# Negative differential resistance of carbon nanotube electrodes with asymmetric coupling phenomena

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An intricate problem in molecular electronics is to control the molecule-electrodes contacts. Asymmetric couplings between both contacts are important in driving novel nonlinear transport characteristics like negative differential resistance (NDR). We find that in the presence of an applied field, metallic carbon nanotubes (CNTs) can form asymmetric couplings even if symmetric structures are employed. This origin is due to the CNT itself, while the NDR phenomenon can be obtained by tuning the threshold voltage for the asymmetric couplings by a proper choice of a molecule.

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Molecular electronics can play an important role in realizing electronic devices to utilize quantum interference phenomena at the molecular level. One of the main problems in current studies of molecular electronics is to find good electrode materials as a part of the device without serious contact problems at the molecular junctions.[1–3] Common metallic electrodes might not be suitable at molecular scales because, as an example, typical metal-molecule junctions like gold-thiol linkage (GTL) show serious reproducibility problems which have been obstacles to overcome.[4–6] To obtain asymmetric couplings between both contacts, which characterize the transport phenomena, both molecule-electrode junctions for GTL have to use different linkages or different electrode materials, which is not practical. We note that a carbon nanotube (CNT) can be a good electrode material to resolve such difficulties. The CNT has the following advantages: (i) it is easy to form a robust and reproducible covalent bond with organic molecules through well-established chemistry,[7] (ii) it is possible to utilize metallic properties of either thin single-walled or multiwalled CNTs,[8] and (iii) CNTs have quasi-one-dimensional structures useful to integrate many individual devices.[9] Based on these facts, we have examined the intrinsic characteristics of a CNT as an electrode material by using first principles methods.

Apart from strong covalent bonding with device molecules, we find that the quantum interference at the interface inherently induces asymmetric couplings in symmetrical molecular devices linked to CNT electrodes. Metallic armchair CNTs have two crossing $\pi$-character bands at the Fermi level[8] ($E_f$) and complex band structures of different characters around $E_f$. These band structures can be exploited for the design of molecular devices having unique transport phenomena, which would not be observed in GTL junctions because gold has a relatively simple *s*-character band structure in a wide energy range around $E_f$.[10] The negative differential resistance (NDR) phenomenon in the molecular electronic devices involving metallic electrodes has not been clearly understood. Here, we first show that even with a symmetric device structure, asymmetric potential drops are induced through a molecule bridging the metallic CNTs, and this drives NDR.

Figure 1 shows a device system composed of two CNTs with chiral vector (5,5) (CNT55) and a molecule. Amide endgroups were used as linkages between a molecule and CNT55. We consider two different molecules, phenylethynyl (PE) oligomers and pyrrollo pyrrole (PP). In the calculations, the end of each CNT is capped by H atoms and the geometry including the H and end carbon atoms (region A in Fig. 1) was fully relaxed by using Gaussian03 suite of programs with 3–21G basis set[11] in density functional theory (DFT). The remaining part of each CNT was fixed at the C–C bond length of graphite (1.421 Å). The DFT calculations were carried out with Becke's three parameter hybrid functional, which employs the Lee-Yang-Parr correlation functional. The transmission calculations were performed using nonequilibrium Green's-function-based program packages[12,13] with the single-zeta polarization basis set and the local density approximation. The current ($I$)-voltage ($V$) characteristics were obtained with the Landauer formalism by integrating the transmission coefficient within the energy ($E$) region restricted by the bias voltage:

$$I(V) = \int_{-\infty}^{\infty} T(E,V)[f(E-\mu_L) - f(E-\mu_R)]dE,$$

where $f$ represents the Fermi function, $\mu_{L,R}$ are chemical potentials of the left and right leads, and $T(E,V)$ is the bias-dependent transmission coefficient.

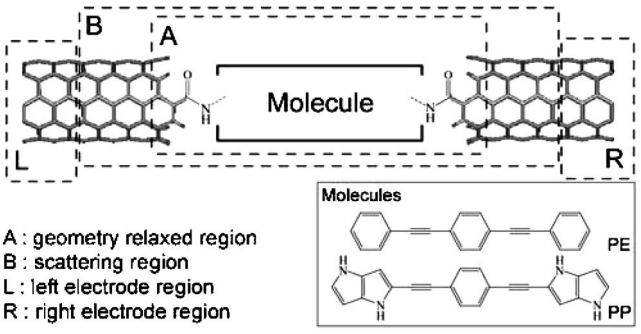


FIG. 1. Geometry of the CNT55-molecule–CNT55 system with amide linkage. PE and PP are the molecules used in calculations.

