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Thermoelectric properties of graphenylene nanotubes with encapsulated fullerenes

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Abstract. Thermoelectric properties of graphenylene nanotubes with encapsulated C_{60} fullerenes are studied by means of the DFT-based calculations. The electrical and thermal conductivities, Peltier and Seebeck coefficients, and thermoelectric figure of merit ZT are estimated for different distances between fullerenes and various chirality of graphenylene nanotubes.

Keywords: graphenylene nanotubes, fullerene, thermoelectric figure of merit

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Термоэлектрические свойства графениленовых нанотрубок с инкапсулированными фуллеренами

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Аннотация. Термоэлектрические свойства графениленовых нанотрубок с инкапсулированными фуллеренами C_{60} изучены с помощью расчетов на основе теории функционала плотности. Электро- и теплопроводность, коэффициенты Пельтье и Зеебека и термоэлектрическая добротность ZT рассчитаны для различных расстояний между фуллеренами и различной хиральности графениленовых нанотрубок.

Ключевые слова: графениленовые нанотрубки, фуллерен, термоэлектрическая добротность

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Introduction

In recent years, a large number of new two-dimensional carbon structures have been proposed and studied for use in nanoelectronics and hydrogen energy storage. Such two-dimensional materials, in particular, include graphenylene [1]. Graphenylene is the first example of a two-dimensional non-delocalized sp2-carbon network consisting of cyclohexatriene units with two completely different C–C bonds within the C_6 ring. It has periodically arranged pores with a diameter of 3.2 Å. Graphenylene is a semiconductor with a narrow direct band gap. Optimization and calculation of the electronic structure of graphenylene were carried out in [2, 3]. The values of the band gap obtained differ from each other, sometimes by an order of magnitude. This is because since the band gap is rather narrow, the value Eg is extremely sensitive to the position of atoms in the optimized structure and strongly depends on the choice of calculation method. In graphenylene, the distribution of electron density is completely different from graphene, since there is a certain alternation between neighboring bonds. Graphenylene nanoribbons were studied in [4]. Electronic spectra indicate that all considered nanoribbons could be classified as direct bandgap semiconductors. The calculated dependencies of bandgap on nanoribbon width show the identical scaling rules for armchair and zigzag graphenylene ribbons. A family-based classification used for the electronic structure of armchair graphene nanoribbons can not be extended to the case of graphenylene ones.

In [5, 6], new van der Waals heterostructures based on graphenylene were proposed and analyzed. In a recent work [7], the optical and thermoelectric properties of graphenylene and octagraphene nanotubes were studied using first-principles calculations. In the present work, the thermoelectric properties of graphenylene nanotubes with encapsulated fullerenes C_{60} for various types of nanotube chirality and different distances between fullerenes. Such structures are promising for thermoelectric power generators. We optimize and study the armchair graphenylene nanotube of 12.99 Å in diameter and zigzag graphenylene nanotube of 11.24 Å in diameter with encapsulated C_{60} fullerenes.

Materials and Methods

Calculations of the thermoelectric properties of the investigated semiconductor graphenylene nanotubes (Fig. 1) were carried out by means of the density functional theory (DFT) and the method of nonequilibrium Green's functions implemented in Quantum ATK [8]. We use the DFT to calculate the electron transmission and the force field method to estimate the phonon transmission. In the force field method, we use Tersoff's optimized empirical potential of the molecular dynamics of carbon systems. We used the PseudoDojo pseudopotential with a linear combination of atomic orbitals (LCAO) basis sets. HibridGGA was chosen as the exchange-correlation functional. The criteria for reliable convergence for the total energy and force are 10^{-6} eV and 0.01 eV/Å. The vacuum region 35 Å is used to eliminate boundary effects.

