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CHEMICAL PHYSICS OF NANOMATERIALS

Peculiarities of the Decoration of Carbon Nanotubes with Transition Metal Atoms

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Abstract—Carbon nanotubes decorated with transition metal, in particular, scandium, titanium, and vanadium, atoms offer promise for use in various applied science fields. We report the results of quantum-chemical calculations of the structure of the metallic layer of atoms of these metals coating the surface of (9, 0) and (10, 0) carbon nanotubes. It was shown that uniform one-layer coating by scandium and titanium could form on nanotubes with diameters no less than the diameter of (10, 0) nanotubes. Vanadium atoms could not uniformly cover nanotubes irrespective of their diameters.

Keywords: carbon nanotubes, decoration, transition metal atoms.
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INTRODUCTION

Currently, interest in systems based on carbon nanostructures decorated with metal atoms has increased substantially. Such structures are, for instance, carbon nanotubes (CNTs) which can serve as matrices for the production of very thin metal filaments with a controlled size [1]. Such filaments can be used as conducting junctions in molecular nanoelectronic devices and are of interest as solid-state material for storage of hydrogen.

Calculations performed jointly by workers of the National Institute of Standards and Technology (USA) and Bilkent University (Turkey) showed [2, 3] that one titanium atom on a single-walled CNT can bind up to 4 hydrogen atoms, and the replacement of titanium with scandium allows 5 hydrogen molecules to be bound. Yildirim et al. suggested a model of coating carbon nanotubes with transition metals. The model was based on the suggestion that coatings were unifiorm and one-layer. Uniformity is here understood as the equality of distances between metal atoms on the surface of CNTs.

This suggestion seems to be not vary accurate for several reasons. First, images of such structures obtained by transmission electron microscopy [1] show that the thickness of coatings, for instance, by titanium atoms is several nanometers, that is, coatings are multilayer. Secondly, the results of quantum-chemical calculations show that scandium atoms more preferably form metal clusters on the surface of (8, 0) CNTs [4], like titanium atoms on the surface of fullerene C_{60} [5]. It follows that coatings under consideration cannot be called uniform. But the idea of the possibility of using carbon nanotubes decorated with light transition metal atoms for the sorption of molecular hydrogen remains fairly interesting. The main question is that of what is the coating in question. Indeed, in the works cited above [4, 5], the interaction of CNTs with several metal atoms was considered, but the situation of a more complete coating was ignored. For this reason, we cannot with certainty say what is in reality the structure of a metallic layer on the surface of carbon nanotubes.

In [6], we considered the interaction of CNTs with separate scandium and titanium atoms. We showed that they could diffuse over the surface under normal conditions and pass from one position into another. This was a substantiation of the ability of light transition metal atoms to cover CNTs by a metallic layer. The purpose of the present work was to study the structure of a surface metallic layer covering (9, 0) and (10, 0) nanotubes and formed by several layers of scandium, titanium, and vanadium atoms separately.

METHOD OF CALCULATIONS AND DETAILS

This is a theoretical study based on quantum-chemical modeling. All the calculations were performed using density functional theory (DFT) [7, 8]

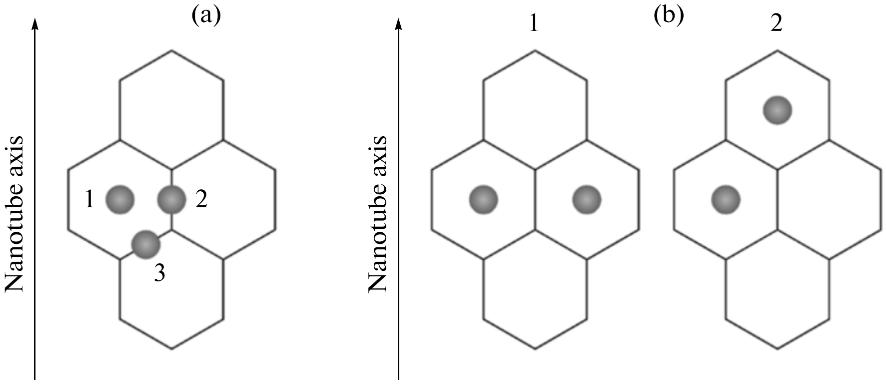

Fig. 1. Possible arrangements of (a) one and (b) two metal atoms above the surface of a CNT.

and the PBE exchange-correlation potential. We used the Vienna ab-initio Simulation Package (VASP) [9–11]. In this package, calculations are performed using the pseudopotential method and the expansion of wave functions in the basis set of plane waves with the kinetic energy 286.7 eV. To effectively decrease the number of basis functions and increase the rate of calculations, Vanderbilt Ultrasoft Pseudopotentials were used for all the atoms [12].

