academy of Sciences, tel. (7-343) 374 53 31, e-mail: ivanovskii@ihim.uran.ru

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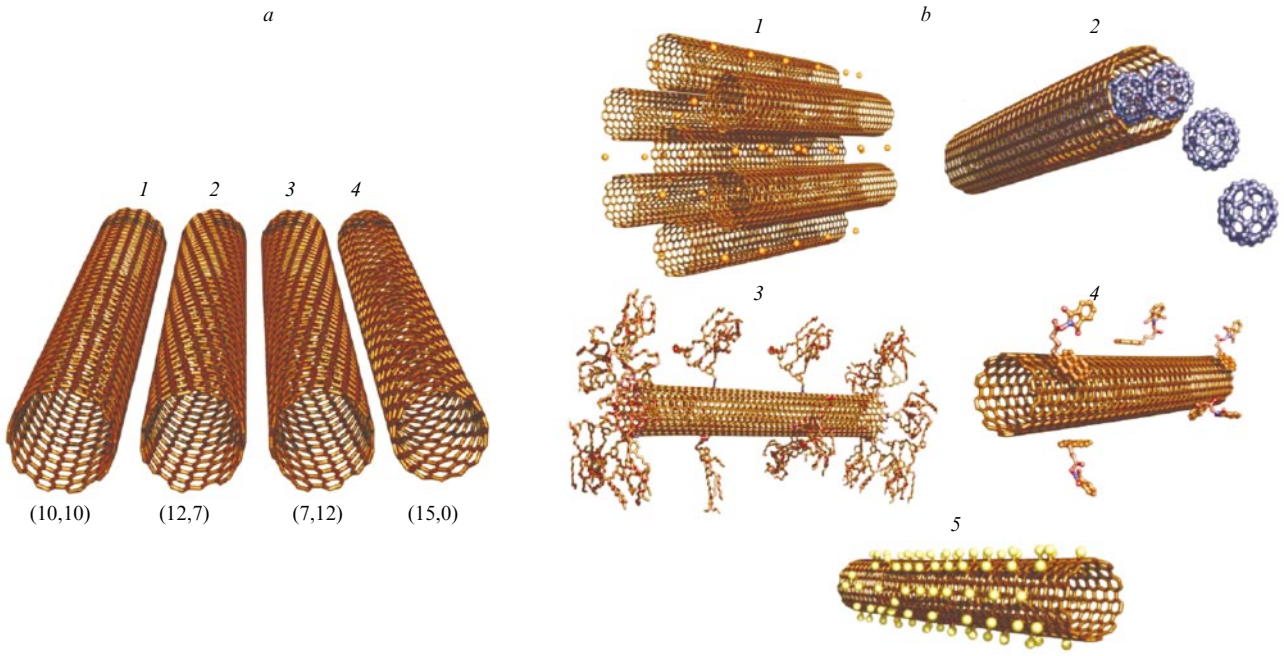


Figure 1. Main types of carbon nanotubes (*a*) and types of their functionalization (*b*);[35]
(*a*) achiral CNTs (*1*, *4*) 'armchair' (*n*,*n*)CNT and 'zigzag' (*n*,*m*)CNT; chiral CNTs (*2*, *3*); *n* and *m* are the chiral indices (integer numbers);
(*b*) particles in the intertubular space within a nanotube bundle (*1*); encapsulation of particles in the inner NT cavity (illustrated by the formation of 'peapods', *i.e.*, fullerenes encapsulated in nanotubes) (*2*); covalent (*3*) or non-covalent (*4*) functionalization of nanotubes; and atomic-decorated nanotubes (taking a fluorine-decorated CNT as an example) (*5*).

— determination of the effect of adsorbed particles on the properties of nanotubes; and

— the possibility of using decorated nanotubes in the design of novel nanomaterials.

To date, considerable progress has been made in solving some of these problems. For instance, advances in the synthesis and investigations of CNTs functionalized with various polymers have been documented in recent reviews,[36–38] as well as the results of studies on the composite materials made of CNTs decorated with noble metal clusters [33, 39] or inorganic nanoparticles [32] were generalized. Possible fields of application of surface-decorated tubular structures have been considered in reviews.[31–40]

Atom-decorated NTs represent a particular large group of quasi-1D tubular nanomaterials. They are formed as a result of, *e.g.*, dissociative chemisorption of fluorine [41–67] or oxygen [68–74] atoms on nanotubes or upon physisorption of inert gas atoms.[75–81] In the text below, nanotubes decorated with A-type atoms adsorbed on the outer nanotube wall will be denoted as A/NT.

Generally, the key factors influencing the formation and properties of atom-decorated NTs include:

— the properties of the medium determined by the pressure, temperature, and chemical composition;

— the properties of adsorbents governed by the NT diameter, chirality, chemical composition and the type of terminal structures (open-end or capped NTs);

— character of the interaction of the medium particles with NTs.

Also, the formation of atom-decorated NTs by physisorption with typical binding energies ($E_b \approx 10-100$ meV, very weak interaction between the adsorbate atoms and CNT) almost does not change the sp^2-like type of hybridization of the nanotube atoms. Contrary to this, in the case of chemisorption (E_b can be as high as 1–10 eV), the adsorbate atoms form strong bonds with the NT carbon atoms. As a result, the effective coordination number of these atoms changes from 3 (for the undecorated nanotube) to 4 and the hybridization of carbon atoms changes from the sp^2-like to sp^3-like. Of course, whereas in the case of physisorption the NT geometry changes only slightly, chemisorption can be accompanied by significant structural distortions and changes in the properties of the initial nanotube.

Decoration of carbon nanotubes with various atoms allows one to obtain novel nanomaterials with unusual properties. For instance, fluorination of CNTs leads to significant changes in their surface polarity, conductivity, sorption capacity and other properties. Therefore, fluorinated nanotubes are promising as reinforcing additives to composites, materials for nanowires and transistors in electronic devices, cathodes for lithium batteries, components of solid lubricants [41, 42, 63–67] and for the design of novel biocompatible materials for medicine.[43] Carbon nanotubes decorated with alkali, alkaline-earth or d-metal atoms are also thought to be promising for hydrogen storage.[82–88] Research on the interactions of individual carbon atoms with the CNT surface is of importance to gain a deeper insight into the growth of nanotubes [2–8, 89, 90] and into the mechanisms of formation of a vast variety of carbon–carbon nanocomposites, such as polymerized CNTs,[91–95] nanofoams,[96, 97] nanobuds (nanotubes whose outer walls are decorated with fullerenes C_n, also known as 'hybrid' nanotube/fullerene nanostructures),[98] composites of the CNT–graphitic nanoflakes type (nanotubes with outer walls decorated with fragments of graphene sheets),[99, 100] CNT–nanodiamond nanocomposites,[101] *etc.*[30]

Atom-decorated nanotubes are of considerable interest for theoretical research as the starting points for the description of more complex systems, such as (i) nanotubes decorated with molecules, various complexes or complex atom clusters, (ii) nanotube/crystal surface interfaces and (iii) various tubular composites.

Modern computational methods used in computer materials science allow one to solve a wide range of problems concerned with elucidation of specific features of the atomic structure and stabilizing factors, microscopic description of the nature of chemical bonding, determination (prediction) of the electronic, structural, thermal and some other properties of atom-decorated nanotubes. It is at least equally important that these methods provide unique possibilities for computer-assisted design of novel materials based on such nanotubes and prediction of their properties.

In this review, we generalize the results of quantum chemical and molecular dynamics studies on the structure and properties of CNTs decorated with hydrogen, oxygen, alkali, alkaline-earth and transition metal, halogen and inert gas atoms. In addition, taking a number of non-carbon nanotubes (boron nitride, boron carbide and boron carbonitride NTs doped with atoms of some s-, p- and d-elements) as examples, we demonstrate the potential of computer materials science in prediction of novel magnetic nanomaterials.

II. Atom-decorated carbon nanotubes

1. The hydrogen/carbon nanotube system

Interest in hydrogen adsorption on CNTs emerged soon after the discovery of these objects. The reason is a very large specific surface area of these quasi-1D structures (to nearly 2200 $m^2\ g^{-1}$). In principle, this is a very attractive factor for the design of CNT-based materials for hydrogen storage. To date, this problem was considered in many experimental and theoretical studies and the results obtained were generalized in reviews.[102–108]

First of all, note that, in spite of the earlier optimistic predictions, according to which nanotubes can store up to 10% of hydrogen by mass,[109–111] more recent studies showed that undoped/undecorated CNTs and their associates (bundles, films, *etc.*) are not promising for the use as hydrogen 'containers'.[102–108] The main reasons are a low energy of hydrogen adsorption ($E_b \approx 0.2-0.4$ eV per atom) and weak H_2-H_2 interactions which prevent nanotubes from 'holding' large amounts of hydrogen.[112]

Nevertheless, theoretical research on hydrogen adsorption on CNTs allowed one to solve a number of methodological problems that are of importance for investigations of more complex systems and to reveal some interesting regularities of changes in the properties of CNTs upon decoration with hydrogen atoms.

There is considerable literature on the molecular dynamics studies of hydrogen adsorption on CNTs and their associates.[113–127] These investigations were focused on calculations of the hydrogen adsorption isotherms and on estimation of the gravimetric hydrogen storage capacity of such systems depending on various parameters including the temperature, pressure, CNT diameter and chirality, intertube distance in NT bundles, NT bundle types (including CNTs of the same or different diameters), impurities or defects (pores) on the surface of nanotube walls.

Quantum chemical methods are used to determine the character of chemical bonding of hydrogen atoms and molecules to CNTs, optimum adsorption sites and to estimate the hydrogen–nanotube binding energies, to study the effect of hydrogen decoration of nanotubes on the electronic states of the H/CNT systems and to simulate structural distortions in CNTs.[107, 126, 128–140] In particular, interesting quantum structures were proposed[132] that can be based on CNTs decorated with hydrogen in some discrete manner. Alternation of the unmodified and hydrogen-decorated fragments causes modulation of the width of the forbidden gap along the nanotube axis, which is accompanied by generation of quantum waves (Fig. 2).

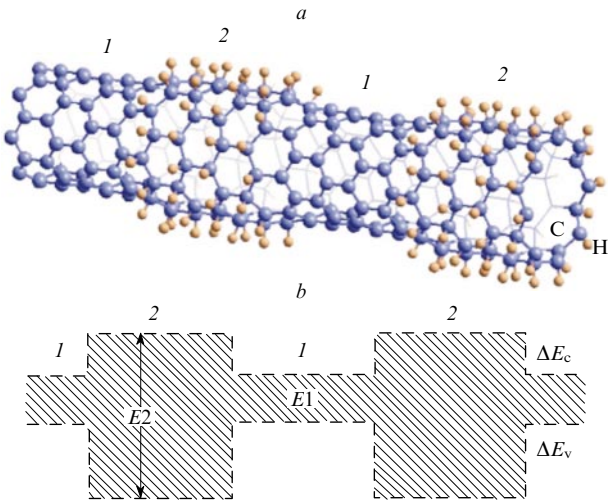


Figure 2. Atomic model for a quantum structure based on a semiconducting CNT decorated with hydrogen atoms in discrete manner (*a*) and a scheme of changes in the forbidden gap (*b*);[132]
(*a*) shown are the pristine (*1*) and hydrogen-decorated (*2*) CNT segments; (*b*) shown are the forbidden gaps along the NT axis for the pristine ($E1$) and hydrogen-decorated ($E2$) CNT segments; ΔE_c and ΔE_v are the conduction and valence band edges, respectively.

A particular role in theoretical search for hydrogen power engineering materials based on CNTs activated by various impurities (see below) is played by quantum chemical methods. Note that theoretical search for 'hydrogen containers' based on quasi-1D forms of carbon with large specific surface areas, of course, is not restricted to the 'classical' nanotubes.

