TEM studies of conical scroll carbon nanotubes formed by aerosol synthesis

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Abstract. Conical carbon nanotubes were obtained by the method of gas-phase chemical decomposition of a carbon precursor on the surface of a catalytic particle suspended in a carrier gas stream (also known as “aerosol method”). TEM study at the JEM-2010 microscope showed that the observed angles at the vertex of the cones (apex angles) were predominantly 5°, 10°, 15° and 20° regardless of the presence of a catalyst particle inside the cone. The analysis of the apex angles witnesses that the nanotubes have a scroll type of structure. Two alternative explanations are proposed for the formation of an unconventional apex angle 5°. The peculiarities of destruction of the catalyst particles inside the nanotubes are revealed.

1. Introduction
Carbon nanostructures have been in the focus of researchers’ attention for several decades. This interest is determined in particular by their interesting electronic and mechanical properties. A detailed structural investigation of carbon nanotubes was given by Iijima [1]. The formation of carbon nanotubes follows different organizational schemes. For example, where they either nest within each other as coaxial graphene cylinders or cones, or where a graphene sheet rolls up into a scroll. Numerous types of helical nanostructures were described such as helix-shaped graphite nanotubes [2], graphitic nanocones [3], nanohorns [4], conical crystals and hollow conical structure [5,6], conical graphitic nanofibres [7] and the helically coiled nanofiber with conical cross-section [8]. There are suggestions that the conical structures can be used in biomedical applications as containers for precision delivery of medicine (nanodroppers) or, as another example, in scanning probe technique applications as cantilevers.

Various conical structures were earlier described in literature [3, 9-11]. The work [3] stipulates that only five angles can exist at the vortex of a single isolated cone, namely: 112.9°, 83.6°, 60°, 38.9° and 19.2°. This phenomenon is related with the limitation in the number of possible pentagon insertions into a graphene sheet, which forms a single cone by scrolling itself. It was shown in [10], however, that a scroll implies larger variety of apex angles. All that variety includes the pentagon-related angles mentioned above. The authors of [10] suggested that a scroll is based on the same graphene packing sequence as in graphite, i.e. ABABAB. This sequence means that neighboring sheets are rotated 30° relative to each other, while every third sheet is rotated 60° relative to the first one. This work reports an attempt of electron microscopy investigation of structural peculiarities of conical scroll carbon nanotubes formed by the aerosol synthesis.
2. Experimental part

The synthesis of carbon nanotubes was performed in a quartz reaction tube (with the inner diameter of 35 mm, 1350 mm long) placed in a vertical tube furnace. Carbon nanotubes were obtained by the method of gas-phase chemical decomposition of a carbon precursor on the surface of a catalytic particle suspended in a carrier gas stream (also known as “aerosol method”) at a temperature of 1150–1200 °C and at a pressure of 1 atm. A schematic representation of the setup is shown in figure 1.

![Figure 1. Schematic representation of the laboratory setup: 1 – He cylinder, 2 – H₂ cylinder, 3 – gas pressure reducer, 4 – valve, 5 – mass flow controller, 6 – fine regulation valve; 7 – input device, 8 – quartz tube reactor; 9 – “catcher”; 10 – nebulizer, 11 – furnace; 12 – temperature regulator; 13 – filter system.](image)

Ethanol was used as the carbon precursor, and the nanotube growth activator was thiophene, while Fe nanoparticles served as a catalyst. Fe nanoparticles were generated from a ferrocene (C₂H₅)₂Fe precursor in the same way as in our earlier works [12,13]. The main difference with earlier works was that the liquid component was introduced in the amount of 1% by a nebulizer device, i.e. it was sprayed into a fine aerosol using an ultrasonic nebulizer. Fine aerosol was directed to the synthesis zone by the carrier gas flow. The use of the nebulizer provided different reaction zone conditions, which allowed us to synthesize a specific nanotube product with structural differences with the results of [12,13].

