Effect of encapsulation of fullerene in semiconducting zigzag carbon nanotubes on optical and thermoelectric properties

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Abstract. We study the optical and thermoelectric properties of carbon nanotubes (CNTs) with encapsulated C$_{60}$ fullerene molecules. Using ab-initio methods, we calculate optical and thermoelectric parameters for CNT with fullerenes periodically located inside the nanotube at different distances from each other. Dependencies of these parameters on fullerene concentration and diameter of CNT are analyzed.

1. Introduction
Nanopeapods discovered by the author of Ref. [1] are hybrid systems of single-wall carbon nanotubes (CNTs) and fullerenes inside and linked with tubes by van der Waals interactions [2-5]. Nanopeapod systems are promising for use in nanoelectronics: solar cells, nano-emitters, etc. [2-4]. Fullerene arranged in an orderly manner represent a set of quantum dots in a one-dimensional superlattice. By varying the concentration of fullerenes inside, and the types of fullerenes, one can modulate the band structure of the CNT-fullerene system and control the electronic and phonon characteristics of nanopeapods.

In this work, using ab-initio methods, we calculate the optical and thermoelectric properties of CNTs (n,0) with fullerenes periodically located inside the nanotube at a fixed distance from each other.

2. Optical and thermoelectric properties
Semiconductor CNTs (14,0), (17,0) are considered. The distances between the C$_{60}$ fullerenes in nanopeapods were chosen equal to 10.32 and 22.74 Å. The diameter of the C$_{60}$ fullerene is 7.1 Å.

Table 1. Parameters of the investigated carbon nanotubes

| Chirality indice of CNTs | CNT diameter, D, Å | The smallest distance from the fullerene to the CNT wall, R, Å |
|-------------------------|--------------------|---------------------------------------------------------------|
| (14,0)                  | 1.096              | 2.03                                                          |
| (17,0)                  | 1.331              | 3.27                                                          |

Optimization of the considered systems CNT (14,0) -C$_{60}$- CNT (17,0) -C$_{60}$ (17,0). was carried out using the density functional method (DFT) implemented in QuantumATK (Synopsys). The cutoff
energy of the electron wave functions is 500 eV. To describe the effects of electron exchange and correlation, we used the Purdue-Burke-Ernzerhof approximation generalized to the case of solids (GGA-PBEsol). To generate k points in the Brillouin zone for all nanotubes, the Monkhorst-Pack method with a $1 \times 1 \times 24$ grid was used.

Transfer coefficients were calculated using the nonequilibrium Green's function (NEGF) method, the DFT method, and nonequilibrium molecular dynamics. We used the standard model, in which the central part of the tube is connected to semi-infinite left and right electrodes (see, for example, [5,6]). QuantumATK calculates the indicated thermoelectric coefficients according to linear response theory. The following relationships are used.

$$G_e = \left. \frac{dI}{dV_{\text{bias}}} \right|_{T=0}, S = \left. \frac{dV_{\text{bias}}}{dT} \right|_{I=0}, \lambda_e = \left. \frac{dQ}{dT} \right|_{I=0, \phi} = \left. \frac{I_{\phi}}{I} \right|_{dfT=0} = SV_{\text{bias}}.$$ 

**Figure 1.** Thermoelectric coefficients of the CNT (14,0) - C$_{60}$ system with distances between fullerene centers $R = 22.64$ Å (red color), $R = 10.32$ Å (black color) and pure CNT (14,0) (blue color).

Figure 1 shows the effect of the encapsulation of fullerenes in CNTs, at which a shift in the spectra readings to the range of negative energies is observed, which leads to a decrease in the Seebeck and Peltier coefficients and causes additional fluctuations in the spectra of electrical and thermal conductivity. The readings of the thermal conductivity coefficients decrease, which can be caused by a change in the Fermi level due to the encapsulation of the tube with fullerenes. Also, the created temperature gradient causes the phenomenon of entrainment of electrons by phonons.

The same calculations were performed for a semiconductor nanotube (17,0) with a distance of 10.32 Å between the centers of two neighboring fullerenes.
Figure 2. Thermoelectric coefficients of CNT (14,0) - C\textsubscript{60} systems with distances between fullerene centers R = 10,32 Å (blue color) and CNT (17,0) - C\textsubscript{60} systems with distances between fullerene centers R = 10,32 Å (black color).

Comparing the readings of the thermoelectric coefficients of CNT (14,0) and CNT (17,0) with the distance between the centers of two neighboring fullerenes 10,32 Å (Figure 2), it can be seen that an increase in the tube diameter leads to a resonance of the Seebeck and Peltier coefficients near zero energy. Also, an increase in the CNT diameter leads to an increase in the thermal conductivity coefficient, which may be associated with a large distance between the fullerene molecules and the tube wall. (see table 1)

Figure 3. a) Transmission spectrum of CNT (14,0) - C\textsubscript{60} (blue color) and CNT (17,0) - C\textsubscript{60} (black color); b) Transmission spectra of CNT (14,0) - C\textsubscript{60} systems with distances between fullerene centers R=10,32 Å (black color), R = 22,64 Å (red color) and CNT (14,0) (blue color).
The transmission coefficient of a CNT system (17,0) with encapsulated fullerenes at a distance of 10, 32 Å from each other is higher than that of a similar CNT system (14,0) (Figure 3 a). Transmission spectra of CNT systems (14,0) - C_{60} is approximately the same (within fluctuations) for the considered distances between fullerenes (Figure 3 b).

![Figure 4](image1.png)

**Figure 4.** The coefficients of dielectric constant and optical conductivity of CNTs (17,0) with encapsulated fullerenes, the distance between the centers of which is 10,32 Å.

![Figure 5](image2.png)

**Figure 5.** The coefficients of dielectric constant and optical conductivity of CNTs (14,0) with encapsulated fullerenes, the distance between the centers of which is 10,32 Å.
The dielectric constant in the short-wavelength spectrum of CNTs with encapsulated fullerenes is higher for the tube (14,0), while an increase in the diameter leads to an increase in the conductivity in the short-wavelength region of the spectrum (Figure 4, Figure 5). Accordingly, we can talk about high readings of the capacity of the considered nanotubes in the short-wavelength region of the spectrum. Also, an increase in the tube diameter leads to the appearance of small fluctuations in the conductivity index in the energy range from 1 to 2.5 eV.

3. Conclusions
Using ab-initio methods, we calculated optical and thermoelectric parameters for CNT (14,0) and (17,0) with fullerenes periodically located inside the nanotube at different distances from each other. Dependencies of these parameters on fullerene concentration and diameter of CNT are analyzed.

With a decrease in the nanotube diameter, the optical conductivity of the CNT-C\textsubscript{60} system in the short-wavelength spectrum increases. The thermal conductivity of CNT-C\textsubscript{60} depends on the distance between the encapsulated fullerene molecules and the diameter of the carbon nanotube.

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