Recently, a rather large number of exotic systems were proposed and their hydrogen capacities were estimated. For instance, the gravimetric hydrogen storage capacity of lithium-intercalated nanoscrolls (in which Li favours, in particular, an increase in the distance between the neighbouring walls in the nanoscroll) can be as high as 5.5% by mass.[141] A theoretical estimation of the hydrogen capacity of hypothetical 'hybrid' nanostructures called pillared graphene (graphene sheets separated by vertically aligned CNT fragments, see Fig. 3) was reported.[142] Other possible candidate materials for hydrogen containers include various types of crystals of single-walled carbon nanotubes, porous nanotube networks[143, 144] and related structures.[145] Of course, the key problem is still the synthetic accessibility of such materials.[146]

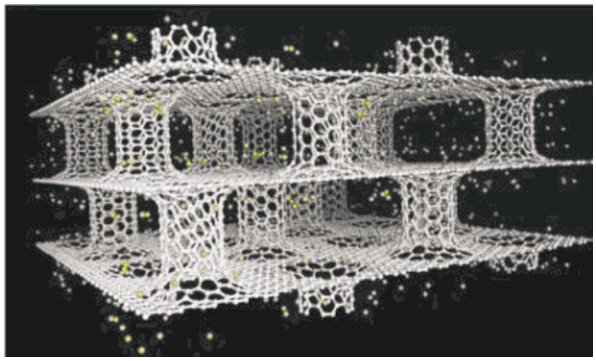


Figure 3. Atomic model for a hypothetical carbon composite called 'pillared graphene', a possible material for hydrogen storage. Shown are the results of a molecular dynamics simulation of filling of this material with hydrogen.[142]

2. The oxygen/carbon nanotube system

Specific features of the interaction of carbon nanotubes with oxygen are of great importance for explanation for the behaviour of CNTs and materials based on them under ambient conditions. Molecular oxygen used for cleaning CNTs favours removal of various carbon particles from the outer nanotube walls.[68,69] Exposure to oxygen significantly changes the electronic, transport and emission properties of CNTs.[70–74]

The $O(O_2)$/CNT systems were studied[147–161] in relation to representative set of carbon nanotubes from 5 to 14 Å in diameter. The emphasis was placed on evaluation of the adsorption energy of oxygen atoms and molecular oxygen and on the possible structural distortions of nanotube walls, changes in the electronic properties of CNTs and on charge transfer upon adsorption of oxygen atoms (molecules) depending on the NT chirality type and diameter and on the particular O (O_2) adsorption site.

The key results of model calculations[147–161] are as follows. Molecular adsorption is an exothermic process, and the adsorbed oxygen molecules are characterized by a binding energy of about 0.5 eV, being located at distances of nearly 2.95 Å from the nanotube wall.[149] The binding energies of individual atoms are much higher (nearly 2.6 eV) and the equilibrium distances O–CNT are much shorter (about 1.57 Å). The $O(O_2)$–CNT binding energy decreases as the nanotube diameter increases, *i.e.*, the $O(O_2)$/CNT system becomes less stable. The system $O(O_2)$/CNT is characterized by charge transfer from the CNT to $O(O_2)$, the degree of charge transfer from the nearest neighbouring carbon atoms being about 0.25 e per oxygen atom. A feature of ultrathin CNTs of the (3,3), (4,2) or (5,0) types having a diameter of about 4 Å is the possibility of both physisorption and chemisorption of oxygen molecules with the formation of various structures on the CNT surface.[155,159] For all semiconducting CNTs, adsorption of oxygen causes a marked narrowing of the forbidden gap.

Molecular dynamics studies of the adsorption of oxygen and O_2+N_2 gas mixtures on CNTs were reported.[162–168] The adsorption isotherms were constructed and it was shown, in particular, that these gases are mainly adsorbed on the outer nanotube walls and that adsorption of oxygen proceeds faster than that of nitrogen under identical conditions.

3. The alkali metal/carbon nanotube systems

The interaction of alkali metals with CNTs is considered in connection with the need to solve problems related to the search for novel materials for lithium batteries[169] and to optimize the properties of CNTs as promising materials for hydrogen power engineering.

The operational quality of a material considered as potential hydrogen accumulator is determined by two critical parameters, *viz.*, the H_2–adsorbent binding energy and the hydrogen storage capacity.[170–178] It is desired that the latter be as high as possible (more than 10% of H_2 by mass, as assumed by the design of 'super-adsorbents' of hydrogen[174,176]), whereas E_b should provide a good initial adsorption of molecules and a quite easy desorption after discharge of the accumulator. For instance, the US Department of Energy 2010 Hydrogen Programme Targets are as follows: the hydrogen storage capacity is higher than 6% of H_2 by mass and the energy of hydrogen adsorption ranges from 0.20 to $\leqslant$0.70 eV per H_2 molecule (at room temperature).[176] These parameters for some systems based on atom-decorated carbon nanostructures are listed in Table 1.

Table 1. Theoretical estimates and experimentally determined values of hydrogen adsorption capacities [c (mass %)] and binding energies of hydrogen molecule to adsorbents (E_b /eV per H_2 molecule) for various systems based on carbon nanotubes and fullerenes C_n.[177]

System	c	E_b	System	c	E_b
Undecorated CNT [a]	~4.2	–	C_{720}	10	–
Li/CNT	~20	–	Li@C_n	13	0.08
K/CNT [a]	~14	–	Na@C_n	9.5	0.08
Ti/CNT	7.7	0.18	Ca@C_n	8.4	0.2–0.4

[a] Experimental value.

The experimentally measured[179–183] sorption capacity of lithium-doped CNTs used as hydrogen adsorbents varies over a very wide range from 2.5 (Ref. 178) to 20% by mass.[182] At the same time, no adsorption was detected.[179]

Using theoretical calculations, one can analyze[82,177,181,183–187] the behaviour of (H_2–Li)/CNT systems depending on a number of important parameters including the type of the adsorption site for lithium adsorption on CNTs and hydrogen adsorption on Li/CNT, the degree of coverage of nanotubes with lithium and the number of adsorbed hydrogen molecules on Li/CNT. As an example, Fig. 4 presents the optimized atomic configurations of the system (H_2–Li)/CNT with possible H_2 adsorption sites and the equilibrium structure of the system with the atomic ratio $(H_2)_{32}:Li_8:C_{64}$ which corresponds to sorption of 6.72 masss % hydrogen. For this system, the adsorption energy of H_2 molecules is about 0.17 eV per H_2 molecule, being close to the optimum value (see above). Similar estimates of the maximum hydrogen sorption on Li/CNT (about 7.6 mass % of H_2) were obtained in a molecular dynamics simulation of this system under atmospheric pressure at 300 K.[82] It should be noted that hydrogen sorption on bundles of lithium-doped CNTs appeared to be significantly lower (nearly 2.7 mass % of H_2),[82] which is close to experimental data.[178]

As the Li:C ratio increases, the energy of the bond between the adsorbed lithium atoms and the nanotube decreases while the Li–CNT distance (l) increases.[82] A decrease in E_b (elongation of the distance Li–CNT) with an

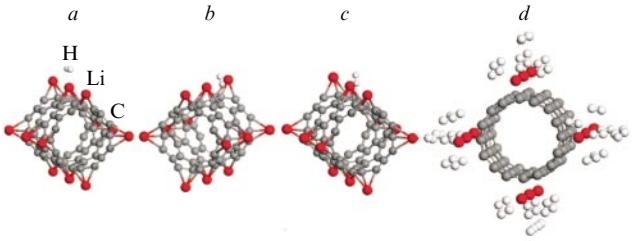


Figure 4. Optimized structures of (H_2-Li)/CNT systems for possible H_2 adsorption sites (*a*–*c*) and the (H_2-Li)/CNT system (*d*) with the atomic ratio $(H_2)_{32}:Li_8:C_{64}$.[177]

increase in the concentration of adsorbed lithium can be explained by a decrease in the ionicity of the Li–CNT bond, *viz*., the effective charges of lithium ions (q_{Li}^{ef}) decrease in the order LiC_{64}, LiC_8, LiC_4 (Table 2).[82] Thus, despite the fact that the hydrogen sorption increases with an increase in the number of lithium atoms on CNTs, the increase in the lithium concentration will be limited by the progressing decrease in E_b(Li–CNT) as the Li:C ratio increases. Mention was made that the introduction of boron impurity into the CNT wall may become favourable for lithium adsorption on the nanotube; the reverse is the situation with a nitrogen impurity.[83]

Table 2. Changes in the parameters E_b, l and q_{Li}^{ef} of compounds LiC_{64}, LiC_8, LiC_4.

Compound	E_b/eV per Li atom	l/Å	q_{Li}^{ef}/e
LiC_{64}	2.11	1.526	0.57
LiC_8	1.65	1.532	0.39
LiC_4	1.60	1.552	0.27

A Monte Carlo simulation[188] of a related system (H_2-K)/CNT showed that the degree of hydrogen sorption increases with the CNT diameter, the tube–tube distance and at particular[188–191] arrangements of potassium atoms on the CNT surface. Thus, by varying these parameters one can control the hydrogen storage capacity of the adsorbent material K/CNTs. In turn, adsorption of potassium on CNTs can be strongly affected by mechanical deformations of the nanotube, in particular, its axial compression or stretching.[191] For instance, stretching of a (5,5)CNT by 10% causes the adsorption energy (E_{ad}) of potassium to increase by nearly 0.87 eV. This effect can be due to an increase in the degree of charge transfer from the potassium atoms to the nanotube carbon atoms on stretching.

Recently, studies on more complex systems formed by decoration of CNTs with two or more different alkali metals, *e.g*. potassium and caesium, have begun.[192]

4. The alkaline-earth metal/carbon nanotube systems

Alkaline-earth metals have attracted the attention of researchers as elements capable of forming rather stable and uniform atomic coatings of carbon nanostructures.[84,193–197] The alkaline-earth metal atom–CNT binding energies and the cohesive energies of these metal atoms (in the crystal or in cluster) are close (~1–2 eV per atom). Thus, unlike transition metals whose atoms adsorbed on the CNT surface are prone to aggregation with clustering (see below), alkaline-earth metals can be used for quite uniform atomic decoration of carbon nanostructures. The Ca/CNT systems are active towards hydrogen[84,193–197] and small organic molecules (*e.g*., dioxin[198] or simple amino acids).[199]

Additional interest in Ca/CNT systems is due to the results of preliminary calculations,[194] according to which the adsorption capacity of calcium-monolayer-coated C_{60} fullerenes with respect to H_2 molecules is much higher than that of uncoated C_{60}. This is due to the polarization of hydrogen molecules in the electric field of the Ca^{2+} ions. For instance, the exo-fullerene $Ca_{32}@C_{60}$ can attach up to 92 hydrogen molecules (about 2.7 H_2 molecules per Ca atom), *i.e*., the storage capacity of this material can be as high as 8.4 mass % of hydrogen.[193] Stabilization of the exo-fullerenes $Ca_{32}@C_{60}$ and $Sr_{32}@C_{60}$ is due to a specific type of the adatom–fullerene bond formed on charge transfer from the outer s-orbitals of the alkaline-earth metal atoms to the fullerene π*-orbital and subsequent partial back charge transfer to the vacant d-orbitals of the metal atoms.[193] Adsorption of beryllium and magnesium is not accompanied by the stabilizing effect.[193]

Calcium-decorated CNTs are characterized by strong Ca–CNT bonds due to, in particular, hybridization of the C 2p orbitals and Ca (s,d) orbitals.[197] At relatively low temperatures ($300 \leqslant T \leqslant 900$ K), the type of the calcium coating is strongly dependent on the NT chirality, *viz*., it can be quite uniform for the zigzag CNTs (the degree of coverage is nearly ~30%–40%), whereas in the case of armchair CNTs, the calcium atoms are prone to clustering. However, the key problem in using Ca/CNT systems for accumulation of gases may be high reactivity of calcium towards gas molecules rather than clustering of calcium atoms on the nanotube surface. This can lead to decomposition of the Ca/CNT system in, *e.g*., hydrogen atmosphere to the undecorated nanotubes and calcium hydride species.[197]

A study[84] of hydrogen adsorption on Ca/CNT systems showed that each calcium atom can interact with a few (at most six) H_2 molecules and that the hybridization of the Ca d-AO and the H s-AO contributes to the H_2–Ca bond (this binding energy is about 0.2 eV per H_2 molecule, see Table 3). The negative (from the standpoint of gas storage) trend towards clustering of Ca atoms on the CNT surface can be minimized[84] by doping the nanotube wall with some impurity (*e.g*., boron or nitrogen atoms) of by forming structural defects. Estimations showed that calcium-decorated boron-doped carbon nanotubes (boron content is 6%) can store up to 5 mass % of hydrogen.

