STM and AFM investigation of coiled carbon nanotubes produced by laser evaporation of fullerene

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Abstract

Carbon nanotubes were grown by the evaporation of a fullerene/Ni particle mixture in vacuum, using 532 nm laser pulses of 12–28 μJ from a Nd YAG laser. The evaporated material was deposited on a freshly cleaved graphite (HOPG) surface and the samples were investigated by scanning tunneling microscopy (STM) and AFM. In the present work, we focus on the Y-branched and coiled carbon nanotubes, the formation of which supposes the incorporation of non-hexagonal rings in the hexagonal graphitic network. The regularity of the observed coils is an indication that the incorporation of the pentagons and heptagons occurred in a very regular way. The possible atomic structure of the coiled carbon nanotubes is discussed.
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1. Introduction

Since their first observation by Iijima [1], carbon nanotubes have been the focus of considerable attention. During the past decade, a rich variety of carbon nanotube morphologies have been studied. The coiled carbon nanotubes are interesting because of their promising potential applications as nanoactuators or nanosprings [2].

Based on molecular-dynamics simulations, helically coiled carbon nanotubes were predicted by Ihara et al. [3] and Dunlap [4]. The coiling of the proposed structures originated from the regular insertion of pentagons and heptagons in the hexagonal network. Multi-wall coiled carbon nanotubes were first observed a year later by transmission electron microscopy (TEM), in samples grown by the catalytic decomposition of hydrocarbons over transition metal catalysts (CVD) [5]. The TEM observation of coiled nanotubes with different pitch values and the observation of tightly wound coils was reported, too [6]. The first experimental observation of single wall coiled carbon nanotubes was achieved in CVD grown samples using scanning tunneling microscopy (STM) [7].

In the present work, we report the observation of regularly coiled carbon nanotubes, which present stable coiling over distances of the order of 100 nm. The relation of the observed carbon nanostructures with the theoretically predicted Haeckelite type structures [8] is discussed.

2. Experimental results and discussion

Carbon nanotubes were grown by the evaporation of a fullerene/Ni particle mixture in vacuum, using 532 nm laser pulses from a Nd YAG laser. The target was heated with pulses of 12 μJ at 5 Hz for 7 min and with pulses of 28 μJ at 10 Hz for 3.5 min. The evaporated material was deposited on a freshly cleaved graphite (HOPG) surface. After deposition, the HOPG surface was examined without any further manipulation by STM and AFM under ambient conditions. This method excludes any artifacts arising from sample handling and preparation. The STM images were acquired with commercially available, mechanically cut PtIr tips using tunneling currents $I_t = 200$ pA and tunneling bias $U_t = 1$ V. Low scan rates in the range of 1 Hz were preferred.

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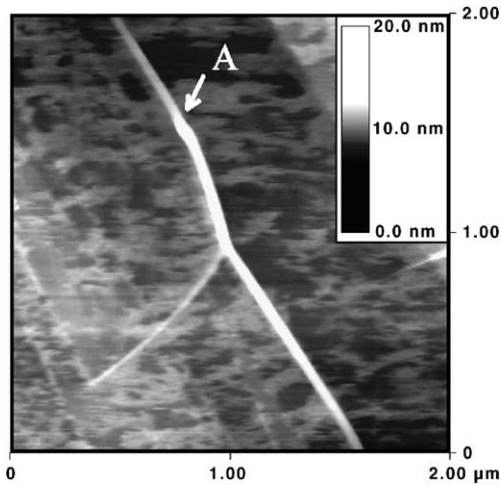
Fig. 1. AFM image of a Y-branched carbon nanotube on HOPG surface.

An AFM image of an Y-branched nanotube is presented in Fig. 1. The heights of the branches near the branching point are 5, 4.2, and 2.4 nm, respectively. The presence of Y-branched nanotubes indicates that the experimental conditions were favorable for the incorporation of non-hexagonal rings in the hexagonal carbon network. On the HOPG substrate, islands of undecomposed C_{60} molecules are visible. It is worth pointing out that at the point labeled A, structural defects are built into the straight nanotube of constant height. The defects produce modification of the growth direction and of the tube diameter.