The obtained samples were studied by high-resolution electron microscopy. The research results showed that the most interesting was the carbon deposit obtained using ferrocene (1 wt.%) as a catalyst precursor. The carbon deposit was analyzed by means of transmission electron microscopy.

3. Results and discussion

TEM showed the presence of conical nanotubes mainly. There were also onion-like structures and fragments of amorphous carbon. Conical nanotubes can either consist of multiple cones stacked inside each other or represent conical scrolls also known as cone-helix structures. The nanotubes of cone-helix structure are visually indistinguishable from stacked cone nanotubes in TEM images. Apex angle is the only reliable distinction between the two types. The measurement of apex angles showed that 5°±1° and 10°±1° are the most common. The former was detected in 17 cases, while the latter was detected in 18 cases. Apex angles of 20°±1° and 30°±1° occurred 11 times each. Apex angles of 25°±1° and 49°±1° were detected 3-4 times each. Some of the nanotubes contained catalyst inside, while the others were hollow. It is interesting that identical apex angles were observed in both filled...
and hollow nanotubes. Figure 2 demonstrates a fragment of a hollow conical nanotube with apex angle of 10° accompanied with corresponding FFT images. Figure 3 shows a filled nanotube with apex angle of 20°.

Figure 2. Carbon deposit obtained using ferrocene: (a) three conical nanotubes are shown by arrows; (b) the fragment of a hollow conical carbon nanotube with apex angle of 10°; (c) FFT image from (b).

Figure 3. (a) The fragment of a conical carbon nanotube, filled by α- Fe with the apex angle of 20°; (b) FFT image from (a).

The formation of multiwalled conical structures instead of double-walled cylindrical nanotubes as in our earlier works [12,13] can be explained taking into account different conditions of formation of the reaction mixture. The nebulizer device, being a very precise mass-flow regulation device, gives, nevertheless, an aerosol of small droplets instead of a homogeneous vaporized reaction mixture as in the earlier used saturator device. The presence of droplets may lead to formation of the catalyst precursor particles as a result of evaporation of ethanol. The formation of Fe nanoparticles from these ferrocene particles would occur not like the formation from vaporized molecules of that same ferrocene and result in larger, differently crystallized catalyst nanocrystals and hence to different structure of the carbon nanotubes.

One can suppose several ways of formation of scroll-type conical structures. First of all, it can be done by insertion of pentagons or heptagons into a graphene sheet. It allows for the formation of structures with five different apex angles. The work [14] considered a conical scroll, where neighboring layers are rotated by constant value θ relative to each other. The θ angle is directly related to the semi-apex angle φ₀ of the cone by the relation:

\[ \Theta = 2\pi \sin \phi_0. \]
One observes pseudo-hexagonal symmetry with ABABAB stacking. This stacking is different from graphite stacking by sheet-to-sheet rotation. It is known, however, that pseudo-orthorombic symmetry may occur in carbon nanotubes with cone stacking ABCABC [15]. In such case, the sheet rotation angle should be multiple of 20°. This packing can be considered as a kind of a turbostratic structure, where the packages of parallel graphenes are inclined by chaotic angles relative to each other.

Braga [6] has shown that a rolled graphene sheet becomes more stable than the undistorted one, and that the curling process becomes self-sustaining, when a minimum overlap of successive layers has occurred. Therefore, in order to start the sheet-to-scroll transition input of a certain threshold energy is required in a first step (excitation by high temperature, sonication, irradiation etc.) [16].

