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The role of impurities on the properties of electron transport through the metal/*trans*-PA/metal system: Green's function approach

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ABSTRACT

In this work, we present a theoretical study on the conductance of *trans*-polyacetylene (*trans*-PA) nanowire in the presence of impurities and use of *trans*-PA as a molecular bridge sandwiched between two semi-infinite metallic electrodes with a simple cubic structure and square cross section. We use a tight-binding Hamiltonian model within the framework of a generalized Green's function technique and rely on the Landauer–Bütikker formalism as the basis for studying the current–voltage characteristic of this system. Our calculations indicate that the presence of impurities gives rise to significant enhancement in the density of states within the bandgap and large enhancement in conductance and the current–voltage characteristic. Also our results show that the electronic properties of the system are sensitive to the molecule-to-impurity coupling strength.

1. Introduction

The study and manipulation of matter on the nanometre scale is a thriving area of research, with profound implications for technology (e.g. nanoelectronics, nanostructure materials and nanobiology). One of the most attractive research areas has been focused on the use of molecular system as electronic devices. So devices have been designed in such a way that a molecule is sandwiched between two electrodes (metallic or organic). Among these compounds, *trans*-PA is the most studied. This is due to the fact that while, being the simplest π-conjugated polymers *trans*-PA has considerable potential applications as an alternative conductor. The possibility of the semiconductor-to-metal transition and the capability of becoming a conductive material have been the reason for the experimental and theoretical investigations on the physical properties of *trans*-PA in comparison with other conducting polymers [1]. Based on experimental data, the metallic phase in doped *trans*-PA is characterized by a conductivity that is on the order of 10^4 s/m, a factor of 10^{12} greater than the conductivity in the insulating forms of the polymer [2–7].

There are a large number of works concerning the study of physical mechanisms behind the metallic transition in *trans*-PA [8–10]. The experimental investigations on the conduction properties of *trans*-PA support the idea that disorder is responsible for insulator to metal transition in *trans*-PA [11–15]. For example, in a series of papers, Harigaya and Teral [16] and Harigaya [17,18] have studied and supported the possibility of survival of the metallic regime in polyacetylene. However, there are still important factors whose influence on the transition to metallic regime in *trans*-PA has not yet been fully studied. There has been an increase in the theoretical modeling for studying how the details of *trans*-PA electronic structures affect the transition to metallic regime in *trans*-PA. Accordingly, here we focus on the presence of a chain impurity that adds as a parallel chain with *trans*-PA (Fig. 1(a)). In addition to showing that the impurity causes reduction of bandgap and getting near the metal phase, we can reach a two-dimensional polymer structure. For example, with the change in the number of vertical coupling, as one among, and the usage of appropriate parameters, we reach the polyacene structure as one of the two-dimensional polymers (Fig. 1(b)).

We numerically investigate the density of state, transmission and current–voltage (I–V) characteristics of *trans*-PA molecule in the metal/*trans*-PA/metal system in the presence of chain impurity. The model and the description of the methods are introduced in Section 2. The results and discussion are presented in Section 3, followed by a conclusion in Section 4.

2. Methodology

Here, we describe very briefly the methodology for the calculation of electronic states of the system, transmission (T) and conductance (g) through a metal/*trans*-PA/metal system in the presence of impurities attached to two semi-infinite metallic electrodes with finite cross sections, simple cubic structure and

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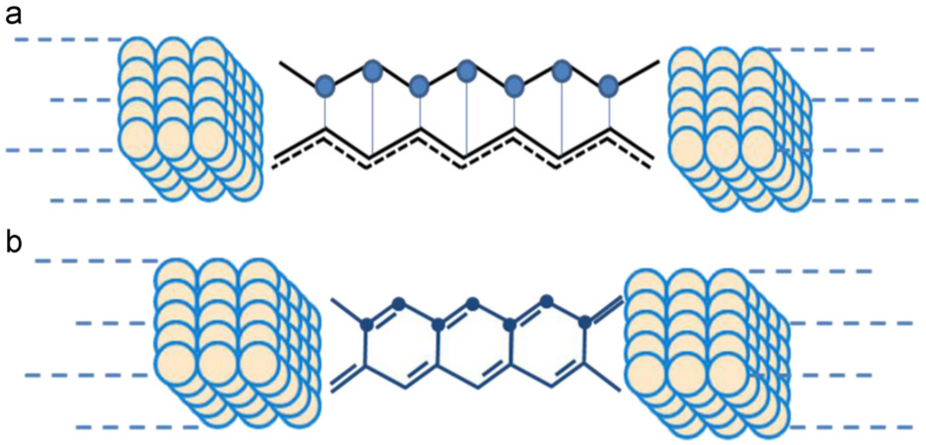

