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Energy gap opening by crossing drop cast single-layer graphene nanoribbons

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Abstract

Band gap opening of a single-layer graphene nanoribbon (sGNR) sitting on another sGNR, fabricated by drop casting GNR solution on Au(111) substrate in air, was studied by means of scanning tunneling microscopy and spectroscopy in an ultra-high vacuum at 78 K and 300 K. GNRs with a width of \(\sim 45\) nm were prepared by unzipping double-walled carbon nanotubes (diameter \(\sim 15\) nm) using the ultrasonic method. In contrast to atomically-flat GNRs fabricated via the bottom-up process, the drop cast sGNRs were buckled on Au(111), i.e., some local points of the sGNR are in contact with the substrate (\(d \sim 0.5\) nm), but other parts float (\(d \sim 1–3\) nm), where \(d\) denotes the measured distance between the sGNR and the substrate. In spite of the fact that the nanoribbons were buckled, \(dV/dI\) maps confirmed that each buckled sGNR had a metallic character (\(\sim 3.5\) G\(_0\)) with considerable uniform local density of states, comparable to a flat sGNR. However, when two sGNRs crossed each other, the crossed areas showed a band gap between \(-50\) and \(+200\) meV around the Fermi energy, i.e., the only upper sGNR electronic property changed from metallic to p-type semiconducting, which was not due to the bending, but the electronic interactions between the up and down sGNRs.

Supplementary material for this article is available online

Keywords: graphene nanoribbon, scanning tunneling microscopy, cross structure, drop cast, energy gap

(Some figures may appear in colour only in the online journal)

1. Introduction

State-of-the-art nano-wiring of electronic circuits is presently based on the 14 nm Fin-FET (field effect transistor) process [1], while the thickness of the wire for interconnects is typically larger than 30 nm and still has room for downsizing. With the use of an atomically thin wire while maintaining high conductance, downsizing the circuits in three dimensions
becomes feasible and single-layer graphene nanoribbons (sGNRs) are one of the most promising candidates [2–5]. GNRs can be fabricated by unzipping carbon nanotubes (CNTs), such that their electronic properties, e.g., the electron mean free path and the maximum allowed current density are quite similar to those of CNTs [6–9]. Although several methods have been reported to fabricate sGNRs on substrates, such as bottom-up processes [4, 5], GNWs fabricated simply by unzipping the multi-walled CNTs along the axis have been used in previous studies [10–12]. Several techniques have been reported in the last five years for unzipping CNTs through the use of (1) sulfuric acid and potassium permanganate as the oxidizing agent [11]; (2) partially embedding in a polymer film and etching by argon plasma [12]; (3) inserting alkali-metal atoms between the concentric cylinders of a multi-walled CNT [13]; (4) catalytic metal nanoparticles; and (5) gas-phase oxidation, where oxygen reacts with pre-existing defects on a CNT, forming pits, and further sonication in liquid unzips the CNT [14, 15].

In contrast to these unzipping processes, atomically-flat sGNRs grown on Au(111) were successfully fabricated by surface-assisted coupling of molecular precursors into linear polyphenylenes and their subsequent cyclodehydrogenation (i.e., bottom-up process) [4], where scanning tunneling microscopy and spectroscopy (STM/STS) have been used as powerful tools to visualize the local density of states (LDOS) of the sGNRs, and to study their dependence with the chirality of the ribbons as well as the existence of edge states [5, 16]. From a theoretical point of view the dependence of the electronic properties of the graphene nanoribbons on the edge’s structure and/or the width has been addressed [17–20]. The growth of sGNRs has been explored as a feasible route to create a band gap around the Fermi level by narrowing the sGNR width (<2 nm) owing to quantization effects; so far, rectification has not been observed [17]. The electronic properties of cross-structured sGNRs are critical for the development of three-dimensional Fin-FETs.

In this manuscript, we have studied the morphology and electronic properties of sGNRs on Au(111) prepared by drop casting GNWR solution by means of STM/STS in an ultra-high vacuum (UHV) at 78 and 300 K. In marked contrast to the atomically-flat sGNRs on Au(111) grown by the bottom-up process [4], our drop casting sGNRs showed unique properties. We used metallic sGNRs to explore, by means of STM/STS, the intrinsic properties of the crossing areas between two sGNRs.

