SURFACE TOPOGRAPHY OF CARBON NANOTUBES

S.Ya. Brichka, M.I. Terets, A.V. Brichka

Institute of Surface Chemistry, G.Naumova str., 17, Kyiv, Ukraine

serg_1971@ukr.net

Carbon nanotube surfaces were investigated by atomic force microscopy. A correlation between the topography and the conditions of nanotube synthesi was established.

INTRODUCTION

In 1986 Binning and co-authors published a study [1] in which interaction forces between a sharp probe and a solid surface were measured by a microconsole (cantilever). The mapping of a surface (including an atomic resolution surface) of any kind of sample (conductor, dielectric, organic matter, living cell, etc.) under various conditions – in vacuum, air or liquid – is possible by controlling the interaction force between a probe and a surface [2]. Atomic force microscopy (AFM) is considered to be the principal method for the analysis of electronic and nuclear structure of carbon nanotubes (CNT). Research on mechanical properties of nanotubes and the production of electronic devices (diodes, transistors, field emitters, memory elements, mini-amplifiers, generators, field sinks) are impossible without AFM [3]. It is obvious that during CNT synthesis, many factors determine the nanotube structure such as the carbon source, the sedimentation technique and the catalyst type. Understanding the interrelation between the morphological features of CNT and its synthesis can help clarify the mechanism of their formation and to predict physical and chemical properties such as the adsorption and catalysis.

The comparative study of the surface topography of CNT synthesized by electroarc, catalytic pyrolysis and by the matrix method is the goal of this research.

EXPERIMENTAL

Single-walled CNT were obtained using an electroarc technique in which metal-graphite electrodes caused thermal evaporation in a ratio of C:Ni:Y_2O_3 = 2:1:1 unit weight. The nanotubes were synthesized at 700°C on an iron-based catalyst by catalytic pyrolysis of acetylene. The synthesis of nanotubes by a matrix technique was carried out for 30 min at 500°C by pyrolysis of dichloromethane in an inert atmosphere with use of Al_2O_3 membranes [4]. CNT were identified by transmission electron microscopy (TEM, JEM-100CXII).

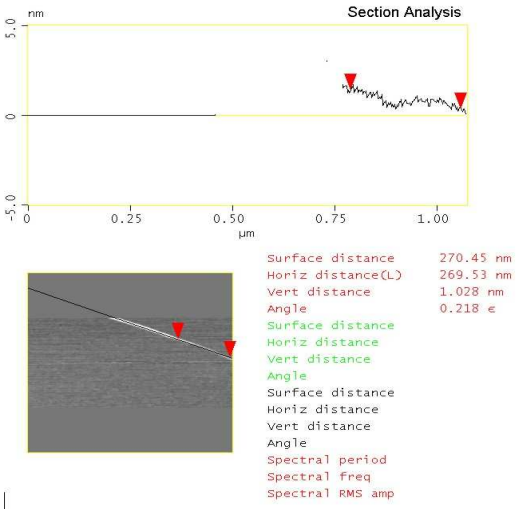
In AFM (Digital Instruments Inc. NanoScope IIIa) the cantilever probe changed in frequency when applied to a surface, scanning the surface of the sample. Cantilever fluctuations were registered as a change in sample surface height. Scanning was carried out with use of a silicon probe. Samples were prepared by dispersion of CNT in isopropanol and ethyl alcohol. Next, the atomically clean surface was covered by mica. The samples were then dried in air for 24 hours.

RESULTS AND DISCUSSION

Due to significant distortion AFM has a number of restrictions concerning images of large surfaces (0,1-100 microns) with developed relief (0,001-5 microns). This restriction depends on two factors: the scanning step and the minimal value of the radius of curvature of the probe. The AFM image of the surface is a result of the real surface and the change of the probe's relative position to the surface. Since the probe has a definite form, the real surface can be reconstructed with the exception of areas forming negative corners with a vertical, and cavities in which the probe does not pass [2]. At the atomic level and for nanoscale surfaces AFM is the

most reliable technique available for imaging.