We considered coating of carbon nanotubes with chirality indices (9, 0) and (10, 0) by transition metal (V, Ti, and Sc) atoms. The distances between supercells in the directions perpendicular to CNT axes were no less than 10 Å to exclude the interaction of metal atoms from neighboring supercells in these directions. That is, we took into account the periodicity of carbon nanotubes only in one direction, along their axes. Quantum-chemical calculations were performed with the optimization of the geometric parameters of all the structures.

The specific energies of metal atom–CNT bonds were calculated by the equation

$$E = \frac{E_{\mathrm{CNT}-n\mathrm{Me}} - E_{\mathrm{CNT}} - nE_{\mathrm{Me}}}{n},$$

where $E_{\mathrm{CNT}-n\mathrm{Me}}$, E_{CNT}, and E_{Me} are the total energies of CNTs with n metal atoms, without metal atoms, and the metal atom itself (in what follows, Me is a metal atom), respectively, obtained in calculations.

RESULTS AND DISCUSSION

At the first stage, we studied the special features of the interaction of one Me atom with the surface of a CNT; that is, we considered the geometric and energy characteristics of compounds. To determine the place and mode of the addition of metal atoms, we analyzed three possible positions (Fig. 1a). It was shown (Table 1) that the addition of a metal atom at position 1, in the center of a carbon hexagon, was most favorable, because the specific Me–CNT bond energies were than highest in magnitude. The distance between Me and the nearest CNT atoms was then 2.08–2.22 Å. Note that the specific energy of Me bonds decreases in (10, 0) compared with (9, 0) nanotubes because of a decrease in the curvature of the surface of nanotubes and, therefore, an increase in the fraction of the sp^2 hybrid state of carbon atoms compared with the sp^3 hybrid state.

Next, we studied systems consisting of CNTs and two Me atoms situated in neighboring hexagons. Two positions of metal atoms with respect to each other were considered (Fig. 1b). It was shown (Table 1) that the occurrence of metal atoms in position 1 was most favorable energetically. This is evidence of the possibility of the formation of a belt of metal atoms around a CNT.

At the next stage, metal atoms placed in the centers of hexagons were arranged in one or two ring belts

Table 1. Specific energies of Me–CNT bonds (eV)

Number of Me atoms	CNT	Position								
		1	2	3	1	2	3	1	2	3
		Sc			Ti			V		
1	(9, 0)	–2.42	–1.67	–1.68	–2.71	–1.76	–1.77	–3.73	–3.44	–2.61
	(10, 0)	–1.83	–1.16	–1.18	–2.05	–1.16	–1.17	–3.01	–1.90	–1.93
2	(9, 0)	–2.78	–2.76	–	–3.41	–3.16	–	–4.75	–4.25	–
	(10, 0)	–2.42	–2.41	–	–3.14	–2.84	–	–4.44	–4.29	–