We used sGNRs unzipped from a double-walled carbon nanotube (DWNT) by following the method used in the previous studies [10–12, 15], i.e., after two hours sonication, more than 95% of the DWNTs were unzipped, producing three kinds of GNWs: double-layer GNWs, Y-shaped GNWs and sGNRs. Markedly, after 16 h sonication, more than 99% of the double-layer GNWs and Y-shaped GNWs split into sGNRs, which was confirmed by Raman spectroscopy and scanning probe microscopy [15]. We used this GNR liquid, and therefore the presence of bilayer or multilayer GNWs could be discarded in our solution. We deposited the resulting nanoribbons placing a drop of the nanoribbon solution on the Au(111) substrates. The samples were then introduced into a home-built UHV setup containing a low-temperature STM. Using a solution with a low concentration the drop casting process created a sample with individual sGNRs deposited on Au(111). The adsorbed sGNRs did not lay completely flat on the surface, some local points of the sGNR were in contact with the substrate (d ~ 0.5 nm), but in other parts the sGNRs were quite far away (d ~ 1–3 nm) from the substrate, where d denotes distance between the adsorbed sGNR and the substrate, i.e., the sGNRs unzipped from the CNTs were buckled. The STS maps clearly show that each buckled sGNR presents metallic properties (conductance of ∼3.5 G0) with a uniform LDOS, independent of the buckling. By repeatedly adding drops of the solution on the substrate, we were able to create a network of intersected sGNRs, the most frequent configuration was the crossing between two sGNRs. Due to the buckling structure on the sGNR, the separation between two sGNRs was between 1.0–1.5 nm. The STS data showed uniform electronic states on the cross areas with a gap around the Fermi level of the order of 250 meV, with a lower limit of −50 meV and an upper limit of +200 meV i.e., the electronic properties of the sGNRs varied from metallic to p-type semiconducting.

2. Results and discussion

2.1. Imaging of drop casting sGNR on Au(111)

The sGNRs were prepared by unzipping DWNTs with careful sonication in solution such that the CNTs were carefully opened but not destroyed and thus the width of the resulting sGNRs could be controlled by the diameter of the CNTs [10–12]. In this work, we used DWNTs with diameters of 5–15 nm, i.e., the widths of the obtained sGNRs were comparable to π times the diameter of the unzipped CNT. Also, two carbon sheets could be initially separated by 1–2 nm, while bilayer GNWs have a separation distance of ∼0.335 nm [21]. As a substrate, we used 200 nm thick gold films deposited on mica. The films present a (111) termination with a grain size large enough to allow STM measurements in a single Au(111) crystallite [22].

Figure 1(a) shows a typical image of the surface of the Au(111) on mica, atomically-flat terraces separated by atomic steps can be observed in the STM image. The inset shows the corresponding low energy electron diffraction (LEED) pattern, the spots corresponding to the six-fold symmetry appear as small arcs due to the small rotational disorder of the different Au(111) crystallites. Figure 1(b) shows an atomically resolved STM image where the atomic periodicity of the Au(111) surface can be observed as well as the modulation...
due to the herringbone reconstruction \cite{22}. First, we used a low concentration solution in order to deposit individual sGNRs and characterize their properties. Figure 1(c) shows an STM image (475 × 100 nm) showing a single sGNR deposited on the Au(111) surface, the width of the observed sGNR was of the order 45 nm, as expected from the diameter of the original CNTs. The line profile (1) in figure 1(d) is measured along the arrow (1) in figure 1(c) and shows a steady increase in height from left to right. The Au(111) film substrate was atomically-flat as shown in figure 1(a), but the terrace width was rather small: 10–20 nm, therefore about 30 steps exist on the substrate from left to right in the STM image in figure 1(c), generating a height difference of ∼6 nm. A single GNR was gently dropped on this substrate, producing a unique shape. In figure 1(d), the line profile (2) obtained on top the sGNR shows a different evolution with the lateral position indicating that the sGNR did not follow the morphology of the substrate. In fact, sGNR along arrow (2) shows clear buckling. Line profiles along the arrows (3)–(5) in figure 1(c) show the separation distance from the substrate (see figure 1(e)). Clearly, the separation distance changed at different positions: the shortest length $d \sim 0.6$ nm to the longest length of $d \sim 3$ nm, suggesting that the sGNR was in local contact with the substrate, but in most of the areas was far away from the Au(111) substrate. We also observed that an sGNR hung on a substrate hole, i.e. an sGNR was able to float from the substrate (see the supplementary information, figure S1 is available online at stacks.iop.org/NANO/29/315705/mmedia.) We can speculate that this configuration may have been due to the drop casting procedure and the subsequent annealing process, because the graphene nanoribbons synthesized in situ always lay flat on the surface \cite{4, 5}.

