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LETTERS

Buckminsterfullerene C_{60}: Synthesis, Spectroscopic Characterization, and Structure Analysis

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We have synthesized C_{60} in gram quantitites using the Krätschmer and Huffman technique. The arc vaporization of a graphite rod was performed at 100 Torr in a static helium atmosphere. The yield by toluene extraction is 7% of the soot produced. C_{60} in the toluene extract was identified by mass, FTIR, and NMR spectroscopy. The result of analytical HPLC showed the content of C_{70} to be 13% in the toluene extract and 9% in the samples sublimated at 400 °C. X-ray and electron diffraction studies show that C_{60} molecules form fcc or hcp crystals, depending on the substrate and sublimation conditions. A new phase with tetragonal symmetry has been found in the sublimated sample, presumably formed by C_{70} or larger C fullerenes.

The success in synthesis of macroscopic quantities of C_{60} by Krätschmer and Huffman group[1,2] has stimulated a variety of studies on its chemical and physical properties. The recent alkali-metal-doped C_{60} sets new T_c records for organic superconductors: 18[3,4] and 19.3 K[5] for K_3C_{60}, 28[6] and 30 K[5] for Rb_xC_{60}. These results will further stimulate intense interest and research on C_{60}. In this short Letter, we present a brief description of the production of C_{60} and its mass, FTIR, and NMR spectroscopy, as well as X-ray and electron diffraction studies.

Synthesis of C_{60}

C_{60} was prepared by using the Krätschmer and Huffman technique, in gram quantities per day.[7] The contact arc vaporization of a graphite rod was performed at 100 Torr of static helium atmosphere. The graphite rod was spectroscopically pure and 6 mm in diameter. For vaporization of the graphite, the power supply was operated in the dc mode at 100 A current and 20–25 V. The black soot was collected from the surface of the stainless steel chamber, which was water cooled. The soot was then scraped and placed in the thimble of an extractor. After 3 h of extraction by toluene, a wine-red to brown liquid, depending on the C_{60} concentration, was collected. The liquid was separated from the

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[2] Krätschmer, W.; Lamb, L. D.; Fostiropoulous, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

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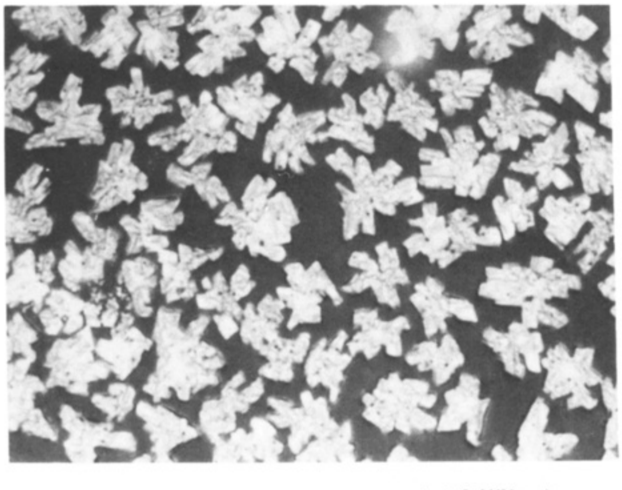

Figure 1. Initial state of growth of C_{60} crystals on a glass plate, optical micrograph. Note the platelets jointed together at one end and deviated with certain angles.

fine soot and the toluene was then removed in an evaporator. The yield of black powder was about 7% of the graphite soot.

Characterization of Spectroscopy and HPLC

The toluene extract and sublimated samples at 400 °C was measured by mass spectroscopy with the electron bombardment source at source/probe temperature of 350/300 °C. The C_{60}^+ ion at $m/e = 720, 721, 722$ are dominant with precisely expected isotopic pattern (100:66.3:20).

