Scanning tunneling microscope evidence of smallest rod presence in nanofilament carbon structure

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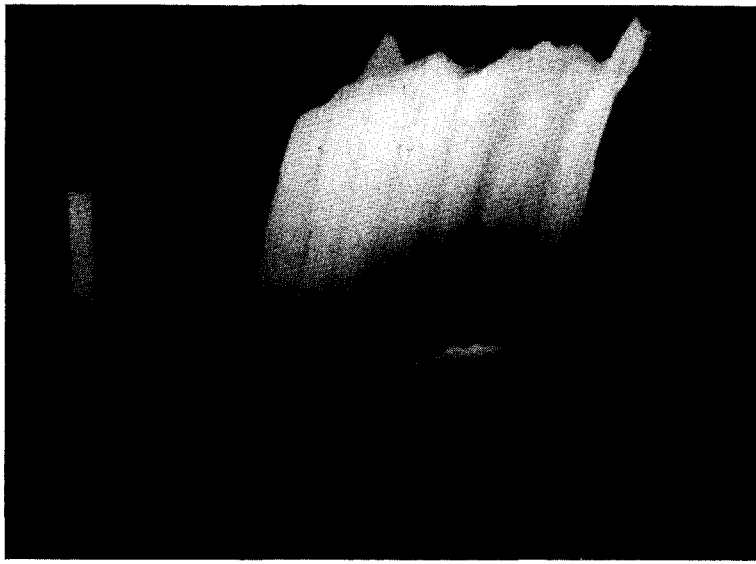
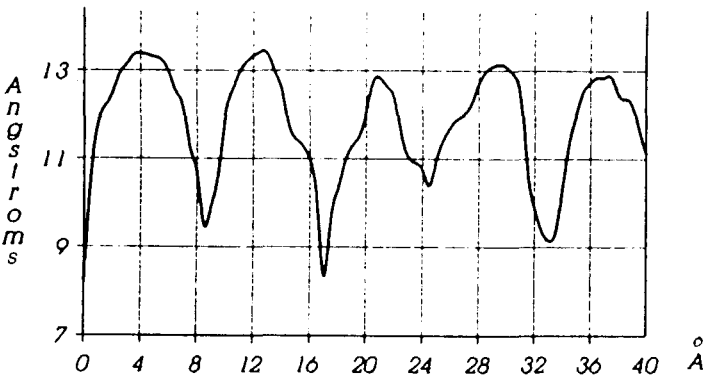
The discovery of helical structure graphite microtubes and extensive study of remarkable molecules C_{60} and fullerenes with increasing number of carbon atoms turned the attention of scientists to the search for carbon tubes of nanometer dimensions. Here we report the first observation with a scanning tunneling microscope (STM) of carbon rods of the smallest diameter (0.8 nm) in nanofilament films synthesized by vacuum electron beam graphite evaporation. These carbon rods are assumed to be tubelenes C_{36+12n} (containing six carbon hexagons in a belt) with a molecular diameter of 8 Å.

Unusual carbon cage molecules with an atomic number between 20 and 600 (Ref. 2) draw attention because of their unique physical–chemical properties. A new direction of such investigations has been opened by S. Iijima,[1,11] who found that helical multilayer carbon nanotubes are terminated by a conoid cap.[7,8] But such carbon clusters, including the well-known C_{60} fullerene,[13,14] were created by laser or arc carbon synthesis in the presence of an inert gas at a pressure of about 100 Torr, at which a sphere-like cluster cage is formed, or at a pressure of about 500 Torr, at which microtubes are formed.[12] Evidence[8,9] of the presence of nanofiber carbon objects during vacuum evaporation of graphite has recently been reported. New carbon filaments[9] consist of rods 1 nm in diameter, which are assumed to be nonhelical tubelenes C_{60+18n} (Refs. 3–5) (n—nine carbon hexagon belts in one molecule) which are closed at both ends by halves of the fullerene C_{60}. At the same time, an analogous tubular object with a diameter of C_{60} was observed with a transmission electron microscope.[10]

We have obtained new structure carbon films by a standard method,[9] in which we used an evaporated carbon particle flow of higher density than that in Ref. 9. Electron micrography of each chip of films has shown that its structure consists of 3 to 20-nm filaments. We detected these films under a high-resolution scanning tunneling microscope[15] at room temperature under normal atmosphere conditions. The resolution of the microscope was 0.1 nm at the surface of the sample (X,Y) and 0.001–0.01 nm in the direction perpendicular to it (the Z direction). 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 during the measurements was no greater than 1 Å/min at the surface of the sample. The scanning during the measurements of the I-V characteristic was 1.5 Å/ms and while measuring the effective tunnel barrier height dI/dZ—0.9 Å/ms. The fixed bias and the tunneling



a



b

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.

current were $U_f = 100$ mV and $I_f = 1$ nA. Voltage modulation of the Z-manipulation changed the tunnel gap within $\Delta Z = 0.5$ Å.