It is known that the high temparetures of CNT synthesis leads to the formation of nanotubes with good graphitized carbon walls. In CNT Raman scattering spectra, two characteristic bands are observed at $\nu_1 \approx 1600$ (G-band) and $\nu_2 \approx 1300$ sm^{-1} (D-band). The range from 1500 to 1600 sm^{-1} is responsible for the tangential mode of valence vibrations of graphite; the band ν_2 is associated with different types of infringements in the structure of the graphene layers. From the ratio ν_1/ν_2 it is possible to determine the degree of deficiency of the graphene layers; for single-wall nanotubes this ratio has an extremely high value. In multi-walled CNT synthesized by catalytic pyrolysis, the band intensity of ν_1 is greater than ν_2. Some CNT syn thesized by



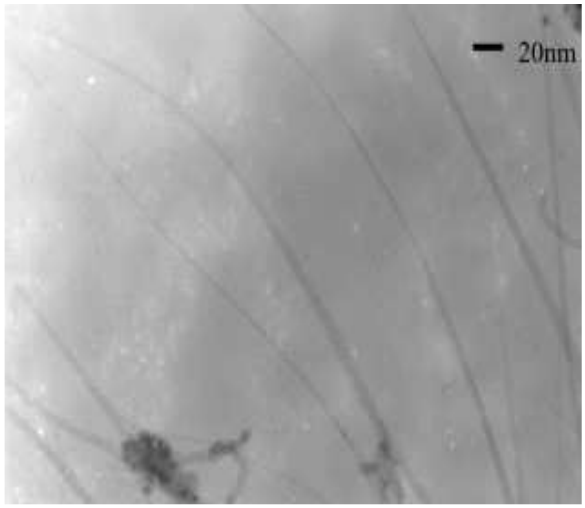
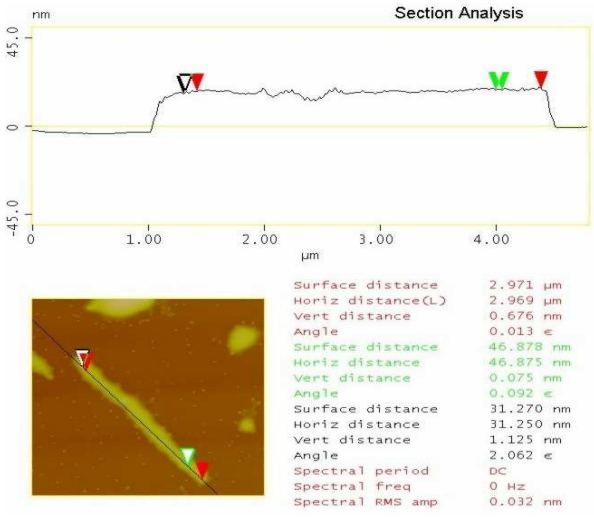


Fig. 1. AFM and TEM images of single-walled carbon nanotubes

the matrix method exhibit the lowest order of carbon walls. In such nanotubes the Raman spectra have wide bands of approximately identical intensity. It is obvious that CNT should have the least amount of defects. In fig. 1 the CNT structure from the AFM profile has much in common with multi-walled nanotube structures. In addition to periodic sinusoidal fluctuations of the probe, there are sites in the profile which can be interpreted as defects in nanotubes.