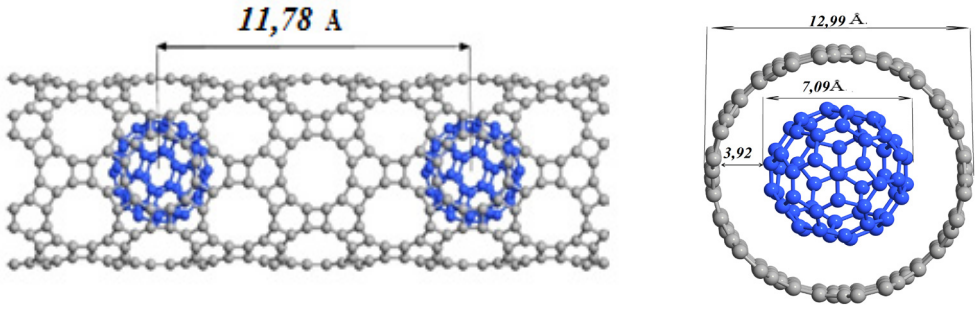

Fig. 1. Structure of a graphenylene nanotube with encapsulated C_{60} fullerenes

A density cut-off grid of 75 Ha (1 Ha = 27.21 eV) was applied, and the Monkhorst-Pack method [9] with a set of k points was used to generate k points in the Brillouin zone 1×1×27.The calculations were carried out for room temperature (T = 300K). The maximum efficiency of the

energy conversion process in a thermoelectric material is determined by its thermoelectric figure of merit ZT, defined by the expression

$$ZT = \frac{S^2 GT}{\lambda} \quad (1)$$

where S is the Seebeck coefficient, G is the electrical conductivity, T is the absolute temperature, λ is the thermal conductivity coefficient, which is equal to the sum of the electron λ_e and phonon λ_{ph} thermal conductivities.

The nonequilibrium Green's function method (NEGF), DFT, and nonequilibrium molecular dynamics were used to calculate the thermoelectric coefficients and the Peltier coefficient. We used the standard model, in which the central part of the tube is connected to the semi-infinite left and right parts. QuantumATK [8] calculates the indicated thermoelectric coefficients and the Peltier coefficient in accordance with the linear response theory. The following relationships are used:

$$G_e = \left.\frac{dI}{dV_{bias}}\right|_{dT=0}; \quad S = -\left.\frac{dV_{bias}}{dT}\right|_{I=0}; \quad \lambda_e = \left.\frac{dI_Q}{dT}\right|_{I=0}; \quad \Pi = \left.\frac{I_Q}{I}\right|_{dT=0} = SV_{bias}. \quad (2)$$

The parameters of the system are given in Table 1.

Table 1

Parameters of the studied structures

Distance between fullerenes, *R*, Å	Tube diameter, *D*, Å
13.60	11.24
11.78	12.99
23.56	12.99

Results and Discussion

Obtaining materials with high thermoelectric figure of merit ZT is complicated by the requirement of independent control of electrical conductivity, thermal conductivity and Seebeck coefficient, which are often interrelated. A thermoelectric material with a high ZT must have low thermal conductivity λ, high electrical conductivity G, and high Seebeck coefficient S. In this paper, we investigate the effect of encapsulation of fullerenes in the cavity of a graphenylene nanotube on the above properties, taking into account chirality of nanotubes and distance between neighboring encapsulated fullerenes.

Fig. 2 shows the calculated thermoelectric properties (electrical and thermal conductivities, Peltier and Seebeck coefficients, thermoelectric figure of merit) of the armchair graphenylene nanotube system with encapsulated C_{60} fullerenes.

Thus, we observe that the introduction of fullerenes into the cavity of a graphenylene nanotube makes it possible to increase the electrical conductivity of the device, but significantly reduces its thermoelectric efficiency by reducing the Seebeck coefficient and increasing the thermal conductivity.

Fig. 3 shows the thermoelectric characteristics of two graphenylene nanotube-C_{60} fullerene systems with zigzag and armchair chirality types. The systems were selected with the closest possible nanotube diameter (a graphenylene nanotube with an “armchair” chirality has a diameter of 12.99 E, and with a “zigzag” chirality, a diameter of 11.24 Å) and the distance between the centers of neighboring fullerenes (11.78 E for an armchair nanotubes and 13.60 Å for a zigzag nanotube).

The graphenylene armchair nanotube-C_{60} fullerene system demonstrates higher electrical and thermal conductivities at zero and near-zero energies, but a low Seebeck coefficient.

