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Letter

Nucleation of WS_2 Fullerenes at Room Temperature

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Abstract. — Inorganic nested fullerene-like particles of layered compound WS_2 were observed by high resolution transmission electron microscopy. It is shown, for the first time, that these structures can be nucleated inside the amorphous matrix at room temperature. At this condition the nucleation process may take 3-4 years.

In 1985 Kroto *et al.* [1] reported of the new modification of carbon - the C_{60} molecule, or fullerene. A related structure to these hollow cages is the nanotubes discovered by Iijima [2]. The great interest in studying fullerenes' and nanotubes' properties has stimulated the researchers to develop the technology for mass production of these amazing structures [3–7]. Previously, cage-like structures were believed to exist only in carbonaceous materials, but in 1992 they were found [8] also in the layered semiconductor WS_2 and later-on in other layered compounds of transition metal dichalcogenides. It is noteworthy that all the reported methods of fullerene and nanotube production require external conditions, like high temperatures in argon arc discharge [3, 6, 7], laser vaporization [4, 5], electron irradiation at high voltage [9], or bombardment of a carbonaceous target with high dosage of ion beam [10]. Here we report on the nucleation of WS_2 fullerenes at room temperature.

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† **In memory of Dr. Lev Margulis.** The Department of Materials and Interfaces of the Weizmann Institute of Science and the many friends and colleagues of Dr. Lev Margulis deeply mourn his recent untimely passing at the age of 54. Lev was a remarkable man and a true friend for many of us. He arrived to Israel in 1987 after having been denied an exit visa for 8 years, during which he was fired from his job as an electron microscopist in the State Institute of Rare Metals in Moscow and forced to do various jobs to make his leaving. After a short adaptation period at the Weizmann Institute, he started to exhibit his skills as a meticulous and innovative electron microscopist. We, that have been exposed to rudimentary electron microscopy prior to his venue, found it a unique opportunity and a privilege to work with him, and enjoy his skills. With him we passed the happiest moments of discovering the power of transmission electron microscopy and unraveling new structures of matter. The legacy of Lev will be followed up by the many students which he had trained and by many of us for whom electron microscopy became almost a second habit. We all mourn the passing of a charming person, who combined the greatest skills with an excellent humor and lasting laughter, which we will always remember.

Prof. Reshef Tenne, Rehovot 4.6.96

A method for obtaining nested WS_2 fullerenes and nanotubes was described by us previously [8]: tungsten films of 20 nm thickness were deposited onto clean quartz substrates by electron beam evaporation. It was found advantageous for the fullerenes' growth, though not absolutely necessary, to oxidize first the sample at $\sim$ 500 °C in open air. The oxide film was subsequently fired at 850 °C for 30 mn in a stream of H_2S (1 ml/mn) and N_2/H_2 mixture (95/5%; 150 ml/mn).

The examination of the films in a transmission electron microscope has shown the presence of giant (several tens of nm in size) nested fullerenes, embedded into amorphous matrix (Figs. 2a, b in Ref. [8]). Clusters of amorphous dots (3-5 nm in diameter) were also observed (Fig. 2c in Ref. [8]), albeit rarely.

One of the samples used in our previous investigation [8] was kept in the drawer at ambient conditions and was periodically examined. The sample was completely amorphous in the early stages of the investigation. After *ca.* one year the first nuclei of a crystalline phase began to appear. They seemed like dots of dark contrast, of 1-2 nm in size, embedded in the amorphous