In fig. 2 TEM photos of carbon nanotubes synthesized by the matrix method are presented. The analysis of TEM images of



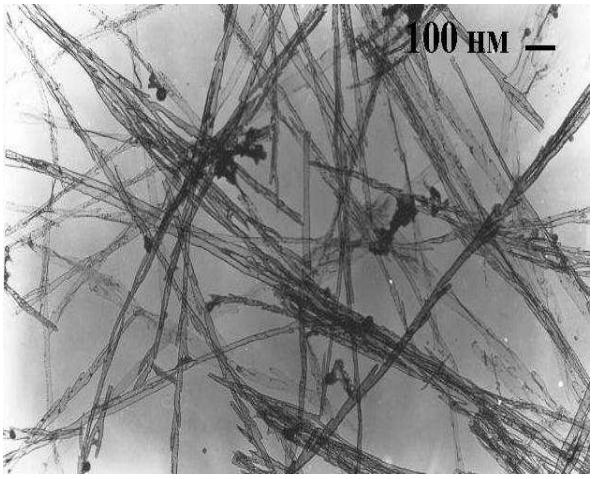


Fig. 2. AFM and TEM images of multi-walled carbon nanotubes synthesized by the matrix method

nanotubes shows that the size of the diameters varies from 18 to 90 nanometers. “Fir tree”-like defects in the form of branches (with lengths of 100-200 nanometers) are the morphological feature of CNT synthesized

by the matrix method. It is possible that the CNT defects are caused by the geometry of the membrane pores in which they are formed. From literary data [4, 5] it follows that, as a general rule, the size of the pores coincides with the external diameter of the CNT. Hence, using matrix synthesis, it is possible to obtain information on the geometrical characteristics of pores of those matrices in which CNT are formed.

Under the action of ultrasonic processing CNTs easily collapse in a perpendicular direction with respect to the nanotubes' axes. The longitudinal AFM profile of truncated nanotubes has rather flat sites as well as obviously defective sites. The depth of roughness of some sites does not exceed 1 Å, which is comparable to the experimental error. It is obvious that the nanotube external surface is laid out mainly by a non-defective graphene layer.

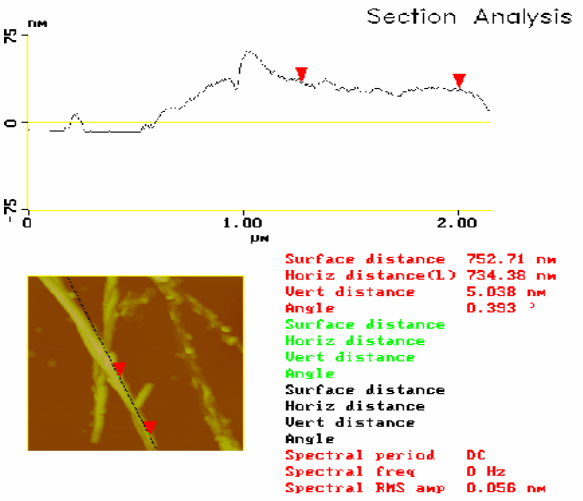
The macrocharacteristics of CNT can influence the form of its structure – *e.g.* elasticity, mechanical damages and other external factors. This is also true for microlevel characteristics – *e.g.* defects in the form of branches, dispositions, point defects of graphene layers. The breaking point (tensile strength) of multilayered CNT reaches 63 GPa, and the rigidity at a curve in graphite-rich CNT is approximately 1 TPa [3]. The elastic properties of CNT should cause smooth, significant differences in the sizes of their profiles. Local changes (up to 100-1000 nanometers) in the nanotube microstructure can possibly cause defects in the tube. By the authors' [6] method, electron microscopy performed at high resolution on multi-walled nanotubes revealed a class of defects similar to regional dispositions in crystals. It is supposed that the regional dispositions are due to chemical interactions rather than Van der Waals forces.

