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Fano Resonance Effect in CO-Adsorbed Zigzag Graphene Nanoribbons *

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Quantum interference plays an important role in tuning the transport property of nano-devices. Using the non-equilibrium Green's Function method in combination with density functional theory, we investigate the influence to the transport property of a CO molecule adsorbed on one edge of a zigzag graphene nanoribbon device. Our results show that the CO molecule-adsorbed zigzag graphene nanoribbon devices can exhibit the Fano resonance phenomenon. Moreover, the distance between CO molecules and zigzag graphene nanoribbons is closely related to the energy sites of the Fano resonance. Our theoretical analyses indicate that the Fano resonance would be attributed to the interaction between CO molecules and the edge of the zigzag graphene nanoribbon device, which results in the localization of electrons and significantly changes the transmission spectrum.

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The 20th century witnessed the development of science and technology, and researchers have entered into a Nano era. Many new nano-materials have been produced, especially for graphene. It is a single atomic layer of graphite. Novoselov *et al.*[1,2] have successfully synthesized it experimentally and demonstrated that it is stable at room temperature. In addition, numerous efforts have been focusing on the researches of graphene-based materials due to their excellent physical properties, such as 2D massless Dirac fermions, unique quantum Hall effect, and giant mobility of charge carriers.[3–5] Moreover, it can also be tailored into armchair graphene nanoribbons (AGNRs) and zigzag graphene nanoribbons (ZGNRs) according to the tailoring direction. Till now, many methods have been proposed to tune their electronic properties. Among them, doping,[6–8] adding electric field[9,10] and building defects[11–13] are the most common ones. Since the band gaps of GNRs are sensitive to their size and geometries, they are excellent candidates for semiconductor devices. To realize different functions of GNRs devices, it is important to manipulate the transport properties with a controllable manner. To date, many methods have been reported.[14–19]

As a nano-electronic device, there is no denying that the particle property plays a leading role in transport properties, while its wave property cannot be ignored. The interference of waves propagated along different paths is one of the distinctive features. Thus quantum interference also plays an important role in the transport properties of devices.[20,21] Many works[22–25] have been devoted to investigate the quantum interference effect of graphene nanoribbons, and significant conclusions have been obtained. Hong *et al.*[21] designed a reversible device consisting of a carbon nanotube decorated with magnetic molecules, and obtained that the coupling between discrete spin-states of a magnetic molecule and continue bands of a carbon nanotube induces the spin-dependent Fano resonance, which can significantly change the conductance property.

In this work, the quantum interference between CO molecules and the ZGNR device is investigated. The Fano resonance effect can be found in the transport property. Moreover, it is sensitive to the distance between CO molecules and the ZGNR device. A detailed theoretical explanation is also given.

Researchers have shown that the electronic properties of ZGNRs are sensitive to the adsorption sites,[26,27] and adsorbing on both edges plays an important function for the electronic properties. Our research is based on the configuration of CO molecules adsorbed on one of the edges of the ZGNR device, as shown in Fig. 1, and each edged carbon atom is terminated by one hydrogen atom to avoid the dangling bonds. The whole system can be mainly divided into three parts: left electrode, central scattering region and right electrode. The left (right) electrode is semi-infinite 6-ZGNRs (here 6 is the ribbon width), and the scattering region is 6-ZGNRs adsorbed one CO molecule at one of the edges. The distance between the CO molecule and ZGNRs is labeled by d, as shown in Fig. 1. In the following we take $d = 1.3$ Å

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as an example (short for M1) to have a detailed study.

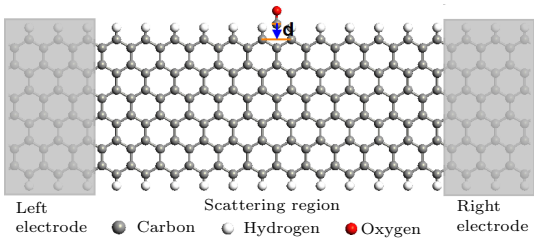

Fig. 1. Geometry structure of the CO molecule adsorbed on the ZGNR device.