 

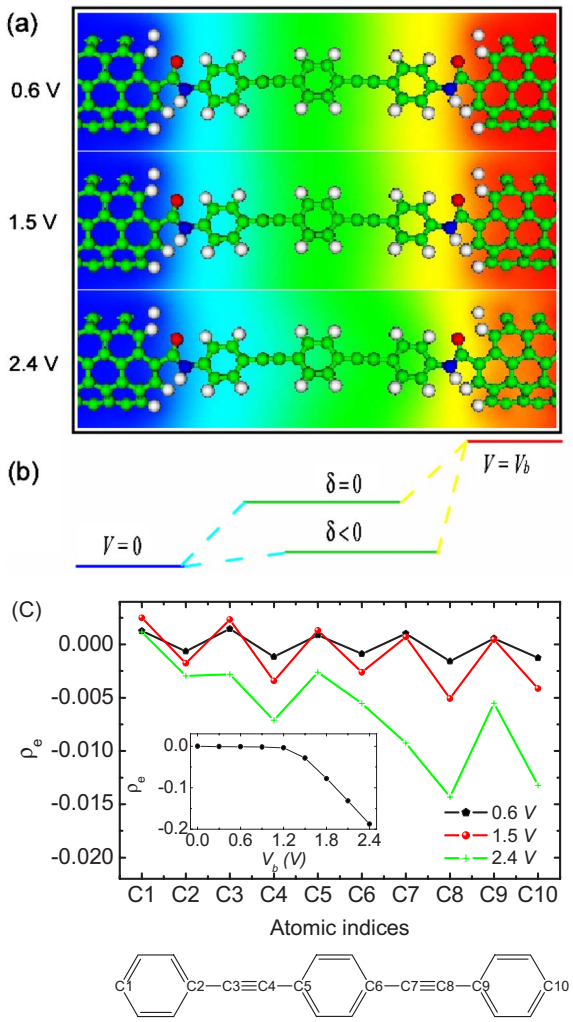


FIG. 2. (Color online) (a) Contour plots of induced potential of the CNT55-PE-CNT55 systems at $V_b$=0.6, 1.5, and 2.4 V. Red to blue color represents high to low potential. (b) A schematic picture of the potential drop through the junction. The case of zero electron loss "$\delta$=0" presents the symmetric potential drop, corresponding to those at $V_b$=0.6 and 1.5 V in (a) and the case of electron loss "$\delta$ <0" presents the asymmetric potential drop due to discharging effect, corresponding to that of $V_b$=2.4 V. (c) Excess electron ($\rho_e$) population on each atom (C1–C10) for the given bias voltage. Inset is the total excess electron population in the molecular part including the linkages, for the given $V_b$, with respect to the unbiased case.

Figure 2(a) presents the contour plots of induced potential of the CNT55-PE-CNT55 system at various bias voltages ($V_b$). It is naturally expected that symmetric and asymmetric junctions would induce symmetric and asymmetric potential drops through the junction, respectively.[14] However, note that even though our system was designed symmetrically in geometric structures, its potential drop in the junctions is asymmetric for $V_b$=2.4 V, while they are almost symmetric at lower bias. To understand this phenomenon, we draw a diagram of the potential drop across the junction in Fig. 2(b). It schematically shows how the induced charge in the molecular region determines the potential drop in the junction. Going into detail, in Fig. 2(c) we analyze the change of real charge distribution in the molecular region due to the finite bias voltage in comparison with the zero bias case. If an external potential is applied to an isolated molecule, the charge in the molecule would be redistributed to screen the potential. At low bias, the induced charges are so small that the molecule retains electronic states almost similar to those of the isolated molecule and the total sum of the induced charges is almost zero. Hence, the potential drop is symmetric as the case of zero electron loss "$\delta$=0" in Fig. 2(b). However, above the threshold voltage (1.2 V), the screening is not fully effective, leading to nonzero value of the total induced charge in the molecule [inset of Fig. 2(c)]. Such a significant electron loss induces a local Coulomb potential with positive charge by electron loss ($\delta$>0) in the molecular region, resulting in asymmetric potential drop at each junction.

When an occupied molecular energy level enters into the current window, the total charge in the molecular region decreases, as the discharging rate on the left side junction is larger than the recharging rate on the right side junction. The coupling strength in the junction is responsible for the charging rate. Therefore, the observed asymmetric potential drop is attributed to the asymmetric coupling strength between the molecule and the left and right electrodes during the transport process.