While observing the structure of a carbon filament profile we have detected adjacent objects of extended shape and 0.8 nm in diameter (Fig. 1a). The corresponding one-pass cut of this filament rising from the graphite substrate is shown in Fig. 1b. The same individual rods are observed at the surface of a $\sim 75°$ texture film prepared on a quartz substrate when a carbon flow is directed at a small angle to its surface. These

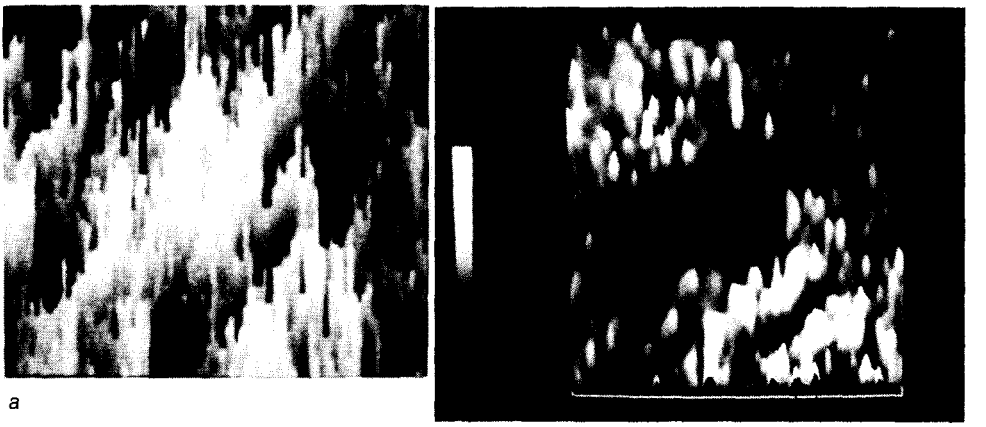


FIG. 2. STM micrographs. a—(rod-like objects at the surface of ~75° texture film on a quartz substrate: "thicker" objects with 1.0–1.1-nm diameter prevail over 0.8-nm "thinner" objects (X:584.4 Å, Y: 657.0 Å, Z: 129.6 Å; I regime); b—object tops at the surface of a normal texture nanofilament carbon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

rods are fewer in number than 1-nm-diameter objects (Fig. 2a). We assume that the pressure of the carbon gas layer at the substrate surface is lower in this case than in the case of a carbon particle flow perpendicular to the surface. In the latter case we observed a predominant presence of 0.8-nm objects (Fig. 2b). We assume that the "thinner" molecules are formed because the carbon "steam" at a pressure of 100 Torr passes very rapidly near the substrate when a high density carbon flow is used. We recall that 100 Torr pressure is essential in order to form C_{60} fullerenes.[13,14]

On the basis of the discussed data we assume that the observed oblong objects 0.8 nm in diameter can be compared with the tube-like cluster models of C_{36+12n} (the left side in Fig. 3) with a corresponding molecular diameter $d=8.2$ Å (Ref. 3) ($d=D+2l_w$, where D is cage diameter, l_w is the van der Waals radius, and $2l_w=3.4$ Å). They have a cylinder graphite fragment with six carbon hexagons in a belt and two lids consisting of a hexagon surrounded by six pentagons, in contrast with C_{60+18n} (the right side in Fig. 3). We found that the electron diffraction of a normal texture film has mainly a sixfold symmetry diffraction pot (the bottom part of Fig. 3). This is an indirect confirmation of our model. Note that more strained cage clusters C_{36+12n} (Ref. 6) are more predisposed to form covalent bond structures than tubelenes C_{60+18n}. Two bound clusters C_{36+12n} are arranged at $d_c=D+a=6.3$–6.8 Å, where $a=1.5$–2 Å is the covalent bond length. This may explain the position of some adjacent objects in Fig. 2b at the distance of 6–7 Å slightly smaller than C_{36+12n} molecular diameter, only if one of those objects is not a tubelene C_{20+10n} with $d=7.4$ Å, $d_c=5.5$–6 Å ($D=4$ Å) and the lids formed by a pentagon surrounded by five pentagons.[3] However, we have not observed a fivefold symmetry pattern in the electron diffractogram of this film surface.

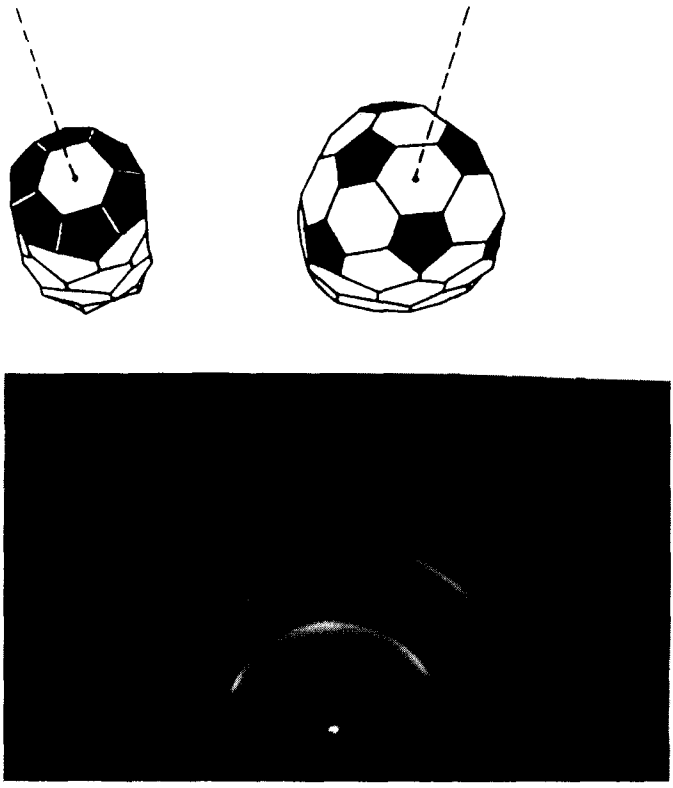


FIG. 3. Models of tube-like carbon clusters: the left one is C_{36+12n} with 0.48-nm cage diameter (the C axis of sixfold symmetry), the right one is C_{60+18n} with 0.72-nm cage diameter (the *C* axis of threefold symmetry).[3] At the bottom the electron diffraction patterns of the normal texture film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

We did not observe the internal structure of an individual tubelene, or its lid, or its cylinder fragment. Evidence of their presence is necessary for a final determination of the structure of these fascinating, very small carbon rod objects.

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