The ^{13}C NMR (Bruker AM500) spectrum of the extract dissolved in C_6D_6 displayed a single peak at 143.24 ppm, which is in excellent agreement with the results reported by other groups.[7–10] Because of the limitation of the integration time, the five ^{13}C NMR peaks of C_{70}[8,9] are not observed.

Fourier transform infrared spectroscopy (FTIR) of the toluene extract pressed in a KBr pellet revealed four strong peaks at 1427.89, 1181.48, 575.21, and 525.65 cm^{-1} in good agreement with the spectrum obtained by Haufler et al.[2,7]

Because of the poor solubility of the extract in most organic solvents, the separation of the mixture of C_{60} and C_{70} is quite difficult. The analytical HPLC performed with hexane on the silica–CN column (150 × 4 mm) gave a satisfactory separation (retention time 2.139 and 2.470 min for C_{60} and C_{70}, respectively, at a flow rate of 1.0 mL/min, detector wavelength 254 nm). The analytical result indicated the content of C_{70} to be approximately 13% (ratio of area) in the toluene extract and 9% in the sublimated sample at 400 °C.

Structure Analysis

The crystalline structure of C_{60}/C_{70} was determined by using optical microscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM) for samples sublimated on glass plates or on Au-coated glass plates as well as powder.

At the initial state of growth on a glass plate, C_{60} forms thin platelets of a deep red color, jointed together at one end, as shown in the optical micrograph, Figure 1. When sublimated at 400 °C for 4 h and then at 500 °C for 2 h, C_{60} grow into larger crystallites with a metallic appearance (see Figure 2). The average size of the crystallites is 3–5 μm. Though many of them show sixfold symmetry, some have rectangular form. No starlike flakes were observed as reported in ref 2. Samples sublimated at 400 °C on Au-coated glass showed only rectangular-shaped crystallites with an average size of 1–2 μm.

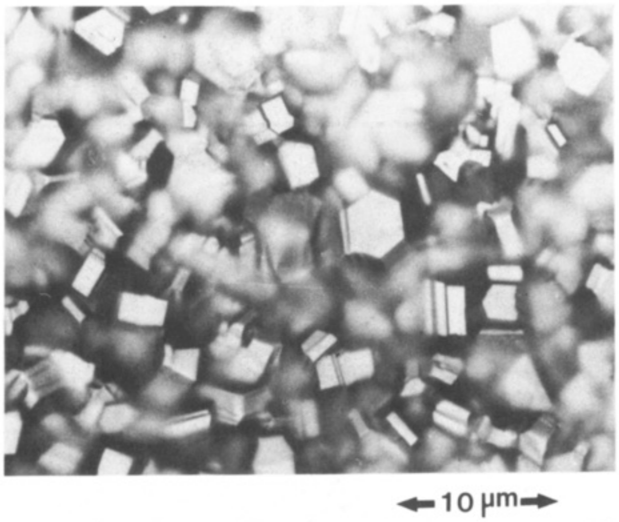

Figure 2. Well-crystallized C_{60} crystals sublimated at 400/500 °C for 4/2 h, optical micrograph. Many platelets have sixfold symmetry. The average size of crystallites is about 3–5 μm. Twinlike defects can be seen across the platelets.

