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STM atomic resolution images of single-wall carbon nanotubes

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Abstract. We have obtained atomically resolved STM images of individual single-wall carbon nanotubes. The interpretation of the apparent lattice is nontrivial. In most cases we observe a triangular arrangement instead of the expected hexagonal carbon lattice. However, the chirality of the nanotubes can be unambiguously determined from the images, which is an important result because the electronic properties are predicted to be strongly dependent on the atomic structure.

Since the discovery of carbon nanotubes [1, 2] much attention has been directed to the electronic properties of these fullerene molecules. A remarkable result of theoretical calculations [2, 3] is the strong dependence of the electronic bandstructure of a nanotube on its chiral structure and diameter. Nanotubes can be either metallic or semiconducting, with energy gaps that depend on the tube diameter. The predictions are based on single-wall nanotubes, which consist of single graphene layers wrapped into cylinders. Only recently has it been possible to synthesize single-wall carbon nanotubes with high yield and structural uniformity [4].

The relation between the chirality of a nanotube and its electrical properties can be explored by scanning tunneling microscopy (STM), since it allows both topographic imaging and scanning tunneling spectroscopy (STS). STS is done by positioning the STM tip above a nanotube, switching off feedback and measuring the tunnel current as a function of the bias voltage. From these measurements, the local density of states can be obtained. To be able to correlate the electronic structure of a tube to its chirality, it is essential to obtain atomically resolved images, from which the chiral structure can be determined. There have been several reports of topographic imaging of bundles and individual carbon nanotubes by STM [5–10], as well as some preliminary STS data on nanotubes [5, 8, 10, 11]. These measurements concerned mostly multi-wall nanotubes. So far, there has been no report of high-quality spectroscopic data in combination with atomically resolved images. Atomic resolution on carbon nanotubes was achieved by Ge and Sattler [7]. In their work a mixture of multi-wall and single-wall nanotubes was produced by vapor condensation of carbon on highly oriented pyrolytic graphite (HOPG) substrates in high vacuum.

In this paper we present atomically resolved STM images of single-wall carbon nanotubes that were deposited on atomically flat gold surfaces. These samples were very suitable for the STM investigation of nanotubes for the following two reasons. First, gold has little structure in the density of states itself, in contrast to HOPG which simplifies interpretation of the STM spectroscopy measurements. Second, the nanotubes were well characterized before the deposition. They were synthesized by a laser vaporization technique [4] and examined by X-ray diffraction, transmission electron microscopy (TEM) and Raman scattering spectroscopy measurements [4, 12]. These measurements showed the high structural uniformity of these tubes. The material consists mainly of single-wall nanotubes of $\sim$1.4 nm in diameter. The small diameter of the tubes confirm that they have to be single-walled. Measurements on these samples demonstrated the possibility to observe with STM both the atomic and electronic structure of carbon nanotubes, which are predicted to be related. From the STS results we can distinguish the two predicted classes of carbon nanotubes: The semiconducting tubes, with energy gaps inversely proportional to the diameters and the metallic tubes. These results will be discussed elsewhere [13]. In this paper we discuss the atomically resolved topographic images of the nanotubes. These atomically resolved images clearly reveal the chiralities of the nanotubes. In most cases the atomic lattice appears to be triangular.

The nanotubes were deposited from a dispersion in 1, 2 dichloroethane on single-crystalline Au(111) facets. The samples were dried within a few seconds by applying a weak nitrogen flow. A home-built STM [14] operated at 4 K has been used for all measurements. We used Pt/Ir tips, cut in ambient by scissors. Atomic resolution was readily achieved on most nanotubes. Typical bias parameters were those of Fig. 1, viz., a tunnel current of 60 pA and a bias voltage of 0.5 V. About 30 tubes were investigated.

Figure 1 shows an image of an individual carbon nanotube. The carbon lattice can be clearly observed from which

