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STM EVIDENCE OF SMALLEST ROD PRESENCE IN NANOFILAMENT CARBON STRUCTURE

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Discovery of helical structure graphite microtubes as well as wide-spread investigations of remarkable molecules C_{60} and fullerenes with a greater number of carbon atoms turned scientists' attention to a search for carbon tubes of nanometer dimensions. Here we report the first observation by scanning tunneling microscope (STM) of carbon rods of the smallest diameter 0.8 nm in nanofilament films prepared by vacuum electron beam graphite evaporation. We suppose them to be tubelenes C_{36+12n} (containing 6 carbon hexagons in a belt) with molecular diameter of 8Å .

Unusual carbon cage molecules with atom number from 20 to 600 [2] draw attention by their unique physical-chemical properties. A new direction of such investigations has been opened by S.Iijima [1,11] who found out helical multilayer carbon nanotubes finished by a conoid cap [7,8]. But such carbon clusters, including the famous C_{60} fullerene [13,14], were created by laser or arc carbon synthesis in the presence of an inert gas with pressure of about 100 torr necessary for the formation of a sphere-like cluster cage or about 500 torr for microtube preparation [12]. Evidence [8,9] of the presence of nanofibre carbon objects during vacuum evaporation of graphite has recently been reported. New carbon filaments [9] consist of rods 1 nm in diameter, which are supposed to be nonhelical tubelenes C_{60+18n} [3-5] (n - number of 9 carbon hexagon belts in one molecule) closed at both ends by halves of the fullerene C_{60}. At the same time an analogous tube object with believed diameter of C_{60} was observed by transmission electron micriscope [10].

We have obtained new structure carbon films by a known method [9] but using an evaporated carbon particle flow of higher density then one in [9]. Electron micrography of each chip of films has shown a structure of 3-20 nm filaments. We watched these films in a high resolution scanning tunneling microscope [15] at room temperature in normal atmosphere conditions. Its resolution was 0.1 nm in the sample surface (X, Y) and 0.001-0.01 nm in perpendicular direction Z. Tunneling bias U between the mechanically ground PtIr needle edge and the sample varied in the interval between -100 mV and +300 mV during constant height mode $I(U)$. Drift in the process of measurement was not greater than 1 Å/min in the sample surface. Scanning rate while measuring current characteristic $I(U)$ was 1.5 Å/ms and while measuring effective tunnel barrier height dI/dZ – 0.9 Å/ms. Fixed bias and tunneling current were U_f = 100 mV and I_f = 1 nA. Voltage modulation of Z-manipulation provided the change of a tunnel gap at the value $\Delta Z = 0.5$ Å.

While observing the structure of a carbon filament profile we have detected adjacent objects of extended shape with 0.8 nm diameter - Fig.1*a*. The corresponding one pass cut of this filament rising from a graphite substrate is shown in