Doping a related system Mg/CNT with boron atoms also favours an abrupt increase in the Mg–CNT binding energy by more than 1 eV per Mg atom (*cf*. E_b ~0.07–0.14 eV per Mg atom for the Mg–CNT bond with the undoped CNT).[201] The reason is that the electron deficiency arising in the CNT in the presence of the boron impurity atom and in the case of local structural distortions of the nanotube wall[202] favours a significant increase in the degree of charge transfer from the magnesium atom to the nanotube, which makes the Mg–CNT ionic bond stronger. This should be taken into account in the design of novel composite materials such as, *e.g*., carbon nanotube-reinforced magnesium matrix composites.[203–206] Informaton on CNTs decorated with other alkaline-earth metals has not been reported as yet.

Table 3. Binding energies of isolated Ca atom (E_b^{Ca} /eV per atom) and H_2 molecule (eV per molecule) to different surfaces of the (7,7)CNT.[84]

CNT	E_b^{Ca}	Number of adsorbed H_2 molecules					
		1	2	3	4	5	6
I	0.88	0.21	0.21	0.21	0.21	0.19	0.17
II	0.61	0.23	0.22	0.21	0.21	0.19	
III	1.82	0.20	0.21	0.20	0.19	0.18	
IV	2.15	0.16	0.17	0.16	0.14	0.13	
V	3.30	0.16	0.16	0.14	0.13	0.12	
VI	2.20	0.20	0.19	0.17	0.16	0.15	

Note. Notations are as follows: (I) a (7,7)CNT; (II) a nitrogen decorated (7,7)CNT (nitrogen is a substitutional impurity); (III) a boron decorated (7,7)CNT (boron is a substitutional impurity); (IV–VI) a (7,7)CNT with the Stone–Wales wall defects (IV), C vacancies (V) and C_2 divacancies (VI). The Stone–Wales defects appear in the graphene sheet upon rotation of a carbon–carbon bond by $\pi/2$; four neighbouring hexagons are transformed to pentagons and heptagons ($4\,C_6 \rightarrow 2\,C_5 + 2\,C_7$).[200]

5. The d-metal/carbon nanotube systems

Among the most intensively studied classes of atom-decorated nanostructures, there are CNTs decorated with d-metals (M); this is due to the variety of possible applications of such systems. For instance, titanium-, palladium- or platinum-decorated CNTs are considered as promising materials for hydrogen storage or gas sensors.[207–211] Decoration of CNTs with magnetic metal atoms (M = Cr, Mn, Fe) is an interesting approach to the design of novel magnetic quasi-1D materials for functional elements (magnetic nanowires) for various electronic nanodevices, which are necessary for, in particular, the development of nanospintronics.[212–214] Nanotubes decorated with noble metal atoms (M = Ag, Au) attract the attention of researchers as electrode materials and materials for gas sensors.[215,216] In addition, CNTs decorated with various metals are of considerable interest as catalysts.[33,39,217,218]

In the early stage of research on the M/CNT systems, it was found that, unlike, *e.g.*, the alkaline-earth metals prone to adsorption on the nanotube surface in discrete manner (see above), the d-metal atoms usually interact with one another, thus forming metal clusters. The d-metal nanoparticles can form quite uniform coatings on the nanotube surfaces,[219] namely, a kind of monolithic metal 'sheath' (so-called nanotube-supported metal nanowires) for M = Ti or Ni or isolated discrete metal nanoparticles for M = Fe, Pd and especially Au (Fig. 5).

Generally, decoration of CNTs with d-metal atoms can lead to the formation of various heterogeneous M/CNT structures (Fig. 6).

Clearly, one of the key factors determining the type of the M/CNT and M_n/CNT systems under study is the character of the metal–CNT interactions. In the earlier calculations,[221–228] it was shown that most d-metals form rather strong covalent bonds with the nanotube surface due to hybridization of C p_z-atomic orbitals with the outer valence states of the chemisorbed metal atoms. This effect is illustrated in the charge density maps for, *e.g.*, the Fe/CNT system (Fig. 7).[225] In addition, the M/CNT systems are usually characterized by partial charge transfer

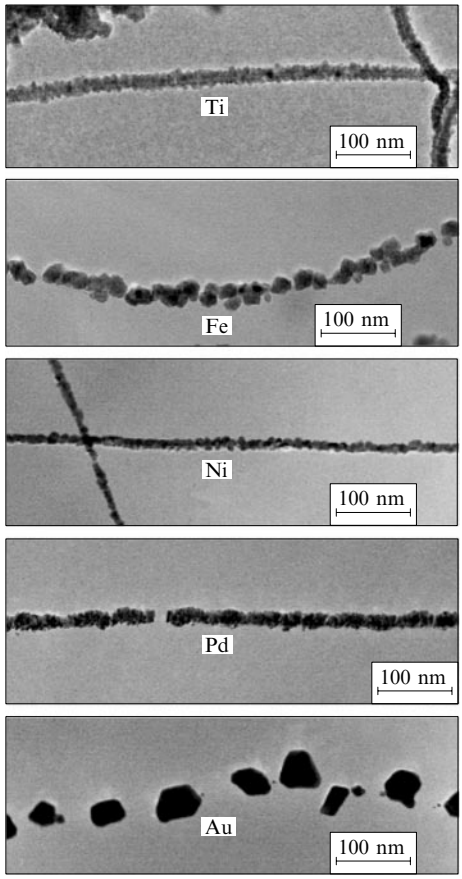


Figure 5. Micrographs of carbon nanotubes decorated with various metal nanoparticles.[219]

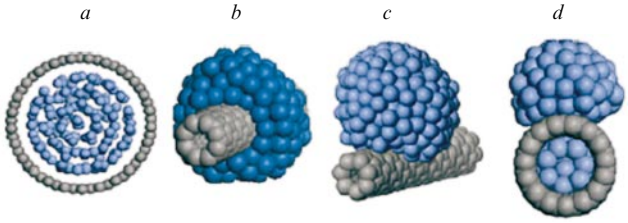


Figure 6. Possible types of heterogeneous structures M–CNT.[220] Metal atoms are encapsulated in the nanotube (*a*); uniform decoration of the outer nanotube surface with metal atoms (*b*); clusters of metal atoms on the nanotube surface (*c*), and a complex type of heterogeneous structure (*d*).

from the metal atoms to the nanotube,[40] which is responsible for the ionic component of the M–CNT bond.

Systematic calculations[226] of M/(8,0)CNT (M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Mo, Pd, Ag, Ta, W, Pt, Au) systems containing individual M atoms located at characteristic adsorption sites (Fig. 8) using a periodic unit cell model allowed one to determine the M–CNT binding energies as

$$E_b = E_{tot}[(8,0)CNT] + E_{tot}(M) - E_{tot}[M/(8,0)CNT],$$

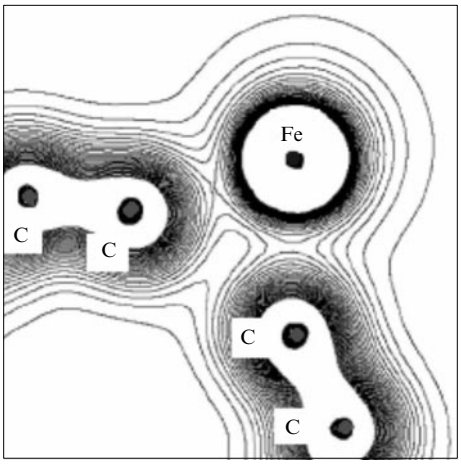


Figure 7. Charge density map of the Fe/CNT system illustrating the formation of covalent bonds between the iron atom and the carbon nanotube wall.[225]

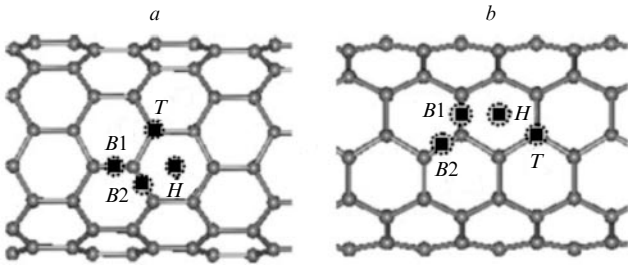


Figure 8. Main sites for adsorption of atoms on the zigzag (*a*) and armchair (*b*) carbon nanotubes.
Adsorption site notations: *T* above the carbon atom; *B*1 and *B*2 above the mid-points of nonequivalent carbon–carbon bonds; and *H* above the centres of C_6 hexagons.

where E_{tot}[M/(8,0)CNT], E_{tot}[(8,0)CNT] and E_{tot}(M) are the total energies of the M/(8,0)CNT system, undecorated nanotube and isolated atom M, respectively. With E_b thus defined, the case $E_b > 0$ corresponds to a stable state of the system. In addition, the equilibrium distances M–CNT and the magnetic moments of the atoms M were evaluated (Table 4). As can be seen, for most atoms M the energies E_b are rather high, *viz.*, $E_b \geqslant 2$ eV per atom. For the elements forming quasi-monolithic structures on CNTs (*e.g.*, Ti), the binding energy (about 2.9 eV per atom) is much higher than for, *e.g.*, gold ($E_b \approx 0.6$ eV per atom) that is deposited on the nanotube surface in the form of discrete nanoparticles Au_n. Yet another important result[226] is concerned with the magnetization of the chemisorbed atoms M on the CNT surfaces. It was reported that the magnetic moments of these atoms differ from those of the same atoms chemisorbed on other carbon materials (*e.g.*, graphite). This was explained by the curvature of the nanotube wall. For most atoms M, the most energetically favourable adsorption site is the position *H* 'above' the centres of the C_6 hexagons (see Fig. 8), which enables the formation of the maximum number (6) of M–C bonds.

Not only the M–CNT interactions), but also the cohesive energies (E_{coh}) of metals are important for the description of the properties of the M/CNT systems. The energy E_{coh} characterizes the energy effect of 'assembling' of a crystal from isolated atoms and is related to the energy of atom–atom interactions in crystals. In the framework of computational approaches, E_{coh} is usually given by

$$E_{coh}(M) = E_{tot}(M) - E_{tot}(M_{at}),$$

where $E_{tot}(M)$ is the total energy of the condensed form of the metal and $E_{tot}(M_{at})$ is the total energy of free (isolated) metal atoms.

Taking into account the aforesaid, a trend towards aggregation of metal atoms on the CNT surface into metal clusters can be explained by the fact that, typically, the cohesive energy of d-metals (about 10 eV per atom) is much higher than the average energy of the bonds formed by these atoms with the CNTs (nearly 1–2 eV per atom).[229,230] Numerical estimation[227] of the metal–metal binding energies (E_b^{M-M}) and the metal–nanotube binding energies (E_b^{M-CNT}) carried out for M_2 (M = Fe, Co, Ni) dimers on a (4,4)CNT showed that E_b^{M-M} (about 1.56, 1.93 and 1.53 eV for Fe, Co and Ni, respectively) are higher than E_b^{M-CNT} (nearly 0.8 eV); this provides an explanation for clustering of the atoms M on the nanotube surface. This is also confirmed by the results of calculations of some monatomic chains ...–M–M–M–... on CNTs;[228] weakening of M–CNTs bonds is particularly pronounced if direct M–M bonds are formed (M = V and Co, see Fig. 9).

The main characteristics of CNTs responsible for control of their interactions with metals include the nanotube chirality and diameter (NT wall curvature).[231,232] Of

Table 4. Distances between the metal atom and nanotube (l), binding energy of the metal atom to nanotube (E_b, eV per atom, obtained from spin-restricted calculations) and the magnetic moments of metal atoms (μ) in the M/CNT systems (isolated metal atom on the surface of a carbon nanotube).[226]

Atom	AS[a]	l/Å	E_b	μ/μ_B	Atom	AS[a]	l/Å	E_b	μ/μ_B
Ti	*H*	2.2	2.9	2.21	Nb	*H*	2.2	3.9	2.86
V	*H*	2.2	3.2	3.67	Mo	*H*	2.2	4.6	4
Cr	*H*	2.3	3.66	5.17	Pd	*B*1	2.1	1.7	0
Mn	*H*	2.4	3.4	5.49	Ag	*B*1	2.5	0.3	0.6
Fe	*H*	2.3	3.1	2.27	Ta	*H*	2.2	2.9	3.01
Co	*H*	2.0	2.8	1.05	W	*H*–*B*1	2.1	3.4	2.01
Ni	*B*1	1.9	2.4	0.04	Pt	*H*	2.1	2.7	0
Cu	*B*1	2.1	0.8	0.53	Au	*H*	2.2	0.6	1.02

[a] The type of the most energetically favourable adsorption site (AS), see Fig. 8.