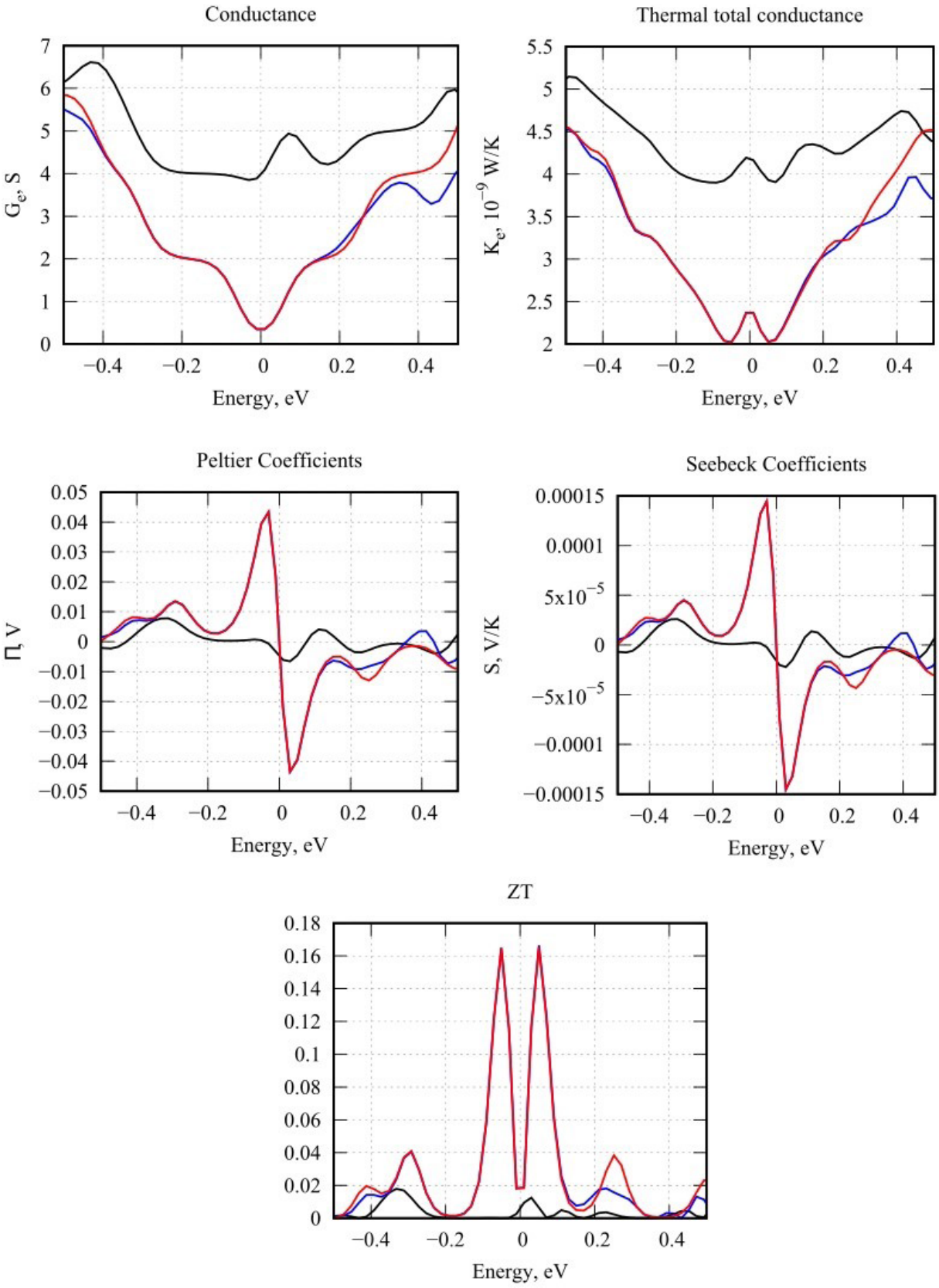

Fig. 2.The results of calculations of the thermoelectric coefficients for a graphenylene nanotube (red line) and graphenylene nanotube-C_{60} fullerene systems with a distance between the centers of two neighboring fullerenes of 11.78 Å (black line) and 23.56 Å (blue line)