2.2. Electronic properties of drop casting sGNRs

By means of STS we studied the electronic properties of individual sGNRs. Figure 2(a) shows the spectroscopy results measured on individual sGNRs, the $dV/dI$ curves shown are obtained at the A, B, C, D, E, and F areas in figure 4(a). It should be noted that all curves have identical shapes and features irrespective of the position they were measured on the buckled sGNRs. In the vicinity of the Fermi energy ($V_s \sim 0$), $dV/dI$ increased linearly for both negative and positive voltages and did not reach zero at zero energy, indicating a metallic behavior as expected from the width

Figure 1. (a), (b) STM images obtained on the atomically-flat Au film (∼200 nm thick) on mica at 78 K, which was cleaned and flattened in UHV by several cycles of Ar⁺ sputtering and annealing before drop casting the GNR solution. (a) Au atomic terraces ($V_s = -1.0 \text{ V}, I = 50 \text{ pA}, 100 \times 100 \text{ nm}$). LEED pattern in the inset image shows six-fold fcc(111) symmetry. (b) Atomically resolved STM image of fcc-Au(111) ($V_s = -70 \text{ mV}, I = 100 \text{ pA}, 8 \times 8 \text{ nm}$). Bright spheres correspond to single Au atoms, while two brighter lines correspond to the Au(111) reconstruction. (c) STM topographic image of a single-layer graphene nanoribbon (sGNR) on the Au(111) substrate ($V_s = -1.5 \text{ V}, I = 50 \text{ pA}, 475 \times 100 \text{ nm}$). The width of the sGNR is ∼45 nm. (d) Line profiles along arrows (1) and (2) in (c). (e) Line profiles along arrows (3), (4) and (5) in (c).
The calculated LDOS of a graphene sheet \(N = \text{in} \text{finity}\) and that of an sGNR with a width of \(N = 19\) are also shown in figure 2(b). Although the finite size effect in the sGNR, as seen in that of \(N = 19\), may have opened an energy gap at the Fermi level, this happened for widths much smaller than the widths of the nanoribbons deposited in our experiments, and therefore, the experimentally observed \(dI/dV\) curves agree well with the behavior expected from the theoretical calculations. In order to test if the observed metallic behavior in the STS spectra was an intrinsic property of the deposited sGNRs or, on the contrary, we measured the metallic character of the Au(111) substrate through the graphene nanoribbon; we measured the electrical conductance along the nanoribbons’ axis in contact with the STM tip at one end of the sGNRs and lifted them from the surface [23, 24]. The experimental procedure was as follows, we approached the W tip towards the sample to make direct contact with the sGNRs avoiding plastic deformation of the sample. During the approach-retract process, the current was measured as a function of the tip-sample separation \((I-z\) curve\) while the bias voltage was fixed at \(+10\) mV. The blue line shows conductance during approach. From \(-180\) pm to \(-220\) pm, we can observe big jumps of the conductance, and around \(-300\) pm, the conductance becomes constant. When we retracted the tip, the conductance was constant (~3.5 \(G_0\)), indicating that the tip is still in contact with the sGNR and the tip started to pick up the sGNR. The conductance through the partially lifted sGNR was ~3.5 \(G_0\).

