Scanning Tunneling Spectroscopy On A Carbon Nanotube Buckle

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Abstract. The topography and electronic structure of a semiconducting carbon nanotube with a sharp bend is studied by scanning tunneling microscopy and spectroscopy. From the increased height it is concluded that the nanotube is 'buckled', i.e. collapsed due to very strong bending. Detailed spatially resolved spectroscopy measurements at the location of the buckle reveal a well-defined localized state inside the semiconducting gap. The spatial extent of this localized state is about 2 nanometers.

INTRODUCTION

Nanotubes are molecular wires that reveal new interesting physical phenomena typical for one dimensional systems [1]. Transport and scanning tunneling microscopy measurements have revealed many of the bulk electronic properties of carbon nanotubes. Attention is now turning towards localized structures such as kinks and bends within tubes.

Two nanotubes with different chirality can be connected together seamlessly by a pentagon-heptagon pair, as is predicted by Lambin *et al.* [2] and Chico *et al.* [3]. This leads to a kink-like structure within that nanotube. Diode behavior has been measured through a kink connecting a metallic and a semiconducting tube [4]. Recently scanning tunneling microscopy (STM) and spectroscopy (STS) measurements on kinks showed that a metallic tube and a semiconducting tube can indeed be connected together [5, 6].

Applying mechanical force on a nanotube can create a bend within that nanotube [7]. If the strain in the tube exceeds a critical limit, the elastically bent nanotube deforms into a buckle [8], a severe distortion of the atomic structure where all the strain is concentrated locally. The buckle is associated with a rearrangement of atoms and bonds which will have a large impact on the band structure in the region of the buckle and thus on the electronic properties of the tube [8, 9]. Buckles made by AFM manipulation were shown to behave as tunnel barriers in transport studies [7]. Here, we will show the first detailed spatially resolved spectroscopy on a buckle. We will show that this buckle strongly affects the local electronic structure.

Experimental details

As a substrate for our STM studies we use gold (111) facets, which form after flame annealing a small (15 mm^3) piece of 99.99% pure gold. Gas-phase catalytically grown carbon nanotubes [10] are dispersed in dichloroethane by sonication. Small droplets are deposited on the facets resulting in mainly individual carbon nanotubes on the atomically flat surface. Such a sample is cooled down in an Omicron low-temperature STM that is operated at 4.6 K. At low temperature there is no movement of the tip with respect to the sample due to thermal drift. This is important as it allows time-consuming spatially resolved spectroscopy measurements. As a tip we use a 0.25 mm diameter 90% Pt / 10% Ir wire which is cut in ambient with cleaned scissors.

During sonication, or when the tubes are deposited on the substrate, mechanical forces can induce strain into a nanotube, which can lead to the formation of bends or even buckles. Once in contact with the substrate the adhesion force, caused by the van der Waals interaction between the tube and the substrate, may be sufficiently strong to lock this deformation. A bend or buckle can thus remain stable on the substrate. In our measurements we frequently observe slightly curved tubes, i.e., bends with very low angles. Occasionally we observe sharper angles such as the one presented here. Figure 1a shows a topography map of such a sharply bent tube with a bend angle of 26 degrees.

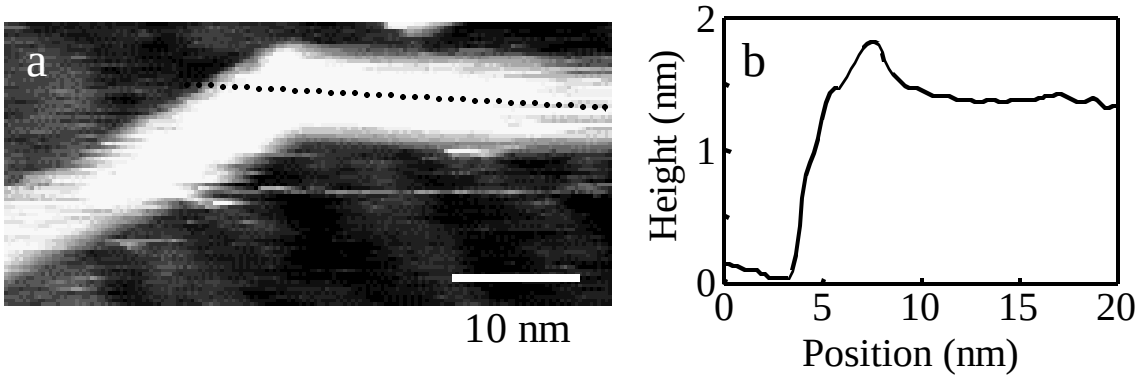

FIGURE 1. a) STM constant current image of a sharply bent individual single-walled carbon nanotube. This image was obtained at a sample bias voltage of V=-1V and a feedback current of I=20 pA. b) Height profile over the bend along the dotted line in figure a. At the location of the bend, the nanotube height of 1.4 nm is increased up to 1.8 nm

Buckle Or Kink?