Our calculations are performed with the Atomistix ToolKit (ATK) package, which is based on the density functional theory (DFT) combined with the non-equilibrium Green function (NEGF) method.[28,29] The structural relaxations of the systems are performed by fixing the CO molecule, then relaxing the device till the residual force on each atom is smaller than 0.01 eV/Å, and the total energy is converged to 10^{-5} eV. The local-density approximation (LDA) is used for the exchange-correlation potential. The real space grid techniques are used with the energy cutoff of 150 Ry as a required cutoff energy in numerical integrations. The k-point sampling is 1, 1 and 100 in the x, y and z directions, respectively, where z is the direction of electron transport. Open boundary conditions are used to describe the electronic and the transport properties of the device. A vacuum layer of 12 Å is added in x and y directions to avoid the interaction between adjacent ribbons. The wave functions of all the atoms are expanded by double-zeta polarized basis set. The NEGF-DFT self-consistency is controlled by a numerical tolerance of 4×10^{-5} eV. The electron temperature is 300 K in the transport calculations. The transmission coefficient $T(E, V_b)$ can be obtained by

$$T(E, V_b) = \mathrm{Tr}[\Gamma_L(E, V_b)G^R(E)\Gamma_R(E, V_b)G^A(E)], \quad (1)$$

where $G^{R(A)}$ is the retarded (advanced) Green's function of the scattering region, and $\Gamma_{L(R)}$ is the contact broadening function associated with the left (right) electrode.

The transmission spectrum $T(E, V_b)$ of the M1 device at zero bias has been calculated, as presented in Fig. 2(c). To have a better understanding about the transmission spectrum of the M1 device, we also give the transmission spectrum of the pristine 6-ZGNR device (short for M0) as a reference, which can be seen in Fig. 2(a). For the transmission spectrum of M0, there are perfect transmission steps. When a CO molecule is adsorbed on one edge of the ZGNR with $d = 1.3$ Å, the transmission spectrum changes a lot, and one can find that the transmission steps are destroyed, instead two transmission dips appear at −0.12 eV and 1.12 eV energy sites, respectively. The transmission peak at 0 eV has decreased from three to two. All of these indicate that the CO molecule adsorption can effectively tune the transport properties of the ZGNR device.

To have a further understanding about the transmission dips of the M1 device, we calculate the density of states (DOS) of M0 and M1, as shown in Figs. 2(b) and 2(d), respectively. Comparing Fig. 2(b) with Fig. 2(d), it can be seen that two more peaks appear in the M1 DOS, corresponding to the energies of −0.12 eV and 1.12 eV. More interesting is that the transmission dips of M1 appear just right in the energies of −0.12 eV and 1.12 eV, which is the same as that of the two more DOS peaks that appear. Thus we can predict that the DOS peaks appearing at the energies of −0.12 eV and 1.12 eV have a close relationship with the transmission dips of the M1 device.

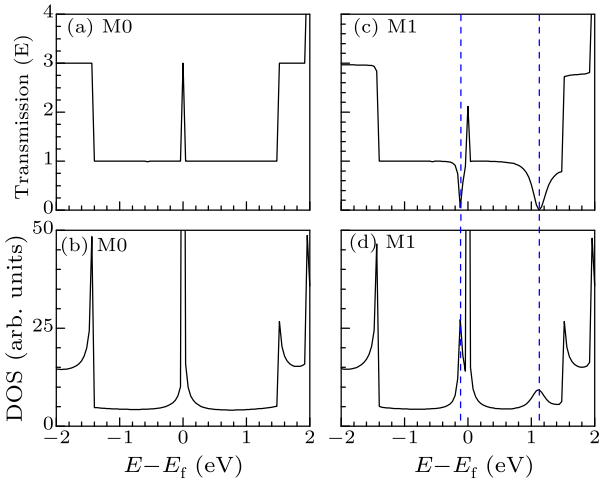

Fig. 2. [(a), (c)] The transmission coefficient of M0 and M1, [(b), (d)] the DOS of M0 and M1.

To continue probing the origin of the transmission dips in the M1 device, we give the project density of state (PDOS) and the local density of state (LDOS) of the M1 device in the following. Figures 3(a)–3(c) are the transmission spectrum of the whole device, PDOS of the CO molecule and PDOS of the carbon atoms in the up side (the green ball inside Fig. 3(c)), respectively. We can find that the peak of the DOS at 1.12 eV mainly comes from the CO molecule, while the peak of DOS at −0.12 eV mainly comes from the edge near the CO molecule of ZGNR. Figures 3(d)–3(f) present the LDOS of the device at different energy sites. Figure 3(d) is the LDOS of the device at 0 eV. We can see that the DOS is nonlocal along the down edge of the device, but is suppressed at the CO molecule adsorbed site along the up edge, thus the corresponding transmission peak decreases compared with that of the pristine ZGNR device. However, for the LDOS at 1.12 eV, shown in Fig. 3(e), there are quasi-bound states, the electrons in these states are mainly located on the CO molecule. Interestingly, the LDOS is mainly located

at the carbon atoms on the up edge at the energy of −0.12 eV, as shown in Fig. 3(f). From the above, we obtain that the interaction between the CO molecule and the up edge of the ZGNR device results in the localization of electrons and then significantly changes the transmission spectrum.

