

Monte Carlo Simulations for Carbon Nanotubes Intercalated with Different Atomic Species

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We performed Monte Carlo simulations for single- and double-walled carbon nanotubes intercalated with different atomic species (Fe, Ni, Co, and B). A relationship was established between the length of a carbon nanotube and the number as well as the type of the intercalating atoms. Carbon nanotube systems intercalated with Ni, Co, and B were shown to be more stable with temperature and retained a greater internal concentration of the intercalate atoms compared to the case of Fe intercalated systems where a substantial extrusion of atoms was observed as a result of thermal treatment.

Keywords: Carbon Nanotube, Intercalate Atoms, Monte-Carlo Method.

1. INTRODUCTION

Design of materials with preset physical and chemical properties determines both the tactics and the strategy of modern materials science. Studies of nanosize clusters are of great interest due to the growing need for new materials in electronics, bioengineering, chemistry, etc. Elucidation of a structure-property correlation for carbon nanotubes (CNT) and their derivatives is of vital importance. As of today, a substantial number of results have been reported on the phenomena related to CNT intercalate systems. For example, the synthesis and structure of alkali-metal- and iodine-intercalated single-walled CNT were studied in detail in papers.^{1–2} The authors of paper³ synthesised Fe- and Co-containing CNT via aerosol thermolysis of a toluene-ferrocene-cobaltocene mixture in inert atmosphere yielding nanoelectronics-grade ferromagnetic composites. Light-emitting diodes, based on CNT composites and ethylene glycol-water mixture with outstanding fluorescent properties, were reported in paper.⁴ Multi-walled CNT intercalation with B and N atoms was presented in papers.^{5–7} The authors of papers^{8–11} investigated the electronic properties of alkali-metal-, FeCl₃-, potassium iodide-, and barium- intercalated single-walled CNT. Modifying the electronic properties of multi-walled CNT by chemical doping with some inorganic fluorides was studied

in paper.¹² Intercalation effect on the Raman spectra and transport properties of CNT was reported in papers.^{13–16} Ref. [17] addressed magnetic properties of single-walled CNT intercalated with such transition metals as Mn, Fe, Co, and Ni.

In this paper we report theoretical results for single- and double-walled CNT intercalated with B as well as such metals (Me) as Fe, Ni, and Co. The comparative studies of the Me–Me and the Me–C (CNT wall) interaction reveal the predominant contribution of the Me–C interaction. The results obtained here are important for understanding of the structural modification, intercalation, and functionalization of CNT.

2. MODEL

Calculations by the Monte-Carlo method were performed as follows. We considered supercells of single-walled CNT (9, 0), each 0.68 nm in diameter, 3.64 nm-long and composed of 324 carbon atoms. One to eight metal atoms were placed inside the CNT at a distance of an effective interaction radius not exceeding 0.140 nm for Fe, 0.135 nm for Ni or Co, and 0.085 nm for B.

To model the double-walled CNT systems the following approximation was used: we employed selections of short CNT fragments made of either three (7.0 nm-long) or five (11.2 nm-long) benzene ring bands. Thus, we investigated a system of coaxial double-walled CNT (9, 0)&(19, 0)

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with the distance of 0.335 nm between the cylinders. The proportions of the intercalate “concentration” relative to the fixed CNT length were the same as for the single-walled CNT case. Like in the case of a single-walled CNT, the metal atoms inside the internal cylinder (9, 0) were placed along its rotation axis. However, the intertube space was filled with the metal atoms bearing in mind that the metal atom positions are less stable in the plane perpendicular to the CNT axis.

In our model, the interaction potential¹⁸ was directly linked to the Born-Mayer repulsion pair potential,¹⁹ which describes high-energy atomic collisions within the range of 0–0.14 nm. Interaction between the carbon atoms was described by the Tersoff-Brenner multi-particle potential²⁰ (with a cut-off radius of 0.21 nm) linked to the Zigler-Birzack-Litmark repulsion pair potential.¹⁹ The distance between the carbon atoms was accepted to be 0.139 nm and the distance between the walls of the double-walled CNT – 0.335 nm. The interatomic interactions for Fe–C, Ni–C, and Co–C (within the range of 0.195–0.375 nm) and for B–C (within the range of 0.170–0.180 nm) were described by the Lennard-Jones pair potential²¹ with the value of the potential energy of the Me–C interaction being ~0.11 eV at a distance of 0.235 nm. The characteristic time to generate a collision cascade was modeled to be 2 ps. The conservation of energy was observed in every cascade with an accuracy better than 0.1%. The initial coordinates of the metal atoms were selected according to the law of random numbers.