Figure 2. (a) \(dI/dV\) curves, proportional to the LDOS, obtained on the sGNR adsorbed on Au substrate at the areas marked by A, B, C, D, E, and F in figure 4(a). (b) Calculated LDOS of sGNR with a width of \(N = 19\) and \(N = \text{infinity}\) (see the supplementary information, figure S3). (c) STM conductance measurement through an sGNR at 78 K. \(z\) denotes the distance of the tip approaching toward the sGNR. Before approaching the STM W tip towards the sGNR on the Au substrate, the tip height position was set as \(V_s = +10\) mV, \(I = 150\) pA. The blue line shows conductance during approach. From \(-180\) pm to \(-220\) pm, we can observe big jumps of the conductance, and around \(-300\) pm, the conductance becomes constant. When we retracted the tip, the conductance was constant (~3.5 \(G_0\)), indicating that the tip is still in contact with the sGNR and the tip started to pick up the sGNR. The conductance through the partially lifted sGNR was ~3.5 \(G_0\).
2.3. Crossing sGNRs by drop cast

By repeating the drop casting on the same substrate, we increased the number of deposited sGNRs and therefore increased the number of sGNRs crossing each other. Figure 3(a) shows the area where three sGNRs (named A, B and C) overlapped. Figure 3(b) is a simple sketch to identify the sGNRs’ positions. By comparing figures 3(a) and (b), we can see that sGNR A and B crossed. The crossing area is marked as A + B. The line profiles along arrow (1) and (2) in figure 3(a) show that the distance between the two sGNRs was always around 1.0–1.5 nm (see figures 3(c) and (d)), so the sGNRs did not lay flat one on top of the other as a consequence of the deposition method. (A wide scan range STM image is shown in the supplementary information, figure S2, where more than 20 sGNRs are stacked.)