Fig. 2a shows a constant current topographic STM image of a coiled nanotube over a Y-branched one, both traversing a cleavage step on HOPG. The higher resolution 3D representation of these objects is shown in Fig. 2b. The distance between the neighboring pitches of the coiled nanotube is 4.6 nm, the apparent height is 0.6 nm at the pitches and 0.4 nm between pitches. The apparent height between pitches is the maximal apparent diameter of the tube. One has to be careful in the interpretation of these values. If the STM tip is not sufficiently sharp, the tunneling current will flow through the pitches (between which the STM tip is positioned) instead of flowing
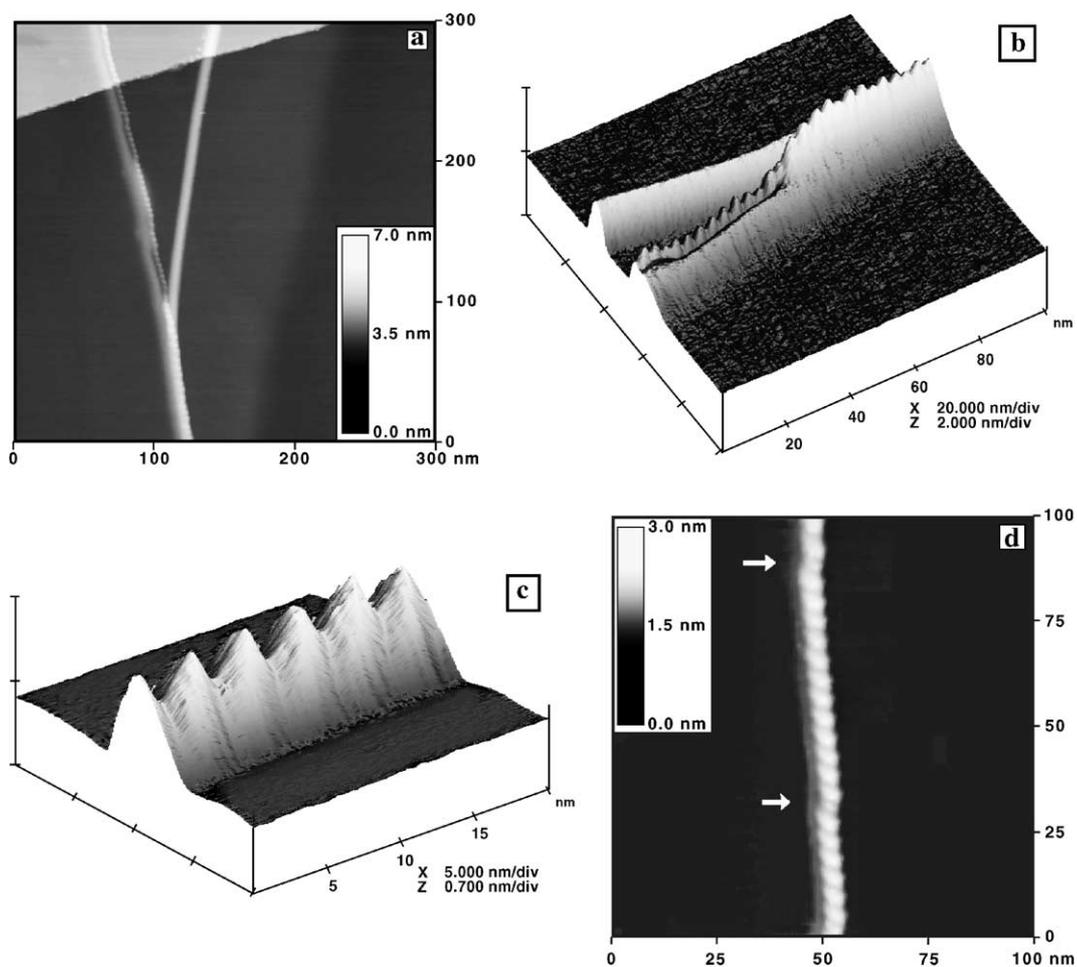
Fig. 2. Constant current topographic STM images of a coiled carbon nanotube over an Y-branched nanotube ($I_t = 200$ pA, $U_t = 1$ V). (a) Top view image of the coiled and the Y-branched nanotubes, both traversing a cleavage step on HOPG. (b) Higher resolution 3D representation of nanotubes. (c and d) The coiled nanotube presented in (a) at a distance of 300 nm from the place where the first image was made.
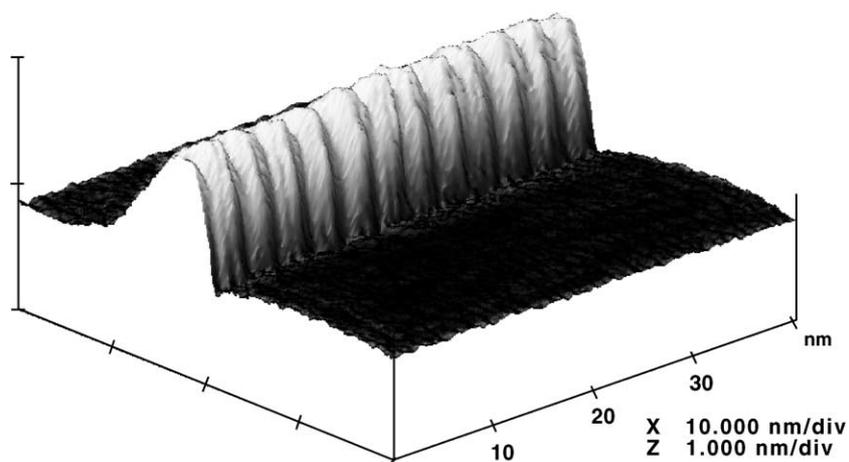
Fig. 3. Constant current topographic STM image of a coiled carbon nanotube in 3D presentation (I_t = 200 pA, U_t = 1 V).