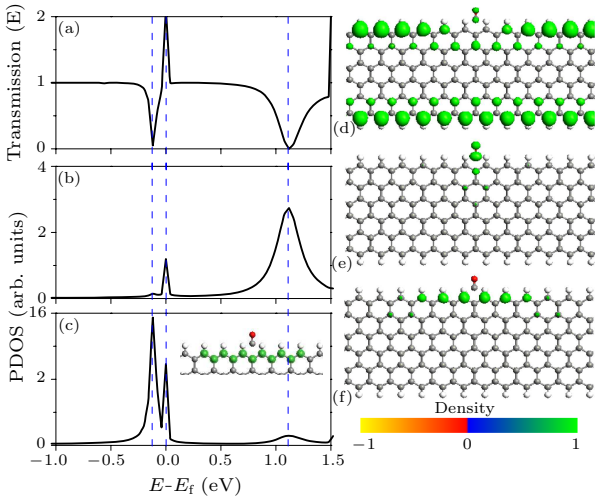

Fig. 3. (a)–(c) The transmission spectrum of M1, PDOS of the CO molecule and PDOS of green carbons shown inside in (c); (d)–(f) the LDOS for M1 at 0 eV, 1.12 eV and −0.12 eV, respectively. The isovalue is 2 Å^{-3}.

The Fano–Anderson model is used to explain this phenomenon.[30] As shown in Fig. 4, the ZGNRs adsorbed with CO molecule can be modeled as a 1D quantum wire (QW) with a side quantum dot (QD). The system Hamiltonian can be written as

$$H = H_{\mathrm{QW}} + H_{\mathrm{QD}} + H_{\mathrm{QD-QW}}, \tag{2}$$

where H_{QW} corresponds to the free-particle Hamiltonian on a lattice with spacing d. Their eigen-function is expressed as Bloch solutions

$$|k\rangle = \sum_{j=-\infty}^{\infty} e^{ikdj}|j\rangle, \tag{3}$$

where $|k\rangle$ is the momentum eigenstate, and $|j\rangle$ is a Wanier state localized at site j. The dispersion relation associated with these Bloch states is

$$\varepsilon = 2t\cos(kd), \tag{4}$$

where t is the hopping coefficient.

The energy level of the QD is ε_{L}, and the coupling between QD and QW is t. The transmission coefficients can be obtained through a series of calculations[20,23] as

$$T(\varepsilon) = \frac{(\varepsilon-\varepsilon_{\mathrm{L}})^2}{(\varepsilon-\varepsilon_{\mathrm{L}})^2+\Gamma^2}. \tag{5}$$

From Eq. (5), we can obtain that the transmission coefficient is zero when $\varepsilon = \varepsilon_{\mathrm{L}}$. To the system of CO molecules adsorbed on ZGNRs, we can see the ZGNRs as QW, and the CO molecule as QD. When the energy eigenvalues of the CO molecule are equal to the energy eigenvalues of the ZGNRs, there will be a transmission dip in the corresponding energy site, which gives a better explanation for the former calculation. As can be seen from Eq. (5), if the parameter ε_{L} is changed, due to the fact that the energy spectrum of ZGNRs is continued, there still exist equal values for ε. Thus the transmission coefficient can also become zero.

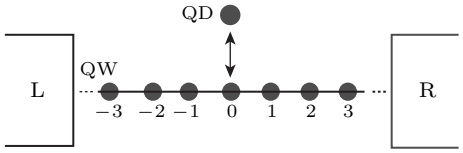

Fig. 4. Model of side-coupled quantum dot attached to a perfect quantum wire.