Figure 4(a) shows an STM topographic image (200 × 180 nm) acquired in another area showing six sGNRs which are marked by numbers: 1–6. There are four sGNRs (1–4) running from left to right and another two sGNRs (5 and 6) running from the bottom to the top of the image. With this configuration GNRs 5 and 6 partially crossed with GNRs 1–4. The crossed areas are marked by G1 and G2. Simultaneously to the topographic image we measured at every pixel of the image the $dI/dV$ curve. Figure 4(b) shows the $dI/dV$ map at +30 mV. The brighter color denotes higher $dI/dV$ [nA/V], i.e., a higher LDOS. By comparing figures 4(a) and (b), we conclude that sGNRs 1–4 show uniform signal in the $dI/dV$ map, which confirms that monolayer sGNRs present a uniform LDOS as long as they are deposited on the Au(111) substrate, as discussed before. However, in all the areas where two sGNRs cross the $dI/dV$ signal is smaller and the areas appear darker in the maps, i.e., there is a clear reduction in the LDOS of the nanoribbons when they are deposited on top of another nanoribbon in comparison to the ones deposited on Au(111). Figures 4(c) and (d) show the line profile along the arrows in the topographic image (figure 4(a)) and the $dI/dV$ map at +30 mV (figure 4(b)), respectively. Since the sGNR surface was not flat, the line profile in figure 4(c) shows height variations within GNR 3. At the position where GNR 3 crossed with GNR 5, the height changed by ∼1.0 nm, which agrees with the average distance measured in the other overlapping areas (see figure 3). On the other hand, the line profile in the $dI/dV$ map along the same path gives us interesting information (figure 4(d)). In spite of the fact that the topographic height varied along GNR 3, the $dI/dV$ values remain constant around 0.20 ± 0.05 nA V$^{-1}$, i.e., the LDOS inside the GNR are quite uniform, independent of the morphology variation. The $dI/dV$ curves obtained at the A–F areas in figure 4(a) are shown in figure 2(a). It should be noted that all curves show similar features, i.e., in the vicinity of the Fermi energy ($V_\text{f} \sim 0$), $dI/dV$ increases linearly for both negative and positive voltages, meaning that the LDOS at different positions on the sGNRs is almost the same. Markedly, at the position where the two sGNRs overlap, the $dI/dV$ signal rapidly dropped down to ∼0.0 nA/V, and remained constant in all the crossing areas. The edge of the crossing area is focused on in figure 4(e), where the height variation of 1.0 nm takes place in Δ ∼ 7 nm distance, however, the $dI/dV$ signal drops within Δ ∼ 3 nm, which indicates that the $dI/dV$ drop was not due to the GNR bending, but the electronic interactions between the up and down sGNRs. Figure 4(f) shows the $dI/dV$ curve obtained at the crossed area (G1 in figure 4(a)), it presents $dI/dV$ values of ∼0.00 nA/V around the Fermi energy (red curve). The blue curve in figure 4(e) was obtained from the crossed sGNR area at G2 in figure 4(a) where GNRs 2 and 6 cross each other. It should be noted that G1 and G2 crossing areas showed exactly the same $dI/dV$ curve, i.e., different crossed sGNRs had the same LDOS and gap, suggesting that there was no crossing angle dependence between two sGNRs, further suggesting that random stacking sGNRs may have a gap. Just by crossing, the sGNRs changed their electronic property from metallic to semiconducting.
In order to characterize with precision the energy position of the gap we measured $dI/dV$ curves with high energy resolution. Figure 5(a) shows $dI/dV$ maps at $-697$, $+10$, $+313$, and $+717$ mV obtained at the boundary between the sGNR and the crossed GNRs. At $-697$ mV, it is hard to see the difference in the map, meaning the sGNR and the crossed sGNRs had a comparable conductance, however, at $+10$ mV, the crossed sGNRs show clear dark contrast, while the contrast becomes weaker with an increase in the bias (see the map at $+313$ mV), and finally at $+717$ mV even the crossed area appears brighter. These variations in the differential conductance maps can be clearly explained by the $dI/dV$ plot on a log-scale shown in figure 5(b). White and red dots are the $dI/dV$ plots obtained at the sGNR and the crossed sGNRs, respectively. Around $-650$ meV, both the sGNR and crossed sGNRs have a similar conductance of $\sim 0.5$ nA/V, then from $-650$ meV to $-50$ meV, the conductance of the crossed sGNRs drastically decays below $0.01$ nA/V. Above $+200$ meV, again the conductance of the crossed sGNRs starts to increase rapidly and above $+600$ meV, the
There are a couple of mechanisms that could explain the presence of a gap in the LDOS of the upper GNRs in the overlapping areas. Botello-Mendez et al calculated that the stacking angle between individual GNRs plays a central role in dictating the probability of transmission of the electrons from one ribbon to the other [21]. In fact, gaps were found in perpendicular conductance at crosses with different orientations. Initially one can think that our STM/STS results agree with these theoretical predictions; however, a detailed analysis of our results indicates that the presence of a gap in the differential conductance must have a different origin. On the one hand, in our experiments, the gap width in the conductance does not depend on the angle between the crossing ribbons, as opposed to the calculations. On the other hand, our experiments measured the tunnel probability when the STM tip was located on top one of the crosses of the graphene nanoribbons and not directly the probability of transmission of an electron from the upper to the lower nanoribbon. The GNRs used in this study are metallic, as demonstrated above, and therefore even if the transmission of electrons between the upper and lower ribbon is prohibited, we should not see a gap in the differential tunneling conductance measured by means of STM since the electrons can reach the Au(111) by moving through the top ribbon.

