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Investigation the thermoelectric properties of M@C60(M=Co, Ni): ADFT study

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ABSTRACT

Density functional theory combined with Nonequivalent Greens Function was carried out to study the $M@C_{60}$ single-molecule junctions between two gold electrodes, where M=Co and Ni. Our results show a smooth transmission coefficient T(E) curve for bare C_{60} in the HOMO-LUMO gap. However, doping C_{60} with transition metals (Co and Ni) reveals two and three prominent peaks in the HOMO-LUMO gap corresponding to Ni and Co respectively. Further, the metals increased the Seebeck (S) and thermal efficiency. Hence, the doping by transition metal is crucial to enhance Seebeck coefficient and figure of merit ZT.

Introduction

Upon the identification of one of the allotropic forms of carbon-fullerene, extensive research into its physicochemical characteristics started to address a variety of practical issues [1,3]. In fullerene, regular hexagons and pentagons have their vertices occupied by carbon atoms, which make up the structure. The unusual electrophysical properties make fullerenes a very promising material for electronics. For instance, semiconductors having a band gap of 1.2–1.9 eV are known as crystalline fullerenes [4,5].

Fullerenes typically take the form of regular truncated icosahedrons, with the most common and chemically stable form being the C60 molecule. Because the carbon atoms in the C_{60} molecule occupy completely comparable locations, the molecule has exceptional symmetry [6].

Next-generation electrical circuits that make use of molecules' spin and electronic properties may employ certain molecules due to their distinct transport characteristics [7,9]. Moreover, the thermoelectric characteristics of these molecular connections have been thoroughly examined. Molecular junctions exhibit a diverse and adjustable variety of thermal transport events. Both empirical and theoretical investigations into the molecular heat transport encounter substantial challenges. Advancements in technology and approach have improved the experimental measurement of molecular spin devices, although uncertainties persist due to their extremely small scale. Furthermore, several transportation mechanisms at molecular junctions require further clarification. Theoretical simulation is essential for studying electron transport in various models of molecular devices and gaining a comprehensive understanding of experimental observations. Molecular devices with specific functions can be created and simulated using theoretical modelling[10].

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Density functional theory (DFT) from first principles in conjunction with the nonequilibrium Green function (NEGF) technique is the most commonly used theoretical approach [11,15].

Gold molecules are of interest for optimising thermoelectric characteristics in junctions. This is due to the variation of the metal atom (referred to as M in Fig. 1) located within the fullerene cage. The objective is to discover novel materials and system architectures capable of implementing these tactics in a laboratory setting. The discoveries are important as they provide new possibilities for harvesting and cooling thermoelectric energy from modified organic molecules. The thermal conductivity of single molecules can only be measured by a limited number of groups worldwide, necessitating theoretical research to explore and study new thermoelectric materials. This work provides a comparative theoretical examination of three distinct metal structures in terms of their electrical and thermoelectric properties. The paper's primary assertion is the adjustability of the transmission coefficient (T), thermopower (S), and the figure of merit (ZT) through the substitution of the central metal ion, conveyed using concise and clear language.

Method

Each structure's geometry comprises gold electrodes and a single fullerene molecule. Employing the SIESTA code [16], We conducted geometry optimization of each molecule positioned between two gold electrodes using a double-zeta polarized base set (DZP) and a generalized functional gradient approximation (GGA-PBE) for functional exchange and correlation [17,18]. We constructed the Hamiltonian for each system, consisting of electrode-C_{60}-electrode, using the ground state geometry. The electronic properties of the molecules in the junction were determined by combining the underlying Hamiltonian (H) with the quantum transport code GOLLUM [19] to calculate the transmission coefficient T(E), Seebeck coefficient S, and the figure of merit ZT for electrons of energy E moving from the left electrode to the right one.

Results and Discussion

To examine the endohedral fullerene's electrical and thermoelectric characteristics M@C_{60} (where M=Co, and Ni), we need to determine the transmission coefficient T(E) for the system shown in Figure 1.