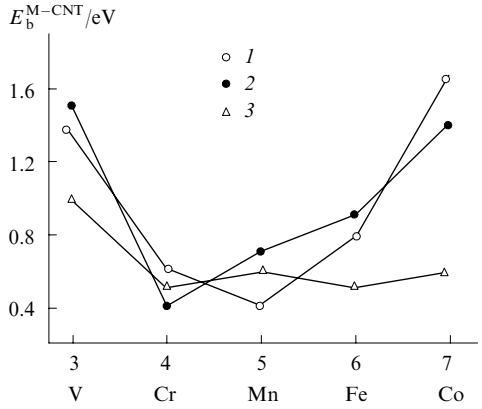


Figure 9. M—CNT binding energies for model calculations.[228] One M atom per cell (*1*), two M atoms per cell (*2*), and a monatomic chain of M atoms ...—M—M—M—... on the nanotube surface (*3*).

course, specific features of CNTs are manifested in the interaction of d-metal atoms with multi-walled nanotubes and various nanotubular associates including whiskers, films (nanopaper), crystals, *etc*., as well as with terminal units of CNTs which can have open ends or be capped.[1–8] In the latter case, one should take into account the type of the NT 'caps' including fullerene-like, conical ones, *etc*. Clearly, the reactivity of NTs towards metals (and other elements used for decoration of nanotubes) can be controlled by introducing various defects into the NT walls.

In the subsequent Sections we will consider the results of computer simulation of particular M/CNT systems that have recently attracted increased interest of researchers.

The Ti/CNT system. Detailed investigations of the properties of this system[85–88,208,233–236] were initiated by a study[87] whose authors showed that a Ti atom on the CNT surface can hold up to four H_2 molecules. The chemisorption of hydrogen on Ti/CNT proceeds by a mixed mechanism. Namely, adsorption of the first H_2 molecule on the titanium atom follows the dissociative channel while the other three H_2 molecules are adsorbed in the molecular form. At high coverages of CNTs with titanium atoms, the hydrogen storage capacity of the Ti/CNT systems can be as high as 8 mass % (Fig. 10). In spite of these optimistic

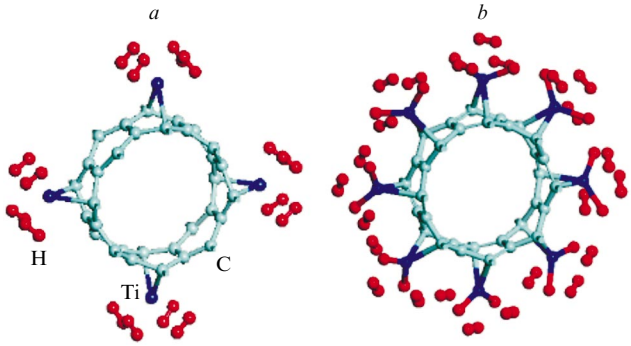


Figure 10. Structural models for hydrogen adsorption on titanium-decorated CNTs.[87]
The (H—Ti)/CNT systems with formal stoichiometries H_8TiC_8 (5.3 mass % of hydrogen) (*a*) and H_8TiC_4 (7.7 mass % of hydrogen) (*b*).

predictions, it's still a problem to synthesize nanotubes uniformly decorated with titanium atoms, because clustering of the Ti atoms significantly reduces the hydrogen storage capacity of the Ti/CNT-materials proposed.[87] This was clearly demonstrated in recent calculations[235] of a related system Sc/CNT. Note also that the hydrogen storage capacity of the proposed[87] model materials (CNTs decorated with d-metal atoms) can be reduced to even greater extent owing to aggregation of metal clusters on nanotube surfaces into larger particles during hydrogenation.[236] This mechanism is illustrated in Fig. 11.

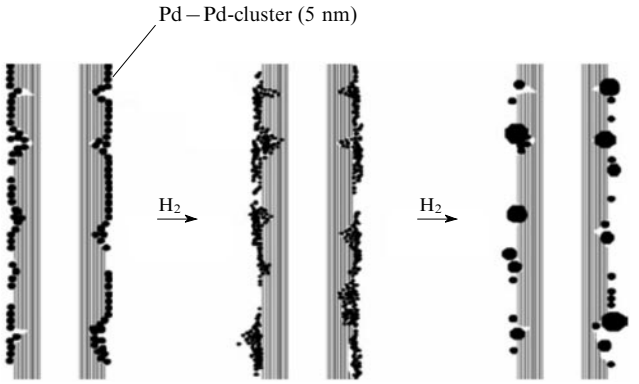


Figure 11. Aggregation of metal clusters on the nanotube surface into larger particles in the course of hydrogenation.[236]

Studies on the Ti/CNT system were concerned with the possibility of simultaneous adsorption of hydrogen on titanium atoms located on the inner and outer CNT walls,[233] the electronic properties of CNT-supported metal nanowires[86] and the magnetic properties of these objects which are expected to behave as ferromagnetic metals.[87] It was shown[86] that the magnetic properties of this type of nanowires depend strongly on the mechanical deformation, *viz*., a positive axial strain favours an increase in the magnetic moment of titanium. However, an external electric field reduces the magnetic moments of titanium atoms in Ti/CNT.[234] Calculations of the interaction of CO molecules with the Ti/CNT system were carried out and the possibility of using this material as CO sensor was discussed.[208]

The Pd(Pt)/CNT systems. The Pd/CNT[237–240] and Pt/CNT[220,237,240,241] systems were theoretically analyzed as candidate materials for gas sensors and hydrogen storage. Experiments showed that palladium-decorated multi-walled CNTs have a hydrogen storage capacity of about 2.9 mass % at a pressure of 1.67 MPa and $T = 298$ K.[242] Platinum-decorated carbon nanotubes are thought to be used as materials for NH_3 or NO_2 sensors.

Calculations[237–240] of Pd-decorated nanotubes showed that a palladium atom on the nanotube can hold two H_2 molecules[237] and two neighbouring Pd atoms can hold up to five hydrogen molecules with an average binding energy E_b of about 0.44 eV.[240] At high coverages of nanotubes with Pd atoms, the theoretical hydrogen storage capacity can be of the order of 2.9 mass %, which is in good agreement with experimental data. It is expected[237,238,240] that chemisorption of H_2 on Pd/CNT will mainly proceed by the dissociative mechanism. The covalent-ionic C—Pd—H_2 bonds (interatomic hybridization C—Pd involves the C $2p_z$ and

Pd 5s, $5p_z$ and $4d_{z^2}$ orbitals) are expected to be much weaker than the C—Pd—H bonds.[240] Interestingly, a study[239] of the Pd/CNT system showed that the energy of hydrogen adsorption on the carbon nanotube (with the formation of a C—H bond) in the vicinity of the Pd atom noticeably increases compared to the corresponding E_b value for the undecorated nanotube.

Simulation of hydrogen adsorption on Pt/CNT showed[237] that this process will also proceed by the dissociative mechanism and that the Pt—CNT bonds become much weaker, but the H—Pt bonds were found to be stronger than the H—Pd bonds.

Adsorption of NH_3 or NO_2 molecules on Pt/CNT[241] is also accompanied by weakening of the Pt—CNT bonds. The molecules being adsorbed on the Pt/CNT surface are oriented in such a manner that the key interactions between them and Pt/CNT involve the Pt—N bonds. The changes in the charge states and electronic structure of the Pt/CNT system interacting with the NH_3 or NO_2 molecules are also very interesting. They can be followed in the differentce electron density maps (Fig. 12) constructed for the $(NO_2—Pt)$/CNT and $(NH_3—Pt)$/CNT systems. One can also compare these maps with the corresponding maps simulating the adsorption of NO_2 and NH_3 molecules on the undecorated carbon nanotube. As can be seen, in both cases one deals with partial charge transfer, Pt/CNT → NO_2 in the system $(NO_2—Pt)$/CNT and NH_3 → Pt/CNT in the system $(NH_3—Pt)$/CNT. Generally, charge transfer is accompanied by changes in the electronic spectrum of the system under study.[241] These features may appear to be useful for the design of Pt/CNT-based materials for gas sensors.

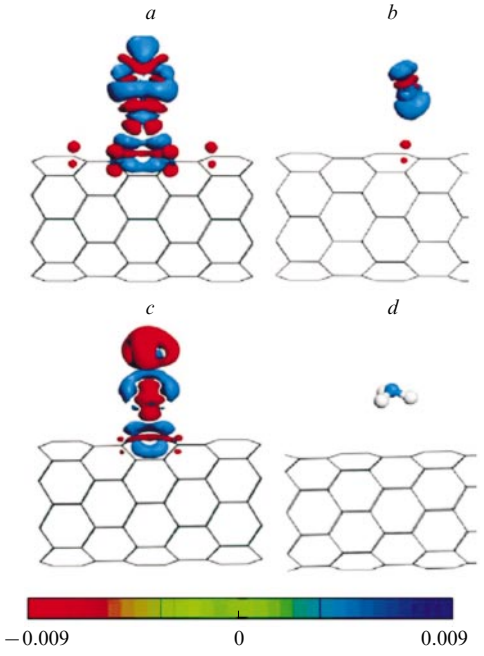


Figure 12. Differentce electron density maps illustrating rearrangements of the charge states of the systems $(NO_2—Pt)$/CNT (*a*) and $(NH_3—Pt)$/CNT (*c*) as well as adsorption of NO_2 (*b*) and NH_3 (*d*) molecules on an undecorated carbon nanotube.[241]

The Au/CNT system. Being a good conductor, gold is considered as the best candidate for the material for contacts between elements of electronic devices including nanotube-based ones. Good biocompatibility of gold allowed one to propose gold-coated nanotubes as biosensors.[243] Recently, a series of studies on the nature of the interaction of single gold atoms and gold clusters with the CNT surface and on the properties of gold particles treated as nanocontacts connecting nanotubes was reported.[216,244–251] To illustrate the latter case, Fig. 13 presents two atomic models, namely, the Au_{14} cluster placed between two parallel CNTs and between the ends of two parallel capped CNTs.[244] According to calculations, electronic transport between nanotubes through such kind of 'contacts' occurs by resonance tunnelling and depends on the orientation of the resonance electronic states of the gold clusters relative to the electronic states of the nanotubes.[244] Model calculations also showed that small gold clusters located between CNTs can undergo spontaneous transformation to monatomic chains ...—Au—Au—Au—... .[246]

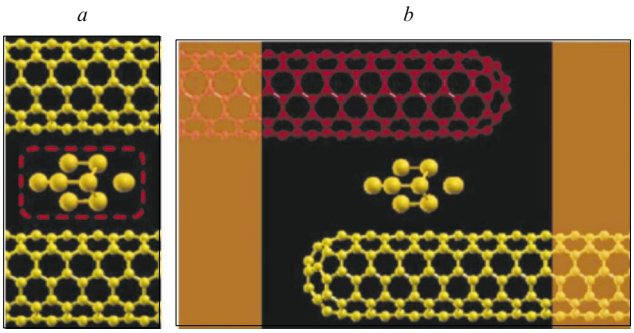


Figure 13. Atomic models used to describe gold clusters as nanocontacts connecting carbon nanotubes.[244]
Shown is the Au_{14} cluster placed between two parallel CNTs (*a*) and between the ends of two parallel capped CNTs (*b*).

The formation of gold clusters on carbon nanotubes is explained[216] by a very low energy of the interaction between an Au atom and CNTs; therefore, gold atoms can migrate with ease across the nanotube surface. In the presence of defects (vacancies or divacancies), the binding energy of a gold atom can increase and the atom now 'attracts' other gold atoms, thus playing the role of a 'nucleus'. Therefore, the pattern of the carbon nanotube decoration with gold nanoparticles can be controlled by creating a necessary configuration of defects in the nanotube walls.[247] Substitutional impurities, *e.g.*, boron or nitrogen atoms, can play a similar role.[248] However, the mechanisms of this effect for these impurities are fundamentally different. Boron impurity atoms favour nucleation of gold clusters due to the formation of strong B—Au bonds. In the case of nitrogen atoms, one deals with the change in the electronic configurations of the nearest carbon atoms and subsequent strengthening of the carbon–gold bonds.

6. The halogen/carbon nanotube systems

High reactivity of halogens (F, Cl, Br) towards carbon nanotubes leads to significant changes in the properties of CNTs.