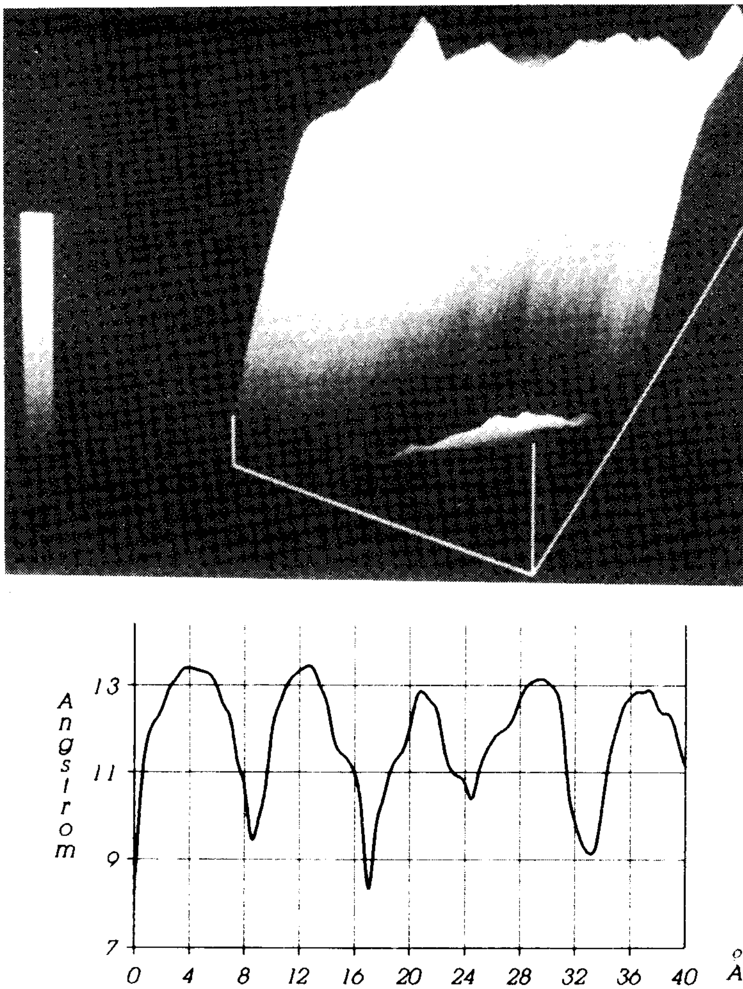
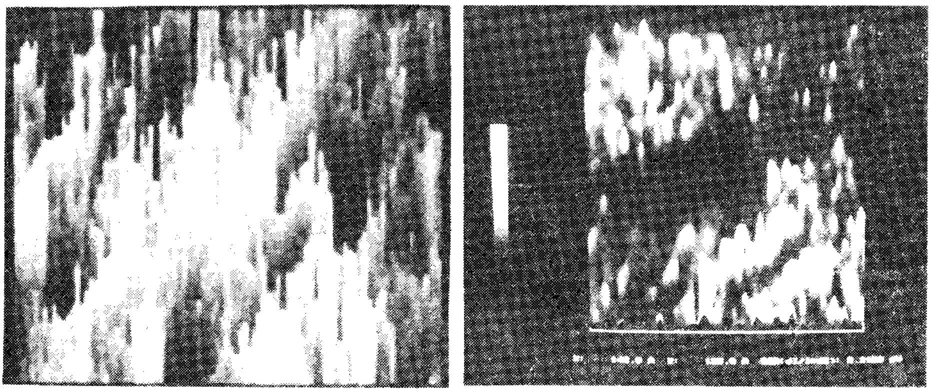


Fig.1. *a* – STM image of a filament profile, substrate-[001] graphite (field of vision X : 65.1 Å, Y : 41.4 Å, Z : 46.6 Å; $I(U)$ regime); *b* – one pass STM cut of this filament.

Fig.1*b*. The same individual rods are observed on the surface of a $\sim 75^0$ texture film prepared on a quarz substrate when a carbon flow has been directed under a not large angle to its surface. Their number is smaller than that of 1 nm diameter objects - Fig.2*a*. In this case as we think the pressure of carbon gas layer over the substrate surface is smaller than that in the case of a carbon particle flow perpendicular to the surface. In the latter case we watch predominating presence of 0.8 nm ojects - Fig.2*b*. We suppose that the "thinner" molecules are formed owing to very fast passing of the 100 torr value by the pressure of carbon "steam" not far from the substrate when a high density carbon flow is used. We remind that 100 torr pressure is essential to form C_{60} fullerenes [13,14].