We need to distinguish whether the local bend of Fig. 1 corresponds to a buckle formed by mechanical strain, or a kink connecting tubes with different diameter and chirality. Spectroscopy measurements performed far away from the bend, to be discussed in further detail below, shows identical semiconducting behavior on both sides of the tube. In addition, the local height at the bent region is clearly higher, as can be seen in Figure 1b. The tube has a height of 1.4 nm which increases up to 1.8 nm near the bend. Note that a small distance of ~0.2 nm between tube and substrate is included in this height due to van der Waals interaction. For a nanotube kink, no height increase is expected. By contrast, in the case of buckled tube, the tube cylinder

is pressed together and the height can theoretically increase up to $(\pi/2)d$, were d is the diameter of the tube. For a tube with a diameter of 1.2 nm this upper bound for the height increase due to a buckle is 1.9 nm. Iijima *et al.* derived an equation for the critical curvature for a buckle to form [8]. For a tube of 1.2 nm in diameter the expected degree of bending necessary to form a buckle is 0.10 rad/nm. Determining the exact radius of curvature of the tube is difficult because the image is broadened by convolution with the shape of the tip. From the height profile we know that the tube has a diameter of 1.2 nm while it appears laterally as broad as 5 nm The tip convolution thus is of the order of 4 nm. As an upper bound we find that the bend is at least localized within the width of the tip since the observed angle is very sharp. This puts a lower limit of 0.11 rad/nm on the curvature.

We conclude that indeed a buckle is formed but the tube may not be completely pressed together since the height does not increase up to its theoretical maximum. To date we have studied only one buckle. Note that the apparent height change can in principal also be caused by a change in the local density of states (LDOS). However, we can rule this out since the profile shown here is taken at a bias voltage of -1 Volt, were the LDOS does not change. Therefor we conclude that the height change is solely due to a topological buckle deformation.

Spectroscopy Over The Buckle

We have performed one dimensional (1D) line scans, measuring the change in the electronic structure as a function of position on the tube. At every point *I(V)* is measured. The derivative *dI/dV(V)* is taken numerically and plotted in grayscale in Figure 2.

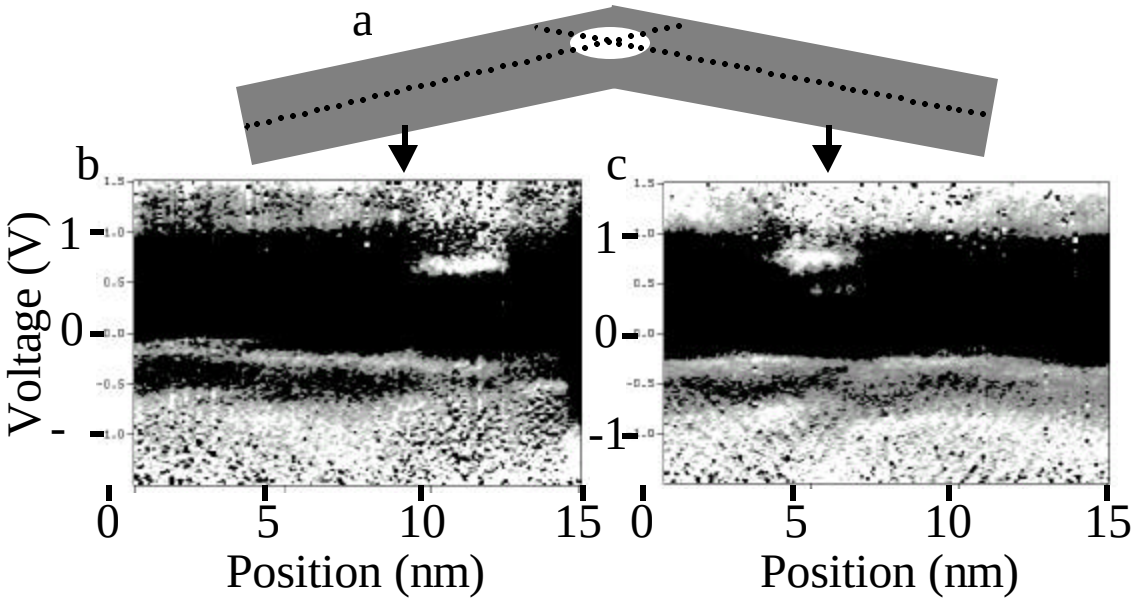

Figure 2. a) Schematic drawing of the buckle. The two dotted lines indicate the tip position for the two spectroscopy plots given at the bottom figures. c) Grayscale plot of dI/dV as a function of voltage (y-axis) and position along the tube (x-axis). At the position of the buckle, a localized state within the semiconducting gap is clearly visible.