3. RESULTS AND DISCUSSION

As a result of our simulations of heating from 300 to 900 K of a single-walled CNT intercalated with a *d*-metal, an important regularity was discovered in the behavior of the CNT&Fe, CNT&Ni, and CNT&Co systems. Two Fe atoms were extruded from the CNT at a distance of 10.0–12.0 nm (Fig.1), while in the case of Ni, with the similar heating rate, only one atom was extruded at a distance of 5.5–6.0 nm. This phenomenon can be explained by a possible coordination of the Fe, Ni, and Co atoms to the π -orbital of a CNT quasiaromatic surface.

The behavior of the double-walled CNT with the intercalate was somewhat similar to that of the single-walled CNT. Figure 2 clearly shows how a previously complete

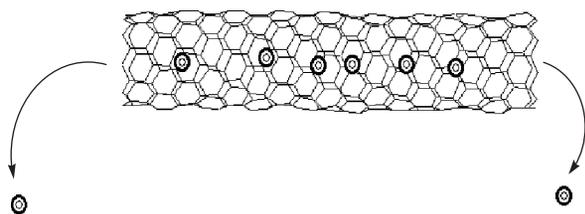


Fig. 1. CNT (9, 0) with Fe atoms. Two extruded Fe atoms are at distances of 12.0 nm and 10.0 nm from the open ends of the CNT.

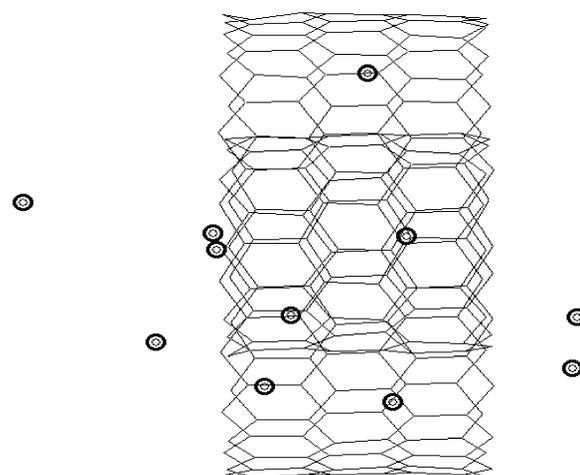


Fig. 2. Orthogonal projection of a fragment of a double-walled CNT (9, 0)&(19, 0) intercalated with Fe atoms.

system easily loses a great number of Fe atoms, in particular six out of eleven atoms, which makes it difficult to distinguish the chain of metal atoms. In their turn, the Ni and Co system proved to be more stable and produced losses of only four out of ten atoms in both cases (Fig.3). Moreover, the Ni and Co atoms formed chains of atoms with interatomic separations between 0.219 and 0.685 nm. The Ni and Co atoms were at a distance of 0.36–0.40 nm from the CNT open end, which is roughly three times the size of the atom itself, and, as a result, they did not feel the impact of the CNT walls (Fig.3).

The temperature dependence of the system potential is shown in Figure 4. As can be seen from the graph, the more stable system is the CNT intercalated with Ni. Moreover, all three cases produced stabilization of the nanostructure within the temperature range of 600–750 K, which was marked by the start and completion of extrusion of intercalate atoms from within a CNT. The start

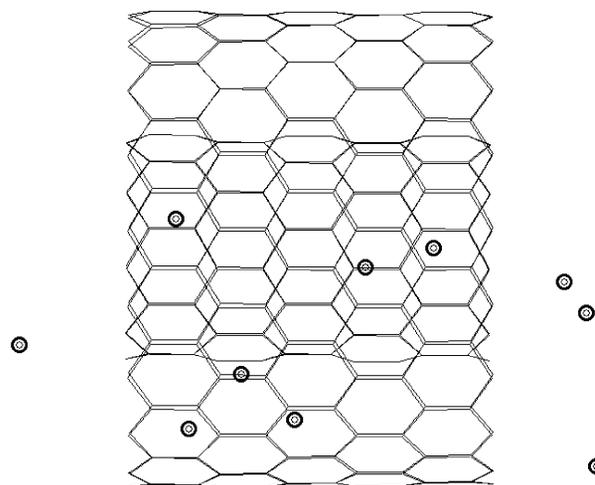


Fig. 3. Orthogonal projection of a fragment of a double-walled CNT (9, 0)&(19, 0) intercalated with Ni atoms.

