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Self-assembly of C_{60} into highly ordered chain-like structures on HOPG observed at ambient conditions

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Abstract

The observation of chain-like structures of self-assembled C_{60} molecules on HOPG surfaces at room temperature in aerial atmosphere by means of scanning tunneling microscopy is reported. The ca. 2.5 nm center-to-center distance between two fullerene molecules is much larger than in the close-packed layered or film structures of C_{60} usually found on HOPG surfaces.
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The discovery of the C_{60} molecule by Kroto et al. [1] has assumed a pivotal role in the development of nanotechnology. First of all, it is extremely rare that new allotrope modifications of the elements are discovered, and secondly the unique physical and chemical properties of this special molecule have spawned numerous speculations on applications of, for instance, its unusual magnetic properties [2] and superconducting properties [3] for various purposes. Also, for more classical chemical purposes fullerenes have attracted attention, for instance in the use of C_{60} as a ligand in complexes like $[C_{60}OsO_4(NC_5H_4Bu^t)_2]$ [4].

Scanning tunnelling microscopy (STM) is an important tool for the study of nanostructures, since it is directly possible to observe single molecules and atoms using STM. A considerable number of STM studies on fullerenes adsorbed on different substrate surfaces have appeared in the literature, e.g. GaAs, [5] Au [6] and highly-oriented pyrolytic graphite (HOPG) [7–9]. By far most of these deal with 2D arrangements of fullerenes, and particularly the growth of C_{60} films and layers on surfaces has attracted considerable attention due to their potential application as new electronic devices [10]. Arrangements of fullerenes in 1D nanostructures is much more uncommon, and have in fact previously been observed only for chemically modified fullerenes [11,12] and for C_{60} arrangements controlled by a porphyrin structured template on a Ag surface [13]. These self-organizing system has attracted attention as potential building blocks in the fabrication of devices using the "bottom-up" approach to nanotechnology.

The most commonly used method for depositing fullerenes onto a substrate surface has been sublimation under ultra-high vacuum (UHV) conditions [8,9,14]. An alternative procedure is to place a drop of a solution containing fullerenes onto the surface and allow the solution to evaporate slowly [7,15]. In previous studies where this sample preparation technique has been used, large clusters and massive stacks of fullerenes are formed. Herein we report the observation of highly ordered chain-like structures of pure C_{60} self-assembled without the use of a structural template on HOPG. The C_{60} molecules were observed to organize into a new 1D nanostructure consisting of a single line of molecules. The measurements were carried out using

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STM in air at room temperature using a surprisingly simple approach in which C_{60} was placed on surface using a solution of C_{60} in toluene. The use of ambient conditions to handle nanodevices increase the possibility implementing application using the "bottom-up" approach in nanotechnology.

In addition to STM studies on layers of fullerenes deposited on HOPG surfaces grown by sublimation [8,9] other approaches for controlling the distribution of the fullerenes have been reported. It is, for instance, possible to use supramolecular 2D structures, on HOPG, to direct the fullerenes into different patterns [16,17]. However, structurally ordered non-layered assemblies of fullerenes on HOPG have only previously been reported for the ferrocene-fullerene cycloadduct, C_{60}ONCFn (Fn = ferrocene), for which closely packed long parallel chains were observed under UHV conditions at room temperature [11]. These closely packed parallel chains had a separation of ~2.2 nm and are presumed to consist of one or two layers of the complexes, however, there was no observation of fullerenes arranged in single-row.

In the present work, the C_{60} molecules were deposited onto the HOPG surface using the following procedure carried out in air. For a typical sample preparation C_{60} (5 mg, Aldrich, 98%) was suspended in toluene (1 ml, Fluka, 99.8%) in a test tube which was sealed with a rubber stopper to avoid evaporation of the solvent. The mixture was sonicated at room temperature for 1 h and allowed to settle for 15 min. The used of ultrasonication is done to accelerate the C_{60} dissolution and to achieve a highly concentrated, saturated solution of C_{60} in toluene [18]. A small portion of the sonicated toluene solution was carefully taken out using a Pasteur pipette and a few drops of this solution were deposited onto a freshly-cleaved HOPG substrate surface with an area of 0.5×0.5 cm^2. The sample was left in a fume hood for 10 min to allow the toluene to evaporate and then mounted onto a commercially available easyScan E-STM apparatus [19] which was used without any modifications. The measurements were always conducted under ambient conditions in constant current mode with a current of 1 nA and a gap voltage between the tip and the sample of 0.01–0.05 V using mechanically cut PtIr (90/10) tips. Fig. 1 shows typical overview STM images of different samples. It is seen that the C_{60} molecules order into chains which are often more than 100 nm long and slightly curved.

