Tuning the Electrical Conductivity of Nanotube-Encapsulated Metallocene Wires

Víctor M. García-Suárez,[1,2] Jaime Ferrer,[2,*] and Colin J. Lambert[1]

[1]*Department of Physics, Lancaster University, Lancaster, LA1 4YB, United Kingdom*
[2]*Departamento de Física, Universidad de Oviedo, 33007 Oviedo, Spain*
(Received 12 September 2005; published 15 March 2006)

We analyze a new family of carbon nanotube-based molecular wires, formed by encapsulating metallocene molecules inside the nanotubes. Our simulations, which are based on a combination of nonequilibrium Green function techniques and density functional theory, indicate that these wires can be engineered to exhibit desirable magnetotransport effects for use in spintronics devices. The proposed structures should also be resilient to room-temperature fluctuations, and are expected to have a high yield.

The ability to fill carbon nanotubes (CNTs) with different compounds [1] has opened a new and growing field of research, where nanowire devices with new electronic properties can be produced using simple chemical methods. A number of experiments [2–5] demonstrate that it is feasible to fabricate long and stable chains of single molecules or atomic clusters by placing them in the interior of CNTs. They also show how the electronic and structural properties of the CNT can be conveniently tailored through the addition of different compounds. Recently, it has been demonstrated that metallocenes may be encapsulated inside single-walled CNTs with diameters of about 1 nm [6].

Bis-cyclopentadienyl TM ($TMCp_2$) is a metallocene composed of a transition metal atom (TM), sandwiched between two aromatic rings made of five carbon and five hydrogen atoms each. It may be formed with the six elements in the middle of the $3d$ row, V, Cr, Mn, Fe, Co, Ni, as well as with those in the column of iron, Ru and Os. All $TMCp_2$ therefore share the same shape, which we depict in Fig. 1. Their electronic structure is also very similar, with differences that can be traced to the diverse electronic filling of the d shell of the TM atom. The crystal field associated with the benzene rings lifts the degeneracy of the d shell into a triplet that lies lower in energy ($d_{x^2-y^2}$, d_{xy}, and $d_{3z^2-r^2}$) and a doublet (d_{xz} and d_{yz}). The levels in the doublet are split into two peaks due to their bonding with the carbon atoms. In addition, there is an exchange field that breaks the spin degeneracy to accommodate the magnetism predicted by Hund's first rule. Accordingly, VCp_2, $CrCp_2$, $MnCp_2$, $FeCp_2$, $CoCp_2$, and $NiCp_2$ have magnetic moments equal to 3, 2, 1, 0, 1, and 2 Bohr magnetons, respectively. $FeCp_2$ is paramagnetic since its core atom has a closed-shell electronic structure. The other metallocenes display a sort of mirror symmetry about $FeCp_2$. To illustrate these points, we plot in Fig. 2 the density of states projected onto the d shell of $CoCp_2$.

Such features are highly advantageous, since by placing metallocenes in the interior of CNTs, one may fabricate chains of molecules, whose electrical and magnetic properties can be tailored at will. We view the CNT as an external coating, whose conducting properties can also be

modified by changing its chirality from armchair to zigzag. Such a coating also provides a strongly enhanced chemical stability to the atomic chain and isolates it mechanically and, to a point, electrically. The simulations that we present here show that the formation energy of these wires is strongly exothermic for CNTs of radii between 4.5 and 7 Å. We therefore argue that these nanometric analogues of conventional electrical wires can readily be fabricated. We note, however, that fabrication and sorting of CNTs of a given chirality is currently a difficult task.

In our search for metallocene nanowires, we have performed an extensive series of *ab initio* simulations of $TMCp_2$ inside CNTs of several chiralities. We have calculated their electronic and structural properties using the density functional theory code SIESTA [7], that uses pseudopotentials, and expands the wave functions of valence electrons by linear combinations of numerical atomic orbitals. To be specific, we have used a double-zeta basis set to describe hydrogen and carbon atoms, and a double-zeta polarized basis set for the $3d$ metal atom. We have also used a number of k points ranging between 20 and 100 to model the periodicity along the axis of the nanotube and the generalized gradient approximation to the exchange
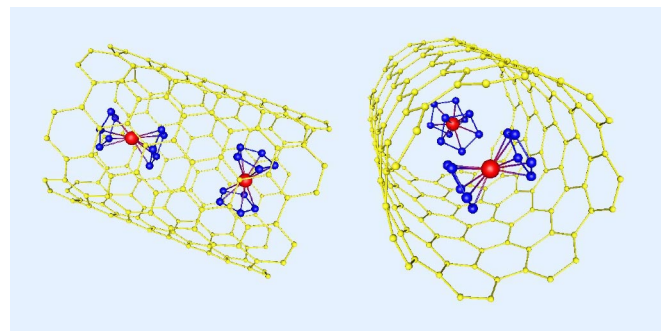