Semi-apex angles for cone-shaped graphene were investigated in [14,17,18]. Table 1 shows the values of semi-apex angles for scrolled nanotubes as a function of the hexagon rotation angle (φ) and as a function of the number of pentagons.

| Table 1. Semi-apex angles in conical scroll structure, formed by two methods |
|-----------------------------|-----------------------------|
| Rolled graphene sheet 0=2π sinφ | Introduction of pentagons |
| ABCABC packing | ABAB packing | φ(°) Semi-apex angles; the number of pentagons (P) is shown in brackets sinφ =1-P/6 |
| 20 | 3,18 | |
| 30 | 4.78 | |
| 40 | 6,36 | |
| 60 | 9.59 | 9.59 (5) |
| 80 | 12.83 | |
| 90 | 14.47 | |
| 100 | 16.12 | |
| 120 | 19.47 | 19.47 (4) |
| 150 | 24.62 | |
| 180 | 30 | 30 (3) |
| 210 | 35.68 | |
| 240 | 41.81 | 41.81 (2) |
| 270 | 48.59 | |
| 300 | 56.44 | 56.44 (1) |
| 330 | 66.44 | |
| 360 | 90 | |

The apex angle of 10°±1° (semi-apex angle appr. 5°) indicates exactly a simple scrolling of a graphene sheet. The apex angle of 30° (semi-apex angle 15°) manifests the scrolling without pentagon insertion as well. As far as the 20° apex angle (semi-apex angle 10°) is concerned, it can be formed by either insertion of five pentagons or by simple scrolling of a graphene sheet. The value of 5°±1° (semi-apex angle 2.5°-3°) can be found in Table 1 as manifestation of pseudo-hexagonal symmetry in a conical nanotube. However, another explanation can be proposed for the 5°±1° apex angle, namely, the insertion of one heptagon as suggested by [10]. Conical nanotubes can also be formed by graphene cones nested inside each other, which can also require the pentagon insertion. The semi-apex angle data shown in Table 1 cannot help distinguishing nested structure from scrolls for all the cases listed in...
the third column of the table. However, the data in the first and second columns witness a scrolled structure.

The presence of conical nanotubes with identical apex angle regardless of the presence of catalyst particles inside witnesses that the formation of cones is not related with a catalyst (figure 4). TEM images in figure 5 show particles inside a nanotube (two particles in figure 5a and three particles in figure 5b). The particle morphology in figure 5a suggests that the observed pattern is the result of destruction of an initial big particle into smaller splinters as cup-cone. Figure 5b manifests a more complicated pattern, i.e. an α-Fe particle in the middle with Fe₃C particles surrounding it. It is necessary to note that a cup-cone pattern is typical for tensile destruction of some cylindrical samples. Investigations show that the destruction proceeds through formation of a neck and consequent fracture forming a crack, which is symmetrical relative to the axis of a sample. Hardness of iron is 180 GPa. Cementite is very brittle but hard (HB more than 800) and is characterized by zero plasticity. Due to three-dimensional stress the neck material is capable of any plastic deformation, so the stress leads to cracking in the neck area, while the other parts of that same particle keep elongating. It explains why the central fracture area of cup-cone type is different from the peripheral areas, where plastic deformation keeps going [19].

Figure 4. (a) the fragment of a hollow conical carbon nanotube with the apex angle of 5°; (b) FFT image from (a); (c) the fragment of a conical carbon nanotube filled with Fe₃C with the apex angle of 5°; (d) FFT image from (c).

Figure 5. (a) Ductile fracture. Cup and cone; (b) Three particles inside a carbon nanotube. An α-Fe particle is in the center and two Fe₃C particles are on the edges.

The metal (α-Fe) takes the shape as determined by the surrounding nanotube. The metal is pressurized by carbon sheets, thus subjecting it to tensile stress up to destruction of the particle. The fracture of a cup-cone type is a sign of plastic deformation, which is followed by carbide formation.
4. Conclusion

Conical carbon nanotubes were formed by the aerosol synthesis. A wide range of apex angles of nanotubes was revealed by TEM methods. Analysis of the values of apex angles shows that at least a part of the nanotubes have a scroll type of structure. The formation of a scroll with ABCABC stacking sequence can explain the unusual apex angle of 5°. It is shown that the metal (α-Fe) inside the nanotube is deformed by elongation along the nanotube axis and shrinking across. This deformation leads to a fracture caused by tensile stress.

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