TABLE I: Diffraction Data of Three C_{60}/C_{70} Phases

					2θ	
h	*k*	*l*	*D*(calc)	*D*(obs)	C	O
Face Center Cubic Phase in C_{60} Deposited on a Au Film $a = 14.17$ Å						
1	1	1	8.185	8.148	10.800	10.84
2	2	0	5.012	5.007	17.679	17.70
3	1	1	4.274	4.277	20.762	20.76
2	2	2	4.092	4.101	21.697	21.66
4	2	2	2.893	2.892	30.873	30.88
5	1	1	2.728	2.732	32.797	32.76
4	4	0	2.506	2.504	35.799	35.82
Hexagonal Phase in C_{60} Thick Film Deposited on a Glass $a = 10.05$ Å, $c = 16.41$ Å						
1	0	0	8.705	8.723	10.153	10.14
0	0	2	8.205	8.185	10.772	10.78
1	0	1	7.690	7.689	11.497	11.50
1	0	2	5.971	5.980	14.823	14.82
1	1	0	5.025	5.021	17.632	17.64
1	0	3	4.631	4.630	19.145	19.14
1	1	2	4.285	4.288	20.707	20.70
0	0	4	4.102	4.101	21.641	21.64
1	1	4	3.178	3.179	28.051	28.04
3	0	0	2.901	2.901	30.788	30.78
0	0	6	2.735	2.736	32.712	32.70
Tetragonal Phase in Film Deposited on a Au Film $a = 10.01$ Å, $c = 18.58$ Å						
0	0	1	18.58	18.60	4.75	4.76
1	0	1	8.81	8.82	10.03	10.02
1	0	3	5.26	5.32	16.82	16.65
2	0	0	5.00	5.02	17.70	17.64
0	0	4	4.64	4.64	19.09	19.11
2	1	2	4.03	4.04	22.01	21.98
1	1	4	3.88	3.87	22.88	22.96
3	1	0	3.16	3.18	28.11	28.04
3	0	3	2.93	2.93	30.40	30.44
3	2	1	2.74	2.74	32.58	32.70

XRD studies were performed on a Rigaku D/MAX diffractometer. Electron diffraction was performed on a JEOL 200CX TEM operated at 200 kV. We have identified three different phases in our samples: fcc, hcp, and a new phase which has not been reported in the literature. The diffraction data for these three phases are listed in Table I. Figure 3 shows the powder diffraction spectra of the phases.

The reflections in the upper spectrum can be well indexed as fcc symmetry. The lattice constant $a = 14.17$ Å was deduced using

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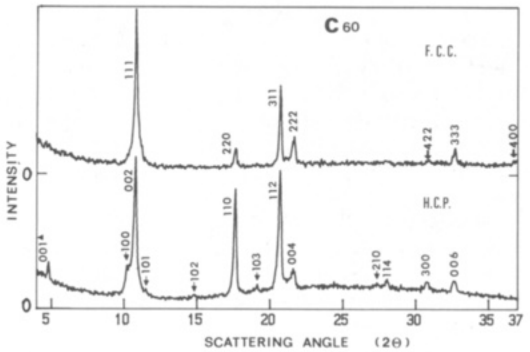

Figure 3. X-ray diffraction patterns of C_{60}/C_{70} samples grown at different conditions. Upper: grown on a Au-coated glass plate, sublimated at 400 °C for 1 h. The pattern can be indexed as fcc symmetry with missing (220), (400), (331), etc. reflections. Lower: grown on a glass plate, sublimated at 400/500 °C for 4/2 h. The hcp symmetry is clear. Most reflections can be indexed as hcp except the line at the lowest angle 4.78 (2θ) as well as some weak reflections.

