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Ring formations from catalytically synthesized carbon nanotubes

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Abstract

Rings of typically 0.5 μm diameter have been observed with the atomic force microscope and the scanning electron microscope in carbon nanotube deposits produced catalytically by thermal decomposition of hydrocarbon gas. The carbon nanotubes are predominantly multiwalled with an average thickness of 20 nm, which is the typical thickness of the rings as well. The observations are discussed in light of the previous discoveries of helical nanotubes in the same material and the observation of rings of similar thickness and diameter (interpreted as toroids) in single wall carbon nanotube material grown by laser vaporization. In our observations, the ring formations can be interpreted as single turn coils with a short overlap between the beginning and end of the coiled nanotube, but the toroidal interpretation cannot be ruled out.

1. Introduction

Since the discovery by Iijima [1] of carbon nanotubes in deposits produced by the arc discharge technique, much experimental and theoretical research effort has been directed towards understanding their structural and electronic properties as well as the conditions for their formation. Carbon nanotubes are found both as single walled (SWNT), with a diameter around 1 nm, and multiwalled (MWNT) with an outer diameter up to several tens of nanometers.

Carbon nanotubes are grown by different methods [2]. The arc discharge method which is widely used for the production of fullerenes, has allowed observations of nanotubes; later the laser vaporization method [3] was introduced and has been very successful in producing high yields of SWNTs. In these two methods, the growth material is graphite, possibly mixed with a catalyst (in order to produce SWNTs). In contrast, in the catalytic growth method [4], a chemical vapor deposition (CVD) method, a carbon containing gas is flowing at a high temperature over a catalyst resulting in the formation of carbon nanotubes.

Several characteristic features have already been observed for carbon nanotube material. The hexagonal graphitic network forming the nanotube wall can in general have a chirality with respect to the tube

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axis, the possible chiral angles ranging from 0° to 30° [2]. Low temperature scanning tunneling microscopy (STM) [5,6], along with electron and X-ray diffraction investigations [7] are currently being employed to study the chirality and its influence on the electronic properties. Furthermore, SWNTs especially have usually been observed to arrange in a regular pattern into ropes consisting of several tens of nanotubes in parallel and in contact with each other. Recently, Liu et al. [8] reported the observation of nanotube rings (called ‘crop circles’) in their laser grown SWNT deposits. The rings typically had a diameter of 300–500 nm and a thickness in the range 5–15 nm, but even a ring of thickness 1.5 nm was observed. The observations were made with an atomic force microscope (AFM), a scanning electron microscope (SEM), and a transmission electron microscope (TEM). The AFM observation of the small 1.5 nm thick ring showed no major discontinuities along the circumference. The authors of Ref. [8] concluded that the observed rings are likely to consist of real SWNT toroids and not to be coiled nanotubes. Furthermore, the typical thickness of the rings was in accord with that of the ropes into which the SWNTs typically order themselves. In the report by Zhang and Zhang [9], it was observed in the TEM analysis of catalytically synthesized MWNTs [the existence of 200 nm sized single turn coils]. They looked deceptively like toroids, where the short overlap between the two ends of the multiwalled coiled tube is discernible.

A related topic is the observation by TEM of helical nanotubes, especially in catalytically grown carbon nanotube deposits. This nanotube material is predominantly multiwalled, with only rare observations of SWNTs [10]. A helical nanotube is described by the coil diameter, where observations range from 10 nm to 1 μm, and the pitch (the distance between adjacent corresponding points along the axis of the helix), which has been observed to take values from 10 nm up to 5 μm. Careful TEM analysis of the helical nanotubes [11] suggests that these nanotubes are in fact polygonized, consisting of straight segments, and the turning being due to the appearance of pentagon–heptagon pairs in the hexagonal network forming the wall of a perfect straight carbon nanotube. Each defect pair would twist the nanotube about an angle α (with $0° < \alpha < 36°$), so that at least 10 pairs would be needed to cause one turn. Growth mechanisms for helical nanotubes have been discussed in Refs. [12,13].

On the theoretical side, carbon toroids can be considered [14] either by introducing curvature inducing defects as in the helical nanotubes or by bending elastically a straight nanotube so that it closes upon itself. In the latter case, the lower limit for the diameter is found to be about 200 nm [14].

In this Letter, we report on the observation by AFM and SEM of ring formations in catalytically grown carbon nanotube material. The rings have the same dimensions (diameter and thickness) as was observed in laser grown SWNT material [8], which may suggest a common origin. Possible links to the observed helical nanotubes in the same catalytically grown material [4] will be discussed.