through the portion of nanotube, which is in tunneling contact with the HOPG surface. On the other hand, the electrons tunneling into the topmost part of the pitches cannot tunnel into the substrate without traveling along the coil to the next lowermost point of the coil with respect to the substrate. Due to these effects, in case of coiled nanotubes the measured height values cannot be converted in a straightforward way into geometric height values. However, the periodicity of the coil along the coil axis, and eventual structural alterations can be measured with very high accuracy by STM. The accuracy of the scanner is ± 0.01 nm.

The apparent diameters of branches of the Y nanotube in Fig. 2b are 1.7, 1.2, and 0.6 nm, respectively. Two effects influence the geometric dimension values of straight carbon nanotubes measured by STM. The geometric convolution leads to a widening in the horizontal plane. In a similar way, this effect produces the widening of the coils, too. The measured height is reduced due to the difference in electronic structure and the existence of two tunneling gaps in the system (STM tip–nanotube and nanotube–substrate) [9,10].

Fig. 2c,d shows the coiled nanotube presented in Fig. 2a at a distance of 300 nm from the Y-branched nanotube. The distance between the neighboring pitches and the height of the coiled nanotube remains unchanged in spite of defects incorporated in its structure (Fig. 2d). This is an indication that the structure responsible for the coiling is a stable one, and it returns to the same atomic arrangement after local structural defects are incorporated accidentally. This behavior cannot be easily explained on the basis of structural models, which presume a non-hexagonal/hexagonal ring ratio far from unity and suppose a very precisely defined location of pentagons and heptagons for stable coiling.

Other coiled nanotubes are presented in Figs. 3 and 4. The distance between the neighboring pitches is 3.3 and 4 nm, and the apparent height is 1 and 0.5 nm, respectively. The nanotube in Fig. 4 was imaged with a multiple STM tip. The tips produce the image independently, and this makes any imaging artifact very unlikely. The different lateral extension of the coil in the two images is due to the deviation of the shape of one of the tips from a shape with rotational symmetry.

The low temperature of the HOPG surface probably promotes the production of Y-branched and coiled carbon nanotubes. Under these conditions, the C atoms and clusters resulting from the decomposition of fullerenes have low mobility, which may enhance the quenching of the non-hexagonal rings into the growing structure.

