Effect of edge states on the transport properties of pentacene–graphene nanojunctions

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We investigate the effect of edge states on the transport properties of pentacene–graphene nanojunctions
on the basis of DFT and NEGF formalism. The calculations reveal that strong interaction between penta-
cene and zigzag GNR leads to edge-induced transmission channels at the Fermi region which controls the
low-bias current. Effects of substitution by electron withdrawing and donating groups on the transport
properties of molecular pentacene have also been discussed, some of which show spin resolved transport
properties with negative differential resistance behavior which may have potential application in spin-
tronics devices.

C O R R E S P O N D I N G   A U T H O R

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1. Introduction

In recent years there is a growing interest in the use of organic semiconductors as the building block of microelectronics or nano-
electronics. Pentacene is one such organic semiconductor which has shown promise in organic thin-film transistors and having high
field-effect mobility [1–4]. The most attractive features which led pentacene to be the most useful are its high electron and hole
mobility, high susceptibility towards thin film formation, and inherent low band-gap owing to its extensive π conjugation and
electron delocalization [5,6]. That is why pentacene-based molecular junctions, using various metal contacts, have been wide-
spread studied both theoretically as well as experimentally and pentacene is considered to be benchmark semiconductor in organ-
ic electronic devices. It has also been used to fabricate organic photovoltaics [7].

During the last couple of years, carbon-based materials such as graphene, carbon nanotube are proved to serve as better contact
moiety for molecular junctions as they are directly synthesized at the contact region using chemical vapor deposition and can be pat-
tened by lithographic technique [8–11]. Moreover, recent advances in material growth and control techniques have made
graphene and its 1D ribbon possible to be synthesized in different orientations. The high conductivity and transparency of graphene
electrodes have been employed in organic field-effect transistors and organic photovoltaic solar cells [12–14]. Graphene or few lay-
ered graphene electrodes have also been used for electron transport through molecular films or molecular junctions [15,16].

Compared to two-dimensional graphene, graphene nanoribbons (GNRs) are distinct by their electronic and optical properties.
The electronic properties of GNRs are sensitive to many factors, edge modification being one of the main control over them
[8,17–20]. It has been show that zigzag graphene nanoribbons (zGNRs) exhibit low band-gap semiconducting properties in its
antiferromagnetic ground state [19], while they show halfmetallic-
ity under the application of external bias [21,22]. The magnetism in
zGNRs is attributed to the peculiar localized states along the zigzag
edges [23,24]. There have been extensive researches on the charge
and spin transport properties of zGNR hetero-junctions [25–29]
showing negative differential resistance, spin filtering effect etc.,
promising them to be useful in magnetoelectronics and spintronics
devices. Charge transport in pentacene–graphene nanojunctions
has recently been investigated employing density functional the-
ory in combination with the Landauer transport formalism [30].
The authors have demonstrated how the transport properties are
influenced by pentacene–graphene coupling pattern and the
energy level sequence. Although the influence of edge states are ta-
ken into consideration, they did not resolve the effect of spin chan-
nels which is crucial for zigzag edged graphene ribbons.

In this Letter, we have considered the simplest way of penta-
cene–graphene nanojunction where the pentacene molecule is
trapped between two zigzag nanoribbons to study the effect of
individual spin channels. Furthermore, the molecular levels of
pentacene have been tuned by the influence of electron donating
or withdrawing functional groups. In order to explore the possi-
bility of practical electronic device application, we have studied the
current–voltage characteristics of these nanojunctions. Thus the
various nanojunctions made of differently functionalized penta-
cene show various types of spin resolved transport properties with
negative differential resistance behavior which are expected to guide while designing spintronics devices.

2. Model and computation

We design our pentacene–graphene nanojunction as the simplest way of molecular contact. The overall model is a two probe system where two edges of the pentacene molecule is linked to the 4-zGNRs via H-terminated graphene fragment as shown in Figure 1. Thus, a well connectivity is always maintained between the scattering region and the electrodes. For functionalized pentacene the functional group is attached preferably to the top of the middle hexagonal ring of pentacene as indicated by the encircled H atoms in Figure 1. For bifunctional attachment the second functional group is attached just opposite side of the first group so as to perform as a fully delocalized system. In each case, the overall system is relaxed until the maximum absolute force was less than 0.001 eV/Å within generalized gradient approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) exchange correlation functional [31]. For k-point sampling we used $1 \times 1 \times 6$ Monkhorst-Pack k-grid along periodic direction while lattice constant (LC) is optimized to be 29.76 Å for pure pentacene–zGNR junction. For functionalized pentacene, however, the optimized LC is varied to some extent. Double-$\zeta$ plus polarization function (DZP) basis set and norm-conservative Troullier-Martins pseudo-potentials (PP) [32] have been used for representing the valence and core electrons as implemented in SIESTA package [33]. A real space mesh cutoff of 300 Ry has been used throughout the entire calculation and the electronic temperature is set to 300 K.