For instance, fluorination of CNTs is accompanied by cleavage of some carbon–carbon π-bonds in the nanotube walls and the formation of strong C—F bonds. The process may involve up to 50% of carbon atoms in the CNT. The formal stoichiometry of the F/CNT systems can correspond to FC_2. Fluorination of CNTs is considered as one of the most efficient methods of changing their physical and chemical properties, such as the surface polarity, conductivity, storage capacity, adsorption capacity, *etc*. (see reviews [41, 42]). Fluorinated CNTs can find application as reinforcing additives to composites, materials for nanowires and transistors in electronic devices, cathodes for lithium batteries, components of solid lubricants and for the design of novel biocompatible materials for medicine (see Ref. 43).

Chlorine and bromine are considered as useful reactants for treatment of various products of CNT synthesis and for nanotube cleaning.[44–49]

Now we will dwell on the key results of studies on the halogen/CNT systems taking the F/CNT system as the best studied example. Since the very beginning of research on the synthesis of fluorinated CNTs,[50, 52] their structure and properties were studied [41, 42, 52–67] by various experimental methods, such as transmission electron microscopy (TEM),[53] X-ray emission spectroscopy (XES),[54] X-ray adsorption spectroscopy (XAS),[55, 56, 60] X-ray photoelectron spectroscopy (XPS),[52, 53, 55, 56, 60] X-ray absorption near-edge structure spectroscopy (XANES),[59] Auger electron spectroscopy,[58] IR and Raman spectroscopies [57] and some other techniques.[42] An interesting series of experimental studies on the mechanism of fluorine chemisorption on CNTs was reported.[61–63] Different fluorination patterns, namely, *exo*-, *endo*- and 'mixed' one were revealed and it was found that the corresponding processes can proceed concurrently (Fig. 14).

Theoretical description of CNT fluorination and the possible structure and properties of the F/CNT systems has attracted considerable attention of researchers.[64–67, 252–261] In the early studies published before 2002 (see reviews [35, 64]), the emphasis was placed on the character of the F–CNT bonding and on the search for the most energetically stable motifs formed upon regular chemisorption of fluorine. Some examples of the structures studied [64] are shown in Fig. 15. Depending on the decoration pattern of fluorine atoms, the stability and the conductivity type of the F/CNT systems will change (the conductivity may change from metallic to semiconducting type [253–255]). In the most stable F/CNT systems, fluorine atoms are arranged either along the nanotube axis or form helical structures (see Schemes *a* and *d* in Fig. 15). The nanotube chirality and diameter are also important parameters that affect the fluorination pattern [256] due to, in particular, steric effects and changes in the repulsion between the adsorbed fluorine atoms.[254] The possibility of fluorine adsorption on the open ends of carbon nanotubes was studied.[256, 257]

Fluorine adsorption may lead to changes in the hybridization type of carbon atoms from the sp^2-like to sp^3-like and to large structural distortions of cylindrical CNTs. Figure 16 presents the results of simulation of CNTs using various irregular fluorination patterns.[257] Regular chemi-

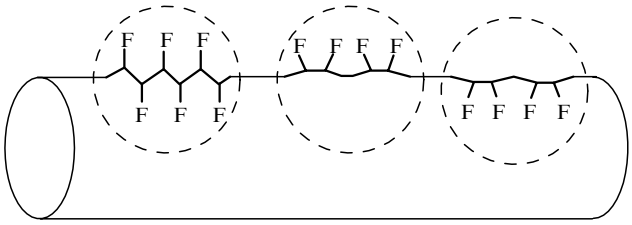


Figure 14. Possible fluorination patterns of carbon nanotubes.[63]

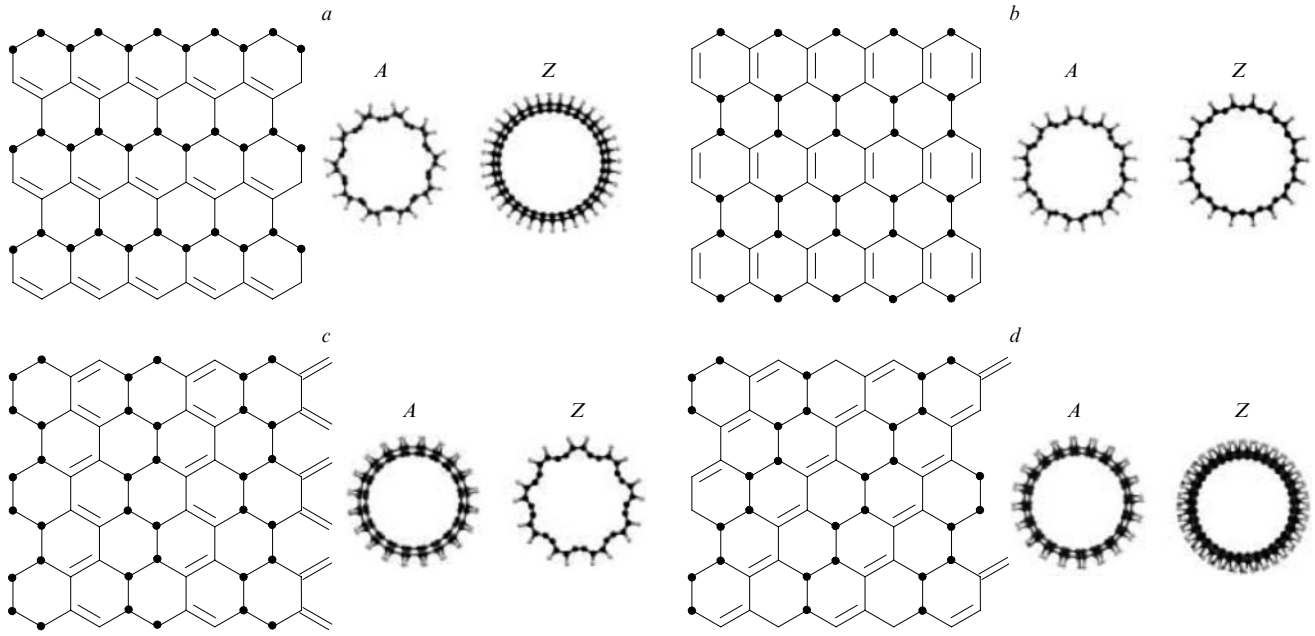


Figure 15. Carbon nanotube surface decoration with fluorine atoms (solid circles): possible decoration patterns and the corresponding cross-sections of the nanotube ends for the optimized F/CNT structures for the armchair (*A*) and zigzag (*Z*) nanotubes.[64]

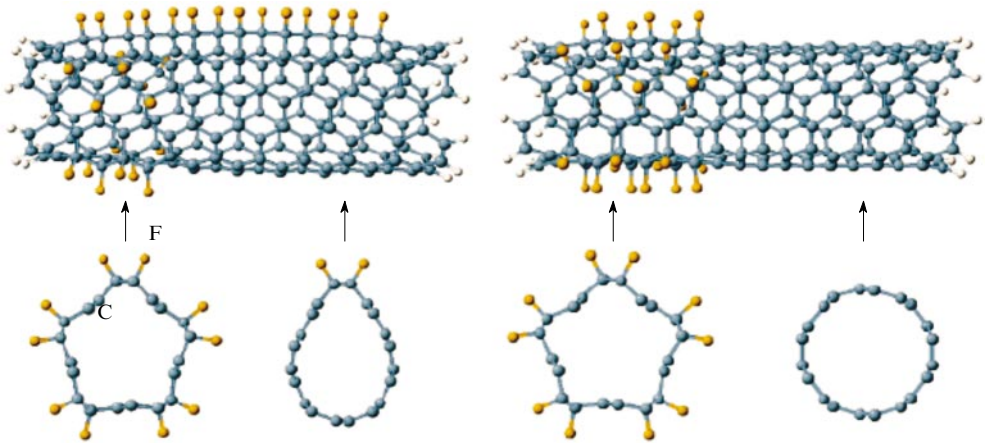


Figure 16. Effect of irregular chemisorption of fluorine on the local structure of carbon nanotubes.[257]

sorption of fluorine atoms can lead to a modification of cylindrical carbon cores of single-walled nanotubes to carbon cores that have a nearly prismatic shape.[259] The mechanisms of fluorine adsorption on carbon nanotubes (including nanotubes with defect walls), changes in the electronic properties of F/CNT systems and aggregation of these systems into bundles have also been analyzed.[256, 260, 261]

Summing up, note that recently, considerable attention has been paid not only to 'simple' fluorination of CNTs (*e.g.*, on exposure of nanotubes to F_2 or its mixtures with inert gases), but also to the formation of more complex (oxyfluoride, fluorohydride) structures on the nanotube surfaces. The properties and possible fields of application of such materials were discussed in a review.[41]

7. The inert gas/carbon nanotube systems

Systematic experimental and theoretical research on the adsorption of inert gases (He, Ne, Ar, Kr, Xe) on carbon nanotubes began quite recently.[75–81, 122, 262–273] These systems are of particular interest because they provide an ideal case of physisorption of various atoms on CNTs. Indeed, the nature of inert gases excludes chemical and(or) polar interactions between the gas atoms and molecules and the nanotube surface (or inner cavity).

One of the most widely used methods of theoretical research on the He(Ne, Ar, Kr, Xe)/CNT systems is the molecular dynamics approach used to calculate the adsorption isotherms, the heats of adsorption, the self-diffusion coefficients, activation energies and structural features of the adsorbed systems including the corresponding temperature and pressure dependences.

As an example, Fig. 17 presents the theoretical isotherms constructed for neon adsorption on an isolated CNT in the gravimetric storage capacity calculations[270] using the expression

$$C_g = \frac{N_{Ne} m_{Ne}}{N_{Ne} m_{Ne} + N_C m_C},$$

where N_{Ne} is the number of adsorbed neon atoms, N_C is the number of carbon atoms in the CNT, m_{Ne} and m_C are the corresponding molar masses at 50, 70 and 90 K and variable pressure (number of neon atoms). It follows that

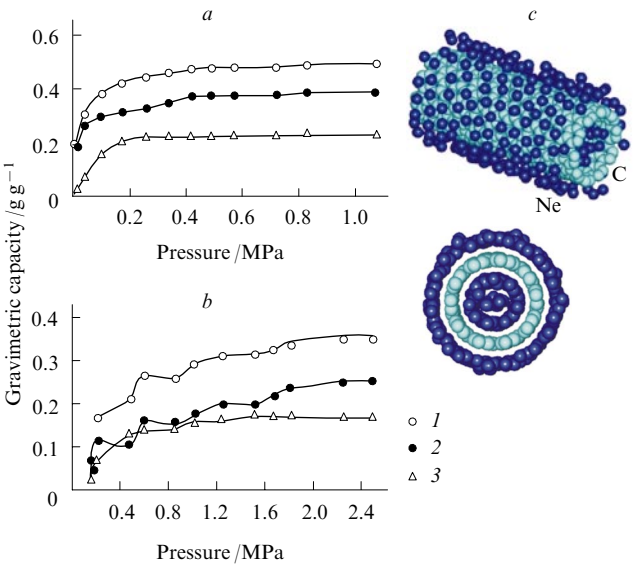


Figure 17. Theoretical adsorption isotherms of neon on isolated CNT at 50 (*a*) and 90 K (*b*).[270]
Total adsorption isotherm (*1*), adsorption on the outer nanotube wall (*2*) and in the nanotube cavity (*3*); (*c*) side view and the cross section of the atomic structure of the (10,10)CNTs bearing neon atoms adsorbed on the outer nanotube wall and in the nanotube cavity at 50 K.

C_g increases as the pressure increases and decreases as the temperature increases (the adsorption energy decreases from 0.17 to 0.09 eV per atom as the temperature increases from 50 to 90 K, see Ref. 270). In other words, the adsorption of neon should proceed most efficiently at low temperatures and elevated pressures.