In Fig. 3(a), we present the transmission curves together with the density of states (DOS) of both electrodes in the CNT55-PE-CNT55 system. The DOS at zero bias was calculated for a single CNT55 without other device parts. Those at nonzero bias voltage $V_b$ are obtained by simply shifting it up and down by $\pm eV_b/2$. Finally, we set up the diagrams by aligning $E_f$ of the calculated transmission peaks with that of the single CNT55. The peaks of DOSs of the electrodes are on the same positions at zero bias on both sides. However, the left and right chemical potentials split off by as much as $(\mu_L-\mu_R)=eV_b$ at finite bias such that the transmission peaks are aligned with the different positions of the DOS on each side (i.e., different band characters or electronic states). Thus, rapidly changing band characters and shapes of DOSs of the electrodes naturally affect the coupling between molecular states and electronic states of the electrodes under a finite bias voltage.[15–17]

The change in coupling triggers drastic effects on the transmission. First, the heights of the transmission peaks change. In Fig. 3(a), the upper peak marked by an arrow at $V_b$=0 V, which corresponds to the lowest unoccupied molecular orbital (LUMO) energy levels, almost diminishes at $V_b$=2.4 V, because there are few available states at the right side electrode. In contrast, the peak corresponding to the highest occupied molecular orbital (HOMO) energy level increases because of the increased available states at the right side electrode. Second, the energies of the peaks shift as shown in Fig. 3(b). At low bias, all peaks remain at the same positions of the zero bias case. However, they begin to shift from the threshold voltage 1.2 V, at which the peak corresponding to the HOMO enters into the current window. These changes are consistent with the change of charge in the molecular region in the inset of Fig. 2(c). This reflects that the shifts of the transmission peaks are closely related to the discharging effect and asymmetric potential drop.

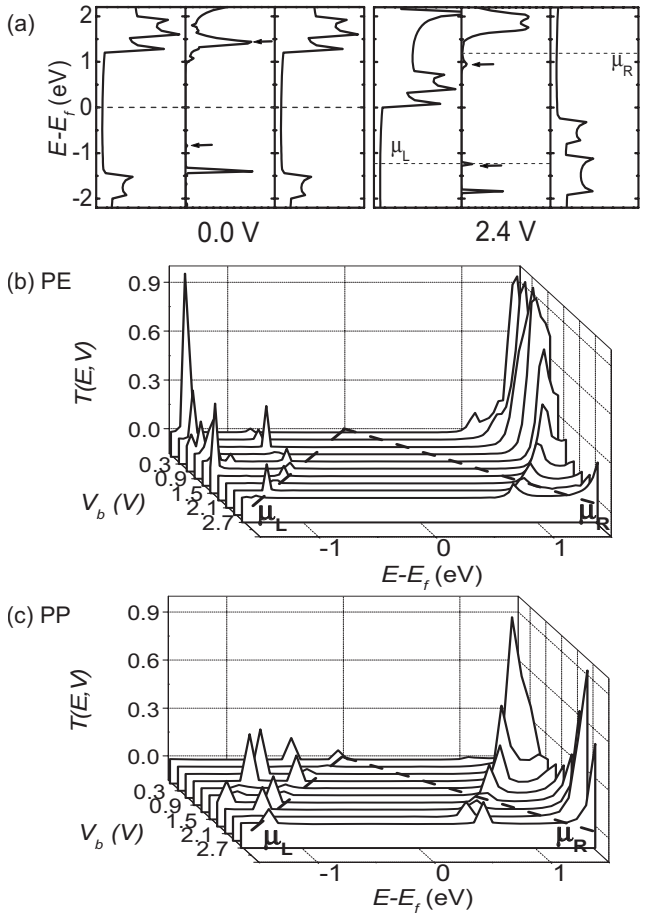


FIG. 3. (a) Bias-dependent transmissions and DOSs of both electrodes in the CNT55-PE-CNT55 system. A left/middle/right inset of each figure denotes DOS of the left electrode/transmission curves of the device system/DOS of the right electrode. Bias-dependent transmission curves for (b) PE and (c) PP.

It is worthwhile to compare the result with that of GTL using the same PE molecule.[14] In GTL, the energies of the transmission peaks do not shift due to the symmetric potential drop when the same linkages are used. The reason is that molecular states couple symmetrically to both electrode states even at high bias voltages because bulk Au has a uniform DOS in a relatively wide range of energy. In contrast, when the different linkages are used, the asymmetric potential drop is induced purely due to the asymmetric coupling of the different linkages, and hence, the energies of the transmission peaks shift. Additionally, the heights of the transmission peaks for the GTL system do not change regardless of used linkages. This difference between CNT and GTL systems results in different behaviors in device applications because the change in transmission peaks drastically affects *I-V* characteristics.