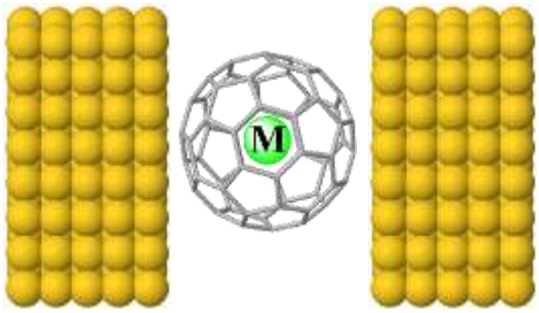

Fig. 1. The structure of the molecular junction which consists of Left gold electrode, fullerene, right gold electrode, and metal atom in the center of the fullerene M where (M= Co, Ni).

Figure 2 illustrates the transmission probability for the C_{60}, Ni@C_{60} and Co@C_{60}. It is clear from Figure 2 that the transmission coefficient of C_{60} is smooth (red line) without any additional features between the HOMO and LUMO gap. Moreover, the addition of transition metals such as Ni and Co can enhance the characteristics of our systems. There are two cases that arise based on the number of electrons in the outer shell of each atom (Co and Ni), whether it is odd or even. The first case is when the electron is odd for the Co atom ([Ar] $3d^7$ $4s^2$), as we can see level 3d has 7 electrons with 3 unpaired electrons in the d orbital this corresponding to the three resonances at -0.1, -1.08, and -1.2 eV (pink line). The second case is for the Ni atom which has two electrons unpaired [Ar] $3d^8$ $4s^2$ in the d orbital caused to appear only two too close resonances located at -0.96, and -0.99 eV (green line). Our calculations have been taken around Fermi level EF = 0 eV. Therefore, the resonance of Co@C_{60} at -0.1 eV is a crucial point in the next calculation because it is very close to the Fermi level.

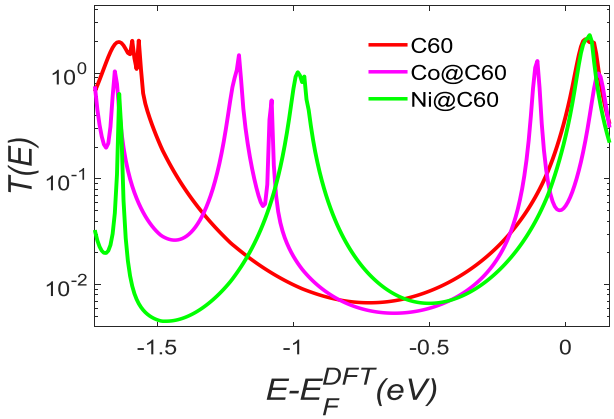

Fig. 2. Transmission coefficients of electrons in relation to energy.

Spin-polarized are calculated due to the individual electrons in the structures of Co@C60 and Ni@C60, which clearly appear in the transmission coefficient. It is clear from Figure SI1, that the C60 does not have spin, while, Co@C60 and Ni@C60 have spin up and down as shown in Figures SI2 and SI3.

The most important quantity calculated is the Seebeck S and thermoelectric efficiency ZT. The ZT is dimensionless figure of merit [20] ZT = S2GT/κ which is proportional to the electric conductance G and the square of the Seebeck coefficient S, and inversely proportional to the thermal conductance κ. Generally, to obtain large S and ZT it is convent to have large features around the Fermi level, these structures could be a very good candidate to act as thermoelectric enhancers. The Endohedral fullerene is based on the transition metal, which has been recently very interesting both theoretically [21,22] and experimentally [23,24]. For certain metallic elements such as Co and Ni as shown in Figure 3, the window shaded in Figure 3 represents the Seebeck for range between 0 and -0.3 eV. The highest and lowest values varied between +105 and -190 μV/K (pink line) for the Co@C_{60} due to the big peak around the Fermi level. Otherwise, the Seebeck for bare C_{60} (red line) and Ni@C_{60} (green line) are between +140 to -146 μV/K and between +192 and -172 μV/K respectively, away from the Fermi level.