FIG. 1 (color online). Two schematic views of a $TMCp_2 @ 3(7, 7)$ nanotube with two encapsulated metallocenes, whose axes are aligned either parallel or perpendicular to the nanotube axis. Each metallocene has a TM atom in the middle, sandwiched by two rings of five carbon and five hydrogen atoms. Hydrogen atoms are not displayed in the figure.
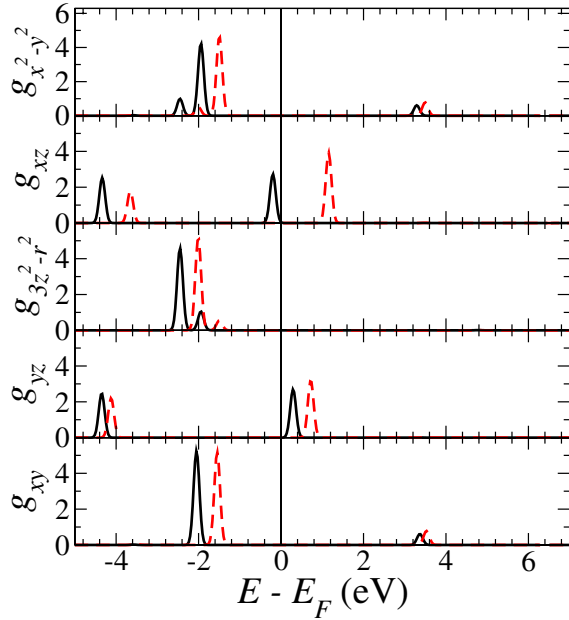
FIG. 2 (color online).   Densities of states g_i of CoCp$_2$, projected onto the d-shell orbitals of the cobalt atom for spin-up (solid line) and down (dashed line). The index i denotes the orbital flavor, $i = x^2 - y^2, xz, 3z^2 - r^2, yz, xy$.

and correlation functional, as parametrized by Perdew, Burke, and Ernzerhof [8,9]. We have relaxed the atomic coordinates of all atoms in the unit cell. Finally, we have calculated the electrical conductance of the devices with the nonequilibrium Green functions [10,11] code SMEAGOL [12], which has been successfully applied to the study of magnetoresistive effects in organic molecules and conductance quantization in atomic constrictions [13,14].

As a first step, we have simulated single-wall CNTs of different chiralities as well as isolated chains of TMCp$_2$. We find lattice constants of 7.88, 7.99, 7.63, 7.55, 7.93, and 8.20 Å for TM = V, Cr, Mn, Fe, Co, and Ni, respectively. Metallocene chains can therefore be accommodated rather well inside armchair (n, n) CNTs, whose theoretical lattice constant is 2.46 Å, with one molecule every three unit cells of the nanotube. They can also be placed inside zigzag $(n, 0)$ CNTs, that have a lattice constant of 4.32 Å, with one molecule every two unit cells. Other chiralities may also be chosen for the CNT. For instance, $(15, 5)$ and $(12, 4)$ CNTs can also host metallocene chains (lattice constant of 15.59 Å, in both cases), with two molecules per unit cell.

To test the stability of the encapsulated chains, we have simulated VCp$_2$, FeCp$_2$, and CoCp$_2$ chains placed inside metallic (n, n) CNTs with n ranging from 6 to 10, which correspond to radii between 3.39 and 6.78 Å, respectively. The structural periodic unit of the simulations comprises $N = 2$, 3, or 4 unit cells of the nanotube and a single metallocene, and is denoted as TMCp$_2$@$N(n, n)$. In addition, the axis of the metallocene has been oriented either parallel or perpendicular to the axis of the nanotube, as shown in Figs. 1(a) and 1(b). We have calculated the bind-

ing energy E_B, per structural unit cell of the whole nanowire, defined as

$$E_B = E_{TMCp_2@N_{(n,n)}} - NE_{(n,n)} - E_{TMCp_2} + \Delta E_{BSSE}, \quad (1)$$