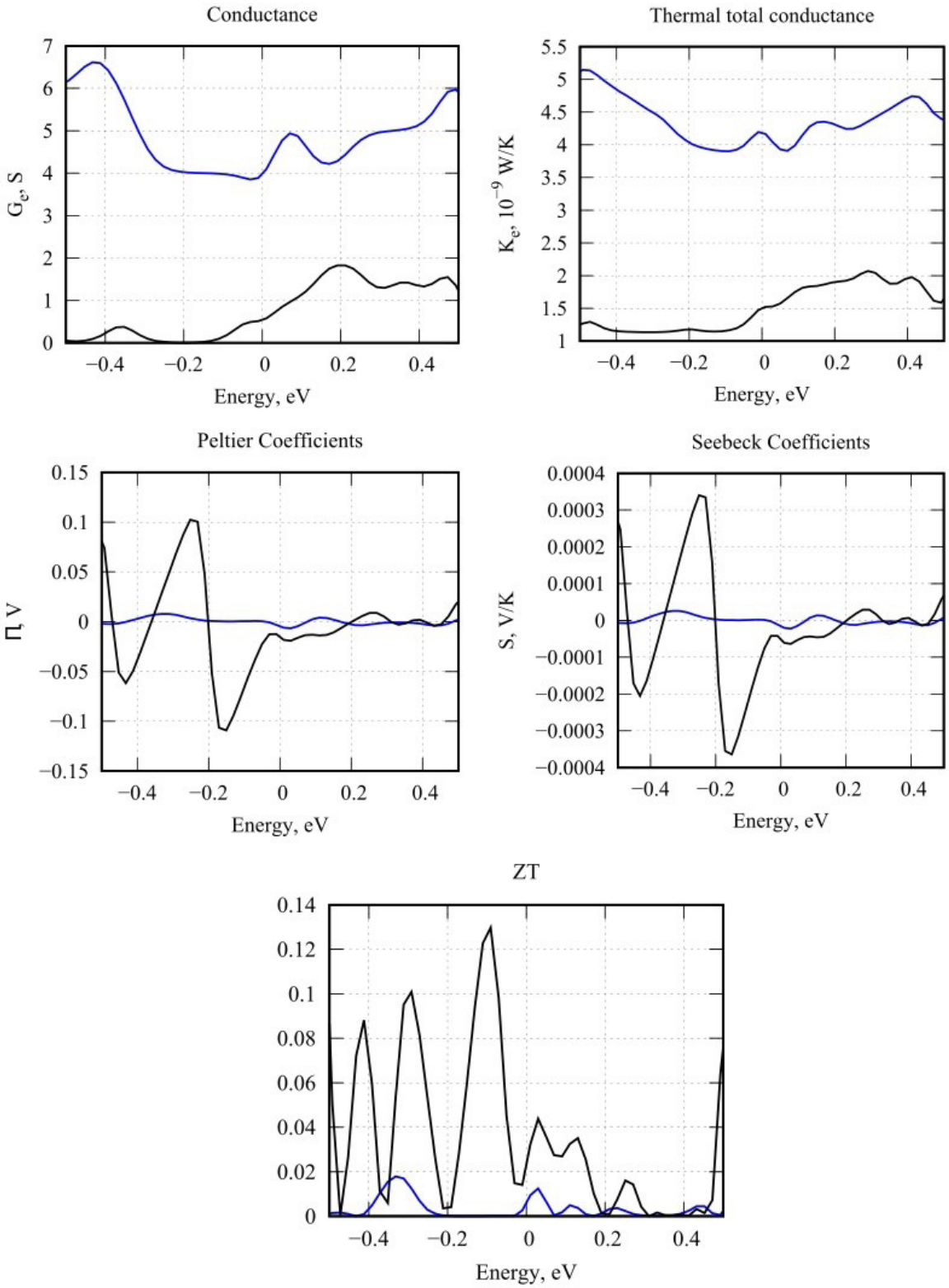

Fig. 3.Thermoelectric properties of graphenylene nanotube with zigzag chirality with encapsulated C_{60} fullerenes located inside the tube at a distance between their centers of 13.60 Å (black line) and a graphenylene nanotube system with an armchair chirality with encapsulated C_{60} fullerenes located inside the tube at a distance between their centers 11.78 Å (blue line)

Conclusion

Using DFT, NEGF and the molecular dynamics method, the thermoelectric properties of graphenylene nanotubes with encapsulated fullerenes are calculated. The thermoelectric figure of merit is significantly higher for the system of "zigzag" graphenylene C_{60} nanotubes than for the armchair graphenelene C_{60} nanotube system due to low thermal conductivity and high Seebeck coefficient. The introduction of fullerenes into the cavity of a graphenylene nanotube makes it possible to increase the electrical conductivity of the device, but, with an increase in the number of fullerenes in the tube, it significantly reduces its thermoelectric efficiency by reducing the Seebeck coefficient and increasing the thermal conductivity.

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