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Efficient Organometallic Spin Filter between Single-Wall Carbon Nanotube or Graphene Electrodes

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We present a theoretical study of spin transport in a class of molecular systems consisting of an organometallic benzene-vanadium cluster placed in between graphene or single-wall carbon-nanotube-model contacts. *Ab initio* modeling is performed by combining spin density functional theory and nonequilibrium Green’s function techniques. We consider weak and strong cluster-contact bonds. Depending on the bonding we find from 73% (strong bonds) up to 99% (weak bonds) spin polarization of the electron transmission, and enhanced polarization with increased cluster length.

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Carbon nanotubes (CNTs) [1] and other graphene-based systems [2] are considered strong candidate materials for future nanoscale quantum electronic devices due to their ballistic transport characteristics. Moreover, the long spin-relaxation length in these materials hold promise for spintronics applications. There is therefore great interest in the possibility of introducing and studying spin-polarized currents in graphene-based systems.

Spin transport has been studied both experimentally [3–6] and theoretically [7] for CNTs in contact with magnetic electrodes. Spin polarization has also been seen in CNTs when doped with magnetic adatoms or molecules [8–10]. These results indicate that one can use CNTs as spin-transport channels with ballistic transport characteristics, with the additional possibility of chemical functionalization. In general, carbon-based systems seem advantageous for spin transport due to weak spin decoherence, and are therefore currently under intense investigation. In addition to CNTs, several experiments regarding spin transport through organic molecules have been done, among them are observation of spin injection and detection in \( \pi \)-conjugated molecules [11], spin transfer across molecular bridges [12], and spin transport in organic tunnel junctions [13]. Theoretical investigations include spin transport through 1,4-benzene-dithiolate molecules [14], spin valves based on two Cobaltocene moieties [15], and evidence of Giant Magnetoresistance (GMR) in alkane-dithiolate and phenyl-dithiolate molecules between nickel contacts [16]. Very recently theoretical studies have indicated that graphene nanoribbons may act half-metallic [17], that is, metallic and semiconducting behavior of the respective minority and majority spins, which in turn means 100% spin-polarized currents for low voltage bias.

Electrically contacted junctions can be manipulated and formed between individual nanotubes [18] or between nanotubes and graphite [19]. In this Letter we propose that an adsorbed layer of benzene-vanadium (VBZ) organometallic molecular clusters can act as a highly efficient spin filter when placed in a junction between carbon electrodes. The junction could, e.g., be formed first adsorbing VBZ on a nanotube or graphite electrode, which is then by manipulation contacted by a nanotube. The spin filter facilitates a highly spin-polarized current in the carbon electrodes even in the case when a weak spin polarization is introduced in one of these by a ferromagnetic contact [5,20]. The role of the ferromagnetic contact being here only to fix the spin of the molecule and thereby the polarization of the current. Our study is based on the *ab initio* pseudopotential spin-polarized density functional theory (DFT), combined with nonequilibrium Green’s function transport calculations. We concentrate on the idealized situation of a single VBZ contact between two nonpolarized carbon electrodes, assuming all clusters in the junction conduct similarly; see Fig. 1. We obtain a large spin-filter effect quite independent of the detailed bonding of the cluster to the electrodes. We find from 73% (strong bonds) up to 99% (weak bonds) spin polarization of the electron transmission, with enhanced polarization for increasing cluster length.

The organometallic cluster we consider is the multi-decker benzene-vanadium sandwich \((V_x BZ_n)_m\) where \(BZ = C_n H_6\) and \(|n - m| \leq 1\), which have been synthesized recently from laser-vaporized vanadium atoms and BZ [21,22]. Mass spectrometric measurements as well as theoretical studies indicate a linear geometry, see e.g. \(V_4 BZ_3\) in Fig. 1, of lengths up to \(n = 6\) (20 Å), and ending with either BZ or V on each side. An integer magnetic moment of 1.00 \(\mu_B\) per VBZ unit cell has been found. Infinite chains of this cluster \((n = \infty)\) have been studied by spin-polarized DFT [23] and they show half-metallic ferromagnetic behavior with a semiconducting gap of 1.12 eV for the majority spin, while the minority spin component is metallic. Very recently, Maslyuk et al. [24] showed that the clusters act as almost perfect spin filters when placed between magnetic contacts of nickel or cobalt.

