The electronic transport properties of N@C_{60}@/(n,m) carbon nanotube peapods

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Abstract

In this paper we use ab initio density functional theory (DFT) to calculate the electronic transport properties of the endohedral fullerene N@C_{60} encapsulated within (n,m) single-walled carbon nanotubes (SWNTs) to produce carbon nanotube peapods (CNPs). By comparing the electronic properties of C_{60}@/(n,m) and N@C_{60}@/(n,m) CNPs, we demonstrate that due to the inertness of the inner surface of the C_{60} cage, the nitrogen is very well protected from its environment.

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Fullerenes [1] and carbon nanotubes [2] provided ideal, fundamental, building blocks for engineering exotic nanoscale geometries [3,4]. An example of the use of these building blocks is the N@C_{60}@(17,0) structure, shown in Fig. 1, which shows a nitrogen atom placed in the center of the C_{60} buckyball, which is in turn located inside a section of (17,0) SWNT. The electronic [5] and transport properties [6] of carbon nanotubes (CNTs) are well documented. More recently, the question of how the encapsulation of molecules within the CNT alters their properties has been addressed [7–9] along with a range of other approaches to engineering transport properties [10,11]. Fullerene are ideal molecular candidates for encapsulation within CNTs, which can be inserted into SWNTs as ordered arrays. For example CNPs of C_{60}@/(n,m) [12,13] have been reported experimentally by a number of groups [14–17]. Theoretical studies of ground-state electronic properties [7,18–20] show that the most energetically favorable encapsulation of C_{60} is within the (10,10) CNT where the insertion reaction is slightly exothermic. The interaction of C_{60} with the (10,10) SWNT is predicted to be weak, ≈ 0.1 eV [20] due to mixing between the p orbitals on the C_{60} shell and nearly free electrons just above the Fermi level of the CNT giving rise to a small charge transfer from the CNT and C_{60}.

The encapsulation of nitrogen within C_{60} forms N@C_{60} and is produced by bombarding the fullerene with a beam of ionized nitrogen atoms [21]. N@C_{60} molecules are stable due to the inertness of the inner C_{60} surface where the curvature is unfavorable to orbital overlap [22]. Previous calculations [23,24] and experiments [25] also indicate that the encapsulated nitrogen atomic state is nearly that of the isolated atom and the usually very reactive atom sits in the center of the C_{60} cage where it is well protected from the environment under ambient conditions.

In what follows, we investigate electron transport properties of CNPs. Our ab initio calculations use density functional theory (DFT) as implemented in the SIESTA code [26], where norm-conserving pseudopotentials and linear combinations of atomic orbitals are employed. The local density approximation [28] with double zeta orbitals is used to perform the structural relaxations, with a plane wave cut off of 150 Ry. Transport properties are calculated with the SMEAGOL code [27], which is interfaced to SIESTA and uses non-equilibrium Green’s functions to obtain, self-consistently, the charge density and the transmission coefficient T(E) for electrons of energy E.

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To start the calculations we examine the effects of encapsulated nitrogen on the band structure of C\textsubscript{60}. The results are shown in Fig. 2 and reveal that the nitrogen causes the lowering of the C\textsubscript{60} \textit{t}{\textsubscript{LU}}M\textsubscript{O} (LUMO) by \( \frac{1}{25} \) eV (together with a splitting of the degenerate levels) and the \textit{H}{\textsubscript{OM}}O (HOMO) levels by \( \frac{1}{25} \) eV. The gap between these levels is reduced from \( \frac{1}{8} \) (C\textsubscript{60}) to \( \frac{1}{66} \) (N\textsubscript{@C\textsubscript{60}}) eV.

The effects of majority and minority spins in the nitrogen basis were found not to have any appreciable further contribution. These small changes to the band gap and Fermi level shifts the support to the evidence that the nitrogen atom is well screened within the cage.

Encapsulating the N\textsubscript{@C\textsubscript{60}} within an \((n,m)\) SWNT should further protect the decoupled spin system from external effects. To demonstrate this, the transport properties were calculated for three examples of N\textsubscript{@C\textsubscript{60}}\((n,m)\).

In each case the model is constructed from perfect \((n,m)\) SWNT leads, which are connected to a self-consistently treated scattering region comprising a molecule of N\textsubscript{@C\textsubscript{60}} encapsulated within a suitable number of unit cells of SWNT. For example the N\textsubscript{@C\textsubscript{60}}\((17,0)\) CNP of Fig. 1 can be considered as such an extended molecule. It has three unit cells of the zig-zag \((17,0)\) SWNT with the molecule placed at the center whereas the N\textsubscript{@C\textsubscript{60}}\((10,10)\) CNP would require five unit cells. The inclusion of unit cells which overlap the N\textsubscript{@C\textsubscript{60}} ensures that the region of contact to the leads represents the bulk properties of the perfect crystalline SWNT leads free from end effects.

Fig. 3 shows \( T(E) \) through a scattering region containing three N\textsubscript{@C\textsubscript{60}}\((n,m)\) buckyballs, for three examples of encapsulating SWNT and lead namely, the armchair \((10,10)\) which is metallic, the zig-zag \((18,0)\) which is semi-conducting and the zig-zag \((17,0)\) which is insulating. In each example the values of \( T(E) \) can be compared with \( T(E) \) for the infinite C\textsubscript{60}\((n,m)\) CNP (dotted line) and the N\textsubscript{@C\textsubscript{60}}\((n,m)\) CNP (dashed line). The figure shows that the inclusion of a finite N\textsubscript{@C\textsubscript{60}}\((n,m)\) scattering region, comprising three buckyballs, lowers the transmission in all cases. For example in the C\textsubscript{60}\((10,10)\) and N\textsubscript{@C\textsubscript{60}}\((10,10)\) CNPs the transmission is reduced from a value of 2 by approximately 50% in the region of the Fermi energy \( E_F \).

However there are negligible differences between the results for C\textsubscript{60}\((n,m)\) CNPs and those of N\textsubscript{@C\textsubscript{60}}\((n,m)\) even at...
energies away from $E_F$. This supports the assertion that the nitrogen is well screened within the C$_{60}$ cage.

In conclusion we have shown that the screening effects of C$_{60}$ cages can isolate even reactive atoms such as nitrogen from the environment. This is demonstrated by calculations which show a negligible difference between the single electron transport properties of N@C$_{60}$@($n,m$) CNPs, when compared with C$_{60}@$($n,m$) CNPs.

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References