Fig. 1. Schematic representation of (a) the metal/*trans*-PA/metal system in the presence of impurities, as described in the text and (b) the metal/polyacene/metal system.

square cross section (x–y plane) [19] using the Green's function method. At low voltage (V) and low temperature limit the conductance of the conductor (*trans*-PA and impurity) can be written by using the Landauer [20] conductance formula:

$$g(E) = \frac{2e^2}{h}T(E), \tag{1}$$

where g is the conductance, T is the transmission probability of an electron through the conductor and E is the energy of the injecting electron. The transmission can be expressed in terms of Green's function of the conductor and the coupling of the conductor with the two electrodes by the expression

$$T(E) = Tr[\Gamma_L(E)G_C^r(E)\Gamma_R(E)G_C^a(E)], \tag{2}$$

where G_σ^r and G_σ^a are the retarded and advanced Green's function of the conductor, respectively. $\Gamma_{L(R)}$ are the coupling terms due to the coupling of the conductor with left (L) and right (R) electrodes, respectively. Green's function is defined as

$$G(E) = ((E+i\eta-H)^{-1}, \tag{3}$$

where η is a very small number that can be put as zero in the limiting approximation. The above Green's function corresponds to the inversion of an infinite matrix that consists of the finite conductor and the two semi-infinite electrodes. Green's function for the conductor can be written as

$$G_C(E) = [EI-H_C-\sum\nolimits_R(E)-\sum\nolimits_L(E)]^{-1}, \tag{4}$$

where H_C is the Hamiltonian for the conductor sandwiched between the two electrodes. The tight-binding Hamiltonian for the conductor within the non-interacting picture can be written in the following form:

$$\begin{aligned} H_C = \sum_{n=1}^{N}\sum_{i,j=1}^{2} & [\delta_{ij}\varepsilon(n,i)|n,i\rangle\langle n,j| \\ & + t_{\text{intra}}(n,i,j)|n,i\rangle\langle n,j| + t_{\text{inter}}(n,i,j)|n,i\rangle\langle n+1,j|], \end{aligned} \tag{5}$$

where $\varepsilon(n,i)$ represents the on-site energy, $t_{intra}(n,i,j)$ the hopping between the atoms within the unit cell n and $t_{inter}(n,i,j)$ the hopping between atoms in neighboring unit cells. The sum over n runs over the unit cells and the sums over i and j run over the atoms in the unit cell. The electron–electron interaction is a minimal effect on the properties of electron transport in our system, since only delocalized π orbitals of the *trans-PA* molecule are involved. However in the present work we do not consider the electron–electron interaction in our model.

In Eq. (4), $\Sigma_L = h_{LC}^\dagger g_L h_{LC}$ and $\Sigma_R = h_{RC} g_R h_{RC}^\dagger$ are the self-energy terms due to the two electrodes g_L and g_R, respectively, which are the surface Green's function for the (L) and (R) electrodes, $h_{\alpha M}$ are the coupling matrices and they will be non-zero only for the adjacent points in the conductor, 1 and $p-1$ as shown in Fig. 2, and the electrodes $\alpha(\equiv L,R)$. The coupling term Γ_L and Γ_R for the conductor can be calculated through the expression [20]