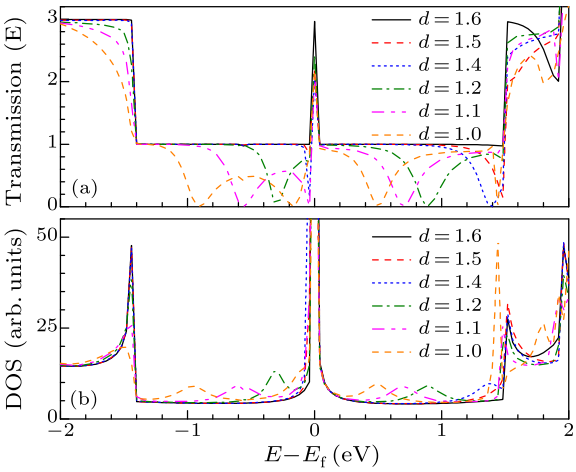

Fig. 5. The transmission spectrum (a) and DOS of the CO adsorbed ZGNR device (b) with different d in the zero bias region.

Next we study the influence of different distances between CO molecules and the ZGNR device (controlled by d) to the system's transmission properties. Figure 5(a) shows the transmission spectra of different systems at zero bias, where d changes from 1.6 Å to 1.0 Å. From Figs. 5(a) and 2(c), we can see that when the distance is increased from 1.3 Å to 1.5 Å, there are still two transmission dips of the transmission spectrum at zero bias. Meanwhile, the transmission dips in the positive energy region are moving to a higher energy site. If the distance d keeps on increasing, the transmission dip will disappear, as well as the transmission spectrum of M0, which indicates that the interaction between the CO molecule and ZGNR is too small to change the transmission spectrum of the device. However, when the distance d decreases from 1.3 Å to 1.2 Å, the transmission dip still exists and the energy site is changed. When d continues decreasing, the transmission dip in the positive energy region

moves to a lower energy site, meanwhile the number of transmission dips is increased. Then we give the corresponding DOSs of different systems in Fig. 5(b). It is clear that the energy sites of transmission dips coincide with the energy sites of the DOS peaks.

To have a clear picture of this phenomenon, we choose the positive energy region as an example; Fig. 6(a) gives the DOS of different devices and Fig. 6(b) shows the PDOS of the CO molecule from different devices. From them we can see that the energy sites of DOS peaks are completely consistent with that of PDOS of the CO molecule, thus the peaks appearing in the DOS mainly come from that of the CO molecule. Thus the variation of d would cause the changes of the DOS distribution of the CO molecule in different energy sites, and results in the Fano resonance in different energy sites. From the above, we can see that the energy positions of the Fano resonance can be controlled by tuning d, and as d decreases, the CO molecule is closer to the ZGNR device, the overlappings of wave functions are increased, thus the Fano dip shifts to a lower energy to stabilize the system.

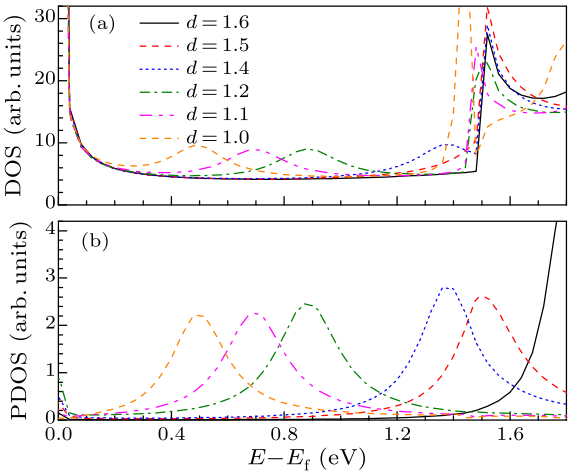

Fig. 6. The DOS (a) and PDOS (b) of the CO molecule in the positive energy area in the zero bias region with different d for the devices.

In summary, we have investigated the influence to the transport property of the CO molecule adsorbed on one edge of the zigzag graphene nanoribbons device. It is shown that, when d is larger than 1.6 Å, the CO molecule adsorption has no influence on the transport property of the ZGNR device. However, when d is smaller than 1.6 Å, the mutual interaction between the CO molecule and the ZGNR edge can result in the Fano resonance effect. Moreover, with the decrease of d, the transmission dip moves to lower energy. Our further analysis indicates that the Fano resonance would be attributed to the interaction between the CO molecule and the ZGNR edge, which results in the localization of the electrons and significantly changes the transmission spectrum. These results would be useful for designing nano-devices.

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