Observations of two-fold shell filling and Kondo effect in a graphene nano-ribbon quantum dot device

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(Dated: October 30, 2009)

A graphene nanoribbon (GNR) with orientation along its principle axis was obtained through a mechanical tearing process, and a quantum dot device was fabricated from the GNR. We have studied the transport property of the GNR quantum dot device down to dilution refrigerator temperatures. Two-fold charging periodicity was observed in the Coulomb-blockade measurement, signaling a shell-filling process with broken valley degeneracy. In one of the smaller Coulomb diamonds, Kondo-like resonance were observed, with two conductance peaks displaced symmetrically from the zero bias voltage. The splitting of Kondo resonance at zero magnetic field suggests spin-polarization of the quantum dot, possibly due to the edge states of a zigzag GNR.

PACS numbers: 72.80.Vp, 73.23.Hk, 73.22.Pr, 73.63.Kv

The discovery of quantum Hall effect in graphene has triggered a lot of studies on this material. Attention has also been paid to the nanoribbon forms of the material, due to their intriguing physical properties for basic research and potential applications in future nanoelectronic circuits. As an unrolled version of single-walled carbon nanotubes, GNRs could be flexibly tailored to various shapes with controlled width, length, orientation and even intramolecular junctions as are suitable as the building blocks for electronic circuits. With the unrolled structures, however, the edges of GNRs are expected to play an important role, introducing new physics different from carbon nanotubes. Theoretical studies show that GNRs with zigzag edges have spin polarized edge states, and are half-metals under a large transverse electric field. Similar prediction has also been made for bilayer zigzag GNRs. Experimentally, GNRs have been fabricated through a reactive ion etching method with the help of electron beam lithography, or via a chemical method. Electron transport measurements reveal that these GNRs are all semiconducting, with a gap inversely proportional to their width. In the experiments of Ref. sub-10-nm wide GNRs along principle axes were also reported. However, there is no systematic experimental study on GNRs with identified edge orientations.

In this paper, we report our electron transport measurement on a quantum dot (QD) device made of a very-long GNR along one of the principle axes of a graphene sheet. Coulomb blockade diamonds with two-fold charging periodicity were observed. Moreover, inside one of the small diamonds a fine peak-dip-peak conductance structure was discerned around zero bias voltage. We believe that these results indicate the breakdown of both the valley degeneracy and the spin degeneracy at different energy scales in the GNR.

We use the “Scotch Tape” technique to exfoliate highly ordered pyrolytic graphite (HOPG) onto degenerate-doped $p$-type Si substrates with a 100 nm thick SiO$_2$ layer. Besides obtaining large pieces (several mm$^2$ and up) of graphene occasionally we can get very long GNRs. Figure 1(a) is a scanning electron microscope image of the GNR used in this experiment. It is about 12 microns long and seems to have a uniform width over its entire length. Atomic force microscope (AFM) shows that the GNR has a width of $w = 60$ nm and a height of $\sim 1.3$ nm. The height of the GNR indicates that it has at most two graphite layers.

The fact that some of the mechanically exfoliated GNRs have a constant width over a very long distance would suggest that they have two extremely parallel and smooth edges. This is most possible when both edges are along one of the principle axes of the graphene sheet. The existence of favorable tearing directions was reported by Geim’s group on large pieces of graphene, and by Dai’s group on some of their chemically derived GNRs. As shown in Fig. 1(a), besides the very long GNR, there is another GNR whose direction changes exactly by 30 degrees across a “kink” structure, presumably from zigzag to armchair or vice versa. The “kink” provides further evidence that mechanically exfoliated GNRs are likely along the principle axes.

Pd electrodes of 50-nm thick, 500-nm wide and 500-nm apart were patterned onto the GNR using standard electron beam lithography techniques (Fig. 1(c)). Two-probe differential conductance between neighboring electrodes of the device was measured using low-frequency lock-in techniques with an ac modulation voltage of 10 $\mu$V. The measurements were performed in a Quantum Design PPMS system with temperatures $T$ down to 2 K, and in a dilution refrigerator with $T$ down to 20 mK.