2. Experimental

The carbon nanotubes were produced by catalytic decomposition of acetylene, carried out at 700°C in a flow reactor at atmospheric pressure [4]. The catalyst, ‘2.5 wt.% Co/zeolite NaY’ prepared by impregnation, was removed from the carbon material (nanotubes + amorphous carbon) by HF treatment.

The purified carbon nanotube material was sonicated with low power in isopropanol and was subsequently deposited onto a piece of silicon wafer. The deposits were imaged with an AFM (Park Scientific Instruments, Autoprobe CP) in non-contact mode as well as with a SEM (Philips, XL-30 FEG).

3. Results and discussion

Fig. 1 shows images of typical ring structures which are observed in our studies with the SEM. Liu et al. [8] estimated that their SWNT material contains between 0.01 and 1% of rings. Based on the SEM studies of our deposits, we found a similar estimate for the concentration of nanotube rings. However, we deposited from very dilute solutions in order to have individual nanotubes clearly separated from each other which may give a distorted estimate. We note that TEM studies published to date have not

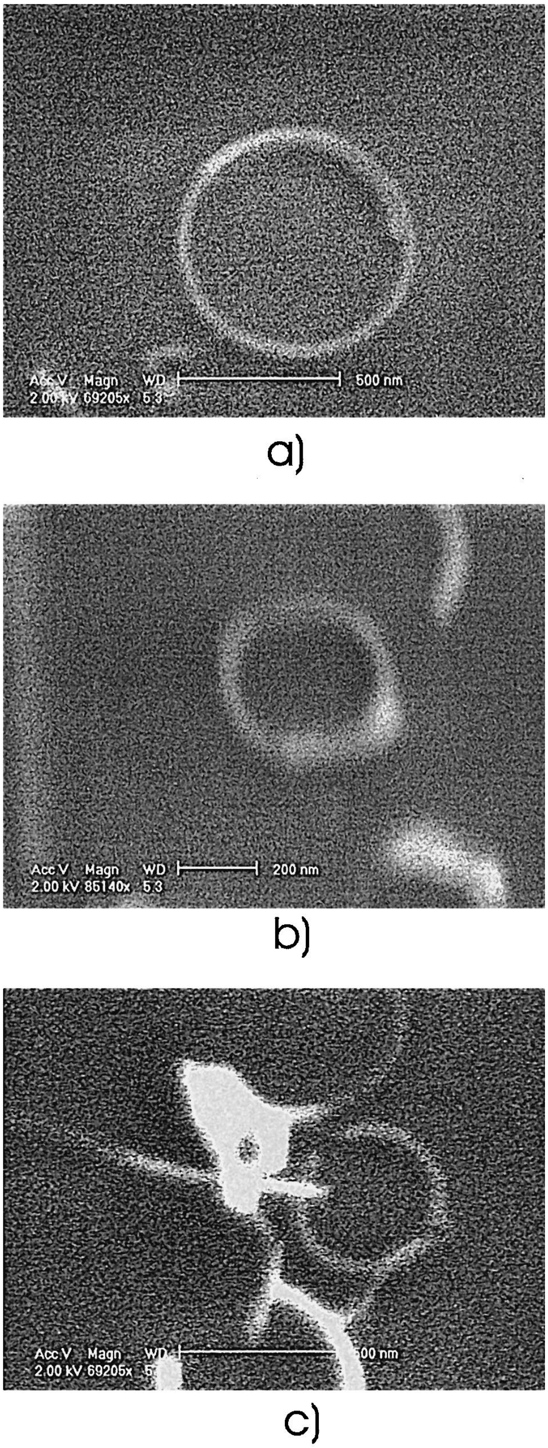

Fig. 1. SEM images of multiwalled carbon nanotube rings.

revealed the presence of ring structures, with the possible exception of Ref. [9].

The SEM cannot resolve the carbon nanotubes of lowest tube diameters that are known to exist. AFM and STM studies have even revealed nanotubes of SWNT thickness (≈ 1 nm), but very infrequently [10,15]. The nanotube ring in Fig. 1a is almost perfectly circular and quite smooth, but the upper section exhibits a thickening which could be explained as two overlapping segments of a nanotube. The ring in Fig. 1b, in contrast, is significantly buckled and is also more inhomogenous in shape along the tube length. Finally, Fig. 1c shows an incomplete ring where a section less than 10% of the circumference is missing. That the shape of the ring is otherwise intact suggests that the ring is in a stress-free state in its curved shape.