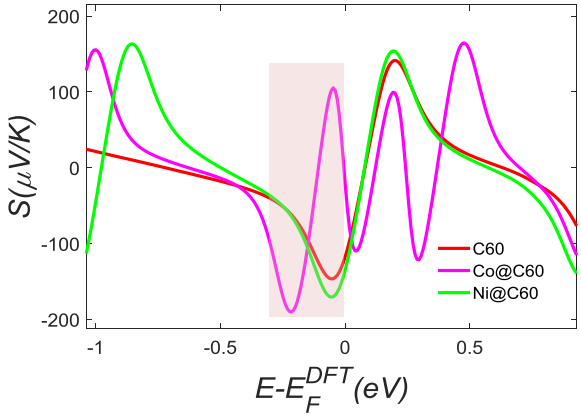

Fig. 3. Thermoelectric coefficients for M@C_{60} between gold electrodes, calculated by density functional theory (DFT) method.

Figure 4 shows the figure of merit for C_{60} doped by Co and Ni elements, the result shaded by the rectangular between 0 and -0.3 eV, the highest value is 1.88 at 0.2 eV for Co@C_{60} structure. These evolutions can be explained by taking into account the resonance, which is a bit lower than the Fermi level. According to this, the most efficient heat-to-electricity conversion (large S and ZT) can be achieved in the case of resonances at an energy close to the Fermi level.

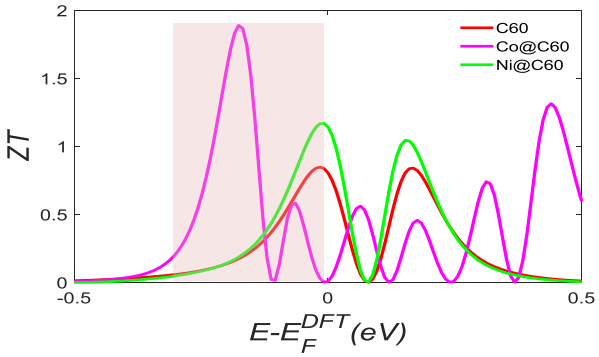

Fig. 4. Figure of merit ZT for M@C_{60} between gold electrodes, calculated by density functional theory (DFT) method.

Conclusions

The thermoelectric properties of the Endohedral fullerene junction between two gold leads and doped by transition metal Co and Ni are calculated by using density functional theory. The resonances greatly support the thermopower and figure of merit when they are close to the Fermi level, this appears at the Co@C_{60} structure and disappears at Ni@C_{60}. The maximum value of thermopower and figure of merit is found for the Co@C_{60} structure.

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دراسة الخواص الكهربائية والحرارية لـــ M@C60 حيث (M=Co, Ni): دراسة نظرية DFT

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الخلاصة:

نظريه كثافه الداله الوظيفية مع دالة كرين غير المتجانسة استخدمت لدراسة الخصائص الكهروحرارية للجزيئات المفردة من $M@C_{60}$ بين قطبين من الذهب حيث ان $M= Co$ و Ni. نتائج الترانزمشن التي تم الحصول عليها تكون خاليه من اي قمم بين الهومو واللومو لل C_{60} النقي اما عند تطعيم C_{60} بالعناصر الانتقالية مثل الكوبلت والنيكل نلاحظ ظهور قمتين وثلاث قمم بين الهومو واللومو للنيكل والكوبلت على التوالي. نلاحظ ان قيمه السيباك تزداد مع التطعيم بالكوبلت والنيكل وكذلك فان الكفاءة الكمية ازدادت. لذلك فان التطعيم بالعناصر الانتقالية مهم جدا لدعم السيباك وال *zt*.

الكلمات المفتاحية. *C60,الاندوهيدرل فلورين، DFT, Co ، Ni*