where ΔE_{BSSE} is the correction for the basis set superposition error [15]. We have also calculated the charge transferred from the metallocene to the CNT ΔQ, and its magnetic moment m, as a function of the radii of the armchair CNTs. Figure 3 shows the results for parallel and perpendicular CoCp$_2$@$N(n, n)$ wires, with $N = 3$ and 4. We note that CoCp$_2$@$2(n, n)$ is energetically unfavorable since the metallocene molecules are too compressed, that CoCp$_2$@$3(n, n)$ accommodates rather well the metallocene chain, and that the wave functions of the metallocene molecules have negligible overlaps in CoCp$_2$@$4(n, n)$.

Figure 3 shows that parallel CoCp$_2$@$N(n, n)$ nanowires are energetically favorable for radii equal or larger than about 4.5 Å, in agreement with the experimental data of Li and co-workers [6], who found a preferred radius of 4.67 Å. The small energy differences between $N = 3$ and $N = 4$ are due to the formation energy of the chain.

We now examine the motion of single cobaltocenes along the nanotube axis. We note that large energy barriers will hinder the fabrication of chains with no faults, while if the barriers are too small, metallocenes will move almost freely. This will render the nanowires useless for operation at room temperature. We have therefore simulated several configurations of parallel CoCp$_2$@$4(n, n)$, where the cobaltocene is placed at different positions along the nano-
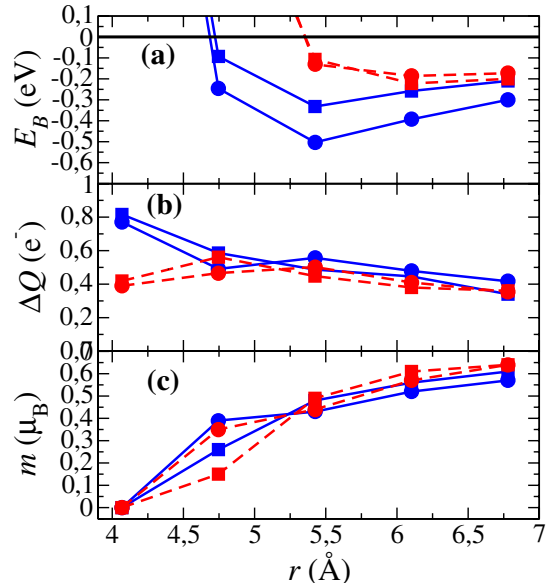

FIG. 3 (color online).   (a) Binding energy E_B, (b) charge transferred to the nanotube ΔQ, and (c) magnetic moment m, of CoCp$_2$@$N(n, n)$ wires, where n varies from 6 to 10. Circles in solid (dashed) lines correspond to parallel (perpendicular) CoCp$_2$@$N(n, n)$. Squares in solid (dashed) lines correspond to parallel (perpendicular) CoCp$_2$@$4(n, n)$.

tube axis. We estimate the energy barrier for motion of the cobaltocene E_M as the energy $E_{CoCp_2@4(n,n)}$ of each configuration, referred to the energy of the most stable position. Thin nanowires have energy barriers of the order of several eV. On the contrary, $CoCp_2@4(7, 7)$ has an energy barrier of only 12 meV, which along with its large binding energy, makes this nanotube a promising candidate for encapsulating cobaltocenes. For larger radii, E_M decreases to values smaller than 3 meV, which allows the molecules to move almost freely along the nanotube, and eventually leave it [6].

To establish whether or not metallocenes remain perfectly aligned at room temperature, we discuss now how easy is to rotate a cobaltocene from a parallel to a perpendicular configuration. We first note that perpendicular cobaltocenes only fit inside CNTs with n equal or larger than 8. We find that the energy cost to rotate the cobaltocene for $CoCp_2@3(8, 8)$ nanowires is as large as 0.15 eV, and therefore they remain aligned at room temperature. In contrast, metallocenes would be missaligned at room temperature in $CoCp_2@4(8, 8)$ nanowires, due to the negligible overlap of metallocene wave functions that leads to an energy difference between both orientations of only 30 meV.