Fig. 2 shows two AFM images of carbon nanotube rings. Fig. 2a shows a ring with a diameter of 180 nm, the smallest diameter that we have observed. As is evident from the figure, the inhomogeneity is substantial. An analysis of the AFM data revealed a minimum thickness of 11 nm and a maximum of 21 nm, and with an average of 18 nm. Fig. 2b shows an image of a very thin ring of 2–3 nm thickness and a diameter of 400 nm. This ring contains one large inhomogeneity in the upper right section.

In all cases, the rings turn out to be not completely smooth and even. This casts some doubt on the assertion that the ring structures are perfect toroids. It is possible that the inhomogeneities are due, at least partly, to residual impurities. Alternatively, however, one could explain the rings as small sections (with one or several turns compressed to the substrate) of the helical nanotubes which have been regularly observed in this material and which seem to be quite unique to it. The helices have been observed with the coil diameter ranging from tens of nanometers to a few hundreds of nanometers [16]. If our rings are cut-off sections of the helices, then they all come from the larger ones of the observed helical nanotubes. In Fig. 3 we show a TEM image of a 0.5 μm coil consisting of 2–3 turns (the figure also includes one small diameter helix). The similarity to the rings observed in the SEM is striking and supports the idea of interpreting the ring formations as deposited segments of the helical nanotubes. In this

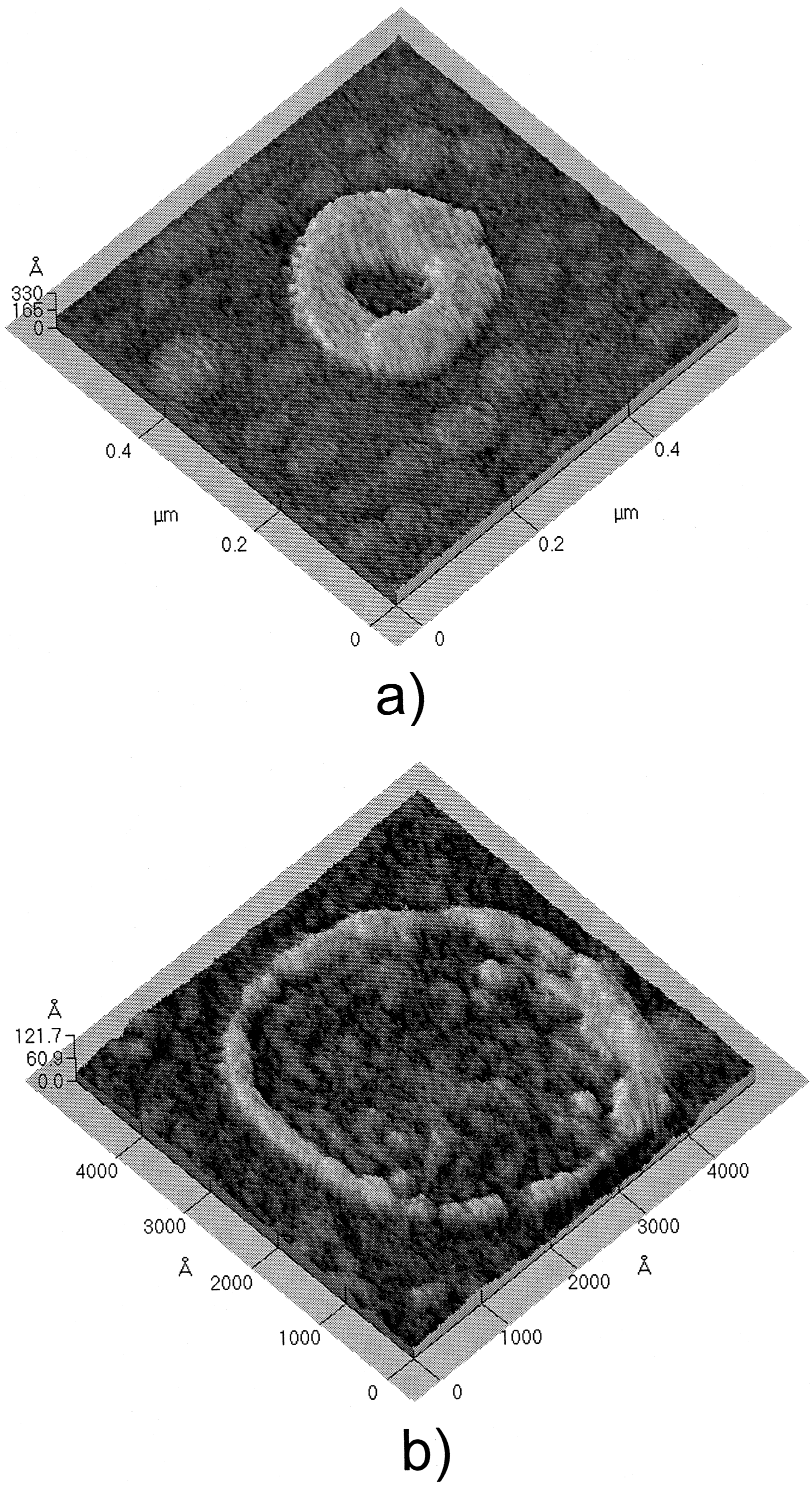

Fig. 2. AFM images a) of a carbon nanotube ring of thickness 20–30 nm and b) of a nanotube ring of thickness 2–3 nm.