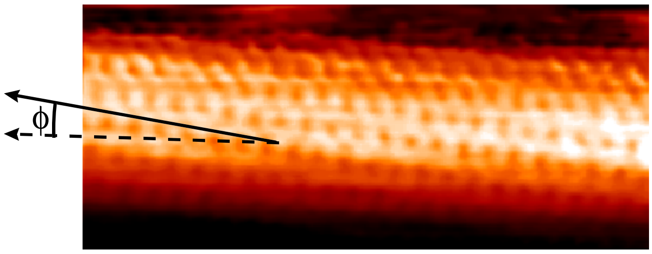

Fig. 1. Atomically resolved image of an individual carbon nanotube. The image size is $6 \times 3\,\mathrm{nm}^2$. The dashed arrow indicates the direction of the tube axis and the solid arrow denotes the direction of the nearest neighbor hexagon rows. The angle between these two arrows is the chiral angle $\varphi = 9 \pm 1°$

the chiral angle of the carbon nanotube is determined to be $9 \pm 1°$. Different chiralities were observed in other nanotubes. In Fig. 2 zoomed images of two different nanotubes are shown. In most cases images with a triangular lattice configuration were obtained, such as in Fig. 2a and b. The nearest-neighbor distance between the white dots is 2.6 ± 0.2 Å , in accordance with the expected value of 2.46 Å.

The interpretation of the observed STM contrast is nontrivial. The observation of a triangular lattice in single-wall nanotubes is unexpected because graphene layers have a hexagonal carbon structure. In the atomically resolved images of multi-wall and single-wall nanotubes obtained by Ge and Sattler [7] both triangular and hexagonal configurations were visible. It is well known that the hexagonal lattice of bulk graphite often appears triangular in STM images [15]. The widely accepted explanation for this observation is that the ABAB stacking sequence of the three-dimensional layered structure results in two inequivalent atomic sites in each planar unit cell, which leads to an asymmetry in STM images [15–17]. Support for this model was provided by an experiment by Olk et al. [18] in which an intercalation technique was used to separate the layers. After separation the hexagonal carbon lattice could be observed. The triangular configuration observed in single-wall nanotubes can obviously not be accounted for by this bulk effect, since these tubes do not have a layered structure. There are several possibilities to consider. Nanotubes can be regarded as rolled up graphene sheets which may lead to a breaking of the symmetry due to, for example, the curvature. Also, one may speculate that the electronic structure of the tip is such that it provides a different tunnel current on the two different carbon atoms in each unit cell. Alternatively, the interpretation of the asymmetry observed in STM images of graphite may have to be reconsidered. For example, Palmer et al. [19] proposed as a possible explanation for the triangular configuration observed in graphite that the protrusions in the STM images may be associated with the centers of the hexagon rings, instead of the atoms. The configuration of the dashed hexagons drawn in Fig. 2a follows this idea. The solid hexagons drawn in the same image illustrates the interpretation that every other atom is imaged. The last possibility seems to be more likely, but a good theoretical footing is lacking. Theoretical studies on the STM contrast of carbon nanotubes are highly desirable.

In conclusion, our measurements confirm the possibility to obtain atomically resolved STM images on carbon nanotubes. The interpretation of the atomic lattice configuration observed in these images is not well understood. However, these images can be used to determine the chirality of the tubes. The combination of atomically resolved images and STM spectroscopy opens the possibility to experimentally investigate the relation between the chiral structure of a nanotube and its electronic properties [13].

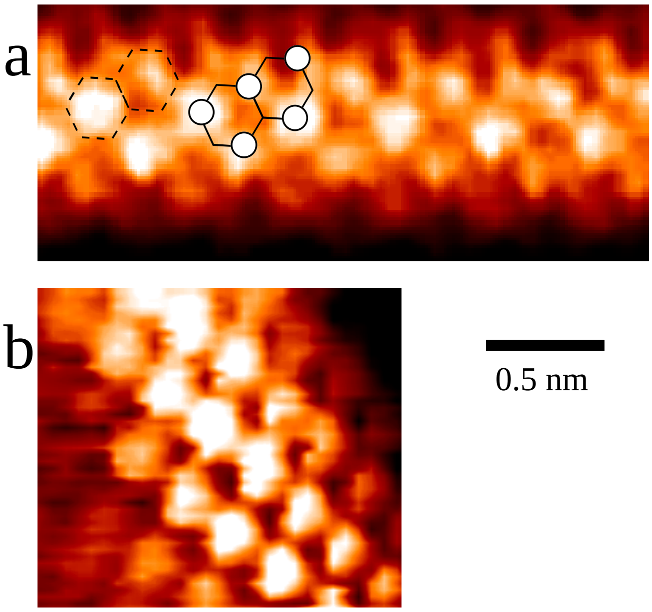

Fig. 2a,b. Zoomed images of two different nanotubes. The carbon lattice is observed to be triangular in most cases. In **a**, two hexagon configurations are drawn to indicate possible interpretations of the apparent contrast. The dashed configuration follows the idea of high contrast in the centers of the hexagons. The solid configuration illustrates the interpretation that every other atom is imaged. The filled black circles indicate the imaged carbon atoms

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