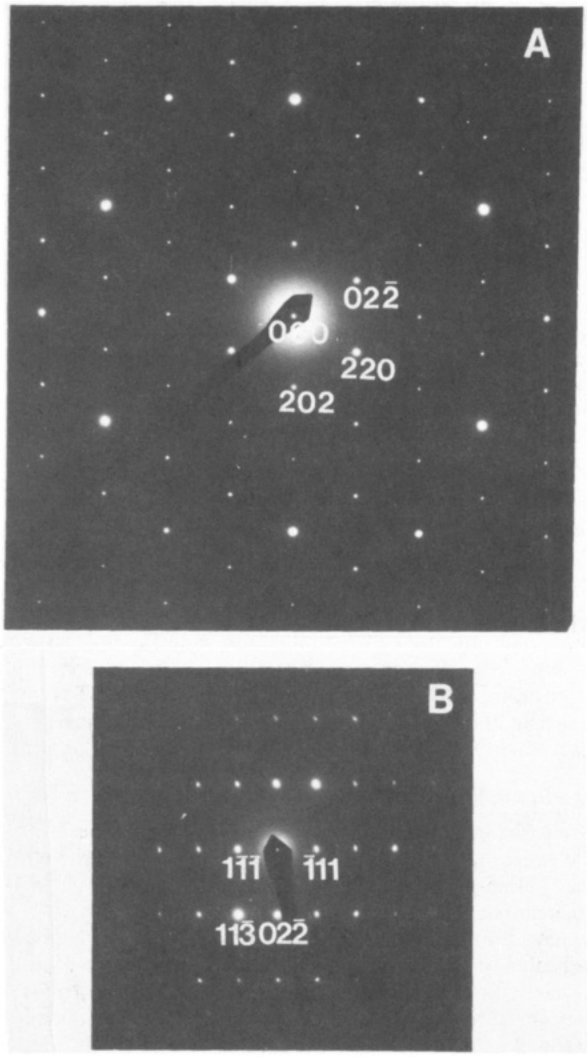

Figure 4. Electron diffraction pattern of the fcc phase. (A) [111] zone axis showing sixfold symmetry; (B) [211] zone axis. The lattice constant a is estimated as 14.2 Å from the above diffraction patterns.

the least-squares method from all reflections observed. The largest spacing, 8.148 Å, corresponds to the (111) interplanar spacing of an fcc structure. It is probable that the fcc Au substrate may play a significant role in the formation of fcc C_{60}. Electron diffraction (ED) along the [111] zone axis shown in Figure 4A has the sixfold symmetry of a fcc structure. The lattice constant as deduced from the reciprocal vectors is 14.15 Å which is consistent with XRD data of 14.17 Å. As one rotates the crystal to the orientation in Figure 4B, the diffraction pattern can be indexed as along [211] axis. This result confirms the XRD observation.

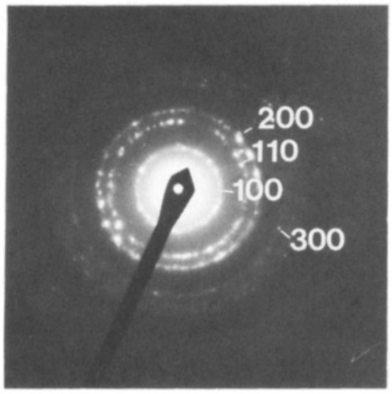

Figure 5. EDP of a polycrystal of the HCP phase. The rings of the pattern are indexed as hcp, a = 10.1 Å, c = 16.4 Å.

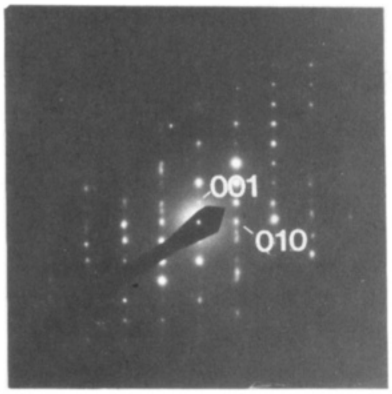

Figure 6. EDP of a new phase. The spacings of the first two perpendicular reciprocal lattice vectors are 1/10 Å and 1/18.6 Å. Combined with the XRD data, the pattern can be tentatively indexed as [100] zone of a tetragonal symmetry with a = 10.02 Å, c = 18.6 Å.