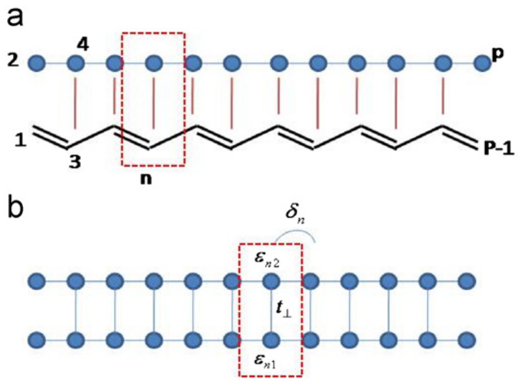

Fig. 2. Representation of polyacetylene and impurities (a) and its topologically equivalent lattice (b). Each unit cell has two atoms. The on-site energies is ε_{n1} and ε_{n2}. Hopping strength in the chain impurity is δ_n and molecule-to-impurity coupling strength is $t_\perp$.

$$\Gamma_\alpha = i\left[\sum_\alpha^r - \sum_\alpha^a\right] \tag{6}$$

where the advanced self-energy Σ_α^a is the Hermitian conjugate of the retarded self-energy Σ_α^r. All the information about the electrode-to-molecule coupling are included in these two self-energies. In this study we have assumed the number of surface atoms to be 25 (i.e. the electrode cross section is 5 × 5 atoms) and only the central atom of electrodes to be linked to conductor. Thus the coupling term can be written as

$$\Gamma_\alpha = -2\mathrm{Im}\left(\sum_\alpha^r\right) \tag{7}$$

g_α is the surface Green's function of the uncoupled electrodes and their matrix elements are given by [19]

$$g_\alpha(m,n;z) = \sum_k \frac{\psi_k(r_m)\psi_k(r_n)}{z-\varepsilon_0+E(k)} \tag{8}$$

where m,n show $m^{\text{th}}(n^{\text{th}})$ site in electrode α, and $r_m \equiv (x_m,y_m,z_m)$, $k \equiv (l_x,l_y,k_z)$, $z = E+i\eta$,

$$\psi_k(r_m) = \frac{2\sqrt{2}}{\sqrt{(N_x+1)(N_y+1)(N_z)}}\sin\left(\frac{l_x x_m \pi}{N_x+1}\right)\sin\left(\frac{l_y y_m \pi}{N_y+1}\right)\sin(k_z z_m) \tag{9}$$

and

$$E(k)=2t\left(\cos\left(\frac{l_x\pi}{N_x+1}\right)+\cos\left(\frac{l_y\pi}{N_y+1}\right)+\cos(k_za)\right) \tag{10}$$

Here $l_{x,y}(=1,\ldots,N_{x,y})$ are integers, $k_z\in[-\pi/a,\ \pi/a]$ and N_β with $\beta=x,y,z$ is the number of lattice sites in the β direction. Note that N_x and N_y correspond to the number of atoms at the cross section of electrodes. ε_0 is the on-site energy in the electrodes, and will be set to $3t$, where t is the hopping strength between nearest-neighbor sites in the (L) and (R) electrodes.

We calculated the current–voltage (I–V) characteristics using the Landauer–Bütikker formula [20]

$$I(V)=\frac{2e}{h}\int_{-\infty}^{+\infty}T(E,V)[f(E-\mu_L)-f(E-\mu_R)]dE \tag{11}$$

f is the equilibrium Fermi distribution and $\mu_{L,R}=E_F\pm eV/2$ are the electro-chemical potentials of the electrodes in terms of the common Fermi energy E_F for the left (L) and right (R) electrodes. For the sake of simplicity, here we assume that the entire voltage drop is across the conductor–electrode interfaces and this assumption does not significantly affect the qualitative aspects of the I–V characteristics. Usually, the electric field inside the conductor, especially for small conductors, seems to have a minimal effect on conductance. Thus it introduces very little error if we assume that the entire voltage is dropped across the conductor–electrode interfaces. On the other hand, for larger molecules and higher bias voltage, the electric field inside the molecule may play a more significant role depending on the size and structure of the molecule [21], though the effect becomes quite small.