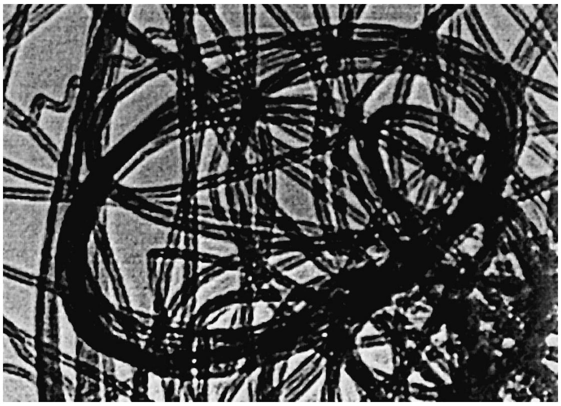

Fig. 3. Low magnification TEM images of carbon nanotubes formed in the decomposition of acetylene at 700°C over '3 wt.% Co/silica' catalyst. A 0.5 μm coil consisting of 2–3 turns is clearly seen. Note the small diameter helix in the upper left corner.

catalytically synthesized carbon nanotube material, TEM analysis [11] gives an estimate of a 10% concentration of helical nanotubes among all nanotubes.

In summary, we have observed rings of carbon nanotubes with SEM and AFM imaging of nanotube deposits. The rings have a typical diameter of a few hundred nanometers. We have compared our findings with a previous TEM analysis of the same material and provided a possible explanation of the rings as compressed sections of helical carbon nanotubes. Our observations contrast with previous reports of the nanotube rings as genuine toroids. Still, since the tools used in this work are not capable of definitely resolving whether the rings are toroids or small coils, we conclude that more elaborate investigations are needed to address this question. In any case, the rings are interesting as objects for various future experiments to study their mechanical and electronic properties.

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References

[1] S. Iijima, Nature 354 (1991) 56.
[2] M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, 1996.
[3] A. Thess et al., Science 273 (1996) 483.
[4] K. Hernadi, A. Fonseca, J.B. Nagy, D. Bernaerts, A. Fudala, A.A. Lucas, Zeolites 17 (1996) 416.
[5] J.W.G. Wildöer, L.C. Venema, A.G. Rinzler, R.E. Smalley, C. Dekker, Nature 391 (1998) 59.
[6] T.W. Odom, J.L. Huang, P. Kim, C.M. Lieber, Nature 391 (1998) 62.
[7] J.M. Cowley, P. Nikolaev, A. Thess, R.E. Smalley, Chem. Phys. Lett. 265 (1997) 379.
[8] J. Liu, H. Dai, J.H. Hafner, D.T. Colbert, R.E. Smalley, S.J. Tans, C. Dekker, Nature 385 (1997) 780.
[9] X.F. Zhang, Z. Zhang, Phys. Rev. B 52 (1995) 5313.
[10] L.P. Biró, S. Lazarescu, Ph. Lambin, P.A. Thiry, A. Fonseca, J.B. Nagy, A.A. Lucas, Phys. Rev. B 56 (1997) 12490.
[11] X.B. Zhang, X.F. Zhang, D. Bernaerts, G. Van Tendeloo, S. Amelinckx, J. Van Landuyt, V. Ivanov, J.B. Nagy, Ph. Lambin, A.A. Lucas, Europhys. Lett. 27 (1994) 141.
[12] A. Fonseca, K. Hernadi, J.B. Nagy, Ph. Lambin, A.A. Lucas, Synth. Met. 77 (1996) 235.
[13] O.Y. Zhong-can, Z.B. Su, C.L. Wang, Phys. Rev. Lett. 78 (1997) 4055.
[14] V. Meunier, Ph. Lambin, A.A. Lucas, Phys. Rev. B 57 (1998) 14886.
[15] M. Ahlskog, A. Depuydt, unpublished results.
[16] S. Amelinckx, X.B. Zhang, D. Bernaerts, X.F. Zhang, V. Ivanov, J.B. Nagy, Science 265 (1994) 635.