The grayscale indicates the magnitude of the differential conductance *dI/dV*, which is a measure of the local density of states (LDOS), as a function of the bias voltage over the tip-tube junction. White is high DOS and black is zero DOS. The horizontal axis is the position on the tube as indicated by the dotted lines in the top illustration of Figure 2. The semiconducting gap is clearly visible as a dark band. The onsets of the first van Hove singularities show up in white. The spectroscopy is featureless along the tube away from the buckle except for small fluctuations in energy. Such fluctuations are also observed in straight tubes [11]. However, at the position of the buckle a clear localized state is visible inside the gap.

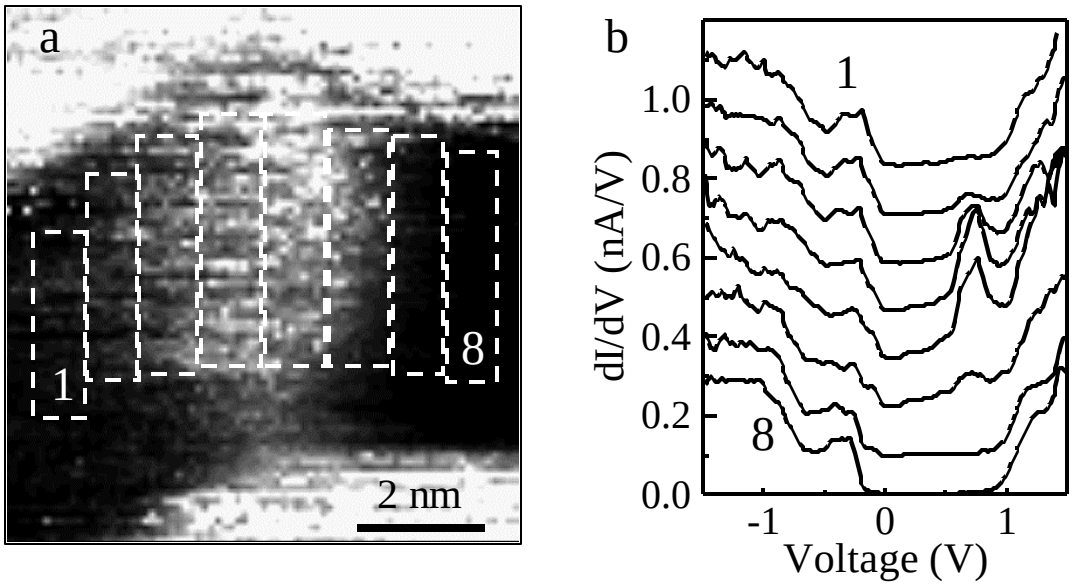

FIGURE 3. a) STM current image in grayscale at +0.72 V of 8 x 8 nm^2. White is high current, black is low current. The semiconducting gap shows up as black. The gold around the tube is white since a current can flow also at low bias. b) Curves 1 to 8 are averaged over the regions indicated in a, starting from the left of the localized state moving gradually to the right. The gap is visible as the flat part with an essentially zero DOS. The curves in b are offset vertically by 0.1 nA/V for clarity.

From spectroscopy measurements over a grid of points on top of the buckle we can gain more insight in the spatial and electronic structure of the localized state. Figure 3a shows a measurement of a current image of the localized state at a bias voltage of 0.72 Volt. Tip convolution broadens the state in the transverse direction but along the tube we can measure the extent of the state away from the buckle. We find that the state extends 2 nm in either direction from the buckle. Figure 3b shows spectroscopy curves averaged over the indicated regions in 3a. The localized state is quite well defined with a full width at half maximum of 0.3 V. Away from the buckle the semiconducting gap is essentially flat. Upon moving over the buckle the sharp localized state appears and decays symmetrically.

Discussion

Several calculations of the electronic structure of kinks and buckles have been reported. However, there are no calculations of the LDOS versus position for this particular measurement layout. We therefore limit ourselves to a qualitative

comparison with related cases. Chico *et al.* showed that defect states appear inside the gap at the interface between two semiconducting tubes connected by topological kink defect [3]. The states fall off within a few unit cells, i.e. within ~1 nm. Here, we measured a buckle and not a kink but we believe that the spatial extent of the defect states is expected to be comparable.

Rochefort *et al.* calculated the effect on the electronic structure caused by bending a metallic nanotube [9]. No significant change was observed for moderate curvature but once a buckle is formed, charge accumulates in the buckled region and additional states appear in between the first van Hove singularities. The states were attributed to a mixing of π and σ states. Since the mixed states have a more local character than pure π states, the transmission through the tube is lower, resulting in an increased resistance. This is consistent with the experimental observation that buckles behave as tunnel contacts. Although we have measured a semiconducting buckle the observation of a localized state is qualitatively consistent with this prediction. A theoretical calculation of the LDOS over a buckle in a semiconducting tube is desirable.

Conclusion

We have shown the first spectroscopy measurements on a nanotube buckle. The formation of a buckle leads to an extra peak within the semiconducting gap. The spatial extent of 2 nm of the localized state agrees with theoretical predictions.

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