3. Results and discussion

Based on the formalism described in Section 2, we have investigated the electronic conduction properties of the metal/*trans*-PA/metal structure. Here we focus on the dependence properties of electron on the presence of impurities in the *trans*-PA nanowire. Using Eq. (5) and Fig. 2, Hamiltonian of the nth cell and the overlap integral this cell and the next cell are given by

$$H_n=\begin{bmatrix}\varepsilon_{1n} & 0\\ 0 & \varepsilon_{2n}\end{bmatrix},\qquad t_{\text{inter}}=\begin{bmatrix}t_{k+1,k} & 0\\ 0 & \delta_n\end{bmatrix}$$

$$t_{\text{intra}}=\begin{bmatrix}0 & t_\perp\\ t_\perp & 0\end{bmatrix},\qquad H_1=\begin{bmatrix}\varepsilon_{11}+\sum_L & 0\\ 0 & \varepsilon_{12}\end{bmatrix} \tag{12}$$

$$H_N=\begin{bmatrix}\varepsilon_{N1}+\sum_R & 0\\ 0 & \varepsilon_{N2}\end{bmatrix},\qquad n=1,\ldots,N$$

N is the number of the cell, ε_{1n} and ε_{2n} are on-site energies in the nth cell related to atoms polyacetylene and impurity, respectively, and the hopping parameters are defined in Fig. 2. Only $t_{k+1,k}$ (here k represents an electron on the kth tight-binding site of *trans*-PA, where the sum $k=1,\ldots,N$ extends over all sites) is the hopping parameter for homogeneously dimerized chain *trans*-PA [14]:

$$t_{k+1,k}=t_0+\gamma(u_k-u_{k+1}), \tag{13}$$

where t_0 is the hopping strength of an undimerized chain, γ is the electron–phonon coupling constant and u_k is the displacement of the kth carbon atom from its equilibrium position. For perfectly dimerized *trans-PA*, u_k is given as $u_k=(-1)^k\,u_0$. Using the parameters of Refs. [22,23], we set $\alpha=4.1$ eV Å^{-1}, $u_0\approx0.04$ Å, $t_0=2.5$ eV and also $\varepsilon_{1n}=\varepsilon_{2n}=0$, $\delta_n=\delta=1$ eV, $N=40$, $N_x=N_y=5$, $t=1$ eV, $t_c=0.5$ eV and $T=300$ K, where t_c is the coupling strength between molecule and electrode, which is an important parameter and could influence the shape of current–voltage and conductance curve [24–26] and we consider it fixed in the calculations.

Fig. 3 illustrates the electronic density of states (DOS) of the metal/*trans*-PA/metal system in the absence ($t_\perp=0$ eV) and in the presence of impurities ($t_\perp=0.45$ eV; panels (a) and (c), respectively), where $t_\perp$ is the coupling strength between molecule and impurity. The plots show that the presence of impurities induces electronic states within the bandgap and causes large enhancement in conductance ($g=g_0T$ where g_0 is quantum conductance) of the system. Also, the logarithm of the transmission through the molecule is shown in panels (b) and (d), which correspond to panels

