Scanning Tunneling Microscopy Characterization of the Electrical Properties of Wrinkles in Exfoliated Graphene Monolayers

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ABSTRACT

We report on the scanning tunneling microscopy study of a new class of corrugations in exfoliated monolayer graphene sheets, that is, wrinkles ∼10 nm in width and ∼3 nm in height. We found such corrugations to be ubiquitous in graphene and have distinctly different properties when compared to other regions of graphene. In particular, a “three-for-six” triangular pattern of atoms is exclusively and consistently observed on wrinkles, suggesting the local curvature of the wrinkle provides a sufficient perturbation to break the 6-fold symmetry of the graphene lattice. Through scanning tunneling spectroscopy, we further demonstrate that the wrinkles have lower electrical conductance and are characterized by the presence of midgap states, which is in agreement with recent theoretical predictions. The observed wrinkles are likely important for understanding the electrical properties of graphene.

Graphene refers to a monolayer of carbon atoms tightly packed into a two-dimensional (2D) honeycomb lattice. The discovery of graphene in an isolated state1,2 has generated widespread research interest.3-5 Graphene initially appeared to be a strictly 2D electronic system, and quantum Hall effects were observed in graphene up to room temperature.6 On the other hand, theory has predicted that strictly 2D crystals are thermodynamically unstable and therefore should not exist at any finite temperature.7

This contradiction was reconciled by recent transmission electron microscopy (TEM) studies on suspended graphene, in which a microscopically corrugated three-dimensional structure was revealed,8,9 overturning the naïve picture of graphene being a flat 2D crystal. The <1 nm local corrugations (“ripples”) discovered in these TEM studies are believed to be intrinsic,10 and so are important for understanding graphene electrical properties.4,11-15 The low resolution of TEM, especially in the vertical direction, however, limits further detailed studies of these corrugations, and how those corrugations can influence the graphene properties. In addition, the structure and properties of suspended graphene may fundamentally differ from graphene deposited on SiO2 substrates, the most widely studied form of graphene.

Scanning tunneling microscopy (STM) provides a probe for the morphology and electrical properties at atomic resolution in all three dimensions. Atomically resolved STM topographs of graphene on SiO2 substrates have been reported,16-20 from which the height of graphene ripples was determined to be 3-5 Å. Meanwhile, attempts to correlate local electrical properties with the observed ripples have achieved only limited success.20-22

Here we report on the STM study of a new class of corrugations in monolayer graphene sheets that have been largely neglected in previous studies, that is, wrinkles ∼10 nm in width and ∼3 nm in height. We found such corrugations to be ubiquitous in graphene and have distinctly different properties in comparison to other regions of graphene that only contain small ripples. In particular, a “three-for-six” triangular pattern of atoms is exclusively and consistently observed on wrinkles, suggesting the local curvature of the wrinkle is a perturbation that breaks the 6-fold symmetry of the graphene lattice. Through scanning tunneling spectroscopy (STS), we further demonstrate that the wrinkles have lower electrical conductance when compared to other regions of graphene and are characterized by the presence of midgap states, which is in agreement with recent theoretical predictions. Our results suggest that, in addition to the previously investigated, low-amplitude ripples, these larger wrinkles likely play an important role in determining the electrical properties of graphene sheets.

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The monolayer graphene sheets investigated in this study were fabricated on insulating SiO₂ substrates through mechanical exfoliation of Kish graphite flakes (Figure S1 in Supporting Information). Monolayer graphene sheets ∼20 µm in size were optically identified and unambiguously confirmed through spatially resolved Raman spectroscopy. As shown in Figure 1A, a symmetric single peak is observed at ∼2700 cm⁻¹ (2D band) in the Raman spectrum, and the peak height is larger than the G band at ∼1580 cm⁻¹. Both features are characteristic of pristine monolayer graphene sheets. Ti/Au electrodes were contacted to the fabricated graphene sheets using electron-beam lithography, and Hall measurements revealed room-temperature carrier mobilities of >6000 cm²/Vs (Figure S2 in Supporting Information), which is typical of high quality graphene at room temperature. For STM measurements, the graphene sheets were then contacted at all edges with gold, so that the tunneling current diffused in-plane through the gold film. The electrodes defined in the previous step served as guides for locating the graphene sheets using STM (Figure S3 in Supporting Information). STM studies were performed using an Omicron low-temperature UHV STM system with mechanically cut Pt/Ir tips. All STM data were taken at liquid nitrogen (77 K) or liquid helium (4 K) temperatures, and a vacuum of better than 10⁻¹⁰ Torr was maintained during experiment.

Figure 1B gives the constant-current STM topograph obtained from a typical graphene device. Atomically resolved, clear honeycomb structures were observed for all samples with bond lengths in agreement with the known graphene lattice constant (Figure 1C). The same honeycomb structures are obtained independent of the specific parameters used for imaging. See Figure S4 in the Supporting Information for additional atomically resolved STM topographs taken with different imaging parameters on different samples.