Structural characteristics of He(Ne, Ar, Kr, Xe)/CNT systems are often analyzed using the radial distribution functions (RDFs). The RDF of, *e.g.*, the Ne/CNT system is defined as the ratio of the probability for the Ne atom to be located at the distance r from the nanotube surface to the probability of random distribution of atoms at the same distribution density of the neon atoms. A sharp RDF peak at $r \approx 3$ Å (at the minimum distance from the neon atom to the CNT surface, Fig. 18) indicates a 'perfect' type of

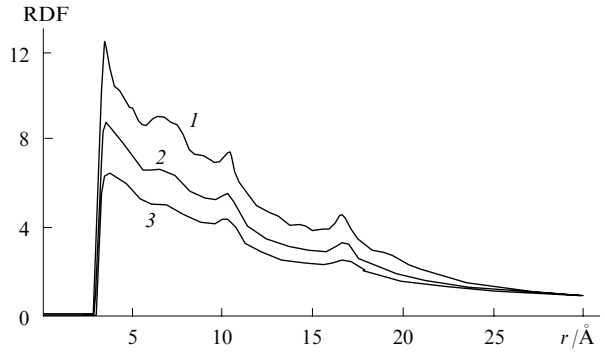


Figure 18. Radial distribution functions of neon atoms for the Ne/CNT system at 50 (*1*), 70 (*2*) and 90 K (*3*).[270]

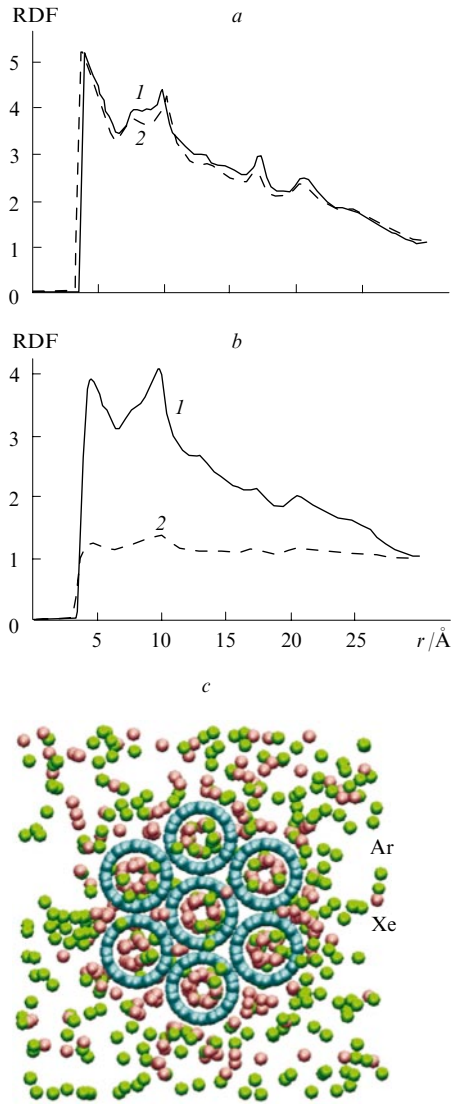


Figure 19. Radial distribution functions of Xe (*1*) and Ar (*2*) atoms for adsorption of Xe + Ar gas mixture on a bundle of (10,10)CNTs at 75 (*a*) and 300 K (*b*) and the atomic distribution pattern for the (Xe + Ar)/(10,10)CNT bundle system at 300 K (*c*).[272]

physisorption of neon atoms. As the temperature increases, the degree of adsorption decreases. Similar dependences were obtained in the studies of adsorption of other inert gases on CNTs.[264–266]

Recently, more complex processes of adsorption of binary [He + Ne,[271] Ar + Kr or Ar + Xe (Ref. 272)] and ternary [Ar + Kr + Xe (Ref. 273)] inert gas mixtures on CNT bundles were reported. As in the case of one inert gas, the gas mixtures are characterized by a general trend towards a decrease in C_g with an increase in temperature. However, they show selective adsorption, *i.e.*, atoms of the heavier inert gas are adsorbed on CNTs much better than atoms of the lighter inert gas. This was explained[272] by strengthening of van der Waals interactions between the inert gas atoms and nanotube in the order

$$\text{He} \longrightarrow \text{Ar} \longrightarrow \text{Kr} \longrightarrow \text{Xe}.$$

The selectivity of adsorption abruptly increases with temperature (Fig. 19). Based on this fact, it is assumed that CNTs may be basic to novel materials for separation and(or) storage of inert gases.

III. Simulation of the properties of atom-decorated non-carbon nanotubes

At present, there is intensive research on the synthesis and properties of nanotubular forms of not only carbon, but also other inorganic substances. Nanotubes based on layered compounds including boron nitride, boron carbides and boron carbonitrides, as well as d-metal dichalcogenides and oxides are best known. Metal, boron and silicon nanotubes were predicted and synthesized and various tubular forms of semiconductor materials were obtained.[4, 6, 24, 25, 274–281]

Materials based on non-carbon nanotubes show a variety of unusual functional properties, which allows one to significantly extend the potential fields of application of these systems and to propose new technological solutions. For instance, boron nitride (BN) nanotubes are suitable for fabrication of nanodiodes, optical fibres, transistors, electromechanical transducers and sensors.[276, 277] Metal dichalcogenide nanotubes are promising for application in microscopy as components of superhard nanocomposites and nanolubricants;[280] metal oxide nanotubes are of particular interest as biomaterials[281] as well as materials for gas sensors and catalysts.[6]

Attempts to control the properties of non-carbon nanotubes in targeted manner through their functionalization were also reported. In these investigations, an important role is played by computer simulation methods.

In this Section, we will discuss the results of simulation of the properties of atom-decorated inorganic nanotubes taking boron nitride, boron carbide (BC_x) and boron carbonitride ($B_xC_yN_z$) nanotubes as examples (Fig. 20). First, we should say that:

— these systems have been studied much poorer than the atom-decorated CNTs;

— heteroatomic nanotubes are characterized by a much larger number of possible adsorption sites compared to CNTs (*e.g.*, five adsorption sites for zigzag BN-nanotubes (Fig. 21); the number of adsorption sites increases as the chemical composition of nanotube walls becomes more complicated);

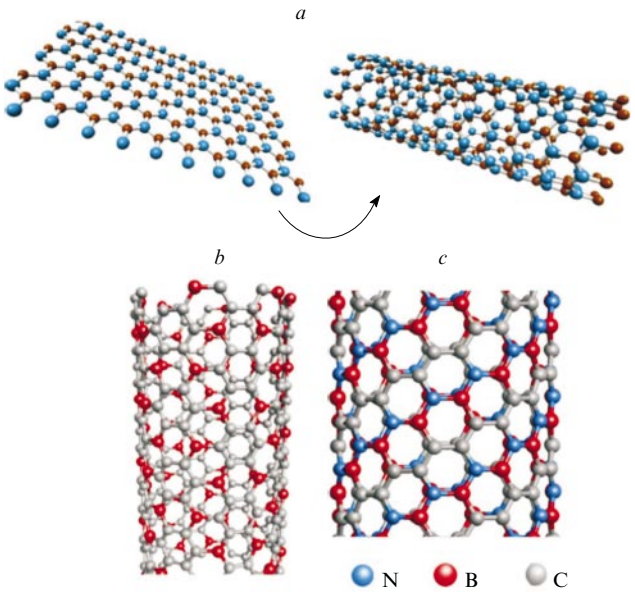


Figure 20. Models for 'rolling' of planar hexagonal boron nitride atomic network (so-called white graphene) into a BN nanotube (*a*) and structural fragments of the BC_3 carbide (*b*) and BC_2N carbonitride (*c*) nanotubes.[275]

— a distinctive feature of all BN, BC_x and $B_xC_yN_z$ nanotubes is their semiconducting character irrespective of the chemical composition, chirality and diameter; combining this feature with high chemical inertness and improved thermomechanical properties significantly extends the potential fields of application of these systems.[274–277]

The interaction of the BN, BC_x and $B_xC_yN_z$ nanotubes with hydrogen atoms and molecules was investigated by quantum chemical and molecular dynamics methods.[282–292] Both undecorated nanotubes (in this case, physisorption of hydrogen is similar to CNTs) and lithium-[290] (or titanium-[291,292]) doped nanotubes were studied. It was found that the Ti/BC_4N-NT systems can store up to 5.6 mass % of hydrogen.[291] Computer simulation of boron nitride nanotubes decorated with carbon,[293] oxygen,[294,295] sulfur,[296] lithium, silicon, tin,[297] fluorine[298–300] and some metal atoms[301] was reported.

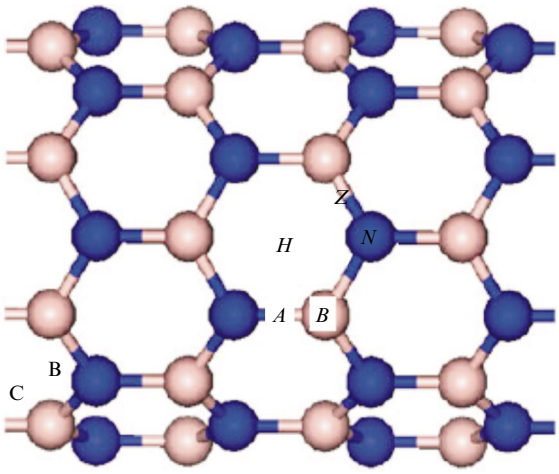


Figure 21. Five main possible adsorption sites on the surface of a zigzag BN-nanotube: 'above' nitrogen atoms (*N*), 'above' boron atoms (*B*), 'above' the mid-points of nonequivalent B—N bonds (*A* and *Z*) and 'above' the centres of B_3N_3 hexagons (*H*).

Now we will dwell on the results obtained in simulation of the magnetic properties of atom-decorated nanotubular systems. Recently, this research avenue has been rapidly developing in connection with the search for novel nanomaterials for spintronics, *e.g.*, for fabrication of magnetoresistive memory cells (spin memory), spin optical fibres, spin field-emitting transistors, spin-valve structures, insulators, magnetic field sensors, qubits for quantum computers, *etc.*[302–317]

The operating principles of such devices are based on the specific features of spin-dependent phenomena, such as spin transport, optical orientation of spins, spin relaxation, spin injection, *etc*. Of course, the corresponding materials should have a high concentration of spin-polarized electrons to allow one to simultaneously influence the charge and spin states of their electronic subsystems in controllable manner.

A promising method for search for such materials is the design of magnetic states of non-magnetic substances, in particular, semiconducting BN, BC_x or $B_xC_yN_z$ nanotubes.

Research in the field of transition of non-magnetic nanotubes to the magnetic state follows various routes. The simplest method consists in functionalization of NTs with atoms of magnetic d-metals which can be introduced into the nanotube cavity or between neighbouring nanotubes in NT bundles, used as dopants to replace some atoms in the nanotube wall, or adsorbed on the outer nanotube surface. The results obtained in the last-mentioned case will be discussed below.

In addition, it was found that the magnetic state of non-magnetic nanotubes can be changed by their functionalization with atoms of non-magnetic s- and p-elements or by creating specific types of structural defects.[306,308–312]

A particular case for transition of non-magnetic nanotubes to the magnetic state is due to the so-called edge effects, *viz*., rearrangements in the spin subsystems at the ends of the open nanotubes. These effects were studied using boron nitride nanotubes (BN-NTs) as an example[313] for BN-NTs with different types of nanotube ends, *viz*., polar ends (the nanotube end is formed by boron or nitrogen atoms) and nonpolar ends (the nanotube end is formed by boron and nitrogen atoms, $B:N \approx 1$). In the former case, each terminal boron or nitrogen atom has an unpaired electron due to the existence of 'broken' bonds. Depending on the even or odd number of boron atoms at the nanotube end, these nanotubes can show a non-magnetic (all boron atoms form dimers) or magnetic behaviour (a magnetic moment of the order of 1 μ_B is induced in the 'remaining' boron atom). The unpaired spin density distribution at the ends of the open BN-NTs is shown in Fig. 22. It is noteworthy that fine 'tuning' of the magnetic state of the open end of a BN-NT can be done by adsorbing hydrogen atoms at the nanotube end, namely, the formation of the B—H and N—H bonds causes the terminal boron and nitrogen atoms to go to the non-magnetic state. This offers prospects for practical application of BN-NTs with 'magnetic edges' as emitters of spin-polarized electrons (these can be, *e.g.*, the probe tips used in magnetic and magnetic exchange force microscopy).[313]

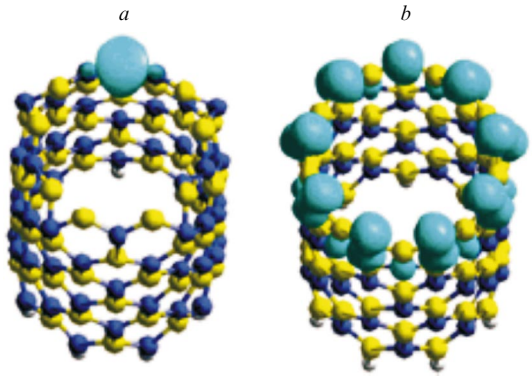


Figure 22. Spatial distribution of the unpaired spin density for the open-end (9,0)BN-NTs.[313]
The nanotube end is formed by boron (*a*) or nitrogen (*b*) atoms.