A Mulliken-population estimate of the total amount of charge transferred from the cobaltocene to the nanotube due to formation of the chemical bond, reveals that the nanotube is always n doped as seen experimentally [6] and does not acquire any spin polarization. The amount of charge transferred is of about 0.4 to $0.6e^-$, depending on the configuration, as shown in Fig. 3. The values of the magnetic moment are considerably smaller than those of the isolated molecule ($1.0\mu_B$), due to the charge transferred from the cobaltocene to the nanotube [4].

This charge transfer is also evident in the band structures shown in Fig. 4, where we plot the spin up and down electronic bands of parallel $TMCp_2@3(7, 7)$, with TM = V, Fe, Co. We note that the relative position of the CNT and the transition metal $3d$ bands indicate the amount of charge transferred and therefore the strength of the chemical bond. The iron metallocene shows three $3d$ bands at the Fermi energy E_F, that are essentially unsplit and dispersionless, whereas the CNT bands show a large dispersion. This implies that the current flowing through these nanowires must be carried only by the external coating. Something similar happens for the vanadium wire, where the bands are now exchange split, but still dispersionless and therefore should not conduct. In contrast, the $3d$ bands of the cobaltocene nanowire are exchange split and dispersive and should carry a spin-polarized current.

The above discussion suggests that parallel $CoCp_2@3(7, 7)$ and $CoCp_2@3(8, 8)$ are the best candidates for spintronics devices and applications. On the one hand, these wires are the most stable devices from a structural point of view. On the other, their band structure shows the presence of a spin-polarized transport channel at the Fermi energy, which can give rise to a magnetoresistive effect.
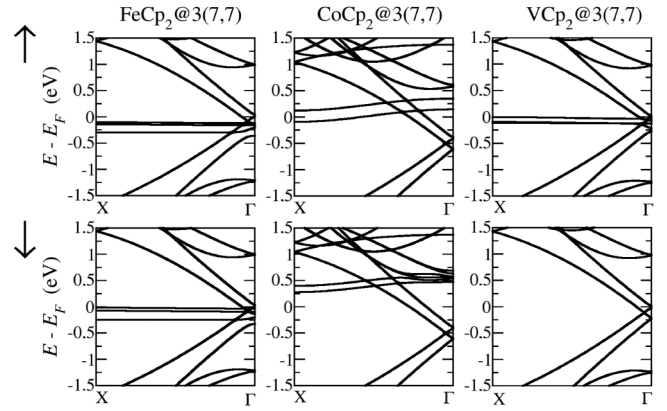

FIG. 4. Band structure of parallel $TMCp_2@3(7, 7)$, for spin-up and -down electrons, where TM = Fe, Co, and V. The perpendicular case is similar but now also the cobaltocene bands are flat. Top (bottom) panels are for spin-up (-down) electrons.

In order to test this possibility we have simulated devices comprised of two leads that sandwich a scattering region, and computed their conducting properties. The leads contain one unit cell of $CoCp_2@3(7, 7)$ with spin-up. The scattering region contains also one unit cell of $CoCp_2@3(7, 7)$ with spin-up or -down. This makes a total of nine nanotube unit cells and 315 atoms for the simulation. We denote each device by the spin (u or d) of the metallocene in the scattering region. Flipping such spin from up to down costs an energy of 0.05 eV, which implies that the ferromagnetic configuration can be stabilized at room temperature, but that a relatively small magnetic field may switch it. We note that we have not included in our simulations contacts between the devices and external electrodes, that should decrease to some extent their conducting and magnetoresistive behavior.

The u configuration, in which the spin of the three cobaltocenes points upwards, corresponds to a perfect ferromagnetic chain, where there is no scattering. In this case, the transmission coefficient is determined from the band structure and is equal to the number of open scattering channels. Figure 5 shows that there are three channels for spin-up in a region around the Fermi energy that extends from -0.1 eV up to 0.4 eV. Two of them correspond to the nanotube and one to the cobaltocene. This excludes a tiny segment, where both cobaltocene bands contribute. On the other hand, there are only two channels at the Fermi energy for spin down, that correspond to the nanotube, while the cobaltocene channels appear 0.3 eV above E_F.