Considering the complexity problem and in order to make the computations tractable, we neglect curvature effects in the nanotube electrodes (Fig. 1 [25]) and use
potential density functional method as implemented in the SIESTA code \cite{27} to obtain the electronic structure from carbon nanotubes \cite{26}. We have used the graphitic sheet model (GSM) of metallic (armchair) carbon nanotubes \cite{26}. We have used the \textit{ab initio} pseudo-potential density functional method as implemented in the SIESTA code \cite{27} to obtain the electronic structure from spin-polarized DFT \cite{28}. Our spin-transport calculation is based on the nonequilibrium Green’s function method \cite{30} extended to spin-polarized systems \cite{31}. We consider here low bias and limit our calculation to transport at the Fermi energy only.

The cluster can end with either a BZ or a V and thus can bond upright to a graphene or CNT electrode with either a strong covalent bond between V and the electrode, or a weak van der Waals bond between BZ and the electrode. Our calculated binding energy between a single V adatom on a graphene sheet is 1.8 eV with a relaxed distance of 1.7 Å. This strong binding is in accordance with previous studies of V adatoms adsorbed on CNTs \cite{9,32}. Different orientations of BZ with respect to graphene are possible. We show the results for the bridge configuration, where the center of BZ is over the center of a bond in the graphene contact. This is one of the most energetically stable arrangements \cite{33}, with a DFT binding energy around 0.24 eV, and BZ-graphene distance of 3.2 Å as in other $sp^2$-like systems. We note that other geometries (“stack” — BZ center above a graphene atom, “hexagon” with BZ above a graphene hexagon) do not change our results significantly.

The setup of the transport calculation for the geometry in Fig. 1 differs slightly from the more standard two-probe setups \cite{30}. The GSM model that we use for contacts is equivalent to using graphene electrodes with periodic boundary conditions in the direction perpendicular to the transport, $x$ direction in Fig. 1. Our results do not change significantly when enlarging the x period, i.e., tube circumference for the GSM. In this geometry, there are four current terminals. The current will enter the cluster from left and right terminals in one graphene sheet (L1 and R1), and exit the left and right terminals in other sheet (L2 and R2). The darker carbon atoms represent the contacting unit cells of the four semi-infinite electrodes. To solve the transport problem we consider a self-energy for each of the four electrodes ($\Sigma_{L1}$, $\Sigma_{L2}$, $\Sigma_{R1}$, $\Sigma_{R2}$). The self-energy, $\Sigma_i$, of each contact $i = 1, 2, 3, 4$ is composed of the two “conventional two-probe” self-energies \cite{31} corresponding to semi-infinite extensions to the left and right,

$$\Sigma_i = (\Sigma_{L1} + \Sigma_{R1}),$$

and similarly for “2”;

see Fig. 1. The transmission function for majority (minority) spin ($\sigma = \uparrow \downarrow$) from graphene contact 1 to graphene contact 2 is calculated using the Landauer formula,

$$T_\sigma(E) = \text{Tr}[G_{D_{\sigma}}^{-1} \Gamma_i G_{D_{\sigma}} \Gamma_{-i}](E),$$

where the trace runs over states in the device region consisting of the VBZ cluster, perturbed graphene parts (light-colored part in Fig. 1), and electrode-connected graphene (black in Fig. 1). Note that $\Gamma_i(E) = \text{Im}[\Sigma_i(E)]$, $i = 1, 2, 3, 4$, is nonzero only in the electrode-connected (black) parts, and are independent of spin since the semi-infinite graphene electrodes (not shown) are not polarized.

We consider the three possible classes of clusters: (I) Vanadium atoms on both end sides (V$_n$BZ$_n$), (II) One vanadium and one benzene on each end side (V$_n$BZ$_n$), and (III) Benzenes on both end sides (V$_n$BZ$_{n+1}$). In Fig. 2 we show the calculated spin-resolved transmission for the three classes of systems. If we, for the moment, ignore the resonant tunneling peak in Fig. 2c, we find that the absolute magnitude of the transmission is determined by the strength of the contact-cluster coupling. The strong covalent vanadium-graphene bond, causes overall larger transmission than weak benzene-graphene bonding. The resonant transmission peak for the class III structures is possible because of the weak interaction between cluster and contact in this case which enables an almost localized state on the cluster. The position of the resonance peak is sensitive to the details of the structure, e.g., exact bonding geometry and size of cluster. However, the spin polarization of the transmission is large even out of resonance.