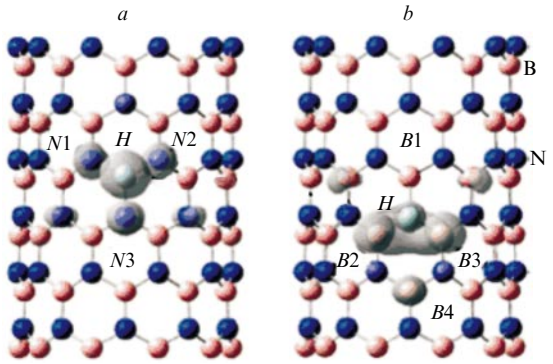


Figure 23. Spatial distribution of the unpaired spin density for a BN-NT bearing a hydrogen atom adsorbed on the boron (*a*) or nitrogen (*b*) atom.[285]

1. Non-carbon nanotubes decorated with atoms of s- and p-elements

Studies on transition of BN-NTs to the magnetic state by adsorption of hydrogen on nanotube walls revealed an interesting effect,[285] *viz*., adsorption of a hydrogen atom on either boron or nitrogen atom leads to the appearance of uncompensated spin density (Fig. 23). In both cases, the magnetic moment of the H/BN-NT system is about 1 μ_B. However, the magnetic state disappears if two hydrogen atoms are adsorbed on two neighbouring nitrogen or boron atoms. The effect was explained by subtle rearrangements of the spin states in the vicinity of these atoms. Based on the results of calculations,[285] a new method of synthesis of non-metallic magnetic nanotubular materials was proposed. Their magnetic characteristics are controlled by varying the degree of decoration of the BN-NT with hydrogen.

Similar predictions concerning the synthesis of magnetic nanotubes were made in studies of the spin states of BN nanotubes decorated with non-metal atoms, namely, C/BN-NT,[292, 293] Si(Sn)/BN-NT [297] and F/BN-NT.[298–300] It was found [293] that, *e.g*., the magnetic moment of the C/BN-NT system containing a single carbon atom adsorbed on the BN-NT ($\sim$2 μ_B) is twice as high as that of the H/BN-NT system. Adsorption of single Si or Sn atoms also causes the nanotube to go to the magnetic state.[297]

This effect is illustrated in Fig. 24 which presents the spin densities of the electronic states (DoS) of an undecorated BN-NT and a BN-NT with single tin or silicon atoms adsorbed on its surface. As can be seen, the Si or Sn atoms cause the appearance of the impurity levels with polarized spin states in the spectrum of BN-NT. The spin-'up' (↑) states lie below the Fermi level on the energy scale (they are occupied), whereas the spin-'down' (↓) states are shifted towards higher energies and lie above the Fermi level. As a result, local magnetic moments are induced on the adsorbed Si (Sn) atom. In addition, the interaction between the Si (Sn) atom and the BN-NT causes induced polarization of the density of states of the nanotube (see Fig. 24). As a

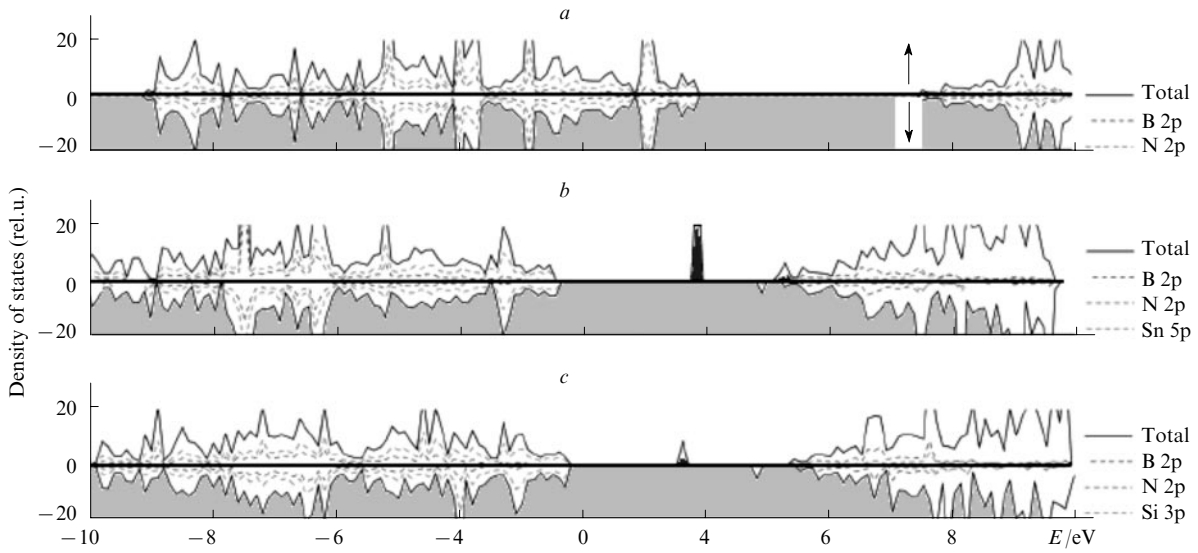


Figure 24. Spin densities of electronic states (DoS): a (8,0)BN-NT (*a*) and the (8,0)BN-NT bearing a Sn (*b*) and Si (*c*) atom adsorbed on the NT surface.[297] Shown are the contributions of the states of the adsorbed atoms that form the DoS peaks in the forbidden gap of the nanotube below the Fermi level.

result, the total magnetic moment of the Si(Sn)/BN-NT system is of the order of 2 μ_B. Interestingly, as in the case of the H/BN-NT system, the non-magnetic state of the BN-NT does not change upon adsorption of Si_2 or Sn_2 dimers.[297]

Chemisorption of fluorine on BN-NTs is also followed by polarization of the spin states (↑)/(↓) of the F/BN-NT system and by induction of a magnetic moment of about 0.99 μ_B.[300] But unlike the Si(Sn)/BN-NT systems whose magnetic moments are strongly influenced by the spin polarization of the states of the adsorbed atoms in the forbidden gap, the nature of the magnetic state of the system F/BN-NT is different. As an example, Fig. 25 presents the spin densities of the electronic states of the (8,0)BN-NT bearing a fluorine atom adsorbed on a boron atom in the nanotube wall. As can be seen, the states of the nitrogen atoms adjoining to the boron atom bearing the adsorbed fluorine atom are characterized by the largest spin splitting. The nature of this effect becomes clear taking into account the fact that the fluorine atom acts as acceptor of the electron density and partially 'devastates' the NT valence band whose edge is mainly formed by the N 2p states. In turn, these states undergo a spontaneous spin polarization, thus ensuring the magnetic state of the F/BN-NT system.[298, 299]

The spectral pattern of the F/BN-NT system[300] is characteristic of magnetic half-metals.[306, 307, 310] These materials have a nonzero charge carrier density at the Fermi level for one spin projection [density of states at the Fermi level $N\downarrow(E_F) > 0$] and a forbidden gap for the spin projection with the opposite sign [$N\uparrow(E_F) = 0$] (see Fig. 25). Therefore, the spin density polarization at the Fermi level for magnetic half-metals can be defined as follows:

$$P = \frac{N^{\downarrow}(E_F) - N^{\uparrow}(E_F)}{N^{\uparrow}(E_F) + N^{\downarrow}(E_F)} = 1.$$

The conductivity in magnetic half-metals is achieved through preferred spin channels. These materials exhibit unusual spin-dependent transport properties.

Generally, the appearance of magnetic states of non-magnetic nanotubes due to their decoration with non-magnetic atoms of s,p-elements can be illustrated by the scheme shown in Fig. 26. The appearance of magnetic states of non-magnetic semiconducting nanotubes (taking a BN-NT as an example) may go by two main scenarios.[312] One of them involves adsorption of the atoms X acting as acceptors of the electron density. In this case, the Fermi level E_F in the X/BN-NT system is shifted towards lower energies relative to its position in the undecorated BN-NT in such a manner that the upper region of the valence band (for BN-NT, it is mainly formed by the N 2p states) is devastated. As a result, a spontaneous spin polarization of the N 2p states appears and the uncompensated spin density ($\Delta\rho$) becomes mainly localized on the nitrogen atoms.

The other scenario assumes decoration of the BN-NT with the atoms Y which form additional 'impurity' levels with polarized spin states in the forbidden gap of the nanotube. The uncompensated spin density localized in the

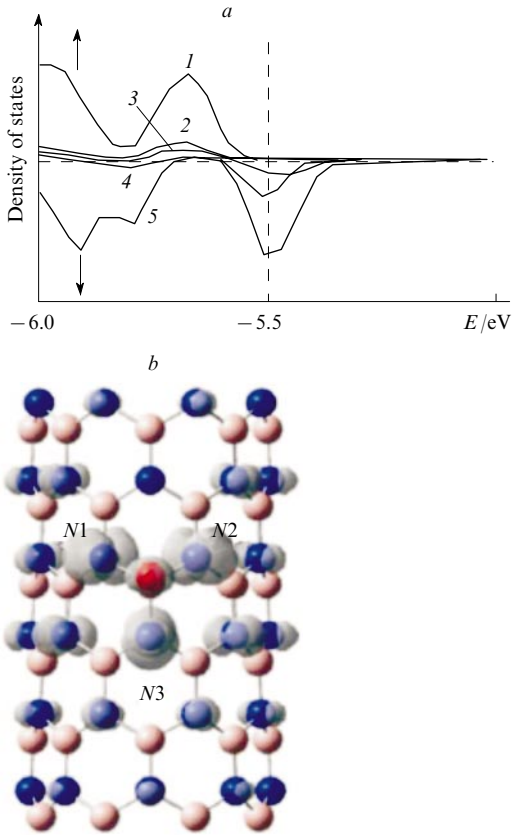


Figure 25. Spin densities of electronic states (DoS) of the (8,0)BN-NT bearing a fluorine atom adsorbed on the boron atom of the nanotube wall (*a*) and the distribution of the uncompensated spin density ($\Delta\rho = \rho^{\uparrow} - \rho^{\downarrow}$) in this system (*b*).[300]
Shown are the DoS of the fluorine (*1*), nitrogen (*N*1 + *N*2) (*2*), nitrogen *N*3 (*3*) and boron (*4*) atoms and the total DoS (*5*).

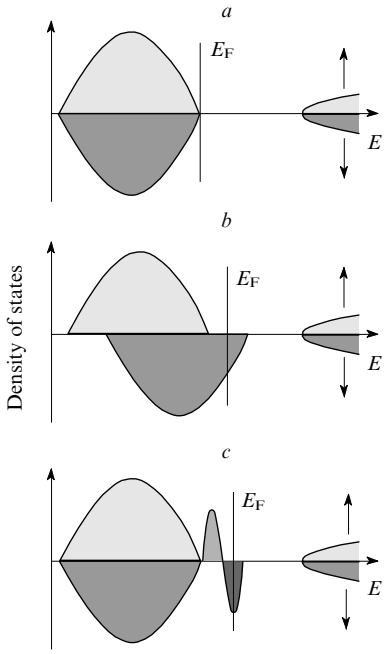


Figure 26. Models for possible mechanisms of transition of non-magnetic nanotubes to the magnetic state upon decoration with non-magnetic atoms of s- and p-elements taking a BN-NT as an example.
Density of spin states for the initial nanotube (*a*) and transition of the BN-NT to the magnetic state owing to spin polarization of the N 2p states (*b*) and the states of the adsorbed atoms (*c*).

Y/BN-NT systems on both the adsorbed atom and the nearest neighbouring atoms of the nanotube wall is due to the induced polarization of their spin density.

2. Non-carbon nanotubes decorated with d-metal atoms

The interaction of BN and $B_xC_yN_z$ nanotubes with particular d-metal atoms was studied experimentally [274–278, 314–317] and theoretically.[292, 301, 318–322] Table 5 presents the results of the binding energy and magnetic moment calculations for single metal atoms M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn. Each atom M was placed in five possible adsorption sites, *viz*., above the nitrogen (*N*) and boron (*B*) atoms, above the mid-points of the non-equivalent B—N bonds (*A* and *Z*) and above the centre of the B_3N_3 hexagon (see Fig. 21). As can be seen, for most 3d-metals one has $E_b > 1.5$ eV per atom (the exceptions are Fe and Cu for which one has $E_b < 0.6$ eV per atom); therefore, chemisorption of these metals on BN-NT is possible. A particular case is zinc characterized by $E_b \approx 0$. In addition, different atoms have different preferred adsorption sites. For instance, the maximum E_b values were obtained for adsorption of the vanadium atom on the boron atom, the manganese atom on the nitrogen atom, the Sc, Ti and Cr atoms on the centre of the B_3N_3 hexagon (*H* site) and the Co, Ni and Cu atoms on the mid-points of the B—N bonds (*A* site). The Fe/BN-NT system differs from the systems decorated with other metal atoms in that one has $E_b < 0$ for the *N* and *H* adsorption sites.