For performing spin transport calculations we employ non-equilibrium Green’s function (NEGF) [34,35] formalism as implemented in TranSIESTA module within the SIESTA package. In our two-probe model as shown in Figure 1, unit cell of 4-zGNR serves the role of both semi-infinite left and right electrode (LHE, RHE). Pentacene or functionalized pentacene is used as the finite part, i.e. the scattering region (SR). Now, under a certain bias $V_b$, the spin polarized current through the scattering region can be calculated using the Landauer-Buttiker formula,

$$I(V_b) = \frac{e}{h} \int_{-\infty}^{\infty} T(E, V_b)\left[f_L(E, \mu_L) - f_R(E, \mu_R)\right]dE$$ (1)$$

where $f_{L(R)}$ is the equilibrium Fermi–Dirac distribution function for left (right) electrode, $\mu_{L(R)}$ is the electrochemical potential of the left (right) electrode such that energy bias $eV_b = \mu_L - \mu_R$, and $T(E, V_b)$ is the spin resolved transmittance of an incident electron with energy $E$ which can be obtained using the equation,

$$T(E, V_b) = Tr\left[\Gamma_L G^0 R G^0 \Gamma_R\right]$$ (2)$$

where $G^0$ is the retarded (advanced) Green’s function of the scattering region, and $\Gamma_{L(R)}$ is the coupling strength of the left (right) electrode. We used finite bias from –3 V to 3 V with small grid of 0.1 V to investigate the current–voltage (I–V) characteristics for both the spin components.

3. Results and discussion

Let us first give some outlines on the geometry and electronic structure of molecular pentacene. It is known that molecular pentacene is planer in its ground state configuration and it is totally symmetric with respect to the two C$_2$ axes perpendicular to each other. Our GGA/PBE calculations also reflect the similar results. Considering molecular specification in the yz plane, the vertical C–C bond distance (along y direction) varies from 1.43 to 1.46 Å while entering from edge to the center of the molecule. The zigzag C–C bond lengths vary from 1.38 to 1.44 Å where the sum of two such bonds in a hexagon is maintained to 2.82 Å. Our results are in excellent agreement with the previously calculated values [36] and experimental observation [37]. However, in the constrained geometry where the pentacene is attached to zGNR leads, the bond length alteration is reduced to some extent. In case of substituted pentacene, the substituent groups (–NO$_2$, –NH$_2$) are essentially in the same plane as that of molecular pentacene which facilitates extended delocalisation. The calculated HOMO–LUMO gap is 1.1 eV, although, in agreement with the previous calculation [36], as the general discrepancy of GGA it is much less than the experimental value (1.82 eV) reported from ellipsometric spectra of thin pentacene films [38].

Before going to details of the transport properties of pentacene–zGNR nanojunction we wish to remember that the ground state of zGNR is antiferromagnetic with zero net magnetization where the magnetization is confined to the spin degenerate edge states which creates an energy gap at the Fermi level [20,21]. Our GGA calculation predicts a band gap for 4-zGNR which is in the order of 0.8 eV. Thus, although molecular pentacene is non magnetic in nature, the overall calculations are performed with antiferromagnetic spin configurations. Consequently, the small transport gap near Fermi energy, in each case, is mainly due to the band opening of the semi infinite leads of zGNRs. This is also reflected from the appearance of threshold voltage in the current–voltage characteristics of the pentacene– as well as substituted pentacene–GNR junctions in each case. However, upon application of finite voltage, in case of the substituted pentacene junctions, two spin components carry electricity through the junction in different extent resulting spin resolved transport properties. The reason behind the spin resolution would be discussed in the subsequent section.