To tune the threshold voltage for the asymmetric coupling, we applied the same analysis for the other molecule (PP) having smaller HOMO-LUMO gap. Indeed, asymmetric potential drops for PP are derived at a lower bias voltage, as compared with that in PE.[18]

The importance of the asymmetric potential drop is clearly represented in *I-V* characteristics, which is the main

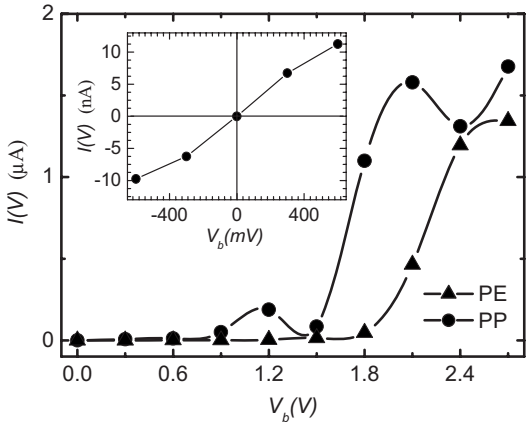


FIG. 4. *I-V* curves at various bias voltages for each molecule of CNT55-molecule-CNT55. Inset: *I-V* curves at low bias for PP molecule.

interest in device applications. Figure 4 shows the *I-V* curve for the PE/PP system. At low bias, the current follows linear behavior and is on the order of 1–10 nA for the PP molecule as shown in the inset of Fig. 4. This behavior is similar to experimental measurements.[3] At high bias, which was not demonstrated in the experiment, however, the nonlinear effects due to the bias-dependent transmission become significant. For example, in the PE molecule [Fig. 3(b)], the energy level of the transmission peak corresponding to the HOMO level, $E_{homo} \sim -1.0$ eV, does not shift much for $V_b < 1.2$ V. However, for $V_b > 1.2$ V, $E_{homo}$ touches the left chemical potential ($\mu_L$), resulting in the onset of current flow to induce the discharging effect. This drives $E_{homo}$ to shift along with $\mu_L$ at slightly lower energy. Such a shift of $E_{homo}$ suppresses the current flow till $V_b = 1.8$ V, at which the LUMO begins to enter into the current window. More interestingly, in the PP molecule [Fig. 3(c)], $E_{homo}$ readily shifts upon the applied voltage because $E_{homo}$ is close to $E_f$. In addition, $E_{homo}$ shows a large peak on the edge of $\mu_L$ for $V_b = 1.2$ and 2.1 V (due to the strong couplings between the molecule and electrodes), highly contributing to the current flow, whereas it shows a small peak between them (due to the weak coupling between the molecule and electrodes), contributing less to the current. The current increment from $V_b = 1.5$ to 2.1 V mainly comes from the LUMO contribution. As a consequence, the PP molecule exhibits the NDR phenomenon at $V_b = 1.2–1.5$ and 2.1–2.4 V.

NDR has been observed from various molecular devices.[2,15–17,19,20] The origin of the NDR observed in molecular devices with semiconducting electrodes is due to band gaps of the electrodes. However, metallic CNTs have no band gaps. Here, the NDR can be explained by considering two effects arising from the band structures: (i) how many states are available to couple with molecular states and (ii) how well each of their state couples with the molecular states.[17] At low bias, molecular energy levels are aligned with the electronic states of electrodes, having equivalent band characters on both sides. Therefore the potential drop through the molecule is symmetric. As the bias increases further, the energy levels are aligned with the electronic

states of different band characters on each side, resulting in asymmetric couplings. This makes the energies of the transmission peaks shift according to the induced potential drop [Figs. 3(b) and 3(c)]. Further, as the coupling at one side becomes weak at a certain bias voltage, the corresponding transmission peaks become smaller and the current is reduced. Thus, the bias-dependent transmission leads to an intriguing feature of *I*-*V* characteristics like the NDR phenomenon.

In summary, apart from the fact that CNTs are promising electrodes with minimal contact problems in molecular electronics due to the strong covalent bonding with a molecule, we find that CNTs generate asymmetric couplings with a molecule beyond a certain threshold bias voltage, which would not be observable in GTL junctions. These asymmetrical couplings give rise to a bias-dependent transmission, and hence, NDR as the threshold voltage for the asymmetric coupling can be tuned by a proper choice of a molecule. Thus, the CNT-molecule-CNT devices could be useful and robust molecular electronic devices in the near future.

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