Changes in the electronic spectrum and magnetic properties of BN-NTs upon their decoration with 3d-metal atoms are very interesting (Fig. 27).[301] Here, the situation goes by the second scenario which assumes the appearance of additional 'impurity' levels in the forbidden gap of the decorated BN-NTs (see Fig. 26).

By and large, the changes in the electronic properties in the systems

$$\text{Sc/BN-NT} \longrightarrow \ldots \longrightarrow \text{Zn/BN-NT}$$

can be described taking into account two factors:

— the shift of the proper energy levels of the atoms M towards higher binding energies with an increase in the atomic number (along the period), and

— the spin polarization of the atoms M.

In the Sc/BN-NT system, the Sc 3d orbitals are admixed to the bottom of the conduction band, being partially filled. As a result, this system behaves as a metal, similarly to the Ti/BN-NT system. The spectrum of the V/BN-NT system is fundamentally different. The Fermi level is in the region of the d↑ states of the vanadium atom and in the gap of the spectrum of the d↓ states of the vanadium atom. As a result, the system exhibits the properties of a magnetic half-metal, as do the Mn/BN-NT and Fe/BN-NT systems. The Cr/BN-NT system shows the properties of a magnetic semiconductor, whereas Co(Ni,Cu)/BN-NT behave as magnetic metals. Finally, decoration of the BN-NT with zinc does not change the semiconducting character typical of the undecorated BN nanotube.

Thus, calculations [301] showed that, in principle, decoration of BN-NTs with various 3d-metal atoms allows one to obtain a variety of nanotubular materials including non-

Table 5. Metal atom – nanotube binding energies and the magnetic moments of the metal atoms in the M/BN-NT systems (isolated metal atom on the BN nanotube surface).[301]

M	AS [a]	E_b /eV per atom	μ/μ_B	M	AS [a]	E_b /eV per atom	μ/μ_B
Sc	*B*	0.386	1.224	Fe	*B*	0.064	3.479
	N	0.859	0.713		***N***	−0.126	3.452
	A	0.505	1.192		*A*	0.034	3.492
	Z	1.283	0.484		***Z***	**0.140**	3.473
	H	**1.625**	0.481		*H*	−0.184	3.464
Ti	*B*	0.711	2.200	Co	*B*	0.993	2.157
	N	0.782	2.278		***N***	0.792	2.074
	A	0.801	2.283		***A***	**1.191**	1.893
	Z	0.786	2.084		*Z*	0.669	2.330
	H	**1.357**	1.693		*H*	0.441	2.476
V	***B***	4.293	3.325	Ni	*B*	1.442	0.200
	N	1.029	3.359		***N***	1.490	0.108
	A	3.749	3.282		***A***	**1.649**	0.113
	Z	2.232	3.271		*Z*	1.546	0.133
	H	3.824	3.211		*H*	0.211	1.175
Cr	*B*	3.243	4.438	Cu	*B*	0.520	0
	N	1.112	4.366		***N***	0.457	0
	A	2.367	4.401		***A***	**0.561**	0
	Z	2.672	4.421		*Z*	0.417	0
	H	**4.006**	4.457		*H*	0.224	0.206
Mn	*B*	4.602	4.439	Zn	*B*	0.007	0
	N	**5.193**	4.562		***N***	−0.001	0
	A	1.853	4.582		*A*	0.005	0
	Z	2.191	4.463		*Z*	0.005	0
	H	3.480	4.566		*H*	0.009	0

Note. The parameters of the most energetically favourable sites are given in semi-bold. [a] The types of the adsorption sites are shown in Fig. 21.

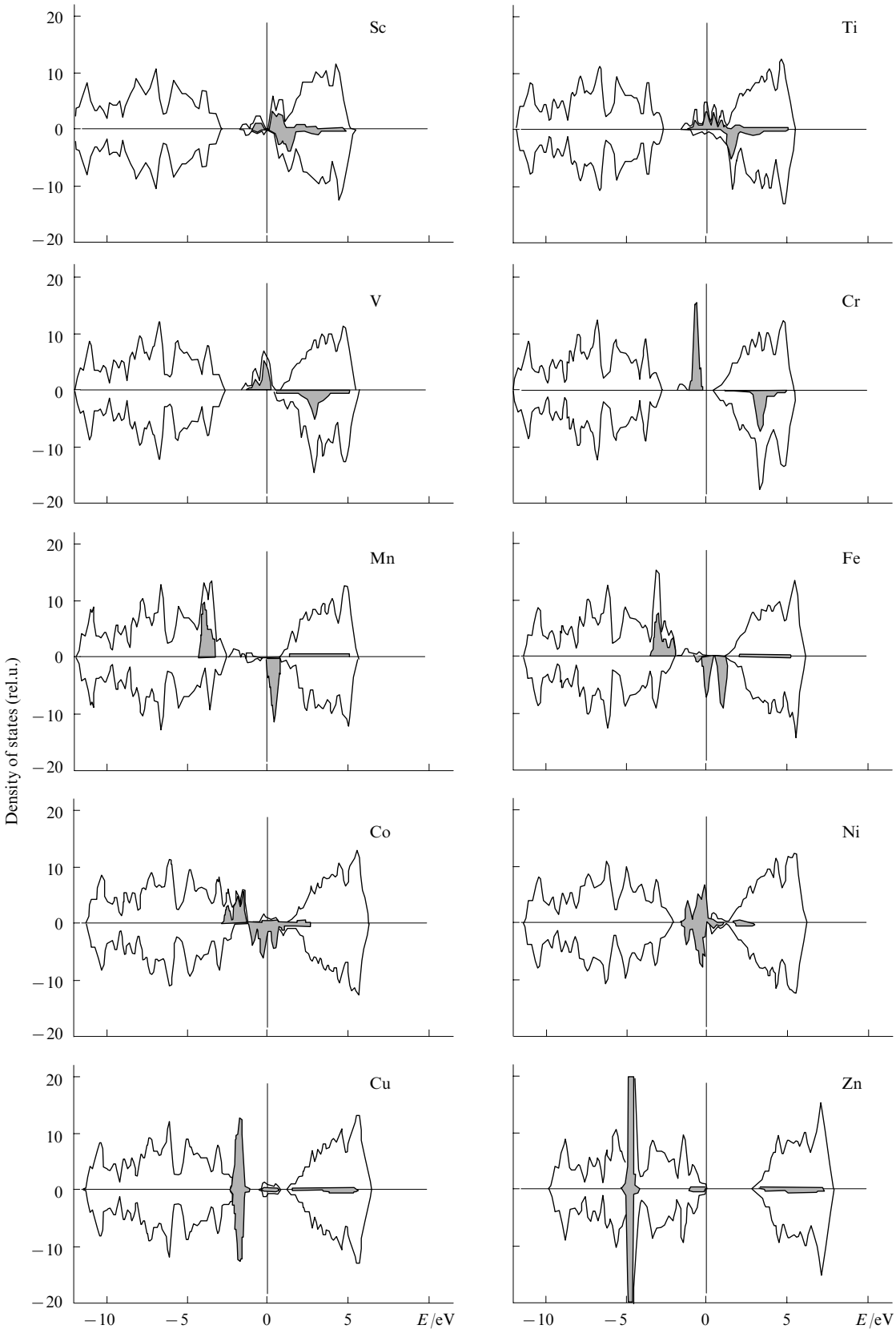


Figure 27. Spin densities of states for the systems M/zigzag (8,0)BN-NT bearing single metal atoms (M = Sc, V, Mn, Co, Cu, Ti, Cr, Fe,Ni, Zn) adsorbed at the most energetically favourable sites (see Table 5).[301]
The densities of states of the M atoms are given in grey.

magnetic (metal Cu/BN-NT or semiconductor Zn/BN-NT) and magnetic ones (metals, half-metals or semiconductors).

Of course, many issues posed in the studies of the systems in question are still to be solved (a key problem concerns the clustering mechanism of metal atoms on the BN-NT surface and their effect on the properties of such systems).

Summing up, mention may be made of a study [318] whose authors simulated the decoration of some edges of an open BN-NT with 3d-metal atoms. It was shown that the formation of metallic 'caps' at the nanotube ends is energetically favourable and that the formation of such structures (Fig. 28) allows one to control the conducting properties and the work functions of such systems; this is of importance for the design of, *e.g.*, field emitters for displays.

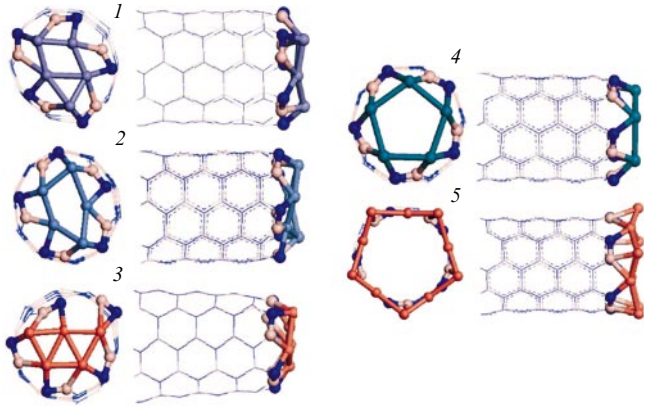


Figure 28. Optimized structures of 'caps' for the open (5,5)BN-NT formed by five (*1*–*4*) and ten (*5*) atoms: Fe (*1*), Ni (*2*), Co (*3*) and Cu (*4*, *5*).[318]
The atomic configurations of the 'caps' differ from one another depending on the type of the metal atom and on the number of metal atoms used for functionalization of the open BN nanotube.

IV. Conclusion

In this review, we tried to present the state of the art in the studies on atom decoration of nanotubes and to generalize the results of investigations carried out by modern quantum chemical and molecular dynamics methods used in computer materials science. These methods are efficient tools for the simulation of atom-decorated nanotubular materials, theoretical research on their properties and elaboration of methods for targeted control of these properties. They are also useful for prediction of novel nanomaterials.

Using the molecular dynamics method, one can solve a wide range of problems first of all concerning the formation of atom-decorated NTs. The method allows one to perform theoretical evaluation of the gravimetric storage capacity of the systems being simulated (depending on different conditions including the composition, temperature and pressure of the gas phase), the nanotube chirality and diameters, the intertube distances in NT bundles, *etc.*, as well as to construct the adsorption isotherms.

Quantum chemical methods are the most efficient for the description of the microscopic properties of atom-decorated nanotubes (the energy and type of the adsorbed atom – NT chemical bond), the choice of the most energetically favourable adsorption sites, the atomic and electronic structures and the magnetic, mechanical and other properties of the modified systems. They are also suitable for simulation of novel types of atom-decorated nanotubes and prediction of their properties.

To date, numerous studies on atom-decorated NTs were performed using both groups of methods of computer materials science. This first of all concerns carbon nanotubes decorated with hydrogen, oxygen, alkali, alkaline-earth metal, transition-metal, halogen and inert gas atoms.

Atom-decorated NTs containing atoms of other elements are studied much poorer. For instance, information on the systems N/CNT,[323] Si/CNT,[324] Ga/CNT [325] and Ru/CNT [326, 327] is scarce. Nanotubes decorated with atoms of 4f- and 5f-elements have almost not been investigated, although the first experimental studies in this field (for, *e.g.*, the system Er/CNT [328]) are now available.

Most data on atom-decorated non-carbon NTs were obtained for the systems based on the BN, BC_x and $B_xC_yN_z$ nanotubes. The results of model calculations for systems containing semiconducting nanotubes made of related materials [329] (AlN, GaN or SiC [330–332]) are available; however, studies of other large groups of inorganic nanotubes (*e.g.*, metal dichalcogenides and oxides) have almost not been carried out. We believe that setting up research in this field will be of great importance for future progress in the materials science of nanotubular systems.

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