In case of unsubstituted pentacene the observed I–V curve (see Figure 2) is antisymmetric in nature, because the whole system has an mirror symmetry. However, spin resolved calculation gives the same spin current for both the spin-up and spin-down with a threshold voltage of around 0.8 V. As there is no direct contact between the two zGNR leads and these are separated by pentacene
molecule, direct tunneling between the leads is not possible. Thus, the appearance of the two zero bias transmission peaks (shown in Figure 3) below and above the Fermi level may be ascribed as the resonance tunneling between the molecular HOMO and LUMO of pentacene and the degenerate edge states of the zGNR, respectively (the corresponding figures are shown in Supplementary Material, Figure S1). Their amplitude (1 $G_0$) indicates a high value of conductance quantum at near about Fermi level. However, as the applied voltage is zero, the integrated current is zero. It should be pointed out that these results are in good agreement with the recent results of Thos et al. in their strong molecule-lead coupling scheme for pentacene-graphene nanojunction through oxygen atoms [30] who also report resonance peaks with unit transmission value near Fermi level. However, we observe no electronic transmission exactly at the Fermi level. Few more transmission functions with similar intensity are also observed within ±2 eV of energy which are essentially resonance tunneling between the other molecular states of pentacene and the dispersed bands of the leads. Due to strong coupling between the molecule and the leads, as also reflected from the broadness of the peaks, it is very difficult to isolate from which molecular states they appear. With increasing the applied bias voltage, transmission value at the Fermi level and within the bias window (from $-eV_b/2$ to $eV_b/2$) first gradually increases resulting overall increase in integrated current up to 2.2 V. It is interesting to note that the a single peak at the Fermi energy at a bias voltage of 0.8 V is first broadened and split with increasing bias. With further increase in bias two peaks near the Fermi level are separated, but the current reaches to the maximum at 2.2 V. Thereafter, the current drops within the bias range from 2.2 V to 2.6 V indicating negative differential resistance (NDR) behavior as also commonly observed for many graphene junctions [39–42]. At the extreme situation (at $V_b = 2.6$ V) the transmission spectra near Fermi region become narrower and they are separated much. Transmission peaks at near about ±0.5 eV are now predicted to be due to weakly coupled molecular states with zGNR. Noticeably, the dips in the transmission spectrum at about −0.5 eV. and at 0.7 eV are again in support of the localized states of molecular pentacene. This discreteness of the transmission functions ultimately leads to reduction of integrated current within the bias region. So, the NDR phenomenon is occurred due to localized states of the molecular pentacene appearing within 2.2–2.6 V of applied bias. In this regard it is worth mentioning that Cheragchi et al. [43] explained the NDR in nanojunction on the basis of sharp features in LDOS and they have also emphasized the charging effect which plays an enhancing role in producing NDR. According to them, a large bias causes asymmetric coupling between the molecule and the electrodes which in turn leads to the appearance of asymmetric potential profile due to depletion of charge and reduction of screening near the source electrode. Consequently, there occurs strong localization of molecular states on different parts of the system thereby reducing transmission and current. NDR behaviors originate from the interaction between the narrow density of states of the doped leads and discrete states in the scattering region as also explained by Ren et al. [39].

Another interesting feature coming out from the transmittance curve is that at low bias region, the finite bias transmission is mainly due to the edge-induced transmission peak with amplitude almost 1 $G_0$ appearing at the Fermi energy. As also described by Thoss et al. [30], these are neither due to direct tunneling between the edge states of the two zGNR leads, nor due to molecular resonance states. The edge-induced transmission channels are direct consequence of strong molecule-lead coupling which have also been reported earlier for molecule-metal contacts [47,48]. It is worth pointing that in our case this peak appears only after the threshold bias (~0.8 V) in contrast to that reported in zero-bias transmission spectrum by Thoss et al. [30] which is presumably due to consideration of nonmagnetic metallic state of zGNR in their calculations. The influence of edge states on the transport properties of pentacene-graphene nanojunctions appears more predominantly when pentacene is functionalized with electron withdrawing or donating groups. Both types of the groups participate in the extended delocalization of the π electrons and consequently they reduce the HOMO–LUMO gap of the molecule. The reduced HOMO–LUMO gap is also reflected from the appearance of the edge-induced transmission peak.
and $R = 2.6$ V for nitro-amine group and thus the spin resolved current is maximum at $-2\,\text{V}$. So, it is expected that the dipolar group at-borod (red) line represents up (down) spin. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

of broader edge-induced transmission channel at the Fermi level. Figure 4 displays the I–V characteristics of nitro-amine bifunctionalized pentacene–zGNR nanojunction, while Figure 5 depicts the transmission spectrum of the same at different bias. At some finite bias (0.8 V), a stronger transmission peak, compared to that of unsubstituted one, at the Fermi level is observed. The additional intensity in the transmission peak of one spin component may be ascribed as the lifting of degeneracy of the edge states of zGNR under the influence of dipolar field of the functional group which will be discussed later. With increasing bias, this peak is broadened and splitted into two peaks of similar intensity. Additionally, from this figure it is also revealed that two spin components are resolved immediately after the threshold voltage. With increasing bias, two spin channels become separated resulting different spin current. However, both the spin currents show NDR phenomena but with different peak positions and different PVR (peak-valley ratio) values.