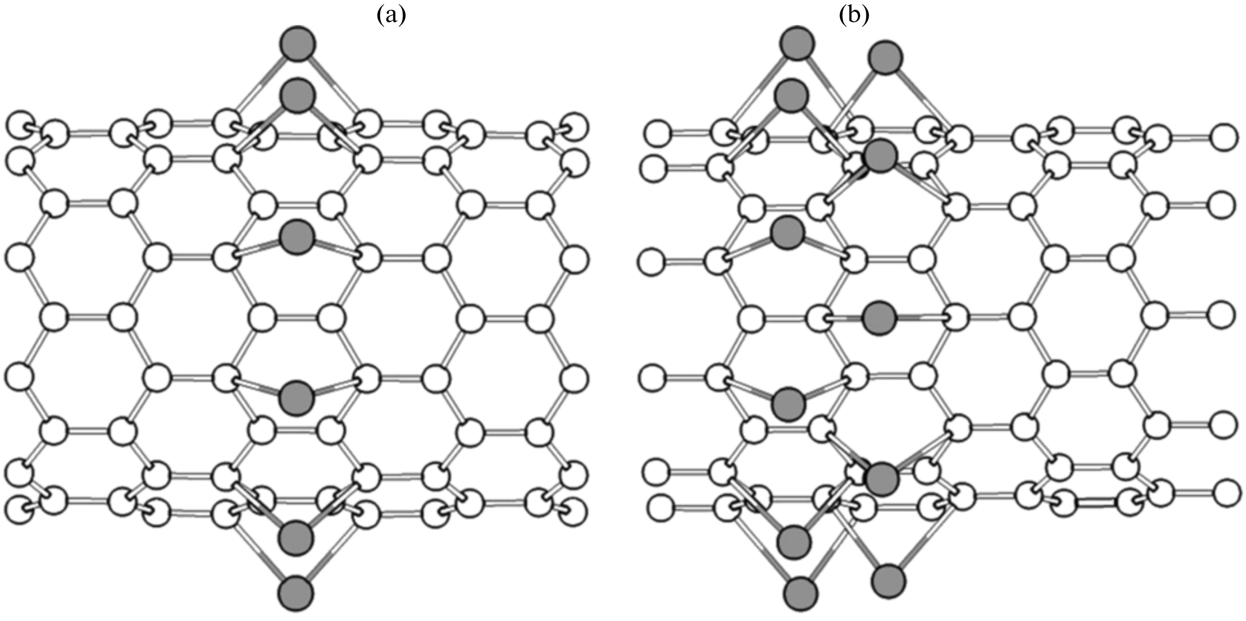

Fig. 2. Optimized (10, 0) CNT structures with (a) one and (b) two ring belts of titanium atoms on the surface.

around nanotubes (Fig. 2). Clearly (Table 2), the specific energies of metal bonds are larger in magnitude when two belts are formed. Indeed, the stabilization of structures and, therefore, a decrease in their total energy additionally occur because of interaction between Me atoms. It follows that the formation of a metallic layer on the surface of CNTs is energetically favorable.

While optimizing the geometric parameters of structures, we found that metal atoms shift from the initial positions at the centers of hexagons toward each other. As a result, small clusters are formed on the surface of CNTs. It then makes sense to consider maximum and minimum distances between Me atoms, which are distances between clusters and between metal atoms within a cluster, respectively. Clearly, the closer the ratio between them to one, the more uniform is coating.

A comparison of these distances (Table 3) leads us to conclude that, with (9, 0) CNTs, coating can hardly be called uniform, because the ratio between the maximum and minimum distances is then 1.17 for scandium and much larger for titanium (1.55) and vanadium (2.39). In (10, 0) CNTs, this ratio decreases for scandium (1.02) and titanium (1.04) because the minimum distance increases and the maximum distance decreases simultaneously. That is, these parameters tend to certain values, which must likely correspond somehow to interatomic distances in crystals of these metals. In scandium crystals, the distance between neighboring nodes is 3.25 Å, and, in titanium crystals, it is 2.89 Å. The distances obtained in this work are slightly smaller than the experimental values, because real crystals have three-dimensional structures, whereas the metallic layer on the surface of CNTs that we are considering can be assumed to be two-dimensional. It follows that uniform coating of carbon nanotubes by scandium and titanium can be obtained by selecting them according to the corresponding diameter. Clearly, these CNTs should be no smaller than (10, 0) nanotubes. In nanotubes with a smaller diameter, clusterization of metal atoms on their surface

Table 2. Specific energies of Me–CNT bonds in one and two rings covering nanotubes (eV)

CNT	Number of rings	Number of Me atoms	Sc	Ti	V
(9, 0)	1	9	–2.63	–2.75	–3.66
	2	18	–2.95	–3.61	–5.06
(10, 0)	1	10	–2.57	–2.72	–3.76
	2	20	–2.78	–3.31	–4.91

Table 3. Minimum (min) and maximum (max) distances between Me atoms covering CNTs by two belts (Å)

CNT	Sc		Ti		V	
	min	max	min	max	min	max
(9, 0)	2.91	3.41	2.43	3.76	1.88	4.50
(10, 0)	3.01	3.08	2.63	2.74	1.96	4.85