Figure 2(a) shows the differential conductance $G = dI/dV_{bias}$ in a color scale as a function of bias voltage $V_{bias}$ and back-gate voltage $V_g$, measured from one of the segments of the GNR at $T = 2$ K in the PPMS. The
The conductance is suppressed at small $V_{\text{bias}}$ due to the Coulomb blockade (CB) effect, and the suppression is enhanced in the vicinity of the Dirac point centered at $V_g \sim 3$ V, where the carrier concentration is the lowest. In Fig. 2(b) we show the zero bias CB oscillations near the Dirac point in the range $V_g = 3.24 - 3.46$ V, measured in a dilution refrigerator at $T = 600$ mK and 20 mK, respectively. The conductance peaks become much sharper at 20 mK. Figure 2(c) shows the stability diagram at this temperature, in the same $V_g$ window as in Fig. 2(b). The most salient feature is the two-fold charging periodicity with varying $V_g$. The bigger CB diamonds are about 23 meV wide, and the smaller ones are about 15 meV wide. The height of the smaller diamonds is around 0.6 meV. Excited states at an energy scale of $\sim 0.3$ meV can be recognized at the edges of the diamonds, as marked by the arrows in Fig. 2(c).

The appearance of CB diamonds with excited states indicates that the GNR forms a QD at low temperatures. The effective size of the QD can be estimated from the width of the smaller CB diamonds, $\Delta V_{g,s} = e/C_g \sim 15$ meV, where $e$ is the electron charge and $C_g$ the capacitance between the QD and the back gate. Assuming a simple parallel plate capacitance, the length of the GNR QD estimated is about 510 nm that happens to be very close to the distance between the contact electrodes $L = 500$ nm. However, a more accurate model taking into account the finite size effect of the GNR plate gives an effective length $L^* \approx 175$ nm. The difference between $L$ and $L^*$ may reflect the existence of long depletion regions that serve as tunnel barriers near the electrodes. We rule out the possibility that the device contains multiple QDs, because no joint CB diamonds are observed.

Apparently, the two-fold periodicity observed in Fig. 2(c) resembles the shell-filling process of a bar-like QD, where the orbital degeneracy is lifted by the spatial confinement while the spin degeneracy is still held. Shell-filling feature is widely observed in QD devices made of carbon nanotubes or semiconductors. When the carrier occupancy of the QD, $N$, is odd, addition of one carrier only needs to overcome the Coulomb energy, whereas it has to pay an extra energy to occupy the upper shell when $N$ is even. As a result, the size of the CB diamonds shows two-fold periodicity, with the smaller diamonds correspond to odd $N$ and the larger ones correspond to even $N$. As it is known, the electrons in 2D graphene exhibit a four-fold degeneracy near the Dirac point, i.e., two-fold spin degeneracy plus two-fold $K$ and $K'$ valley degeneracy. The observation of a two-fold charging periodicity possibly signals the lifting of the valley degeneracy due to the existence of edges in the GNR.

Another interesting feature of the data is the appearance of a Kondo-like conductance enhancement in one of the Coulomb diamond centered at $V_g = 3.35$ V (the sixth diamond from the right in Fig. 2(c)). Since this diamond is smaller than its neighbors, the electron occu-
FIG. 3: (color online) (a) Color-scale plots of the conductance $G$ in one of the Coulomb diamonds with odd number of carrier occupation (the sixth diamond from the right in Fig. 2(c)). Conductance peak-dip-peak structure near zero bias voltage and its evolution with $V_g$ can be resolved. $T = 20$ mK. (b) Peak position as a function of $V_g$. (c) $G - V_{\text{bias}}$ curves measured at different temperatures. The peak-dip-peak structure disappears above $\sim 400$ mK. (d) The amplitude of conductance enhancement $\Delta G$ in (c) as a function of temperature. Insets of (d) depict two different ways of estimating $\Delta G$.

Kondo resonance usually appears as a single conductance peak at zero bias voltage (Fig. 4(a)). However, the conductance enhancement observed here exhibits a peak-dip-peak structure around zero bias. The two peaks are $\sim 0.1$ meV apart at the most left side of the diamond, getting closer with increasing $V_g$, and apparently merging together in the right half of the diamond.

Usually the height of a Kondo conductance peak follows a logarithmic temperature dependence below the Kondo temperature, and saturates gradually at very low temperatures. The temperature dependence data of the peak-dip-peak structure are shown in Fig. 3(c). As can be seen in Fig. 3(d), the amplitude of the overall structure, $\Delta G$, extracted using two different ways (depicted in the insets), does roughly follow a logarithmic temperature dependence below $400$ mK.