For investigating the origin of the spin transport properties of the pentacene–zGNR nanojunction we recall that under transverse electric field, zGNRs show halfmetallicity [19] which is supposed to be originated from a unique interplay between the inter-edge antiferromagnetic ordering and the relative potential shift between two edges. Many researchers have also suggested diverse methods for showing halfmetallicity without external electric fields, such as introducing quantum dots with the zigzag edges, functionalizing edges of zGNRs, substituting edge carbon atoms by boron, nitrogen etc. or by depositing ferroelectric material on functionalizing edges of ZGNRs, substituting edge carbon atoms by both nitro and amine group placed anti to each other, i.e. when $R = \text{NO}_2$ and $R' = \text{NH}_2$ in Figure 1. Here, the opposing electronic effect of the two groups produces pronounced dipolar effect which results relatively much more spin resolution in transmission channels. We wish to mention here that Kan et al. [45] reported that bifunctionalization of zGNR with nitro and amine groups results metallic spin-down and semiconducting spin-up channels which can be elucidated to explain the difference in transmission values at the Fermi energy for the two spin components in case of nitro-amine bifunctionalized pentacene as shown in Figure 5.

We have also studied some nanojunctions with wider ribbon (6-zGNR) to see the effect of width on the transport properties. It is quite obvious to see similar type of behavior in the I–V characteristics; the unsubstituted pentacene shows spin independent NDR phenomenon, while the substituted one shows spin resolved transport properties as displayed in Supplementary Material, Figure S2. However, the peak and valley positions of I–V curves are shifted for both the cases as compared to the narrower ribbon.

The consequence of spin resolution is the spin filtering ability which can be quantified in terms of spin resolved current at finite bias ($I_s$) and is defined as $I_s = \frac{I_{up} - I_{down}}{I_{up} + I_{down}}$. We have found the highest value of $I_s = 0.41$ at an applied bias $V_b = 2.6$ V for nitro-amine bifunctionalized pentacene. Although the spin filtering ability is predicted to be low, the spin resolved current may be utilized in spintronics devices. The mechanism of spin dependent NDR phenomena may be understood on the basis of variation of spin induced transmission function as a function of applied bias as shown in Figure 5 in case of nitro-amine bifunctionalized pentacene as an example. It is clear from the figure that at 0.8 V of applied bias the transmission functions are almost inseparable. With further increasing the bias up to 1.8 V transmittance ($T(E)$) and hence current increases for both the components. With further increase in $V_b$, $T(E)$ for spin up component decreases resulting decrease in up-current, while that of spin down component still increases up to 2.2 V. At that bias spin down channel gives maximum current owing to its two bifurcated strong transmittance peaks whereas that of spin up component is almost half and it still decreases. This explains the different peak current positions for individual spin components and thus the spin resolved current also varies accordingly, however, both the components show NDR behavior. The difference between the spin down and up current is maximum near the valley position of the I–V curve (precisely at $V_b = 2.6$ V) and thus the spin resolved current is maximum at that bias.

4. Conclusion

Summarizing, we have performed a first principle calculations based on spin resolved density functional theory and non equilibrium Green’s function analysis to study the transport properties of various pentacene–graphene nanojunctions where the molecular pentacene is strongly coupled to zGNR leads. As a result of this strong coupling there appear edge-induces transmission channels at finite bias voltage. Functionalization of molecular pentacene with dipolar groups creates an internal field which subsequently lifts the degeneracy of the edge states of the zGNR leads and thus the substituted pentacene–graphene nanojunctions show spin resolved transport properties. Spin dependent current–voltage characteristics of these devices show negative differential resistance behavior which is attributed to the localization of the molecular states at some particular bias region. Although the spin filtering
ability of the devices are predicted to be low, the spin resolved transport properties may be useful for designing bias dependent spintronics devices.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2014.02.027.

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