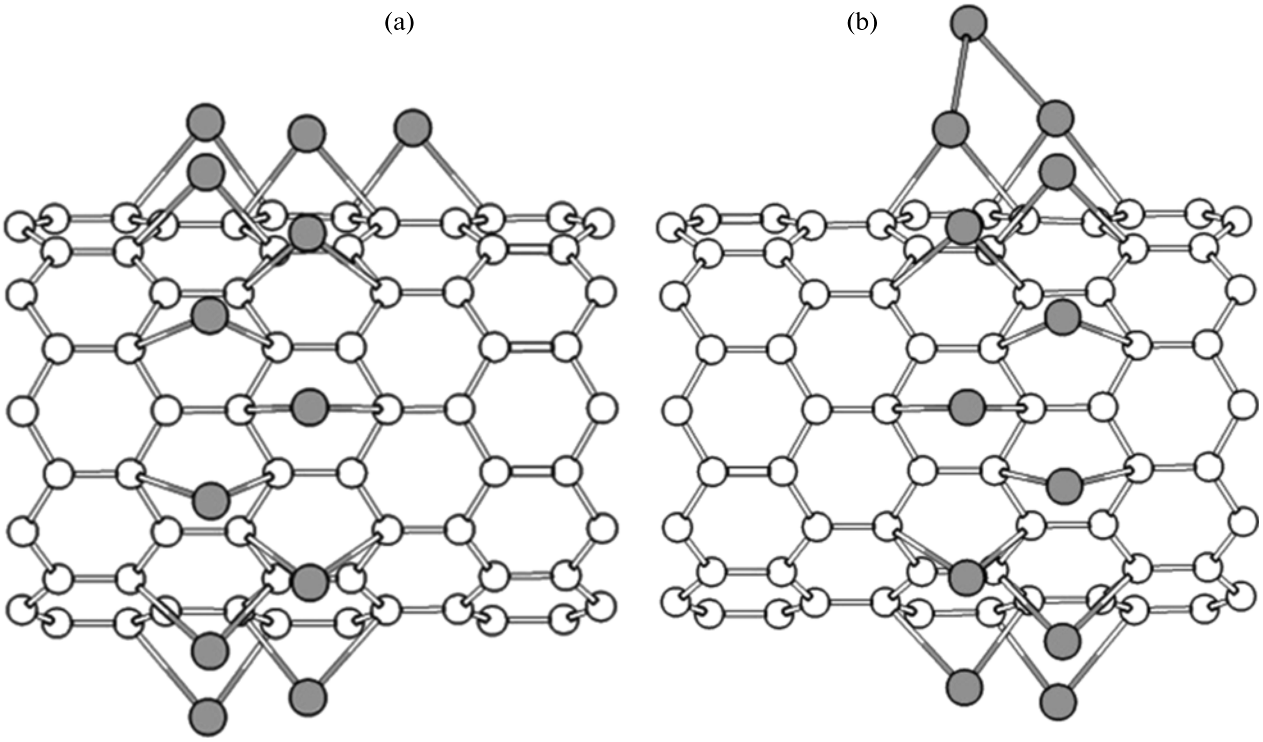

Fig. 3. Optimized (10, 0) CNT structures with two ring belts of titanium atoms and one atom (a) near and (b) above them.

rather than the formation of a uniform layer should occur.

The situation with vanadium is somewhat different. The point is that the interatomic distance in vanadium crystals is 2.62 Å. Since the values obtained for scandium and titanium are on average smaller than interatomic distances in their crystals by approximately 0.2 Å (in (10, 0) CNTs), a similar difference should be observed for vanadium in the most uniform coating of CNTs. That is, the mean distance between V atoms in a layer on the surface of a carbon nanotube should be ≈2.42 Å. This creates a problem for uniform coating of CNTs, because the distance between the centers of hexagons in the graphite plane is ≈2.46 Å, and graphite can be treated as a carbon nanotube with an infinitely large diameter. It follows that vanadium atoms will always combine into clusters on the surface of arbitrary CNTs irrespective of their diameters, and a uniform coating will not form.

At the final stage, we modeled the interaction of two metallic rings on CNT surfaces with a separate metal atom situated either near them in the center of a neighboring hexagon or above them (Fig. 3). We found (Table 4) that the energy difference between these two situations was insignificant. It follows that the formation of one or two metallic layers on the surface of CNTs is equiprobable. This means that the decoration of carbon nanotubes with light transition metal atoms should occur with the formation of a multilayer surface coating.

Table 4. Specific Me–CNT bond energies in two ring belts covering nanotubes and a separate metal atom above them and near them (eV)

CNT	Number of Me atoms	Sc		Ti		V	
		above	near	above	near	above	near
(9, 0)	19	–2.92	–2.96	–3.63	–3.64	–5.04	–5.06
(10, 0)	21	–2.78	–2.77	–3.39	–3.31	–5.01	–5.01

CONCLUSIONS

Quantum-chemical modeling showed that scandium, titanium, and vanadium atoms more preferably add to (9, 0) and (10, 0) carbon nanotubes in the centers of their six-membered rings. The strength of bonds increases in this series of metals. The addition of the second metal atom is more favorable energetically into a neighboring six-membered ring in the direction perpendicular to the axis of the nanotube. More complete coating of the objects studied is also energetically favorable. Uniform coating in the first layer can be formed by scandium and titanium atoms on the surface of nanotubes with diameters no smaller than that of (10, 0) nanotubes. Vanadium atoms cannot create a uniform coating in the first layer, because the distance between them should then be smaller than the distance between six-membered rings even in the graphite plane.

Generally, the decoration of carbon nanotubes by light transition metal atoms should produce multilayer coatings. This is a negative point in the potential use of these objects for the storage of molecular hydrogen. First, its weight fraction will be fairly small, and, secondly, the role played by carbon nanotubes in this process decreases, and the point is the interaction of hydrogen directly with the surface of a metal. It was shown in [4] that, in this situation, we should observe the dissociation of hydrogen molecules, which is undesirable, because atomic rather than molecular hydrogen is then retained, which hinders its desorption in practical use of carbon nanotubes decorated with metals. For this reason, the possibility of their use for this purpose is very questionable. In the future, it is suggested to consider these objects from the point of view of their potential use in molecular nanoelectronics.

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