No lattice defects were ever observed during our atomically resolved STM study over an accumulated area of ∼10⁴ nm² on different samples, corresponding to >10⁵ atoms. This is in agreement with the measured high carrier mobilities, but in contrast with STM results obtained on graphene epitaxially grown on conductive substrates in which lattice defects are observed at the nanometer scale. Surface corrugations (ripples) of ∼4 Å in height are observed for most regions of our graphene samples (Figure 1B and Figure S4 in Supporting Information), which is in agreement with previous studies. In addition to the previously observed ripples, we also frequently encounter larger-amplitude wrinkle-like structures that are 5 to 20 nm in width, 2 to 5 nm in height, and have lengths from ∼100 nm to ∼1 µm. Figure 2A presents the topograph obtained from a region of a graphene sample in which multiple wrinkles are observed. Additional representative topographs of the observed wrinkles are included in Figure S5 in the Supporting Information. The wrinkles appear to be continuous parts of the graphene sheet that buckle up from the underlying substrate (Figure 2B), reminiscent of wrinkles that spontaneously occur in thin elastic sheets under stress. However, quite different from a conventional thin sheet, the observed graphene wrinkles are found to be accompanied (both on and near the wrinkles) by the ∼4 Å
small ripples that are known to be intrinsic\textsuperscript{10} to graphene (Figure 2B).

Wrinkle-like structures have been seen before in TEM images of suspended graphene sheets\textsuperscript{24} and in STM and high-resolution scanning electron microscope (SEM) images of graphene grown on conducting substrates\textsuperscript{28,29} but their structure and properties have not been carefully characterized. Moreover, wrinkles were not previously known to be present in the high-mobility, mechanically exfoliated graphene sheets on SiO\textsubscript{2} substrates, presumably due to their low occurrence rate and small physical dimensions; features with such dimensions are hard to detect optically or with an SEM or atomic force microscope. High-resolution STM topographs were only recently achieved for graphene sheets on insulting substrates\textsuperscript{16--20}

The wrinkle structures were found to be ubiquitous on our exfoliated graphene sheets on SiO\textsubscript{2}. Wrinkles appear randomly across the sheets, and one or more wrinkles are typically observed when the scanning area is larger than \(\sim 2 \mu\text{m}^2\). Previous STM studies have indicated that wrinkles of similar physical dimensions appear at a similar density on freshly cleaved graphite surfaces obtained through mechanical exfoliation using adhesive tapes\textsuperscript{30}. Because a similar exfoliation technique is employed in the fabrication of graphene sheets (Figure S1 in Supporting Information),\textsuperscript{2,23} it may be that wrinkles are unavoidable for graphene on SiO\textsubscript{2}. Recent theoretical studies have also proposed the spontaneous formation of wrinkles for graphene on SiO\textsubscript{2} substrates.\textsuperscript{31} We, however, do not dismiss the possibility that the standard microfabrication procedures employed in this study might result in additional wrinkles in the graphene sheet.

Surprisingly, atomically resolved topographs (Figure 2C,D) reveal very different structures for the wrinkles in comparison with other parts of graphene. A triangular pattern is observed over the entire graphene wrinkle (Figure 2C,D), and the distance between adjacent bright spots is \(\sim 2.5\ \AA\), indicating the honeycomb 6-fold symmetry of the graphene lattice is broken, and only three of the six carbon atoms in each hexagonal ring is observed (Figure 2D). In comparison, the topograph taken on the same graphene sheet adjacent to the wrinkle (Figure 2E) reveals the honeycomb structure that is consistently observed on the “flat” (by “flat” we mean only the \(\sim 4\ \AA\) ripples are present) parts of the monolayer graphene sheets investigated in our study. The “three-for-six” triangular patterns were observed on all (\(\sim 10\)) the wrinkles we investigated over a couple of different graphene samples. For example, Figure 3 shows the triangular patterns observed on another wrinkle in another graphene sheet.