An alternative explanation for our experimental results is the existence of a gap in the electronic structure of graphene bilayers. It has been shown that breaking the inversion symmetry in graphene bilayers by applying an electric field perpendicular to the plane of the graphene bilayer opens a gap [25, 26]. A similar way of getting the same results is growing or depositing the bilayer on a substrate, which modifies the density of carriers differently in one of the layers of the bilayer [9, 27]. In all cases gaps observed are of the order 250 mV. Figures 5(c) and (d) show schematics of electron transfer between the tip and the sample when positive (+200 mV) and negative (−50 mV) bias voltages are applied. At the crossed structure, upper and lower GNR layers were stacked. We know that the lower GNR layer has a metallic property, thus electrons fill up to the Fermi energy (E_F). However, the situation of the upper GNR layer is totally different; from the STS results in figures 5(a) and (b), we know that the LDOS of the upper GNR layer has a gap. In figures 5(c) and (d), blue and red lines denote the valence band edge (E_v) and the conduction band edge (E_c) of the upper GNR layer, respectively. When a positive bias was applied to the sample, electrons from the tip Fermi energy tunneled into the unoccupied states of the sample substrate through the conduction band of the upper GNR layer (see figure 5(c)). Reversely, when a negative bias was applied to the sample, electrons tunneled from the Fermi energy of the substrate to the tip unoccupied states through the valence band of the upper GNR layer. Considering that Fermi levels in the lower GNR and the Au substrate were in equilibrium whereas the upper GNRs was electrically isolated from the lower one by 1.0 nm spacing, the vertical electric field of around 400 MV m⁻¹ could have been caused between the two GNRs layers by the difference in work functions of Au and the GNR; 5.1 eV for Au and 4.7 eV for conductance of the crossed GNRs becomes higher than that of the GNR. From this plot, if we define the dI/dV values lower than 0.002 nA/V as insulating, we can say that the crossed GNRs have a gap between −50 and +200 meV around the Fermi energy (an energy gap width of E_g = 250 meV), i.e., the crossed GNRs have p-type semiconducting characteristics.

Figure 5. (a) dI/dV maps at −697, +10, +313, and +717 mV obtained from the crossed sGNRs areas. Brighter areas denote higher conductance. (b) Differential conductance (dI/dV) plot on a log-scale as a function of energy, where zero corresponds to the Fermi energy, and positive and negative energy denote unoccupied and occupied states, respectively. White and red dots show dI/dV values obtained on the sGNR area and the crossed sGNRs area, respectively. Two dashed lines suggest a band gap. (c), (d) Scheme showing the electron transfer between the tip and the sample at the crossed sGNRs areas. From the left side, the lower sGNR/Au(111) substrate, the upper sGNR, and the W tip energy diagrams are shown. Bias voltage is applied between the substrate and the tip. The substrate and the upper GNR are separated by ~1.2 nm, and the W tip and the upper sGNR are separated by ~1 nm. In (c), a positive bias voltage of +200 mV and, in (d), a negative bias voltage of −50 mV is applied. E_v and E_c denote conduction and valence band edge, respectively.

-700 -350 0 350 700 E - E_F [meV]
-0.0001 -0.00001 0.00001 0.0001 0.001 0.01 0.1 1 10 dI/dV [nA/V]

Conductance. White and red dots show dI/dV values obtained on the sGNR area and the crossed sGNRs area, respectively. Two dashed lines suggest a band gap. In (c), a positive bias voltage of +200 mV and, in (d), a negative bias voltage of −50 mV is applied. E_v and E_c denote conduction and valence band edge, respectively.
3. Materials and methods

3.1. STM setup

All experimental studies were performed with home-built UHV-STM equipment [29], which consists of introduction, preparation, and analytical chambers. The scanning head of the equipment was located inside the analytical chamber and was cooled down to low temperatures with a cryostat. We achieved 78 K by filling liquid nitrogen (LN2) in the cryostat (4 liters of LN2 remained at 78 K for more than 80 h). W tips were fabricated by chemical etching from a commercial polycrystalline W wire (99.9% purity) with KOH aq. under air. The etched W tip apices were quickly checked by SEM (Technex Tiny-SEM, ∼10−3 Pa). Sharp tips were subsequently introduced into the UHV-STM setup. In the preparation chamber, the tip apex was properly annealed by electron bombardment (10–30 W, 10 s, once) to remove oxide layers coating the apex [30], then without breaking UHV, the tip was set into the STM.

3.2. STM spectroscopy

All STM topographic images were obtained in constant-current mode using a feed-back loop. With the use of STM spectroscopy, the LDOS of each atomic position could be directly obtained [29, 31–33]. The tunneling current as a function of the sample bias voltage (I−V curve) was measured at each pixel position in the STM topographic image. The differential conductance (dI/dV) was obtained by numerical differentiation of the I−V curve. Since the experimentally obtained dI/dV is proportional to the sample LDOS [29, 31–34], the zero voltage corresponded to the Fermi level and dI/dV in the positive (negative) voltage range denoted the unoccupied (occupied) state. Conductance through the sample could also be measured by approaching the W tip to the sample to make direct contact without plastic deformation of the sample [23, 24]. During the approach-retract process, the current was measured as a function of the tip-sample separation (I−z curve). We set the constant voltage at +10 mV during the I−z measurement. Typically, the tip detected the tunneling current increasing exponentially when the tip started to approach the sample. The current (and thus the conductance) was drastically increased by a factor of more than 10 when the tip made contact with the sample. Further approaching the sample did not significantly increase the current. Here, we used G0 = 2e2/h ∼ 1/12.9 kΩ [23, 24], where e is electron charge, and h is Planck’s constant.