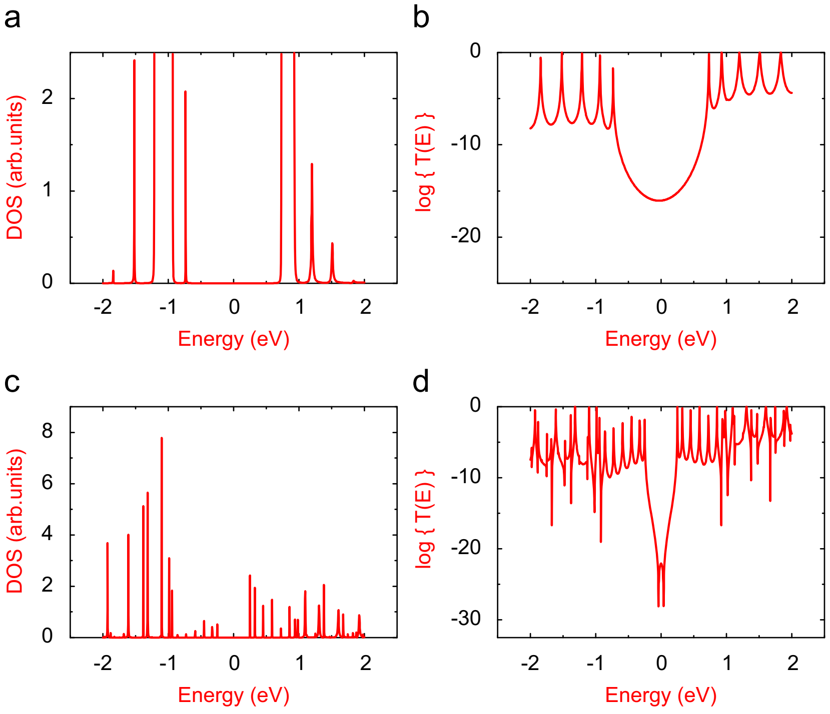

Fig. 3. Panels (a) and (c) show the density of state (DOS) versus energy for the metal/*trans*-PA/metal system without ($t_\perp=0$ eV) and with impurity ($t_\perp=0.45$ eV), respectively. Corresponding to plots (a) and (c), logarithm of the transmission (log $\{T(E)\}$) is illustrated in panels (b) and (d), respectively.

(a) and (c), respectively. Curves of density of states and transmission exhibit sharp resonant peaks for some particular energies, while they almost vanish for all other energies. It emphasizes that fine tuning in the energy scale is necessary to get electron conduction across the molecule. All these resonant peaks are associated with the energy eigenvalues of the molecule, and hence, we can predict that the electronic density of states and transmission spectrum manifest themselves in the electronic structure of the molecule. In the presence of impurities, more resonance peaks appear in the electronic density of states and the logarithm of the transmission spectrum, which reveals that more energy levels appear in the system (Fig. 3(c) and (d)). The physical reason is that the effect of quantum interference of the electronic wave's passing through different branches of the conductor provides different paths for electron transmission between the electrodes. Thus, we can predict that electronic transport is significantly influenced by the quantum interference effect, i.e. the molecule–impurity interface structure [26].

The calculated current–voltage (*I*–*V*) curves for the molecule attached to metallic electrodes are shown in Fig. 4. The effect of an applied voltage is from the shifting of the chemical potentials of the two electrodes relative to each other by *eV*, where *e* is the electronic charge. Currents will flow whenever a molecular level (either the highest occupied molecular orbital or the lowest unoccupied molecular orbital) is positioned within such a bias window. The appearing of molecular levels in the bias window when the potential is increased typically leads to changes in the slope and a step-like behavior of the *I*–*V* characteristics. Additionally, it is also important to note that the non-zero value of the current appears beyond a finite value of *V*. In presence of impurities, the step-like feature almost disappears and the current varies quite continuously with the bias voltage *V*. Here the non-zero value of current is observed for a small value of bias voltage *V*. Also, it is clearly observed from this figure that the current shows more steps (Fig. 4(b)) compared to the without impurity system, which reveals that more resonance peaks appear in the logarithm of the transmission spectrum for non-zero values of $t_\perp$.

Note that with changes in the number of vertical coupling and use of the equation $\delta_{k+1,\,k}=t_0+\gamma\,(u_k-u_{k+1})$ for the hopping parameter for chain impurity, we obtain the structures of polyacene shown in Fig. 4(c) and here the molecule-to-impurity coupling strength is $t_\perp=1.08$ eV [27–30]. Note that the molecule is attached to the electrodes in the *trans* configuration [31].

Finally, in Fig. 5 we show the changes of conductance for different values of $t_\perp$. With increase in molecule-to-impurity coupling strength, the conductance varies almost continuously

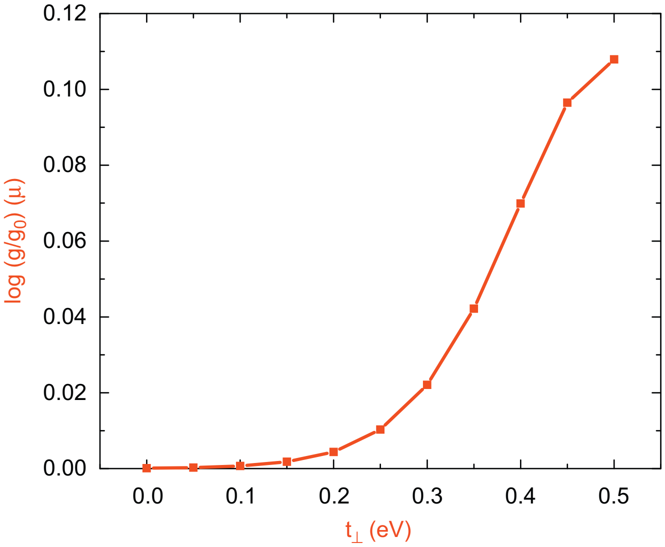

Fig. 5. Logarithm of conductance (in units of g_0) versus the molecule-to-impurity coupling strength, $t_\perp$, in the metal/*trans*-PA/metal system for $N=40$.