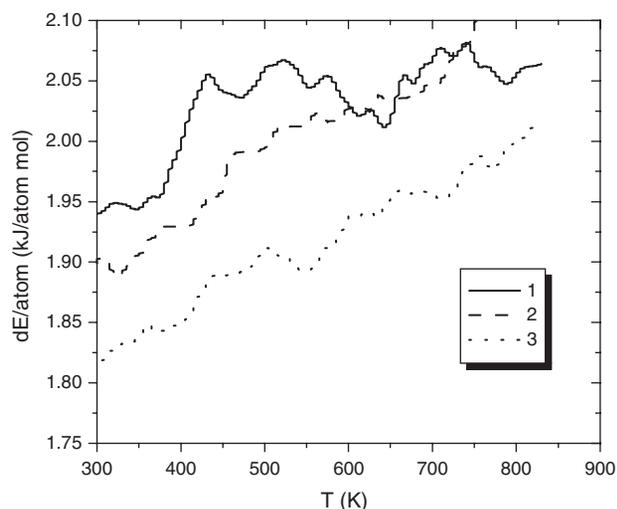


Fig. 4. Temperature dependence of stability of intercalated CNT systems: 1—CNT (9, 0) intercalated with Fe atoms; 2—CNT (9, 0) intercalated with Co atoms; 3—CNT (9, 0) intercalated with Ni atoms.

and completion values differed from system to system and varied within the range of 40–60 K.

Thereby, as the temperature increased (the temperature increase rate was the same in all the three cases), a less stable system (CNT&Fe) began extruding the intercalate atoms earlier (by ~ 40 K) compared to the CNT&Ni and CNT&Co systems. In their turn, the latter two nanostructures released part of the internal metal atoms only at 640–650 K remaining stable while heated up to 745 K.

Importantly, for the CNT&Fe system, there is a distinctive extremum feature within 640–655 K in the temperature dependence of the potential. This can be explained by a fast extrusion of redundant atoms, with eight Fe atoms per CNT length of 3.64 nm. From Figure 4 it is clear that the CNT&Fe system is more stable kinetically compared to the CNT&Co system due to the slower rate of Co atom extrusion.

When heated up to 750 K, all three systems exhibit a similar behavior indicating the lack of extrusion of the internal metal atoms and the increasing influence of the temperature on the system potential.

Furthermore, we performed temperature-dependent calculations for a system of a single-walled CNT of a similar size (9,0) intercalated with boron. We placed fifteen boron atoms inside the CNT. Simulations of the system demonstrated that at the temperature of 800 K the system lost four boron atoms, which represented a significant reduction of the boron concentration inside the CNT. Upon further heating, the thermally stable configuration of the system remained the same.

Unlike the CNT intercalated with Fe, Ni, and Co, the CNT&B system revealed an expected effect of system stabilization due to a greater $\pi \rightarrow p$ interaction of the CNT aromatic surfaces with the free p -orbitals of the boron atoms. The size of the d -orbitals in the Fe, Co, and Ni

atoms reduces this type of interaction, which impacts the thermodynamic properties of those systems.

Calculations were also performed for the system of double-walled CNT intercalated with boron atoms. The criteria for the selection of parameters for this system were similar to those for the double-walled CNT with Fe, Co, and Ni. Similarly to the case of the single-walled CNT&B, the behavior of the double-walled CNT&B system can also be predicted. Surprisingly, it turned out that the double-walled CNT&B are less stable compared to the single-walled CNT&B, contrary to the experimental results of⁷ where it was shown that the double-walled CNT&B systems survive up to 2473–2573 K. The authors of⁷ reported on the diffraction spectra of the synthesized compounds, consistent with clusters of a C_4B structure. It should be noted that the numerical simulations were starting from 0 K to ensure that no anomalies of the system's behavior would be lost in calculations up to 298.15 K.

4. CONCLUSION

Monte Carlo simulations for CNT intercalated with different atomic species demonstrated a correlation between the CNT length and the number and type of the atoms that CNT can retain as a result of thermal treatment. Thus, for the case of a 36.0 nm-long CNT (9, 0) supercell, extrusion of the Fe atoms was observed provided the number of the Fe atoms initially placed inside the CNT supercell was greater than seven. This phenomenon was specific to case the Fe atoms only and has to be born in mind during the process of modification of CNT with Fe either chemically or via ion impact. By the same token, CNT&Ni, CNT&Co, and CNT&B systems were shown to be more stable and retained a greater internal concentration of the intercalate atoms.

The systems studied were stable for 0.18–0.20 nm coordination distances of the $3d$ -metals near the CNT walls.

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