It is known that the Kondo resonance peak splits into two peaks that are symmetrically displaced from the zero bias if there is a preferred spin orientation (i.e., when the spin degeneracy is lifted, as illustrated in Fig. 4(b)) [33]. Such splitting has been observed in both 2D semiconductor QDs and carbon nanotubes, where the spin degeneracy is lifted by either an applied magnetic field [34] or by the exchange coupling to ferromagnetic contacts [35]. The lifting of spin degeneracy in this experiment is surprising in that there is neither external magnetic field nor ferromagnetic contacts.

Although the exact nature is obscure, the observed peak-dip-peak structure may be qualitatively understood by assuming some degree of spin polarization on the GNR QD itself. As aforementioned, preferred spin orientation is expected at the edges of a zigzag GNR [7, 8, 16, 17]. In following paragraphs, by analyzing the CB data in Fig. 2 we will show that the GNR measured in this experiment is quite likely to be a zigzag one.

Let us first show that the QD is unlikely made of an armchair GNR. The band dispersion of an armchair GNR takes the same Fermi velocity ($v_F = 1.0 \times 10^6$ m/s) as in a bulk graphene, except a gap near the neutral point in the semiconducting cases. Taking $L^* \approx 175$ nm, the level spacing due to longitudinal confinement for this bar-like GNR is $\epsilon_L = h v_F / 2 L^* \approx 12$ meV, and the energy spacing between subbands is $\epsilon_w = h v_F / 2 w \approx 34$ meV. In order to explain the excited state energy of $\Delta \approx 0.3$ meV as observed in the CB measurement, one has to assume that there are many subbands across the Fermi level. Simple estimation shows that the Fermi energy $\epsilon_F \approx 430$ meV, and the number of carriers in the GNR $N \sim 710$. This would lead to a Dirac point (the neutral point) that is located $20$ V away from the $V_g$ window of Fig. 2(c). However, the experimental data indicate that the Dirac point is located at several volts of $V_g$, or at worst within $10$ V from the $V_g$ window. In addition, if the GNR is armchair, in the regime near the Dirac point there should be at least a few big CB diamonds whose height is comparable to the confinement energy spacing of $12$ meV and whose width is wider than $250$ meV in $V_g$. However, as shown in Fig. 2(a), there is no CB diamond having these large sizes.

On the other hand, for a zigzag GNR, the energy bands near the Fermi level is nearly flat due to the existence of edge states. Therefore, the confinement along its length direction yields a relatively small energy level spacing, so that the lack of large CB diamonds is naturally understood. To estimate the level spacing (the excited states energy), we recall that the bands of edge states in a zigzag GNR are nearly flat near the Fermi level $\approx 3$ meV, consistent with the observed values. Therefore, we believe that our GNR is most likely to be a zigzag GNR rather than an armchair one.

Based on the spin configuration of the edge states in a zigzag GNR [7, 8] that the spins on the same edges are
parallel but on opposite edges are antiparallel, we present a toy-model in Fig. 4 (c) to account for the lifting of spin degeneracy. In this model, electrons with different spin will fill onto different edges. When the local electrostatic environment of the two edges are different, filling to different edge will cost different energy. This would lead to the observed spin splitting in odd $N$ GNR QD. In this scenario, the gate-voltage dependence of the Kondo peak splitting can also be naturally explained through the dependence of local electrostatic environment on the gate voltage. In fact, it is almost unavoidable to have randomly trapped charges in SiO$_2$ surrounding the GNR. The distribution of these charges, thus their stray field, is tunable by applying a gate voltage. To further clarify the issue, more experiments such as magnetic field dependence of the peak splitting are demanded.

To summarize, we have observed two-fold charging periodicity in a QD device made of a GNR. We also observed Kondo-like conductance peaks in one of the Coulomb diamonds. The observation of Kondo splitting at zero magnetic field suggests the lifting of spin degeneracy due to spin polarization on the QD itself, in favor of theoretical predictions on a zigzag GNR where the spin polarization is due to its highly degenerate edge states.

We would like to thank H. F. Yang and X. N. Jing for experimental assistance, Y. Q. Li, Q. F. Sun, W. J. Liang, and K. Chang for helpful discussions. This work was supported by the NSFC, the National Basic Research Program of China from the MOST, and by the Knowledge Innovation Project of CAS.

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