To quantify the results, we use the transmission spin polarization (TSP) and charge spin polarization (CSP) measures defined as,

$$\text{TSP} = \frac{T_{\text{Min}} - T_{\text{Maj}}}{T_{\text{Min}} + T_{\text{Maj}}}$$

$$\text{CSP} = \frac{Q_{\text{Maj}} - Q_{\text{Min}}}{Q_{\text{Maj}} + Q_{\text{Min}}}.$$
of the geometrical arrangement of the junctions, we enhance the TSP with cluster length. Additionally, increasing the length of cluster causes the transmission for minority component to decrease exponentially while the transmission for the majority spin component to increase. In agreement with earlier studies, we find 3 crossing bands (2 degenerate) corresponding to Bloch waves with $d_{xy}/d_{x^2-y^2}$ and $d_{z^2}$ character on the V atoms, see Fig. 3(a) and 3(b). The $d_{z^2}$ band displays little dispersion since the $d_{z^2}$ are only able to couple weakly through the BZ via the hydrogen atoms. On the other hand, the degenerate $d_{xy}/d_{x^2-y^2}$ bands couple strongly through the BZ, $\pi$-orbitals leading to larger dispersion. From the band structure, we anticipate a maximum of 3 transport channels for the finite cluster. However, in our transport calculations of the finite cluster, we find only 2 equally contributing minority spin transmission eigenchannels corresponding to scattering states with $d_{xy}/d_{x^2-y^2}$ character. The more localized $d_{z^2}$ states only contribute to the spin polarization and not to the transport. The scattering states of the two highest transport eigenchannels [34] are presented in Fig. 3(c) for $V_4BZ_3$ for each of the two spin components. The corresponding transmission eigenvalues are $T_1 = 0.10$, $T_2 = 0.05$ and $T_1 = 0.60$, $T_2 = 0.59$ for the majority and minority spin components, respectively. A decaying behavior through the layer is observed for the minority spin wave functions which explains the increase in TSP with layer length. We draw similar conclusions about transport channels for the other structures we have studied. The appreciable spin-filter effect found even for the strongly bound, short $V_3BZ_2$, is presumably due to the rather similar type of bonding of vanadium to graphene and benzene.

In summary, we have shown a high degree of spin polarization of electron transmission in a class of molecular systems consisting of organometallic half-metallic benzene-vanadium clusters sandwiched between CNT or graphene contacts. So far, the majority of studies in molecular spintronics have focused on ferromagnetic contacts. In this work we have investigated another category of systems where the contacts are nonmagnetic and magnetization is solely due to the molecule. The TSP depends on the nature of bonds between cluster and contacts; however, the high values for TSP (from 73% to 99%) in the different structures show that this effect does not depend critically on a specific structure or orientation of $V_nBZ_m$ cluster. We suggest these could be used to spin filter electronic current in graphene-based nanodevices when the molecular spin is fixed by external means.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>TSP(%)</th>
<th>CSP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_3BZ_2$</td>
<td>73</td>
<td>4.9</td>
</tr>
<tr>
<td>$V_4BZ_3$</td>
<td>77</td>
<td>5.8</td>
</tr>
<tr>
<td>$V_5BZ_4$</td>
<td>81</td>
<td>6.8</td>
</tr>
<tr>
<td>$V_3BZ_3$ (Bridge)</td>
<td>91</td>
<td>6.6</td>
</tr>
<tr>
<td>$V_4BZ_4$ (Bridge)</td>
<td>80</td>
<td>7.6</td>
</tr>
<tr>
<td>$V_5BZ_5$ (Bridge)</td>
<td>84</td>
<td>8.3</td>
</tr>
<tr>
<td>$V_2BZ_3$ (Bridge-Bridge)</td>
<td>93</td>
<td>2.4</td>
</tr>
<tr>
<td>$V_3BZ_4$ (Bridge-Bridge)</td>
<td>99</td>
<td>3.6</td>
</tr>
<tr>
<td>$V_4BZ_5$ (Bridge-Bridge)</td>
<td>99</td>
<td>4.7</td>
</tr>
</tbody>
</table>
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[25] Relaxed geometries: $d_{\text{VBZ}} = 1.695 \text{ Å}$, $r_{\text{CC}} = 1.45 \text{ Å}$, and $r_{\text{CH}} = 1.09 \text{ Å}$ in accordance with [24]. We used the most stable structure with $D_{6h}$ symmetry.
[28] DZP basis (energy-shift 0.01 Ry), grid cut-off 150 Ry, GGA-PBE for exch.-corr. [29]. The GSM was tested using 10 $k$ points in the periodic $x$ dir.: The $k$-averaged transmissions did not change noticeably.
[34] A. Paulsson and M. Brandbyge, cond-mat/0702295.