3.3. Au111/mica substrates

Commercial Au films (∼200 nm thick) deposited on mica were used as substrates. The observation of atomically-flat sGNRs required atomically-flat substrates. In the present study, we used two methods: (1) the Au/mica was heated in air by flame for 5 s (we used the top of the orange-flame, C2H10 gas). (2) the Au/mica was sputtered by Ar⁺ (+1 kV, 10 min) and annealed (853 K) in the UHV preparation chamber. We repeated these cycles five times (too much sputtering removes the entire Au film). LEED located inside the preparation chamber showed six-fold fcc-Au(111) spots. STM topographic images showed atomically-flat terraces.

3.4. GNR preparation

First, the atomically-flat Au(111) substrates were confirmed in our STM setup, and then the substrate was taken out of the setup. GNRs were produced by unzipping the DWNTs in liquid [10–12, 15]. Under sonication (37 kHz, 600 W) for 2 h, more than 95% of the DWNTs were unzipped, producing double-layer GNRs (∼20%), Y-shaped GNRs (∼30%), and sGNRs (∼45%) (see the supplementary information in ref. [15]). Further sonication for more than 16 h split more than 99% of the double-layer GNRs and Y-shaped GNRs into sGNRs. We used this solution in this study. The sGNR liquid was drop cast at the center of the substrate under air. The size of the substrate was 10 × 5 mm² with a thickness of ∼0.5 mm. The sample was then annealed up to 623 K for 3 h in air to remove poly (m-phenylene vinylene-co-2,5-dioctoxy-p-phenylene) (PmPV). Again, the sample was set into the UHV setup, and annealed in the preparation chamber at 853 K for 10–30 min. The sample was transferred to the analytical chamber and we performed the STM/STS measurements.

3.5. Theoretical calculations

As a theoretical model of the GNR, we adopted an armchair ribbon with a width of N atomic rows of carbon, where both edges were terminated by hydrogens to remove the effects of the dangling bonds (see the supplementary information, figure S3). The bond length was taken to be the experimental value of graphite, 0.142 nm. Calculations were performed based on the local spin density approximation using the full-potential linearized augmented plane-wave method with a single slab geometry [35–37]. Linearized augmented plane-wave functions with a cutoff of |k+G| < 5.0 a.u.−1 and muffin-tin (MT) sphere radii of 1.2 and 0.8 a.u., respectively, were used for the C and H atoms, where the angular momentum expansions inside the MT spheres were truncated at l, 6 and 4 for the wave functions, charge density, and potential.

4. Conclusion

In this study, single-layer metallic graphene nanoribbons unzipped from double-walled carbon nanotubes with a sonication method were deposited on Au(111) by drop casting the sGNR solution in air with subsequent annealing (853 K) in
UHV. In contrast to the bottom-up CVD process, the drop cast sGNRs were buckled, i.e., some local points of the sGNRs were in contact with the substrate (d ~ 0.5 nm), but other parts were further apart (d ~ 1–3 nm). The STS maps clearly showed that single buckled sGNRs on Au(111) have metallic properties (conductance of ~3.5 G_0) with considerable uniform LDOS, independent of topographic variations. On the contrary, the areas where two sGNRs overlapped show a uniform electronic structure with an energy gap between ~50 and ~200 meV around the Fermi energy, i.e., the electronic properties of the sGNRs varied from metallic to p-type semiconducting, which was not due to the bending, but the electronic interactions between the up and down sGNRs. These findings in our STM/STS studies of the crossed sGNRs could be useful with regard to future architecture of cross bridging array structures in nanodevices using sGNRs.

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