The center-to-center distance between two fullerene molecules in C_{60} films usually found in studies of fullerenes on HOPG is normally ca. 1.1 nm [9]. This is comparable to distances of ca. 1 nm seen in C_{60} films on GaAs [5] and Au [14] substrates and also to the center-to-center distance of 1.0 nm in crystalline C_{60} [20].

Fig. 2 shows a single-row of C_{60} molecules next to multiple rows of C_{60} molecules. As is seen in Fig. 2, the fullerene molecules order into highly ordered 1D chain-like structures with a slightly larger, and highly uniform, center-to-center distance between two fullerenes (2.5 nm) than the distance observed for C_{60}ONCFn (2.2 nm) [11]. The size of a single fullerene molecule is measured to be ca. 1 nm, which compares well with the calculated diameter (7.1 Å) of C_{60} [1], when taking into account that STM probes electron density rather than topology. Thus, the arrangement

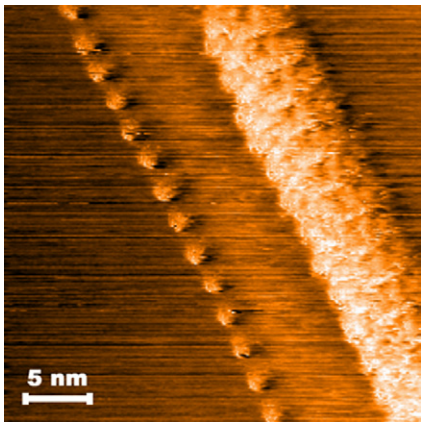

Fig. 2. A single-row of fullerene molecules left to multiple rows. The very uniform center-to-center distance of the molecules is ca. 2.5 nm, and the diameter of an individual fullerene molecule is ca. 1 nm.

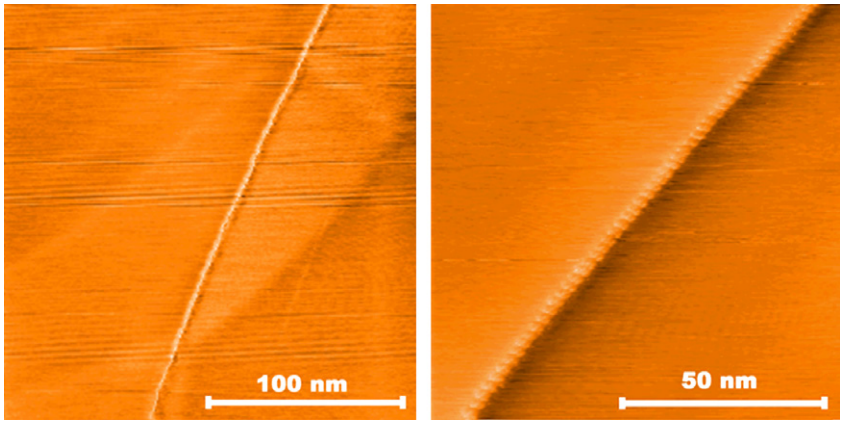

Fig. 1. Overview images of self-assembled rows of fullerenes on HOPG showing long slightly curved chains of fullerenes.