Knowledge of CNT formation mechanisms makes it possible to develop more effective methods for their synthesis. The current mechanism of catalytic growth of CNT on iron-based catalysts includes stages of formation and sedimentation of carbon vapor, its dissolution in the catalyst and the diffusion of carbon atoms to the free end of the growing nanotube. Based on our experimental data [7] a template model of CNT synthesis is constructed, which consists of the stages of carbon vapor formation and its sedimentation on a firm surface (in pores). During sedimentation, carbon-carbon covalent bonds and graphene layers of nanotubes are formed on the template surface. Thus, the hypothesis is that nanotubes (diameters up to 100 nanometers) are formed as a result of carbon vapor condensation along its length in template pores (the "condensation" mechanism). Random external surface defects are inevitable in this graphene layer formation process. In our opinion AFM images of matrix-synthesized CNT indirectly confirms the proposed mechanism of their formation.

Nanotubes (fig. 3) synthesized by catalytic pyrolysis have a number of morphological features. They form files by mutual interlacing that considerably affects the density of the macrosample. Fig. 3 shows an AFM picture of nanotubes laying cross-wise on a substrate, in isopropyl solution. Different CNT can have heights from 39,2 to 40,5 nanometers. Possibly the CNT longitudinal profile can give information about its diameter. Assuming that CNT on a substrate have a cylindrical form, then the heights of the profile can have commensurable values and correspond to CNT diameter. Comparing TEM images with AFM confirms that CNT diameters lie between 38 and 60 nanometers.

In fig. 3 sections of CNT are shown: the profile of two tubes crossing causes a vertical drop of 10 to 15 nanometers. The nonlinearity of the profile on sites up to 10 nanometers can be explained by the internal structure of synthesized CNT and defects of external graphene layers. It is possible to assume that observable defects in the size 46, 88, 31, 25 nanometers with depth of 1-3 nanometers are consequences of damage to the integrity of the external graphene layer.

The absence of atoms leads to the formation of heterogeneous "holes" and to the formation of dangling bonds on the external and internal CNT surfaces. X-ray electron spectroscopy confirms the presence of dangling bonds C-O, C=O [8].



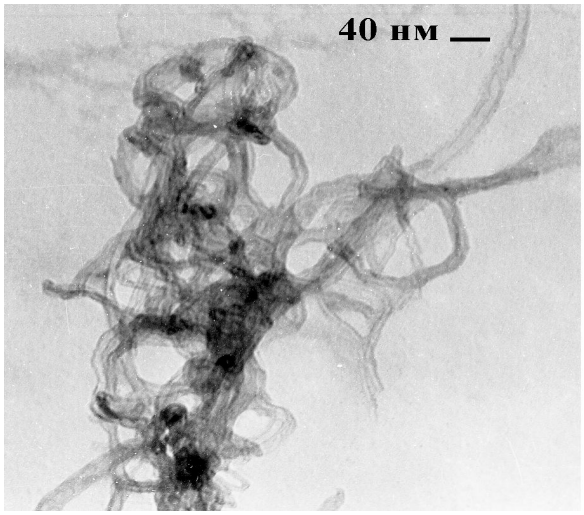


Fig. 3. AFM and TEM images of multi-walled carbon nanotubes synthesized by catalytic pyrolysis

It is shown that on single-layered and multilayered CNT surfaces the quantity of oxygen is about 6-12%, which can be chemically adsorbed not only at the ends of the CNT, but also along the lateral surfaces. Hence AFM is useful for studying external surface CNT defects.

Calculations were performed on the influence of defects on CNT mechanical properties [9]. It is shown that defects in the form of one-atom and two-atom vacancies lead to a reduction of their durability by 25%. That is why the problem of searching for non-defective nanotubes is important (*e.g.* for creating nanodevices). Thus AFM is informative and useful for studying defects in CNT.

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ТОПОГРАФИЯ ПОВЕРХНОСТИ УГЛЕРОДНЫХ НАНОТРУБОК

С.Я. Бричка, М.И. Терець, А.В. Бричка

Институт химии поверхности НАН Украины, ул.Г.Наумова, 17, Киев

serg_1971@ukr.net

Методом атомно-силовой микроскопии изучена поверхность углеродных нанотрубок. Установлена взаимосвязь между топографией и условиями синтеза нанотрубок.