On the base of discussed data we consider that observed oblong objects with 0.8 nm diameter can be compared to the tube-like cluster models of C_{36+12n} - on the left in Fig.3 - with corresponding molecular diameter $d = 8.2$ Å [3] ($d = D + 2l_w$, D is cage diameter, l_w is van der Waals radius, $2l_w = 3.4$ Å). They have a cylinder graphite fragment with 6 carbon hexagons in a belt and two lids consisting of a hexagon surrounded by 6 pentagons as distinct from C_{60+18n} - on the right in Fig.3. We have observed that the electron diffraction of a normal texture film has mainly 6-fold symmetry diffraction pot location - on the bottom in Fig.3. This fact obliquely confirms our model. Note, that more strained cage clusters C_{36+12n} [6] are more predisposed to form covalent bond structures than tubelenes C_{60+18n}. Two bound clusters C_{36+12n} will be arranged at $d_c = D + a = 6.3 - 6.8\,\mathring{A}$, where $a = 1.5 - 2\,\mathring{A}$ is covalent bond length. This may explain the position of some adjacent objects in Fig.2*b* at the distance of 6–7 $\mathring{A}$ a bit smaller than C_{36+12n} molecular diameter, only if one of those objects is not a tubelene C_{20+10n} with $d = 7.4\,\mathring{A}$, $d_c = 5.5 - 6\,\mathring{A}$ $(D = 4\,\mathring{A})$ and lids formed by a pentagon surrounded by 5 pentagons [3]. However we have not revealed 5-fold symmetry pattern in electron diffractogramme of this film surface.



a *b*

Fig.2. STM micrographs: *a* - rod-like objects at the surface of ~ 75° texture film on a quartz substrate: "thicker" objects with 1.0-1.1 nm diameter prevail over 0.8nm "thinner" objects (X : 584.4 Å, Y:657.0 Å, Z : 129.6 Å; I regime); *b* – object tops at the surface of a normal texture nanofilament carbon film on a Si substrate: "thin" 0.8 nm objects prevail (X : 142.0 Å, Y : 125.0 Å; dI/dZ regime), □ 0.8nm distance between two neighbour rod tops. The percent of objects with {10-11; 8; 6-7} Å distance between their neighbouring tops (or their diameters) is correspondingly in images a) {60; 18; 22}% and *b*) {16; 60; 24}%.

We didn't manage to observe the internal structure of an individual tubelene, neither its lid nor its cylinder fragment. Such an evidence is certainly necessary for a final determination of the structure of these fascinating smallest carbon rod objects.

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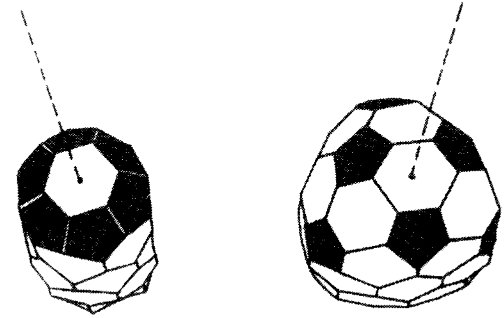

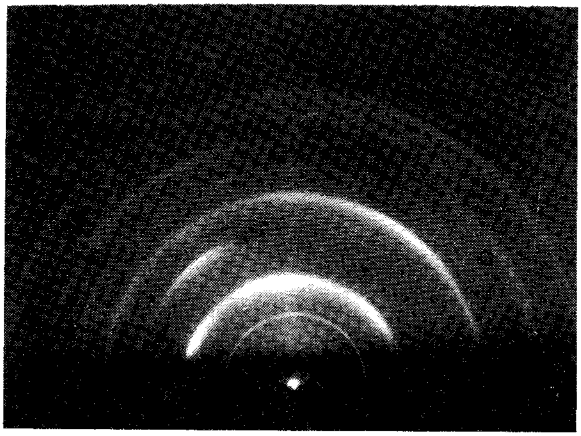

Fig.3. Models of tube-like carbon clusters: the left one is C_{36+12n} with 0.48 nm cage diameter (C axis of 6-fold symmetry), the right one is C_{60+18n} with 0.72 nm cage diameter (C axis of 3-fold symmetry)[3]. In the bottom electron diffraction patterns of the normal texture film (Fig.2b) indicate mainly 6-fold symmetry of carbon location in its surface.

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