**Figure 2.** STM topographs of graphene wrinkles. (A) A large-area (500 nm by 500 nm) scan of wrinkles in a graphene sheet. A small color scale is used to accentuate the coexisting small ripples. The largest height in this topograph is \(\sim 6\ \text{nm}\). (B) A three-dimensional plot of the topograph of a typical wrinkle structure. The coexisting ripple structures are also observed. A height profile through the green line is given. (C) Atomically resolved topograph obtained on the top of the wrinkle. Scale bar: 1 nm. (D) A close-up of the observed “three-for-six” triangular pattern on the wrinkle, corresponding to the green square in (C). Scale bar: 2 Å. The blue hexagon has sides of 1.42 Å, corresponding to the size of one hexagonal carbon ring. (E) Atomically resolved topograph taken right next to the wrinkle on a “flat” region of the same graphene sheet. Scale bar: 2 Å. The blue hexagon has sides of 1.42 Å.
Most previous STM studies on monolayer graphene sheets on SiO₂ substrates reported honeycomb patterns. Small (<1 nm) and random regions of “three-for-six” triangular patterns mixed with honeycomb patterns have been observed in one individual sample. The origin of such patterns was unclear, but was conjectured to be due to the presence of “strong spatially dependent perturbations”, including local curvature or trapped charges. In our study, honeycomb patterns are observed for all “flat” parts of graphene (with ∼4 Å high ripples), while triangular patterns are exclusively and consistently observed on the ∼3 nm high wrinkles. These results indicate that increased local curvature (and the associated strain) on the wrinkles can provide strong enough perturbations to break the 6-fold symmetry and degeneracy of the electronic states in graphene.

Because STM topographs represent the local density of states (DOS) distribution, we were able to further investigate how the “three-for-six” pattern characteristic of the wrinkles reflected the local electronic states and geometric structure of graphene. This can be probed by measuring topographs at both positive and negative sample biases, since such STM measurements will respectively probe the LUMO (empty states) and HOMO (filled states) of the sample.

Figure 3A,B gives the atomically resolved STM topographs of the top surface of a graphene wrinkle, obtained at positive and negative sample biases. The same “three-for-six” triangular patterns are observed for positive and negative biases (Figure 3C); the center parts of the two topographs, which correspond to the crest of the wrinkle, overlap with each other exactly, and a regular triangular lattice is observed. Small distortions of the triangular lattice are observed for regions away from the center, and the patterns obtained from the two scans gradually mismatch with each other. This suggests that the wrinkle is flexible, and the force from the STM tip causes a slight deformation of the wrinkle during scans. In comparison, on the “flat” part of the same graphene sheet (Figure 3D–F), although ∼4 Å ripples are present, clear honeycomb structures were observed for both positive and negative biases, and the obtained topographs always exactly overlap, suggesting the ripples are more rigid compared to the wrinkle.

The same “three-for-six” patterns obtained on the wrinkle at positive and negative sample biases suggest the patterns reflect the actual topology of atoms in graphene. Recent experiments on hydrogenation of graphene have suggested that local bending/curvature in graphene may induce some sp³ hybridization component in the otherwise sp²-hybridized carbons, which facilitates the breaking of delocalized π-bonds in graphene. With a tendency toward sp³ hybridization, the six carbon atoms in each hexagon ring of graphene may start to adopt a structure similar to the chair conformation of cyclohexane, and so three
of the six atoms protrude up and out of the hexagon ring, leading to the “three-for-six” pattern seen in our STM tographes.

We have also characterized the electrical properties of graphene wrinkles through spatially resolved STS. Theoretical studies have suggested that corrugations and the associated strain in graphene may alter the local electrical properties of graphene. On the other hand, recent STS studies on graphene have found very limited or no correlations between corrugations and local electrical properties. This is presumably because the previously studied ripples on “flat” parts of graphene were too small (~4 Å in height).

We have found distinctly different electrical properties for the ~3 nm high wrinkles. Figure 4B presents the differential conductance behavior of a wrinkle, in comparison with other parts of the graphene sheet, where small ripples are present. Lower conductance is observed for the wrinkle at low bias voltages, indicating the wrinkle is less conductive than other parts of graphene. This is in agreement with our previous discussions that the local bending/curvature effects may weaken delocalized π-bonds. For the “flat” part of graphene, in addition to a soft gap at zero bias, a clear dip (local minimum) of differential conductance is observed at $V_D = -0.12$ V (Figure 4B). This corresponds to the charge-neutral Dirac point of graphene, at which energy the conduction and valence bands of graphene meet at a single point in $k$-space, and so charge carriers vanish. Interestingly, this dip disappears on the wrinkle (Figure 4B). This may be explained with recent theoretical studies, which suggest large local corrugations may lead to midgap states, and so a finite density of state is present at the neutrality point.

We have utilized cryo-STM to investigate a new class of corrugations in monolayer graphene sheets, that is, wrinkles ~10 nm in width and ~3 nm in height. We found such corrugations to be ubiquitous in graphene and have distinctly different properties in comparison to “flat” regions of graphene that only contain small ripples. The observed wrinkles are likely important for understanding the electrical and mechanical properties of graphene. Recently developed graphene manipulation methods would be a first step toward harnessing wrinkles to control the electronic landscape of graphene sheets.

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Supporting Information Available: Supplementary figures describing the fabrication and measurement processes and additional STM topographs. This material is available free of charge via the Internet at http://pubs.acs.org.

References