The earlier structural models for regularly coiled carbon nanotubes are based on the regular incorporation of pentagon–heptagon pairs in the hexagonal network [4,7,11]. These models describe the coil as the succession of short knees with the same diameter on both sides of the knee [12]. The question remains why such defects
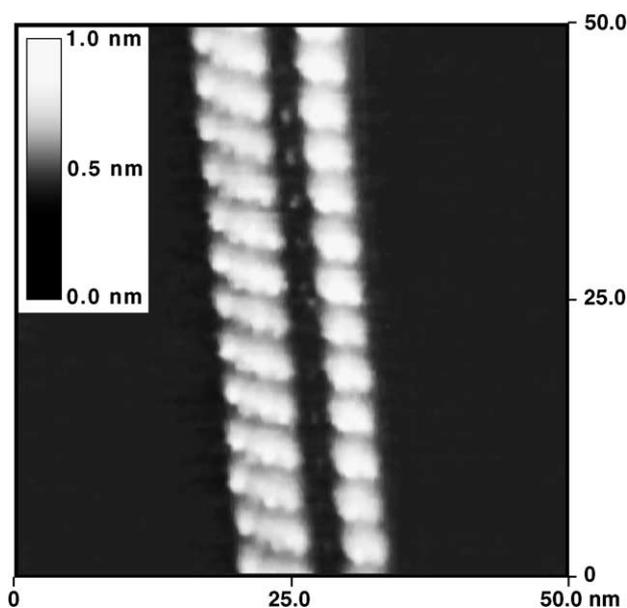
Fig. 4. Top view, constant current topographic STM image of a coiled carbon nanotube imaged with a multiple STM tip (I_t = 200 pA, U_t = 1 V).
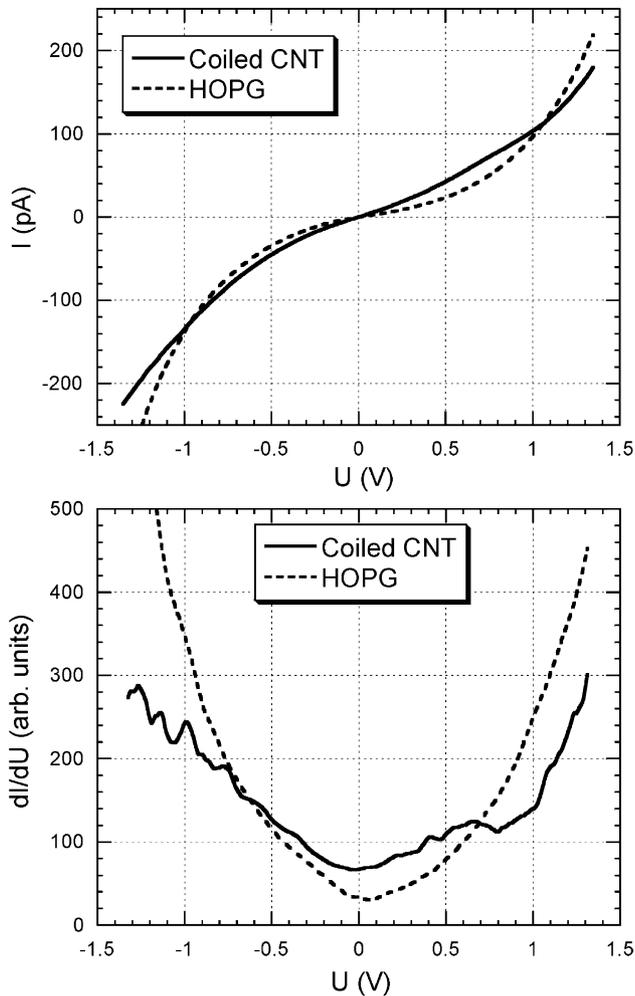
Fig. 5. Scanning tunneling spectroscopy (STS) on the coiled nanotube presented in Fig. 2a.

appear periodically to form the helical structure [2]. If the pentagonal and heptagonal rings are not regarded as defects, but as regular building blocks, then their very precise positioning may be regarded as an inherent property of the structure. According to theoretical calculations, carbon nanotubes built from pentagons, hexagons, and heptagons or only from pentagons and heptagons—named Haeckelite tubes—are energetically more stable than C_{60} [8]. This is in agreement with experimental observations, which shows that coiled nanotubes despite the large number of non-hexagonal rings they must contain are not attacked during wet oxidation [13]. Theoretical calculations show that the coiling of Haeckelite nanotubes may be attributed to the relaxation of bond strain [14]. In this case, the formation of carbon nanotube coils has a structural origin.

Fig. 5 shows the current–voltage curve and its derivative (dI/dU) obtained by scanning tunneling spectroscopy on the coiled nanotube presented in Fig. 2a. The

metallic density of states near the Fermi level is in agreement with the density of states calculations for Haeckelite nanotubes [8], which showed that the metallic behavior is an intrinsic property, independent of orientation, tube diameter, and chirality.

3. Conclusions

Carbon nanotubes were produced directly on HOPG substrate and examined by STM and AFM without further manipulation. The observed coiled nanotubes are regular and present stable coiling over distances on the order of 100 nm. The regularity of the observed coils, which is the consequence of the very regular incorporation of the pentagons and heptagons, suggests that the pentagons and heptagons should be regarded as regular building elements of coiled nanotubes. It is proposed that coiled nanotubes are built from a theoretically predicted material, the haeckelite, in which pentagons, hexagons and heptagons are equally considered as regular building elements.

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