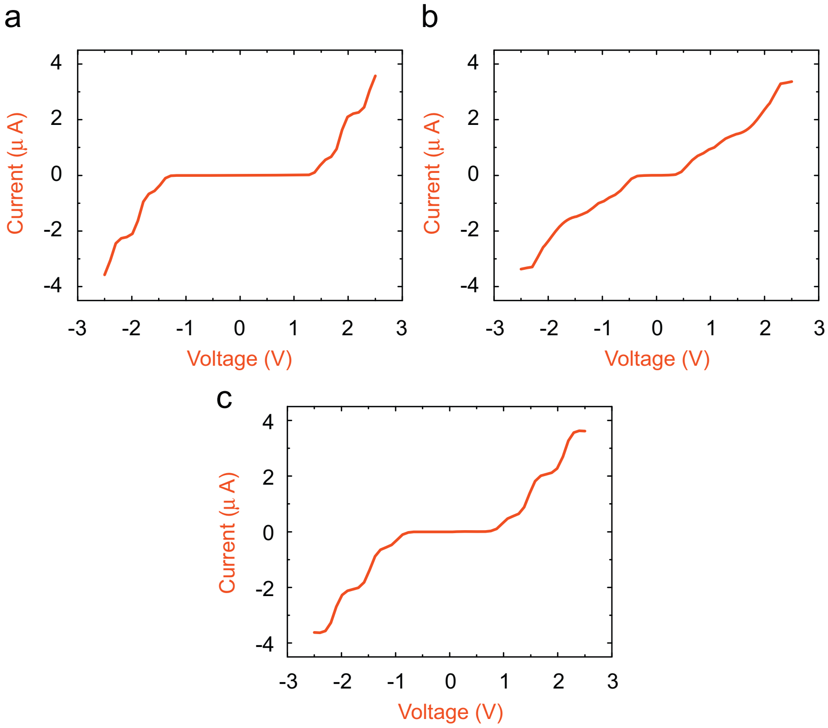

Fig. 4. Plots (a)–(c) show the current–voltage characteristics for the metal/*trans*-PA/metal system with $t=1$ eV and $t_\perp=0$, 0.45 and 1.08 eV, for $N=40$ carbon atoms, respectively. Note that plot (c) is the structure of polyacene (see Fig. 1(b)).

with injecting electron energy, so that any increase in $t_\perp$ gives rise to a considerable enhancement in the conductance of the system and illustrates this aspect of the conductance clearly. With increasing $t_\perp$, new peaks appear in the electronic density of states and the logarithm of the transmission spectrum, which cause reduction of bandgap and increase in conductance (see Fig. 3(c) and (d)).

4. Conclusion

In brief, we have studied in detail the role of impurities on the properties of electron transport of the metal/*trans*-PA/metal system. We have applied some well-known approaches and methods based on Green's function theory and Landauer formalism to investigate electron conduction through the metal/*trans*-PA/metal system. Our results show that (i) the presence of impurities in the *trans*-PA chain induces electronic states within the bandgap of the molecule, which give rise to large enhancement in the density of states and conductance and (ii) conductance is sensitive to the molecule-to-impurity coupling. Electron conduction through the molecule is strongly influenced by molecule-to-electrode interface structure, length of the molecule [32] as well as molecule-to-electrode coupling strength. The conductance properties of the system are studied for a *trans-PA* molecule of fixed coupling strength of the electrode to molecule and length.

Throughout this study, we have ignored the effects of inelastic scattering such as the electron–phonon interaction, electron–electron correlation [32], etc. These factors can affect the electron transport. Another improved method is needed for better results and we need further study for considering all these effects.

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