In order to study the change of resistance as a function of the magnetic configuration we have also calculated the conductance of the d configuration. In this case, the cobaltocene channel has moved to energies way above E_F due to the exchange splitting, whereas the transmission for spin-down is unaffected. As a consequence, the difference in conductance between u and the d configurations is $0.9e^2/h$. Defining the magnetoresistance ratio as $\delta G = (G_u - G_d)/G_d$, the predicted ratio is $\delta G = 20\%$.
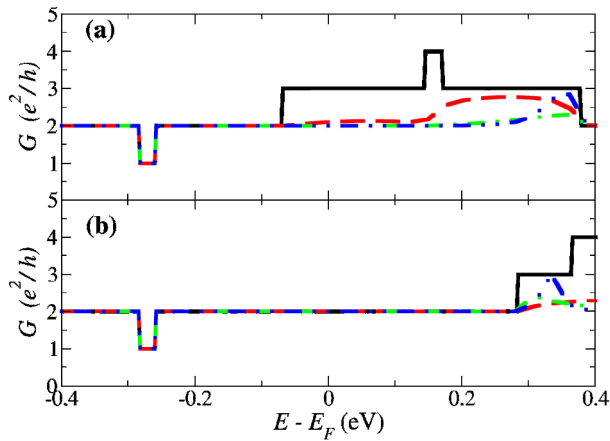
FIG. 5 (color online). Conductance of the $CoCp_2@3(7,7)$ magnetoresistive devices for (a) spin-up and (b) spin-down electrons. u, d, dd, and ddd conductances are plotted with solid lines, dashed lines, dash-dotted lines, and dash-double-dotted lines, respectively.

FIG. 6. Band structure of parallel $CoCp_2@2(11,0)$, $VCp_2@2(11,0)$, and $2CoCp_2@1(12,4)$ for spin-up (top panels) and -down electrons (bottom panels).

Since the spin flipping of only one cobaltocene may be difficult to achieve in practice, we have simulated two other configurations that have two and three $CoCp_2@3(7,7)$ unit cells in the scattering region, with all its metallocenes pointing downwards. These configurations, that have a total of 420 and 525 atoms, are denoted by dd and ddd, respectively. As shown in Fig. 5, the resulting transmission for spin-up channels around the Fermi energy decreases slightly. This yields an additional increase in the magnetorresistance ratio to 25%. We have also simulated devices where the spin of the leads are either aligned or antialigned, but where there is no cobaltocene in the scattering region. In this case the magnetoresistance ratio vanishes. This confirms the fact that the spin-polarized channel is present only when the cobaltocenes form an unbroken conducting chain, with dispersive bands.

Finally we have examined the effect of the conducting properties of the CNT coating. With a view to improving the magnetoresistance ratio, it is desirable to increase the fraction of the current passing through the metallocene chain and so instead of using armchair CNTs, which are always metallic, the question arises of whether we could engineer an insulating coating by choosing nonconducting zigzag or chiral CNTs. Our calculations show that the charge transferred from the metallocene to the CNT due to the chemical bonding brings the CNT valence bands down in energy. The CNT coating becomes either conducting or semimetallic, as we show in Fig. 6 for $CoCp_2@2(11,0)$, $VCp_2@2(11,0)$, and $2CoCp_2@1(12,4)$.

In summary, we have demonstrated that electrical nanowires consisting of a core made of a metallocene chain and a CNT coating may be fabricated, whose magnetic and electrical properties can be tailored by the appropri-
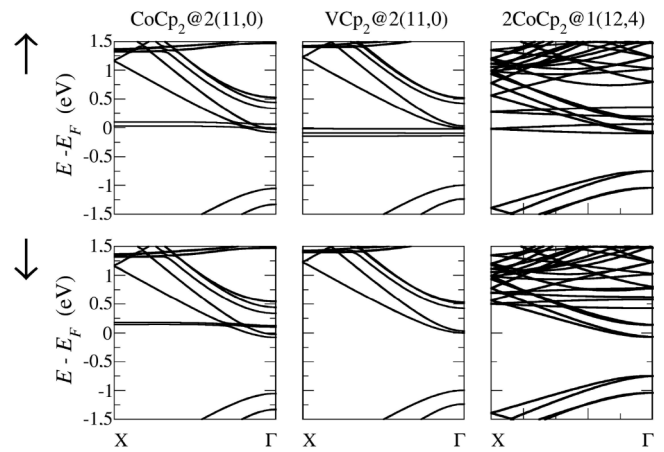
ate choice of metallocene molecule and chirality of the CNT. We have performed a series of *ab initio* simulations of the electronic and structural properties of several $TMCp_2@(n, n')$, which agree very well with recent experiments and show that engineering of molecular spintronics properties is possible.

*Electronic address: ferrer@condmat.uniovi.es
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