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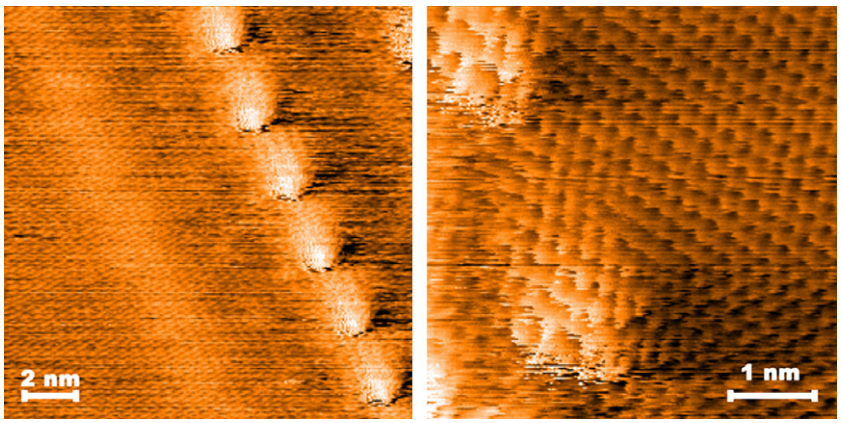

Fig. 3. High-resolution images of fullerene chains on the hexagonal HOPG surface showing (left) six fullerenes on the flat HOPG surface, and (right) zoom in on the hexagonal HOPG surface and two C_{60} molecules. The surface height on different sides of the chains is the same, plus/minus ca. 1 Å.

of the fullerenes in rows as in the present structure is much less dense than crystalline C_{60} or in fullerene films.

Fig. 3 illustrates high-resolution images of the fullerene chains. These images clearly show that the self-assembly does in fact not take place on HOPG step sites, since no step sites are visible in the images. Furthermore, as may be seen from Fig. 3, the hexagonal pattern of the HOPG structure is readily identifiable on both sides of the C_{60} molecules. Moreover, the surface height on different sides of the chain is the same, plus/minus ca. 1 Å, i.e. significantly less than the graphene layer distance of 3.34 Å.

The comparatively large and very uniform intermolecular distance suggests the presence of solvent molecules during the self-assembly of the fullerenes. Thus, we suggest that it is solvated fullerene molecules that self-assemble before the complete evaporation of the solvent, since solvated fullerenes should be much more mobile on the HOPG surface than their solvent-free counterparts. We suggest that the individual C_{60} molecules interact with the HOPG surface and also with each other, through van der Waals type and π-type interactions and propose that the ability of toluene to π-interact with the fullerene molecules, or rather, the ability of solvated fullerenes to π-interact with each other through an adhering solvent layer makes possible the ordering of the fullerenes into chain-like structures. Because of the large and very uniform intermolecular distance between the C_{60} molecules one might speculate that a number of toluene molecules are able to π-stack and that the π-stacking gives rise to the 1D arrangement. The comparatively large distance between two C_{60} molecules similarly observed for C_{60}ONCFn mentioned earlier is not fully understood but may be caused by the 1,2-dichloroethane solvent and/or the ferrocene group [11]. In order to understand the influence of the solvent we tried to use other solvents, i.e. ethanol, acetone and 1,2-dichloroethane, without any success since no chain-like structures were observed. The solubility of C_{60} as well as the volatility of the solvent may also have a great influence. The volatility and the evaporation of the solvent might be important factors in the self-assembled and the formation of the 1D arrangements. The fullerene assembly may take place during solvent evaporation and retraction of the solvent drops. This could explains the very long and curved 1D assemblies, and is indeed backed up by the curvature of chains which actually rule out the possibility of step decoration by the fullerenes, i.e. adsorption of the fullerenes on HOPG step edges. The curvature may also indicate that the formation of the 1D arrangement is rather independent of the HOPG.

These results suggest that self-assembly of fullerenes on HOPG leads to new and interesting 1D chain-like nanostructures. The mechanisms involved in this process are not fully understood, however, we have provided a possible explanation of this observation, namely, that solvation of the molecules during the process is of crucial importance. Further investigations of the possibility for more controllable depositions of fullerenes onto HOPG surfaces, as well as onto other surfaces and using other solvents, must be done. These 1D self-assembled fullerene chains may in the future find application in the construction of other potentially interesting nanostructures.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.susc.2007.03.022.

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