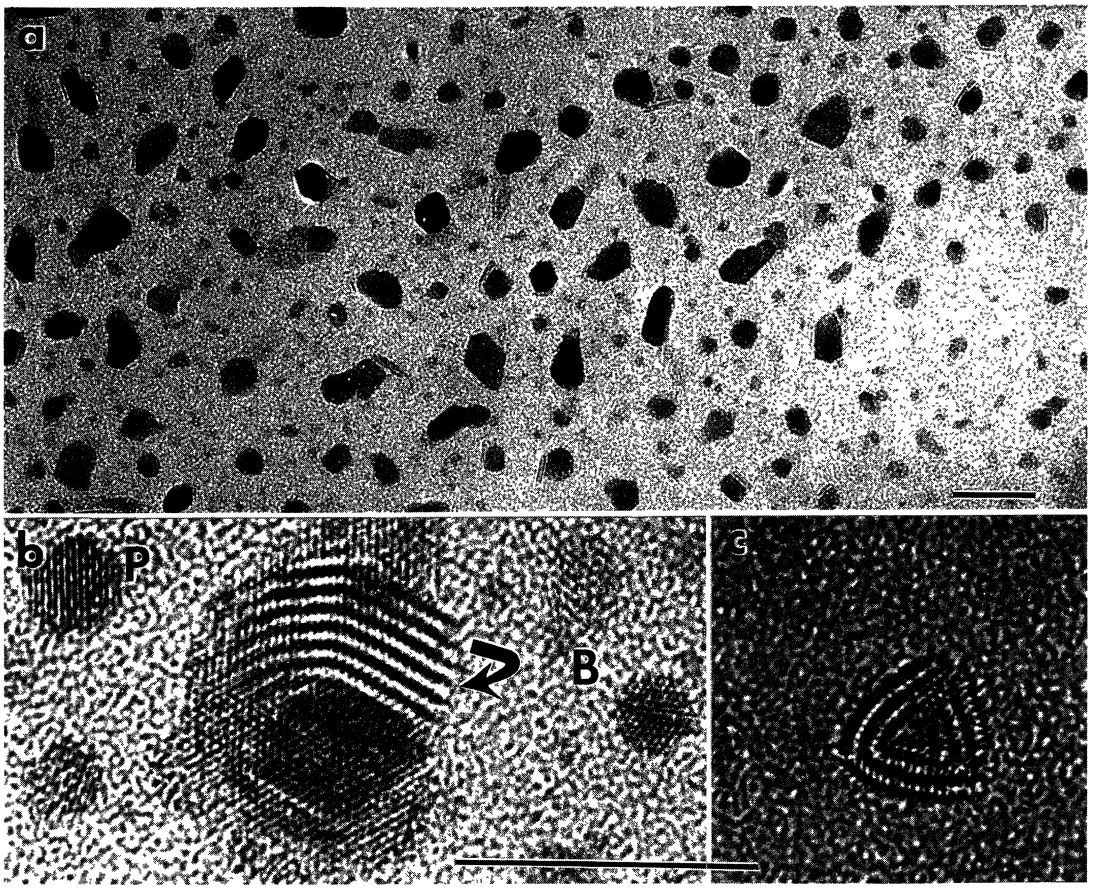

Fig. 1. — a) Distribution of nested WS_2 fullerenes ($\sim$ 10 nm and smaller) nucleated at room temperature inside an amorphous phase during four years. The lattice image is not resolved because of low magnification. b) High resolution image of plate-like nuclei oriented with basal (B) or prismatic (P) plane perpendicular to the incident electron beam. Note the curling of the largest nucleus (arrow). c) Tetrahedral four-shell fullerene. Scale bars = 10 nm.

matrix. The crystallinity of these tiny nuclei can be revealed due to a fringe interference contrast. Now, that *four* years have elapsed, the average volume density of nuclei has reached a huge value of approximately 5×10^{17} cm^{-3} (Fig. 1a). High resolution transmission electron microscopy (HRTEM) discloses two kinds of nuclei - the flat, layered nuclei and fullerene-like ones.

The flat nuclei (Fig. 1b) can be oriented with basal (B) or prismatic (P) planes parallel to the amorphous substrate. The arrow in Figure 1b indicates an interesting phenomenon-spontaneous curling of a 7-layered nucleus. But the most impressive observation is a projection of a four-shell tetrahedron (Fig. 1c). Actually, this is the first direct confirmation of our model proposed previously [11]. According to this model, an apex can be created by folding the flat MoS_2 (or WS_2) layer around a triangle which is a stable topological element of the trigonal prismatic lattice of WS_2 [12]. Due to Euler's theorem, only four triangles are required for closing a cage with tetrahedral fullerene shape, the projection of which is seen in Figure 1c. Unfortunately, the tilt angle was very limited in the HRTEM used in this work ($\pm 10°$) and consequently only limited information regarding the detailed structure of the tetraheder could be obtained. In addition to the triangle of Figure 1c, many fullerene-like structures among them a few with triangular shape have been observed. Electron diffraction confirmed that both platelets and fullerene-like structures have WS_2 unit-cell.

In analogy with the phase transformation of the Mo-S [11], we may schematically represent the following series of phase transformations which occurred in the present material: $a - W > a - WO_3 > a - WS_3 > c - 2H - WS_2$ (where "a" means amorphous and "c" - crystalline phases). We concluded earlier [11] that the fullerene-like phase may be considered as an intermediate stage appearing between the last two phases. Since the phase boundary between these two phases extends down to room temperature, it is not surprising that the fullerenes coexist with nuclei of the crystalline WS_2-phase at ambient conditions (Figs. 1b, c).

Acknowledgements

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