When the toluene extract was sublimated at 400/500 °C for 4/2 h on a glass plate, the sample was well crystallized as indicated by the low background in the XRD pattern (see the lower part of Figure 3). Most of the reflections have been indexed for a = 10.05 Å and c = 16.41 Å of a hcp symmetry. Both a and c are slightly larger than those reported in ref 2. Electron diffraction (Figure 5) confirmed this conclusion. From the diameters of the rings and their relative positions, one can index the pattern as [001] zone with a = 10.1 Å and c = 16.4 Å. Depending on the growth kinetics, the stacking sequence of C_{60} molecules may vary from ABABAB... of an HCP structure to ABCABC... of an fcc. From Figure 3, one can see the reflections from the crystalline planes with more or less identical spacings of both hcp and fcc, e.g. $(111)_{\mathrm{fcc}}$ and $(002)_{\mathrm{hcp}}$, $(220)_{\mathrm{fcc}}$ and $(110)_{\mathrm{hcp}}$, etc. In the worst case, the stacking sequence is disordered, showing elongated EDP or commensurate types of patterns (not shown here). From our results, the controversy over whether C_{60} forms fcc[11] or hcp[2] can be resolved.

It is interesting to note that an extra line was observed in XRD of the lower spectrum of Figure 3 with d = 18.6 Å, along with some weak reflections not expected from by hcp phase. This is an indication of the existence of a new type of fullerene phase with a larger lattice parameter. From EDP in Figure 6, the first two perpendicular reciprocal lattice vectors are measured as 1/10 and 1/18.6 Å. It must be different from the known fcc or hcp structure. We tentatively assign the new phase as tetragonal with a = 10.01 Å and c = 18.58 Å based on the calculation of both XRD and EDP. The weak reflections unindexed in HCP phase can now be explained. Since the sample was obtained by sublimating the toluene extract at a temperature higher than the C_{60} sublimation temperature for a certain period of time, it is probable that heavier fullerenes, such as C_{70} or larger, may also be sub-

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limated on the substrate and form their own unique ordered array. This speculation will require further TEM study. Recent STM studies indicated the presence of C_{70} on top of C_{60} clusters[12] and a new type of ordering of fullerenes and islands.[13] The combination of XRD, ED, and STM may provide concrete information of the internal structures of individual fullerenes and the new type of structure.

Conclusions

Buckminsterfullerenes were synthesized in gram quantities by the Krätschmer–Huffman technique. The toluene extract from soot mainly consisted of C_{60} and C_{70}. Analytical HPLC showed the content of C_{70} to be 13% in the extract and 9% in the sample sublimated at 400 °C. The results of FTIR and ^{13}C NMR provided evidence for symmetrical cage structure of C_{60}. C_{60} may form fcc or hcp crystalline structures, depending on the sublimation conditions. A new phase with tetragonal symmetry has been found, possibly formed by C_{70} or even larger fullerenes.

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Registry No. C_{60}, 99685-96-8; C_{70}, 115383-22-7; graphite, 7782-42-5.

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Scanning Tunneling Microscopy Studies of Iodide Adsorption on Au(111): Direct Observation of Adlattice Orientation

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Scanning tunneling microscopy is used in air to image iodide adlayers on Au(111) with atomic resolution over areas as large as 625 nm^2. Dosing of the Au surfaces with aqueous KI results in only one observable adsorbate structure over the iodide concentration range of 10^{-2}–10^{-5} M. The I/Au layer has a nearest- and next-nearest-neighbor spacing of 0.50 ± 0.03 and 0.88 ± 0.05 nm, respectively, consistent with a $(\sqrt{3}\times\sqrt{3})R30°$ adlattice structure on Au(111). Direct evidence for the adlayer structure is obtained from atomic resolution images of an interface between iodide-coated and bare Au(111) regions.

Introduction

We report here ex situ, atomic resolution scanning tunneling microscopy images of iodide adsorbed from aqueous solution on Au(111) films on mica. In addition, we have been able to image an interface between iodide-coated and uncoated regions, allowing direct observation of the adlattice orientation with respect to the underlying Au(111) substrate.

Adsorbed molecules and ions play an important role in many interfacial processes, especially electrochemistry. The high lateral and vertical resolution of scanning tunneling microscopy (STM) has allowed imaging of adlayers on substrates in various environments.[1] Sulfur or sulfide monolayers on metals have been atomically resolved with vacuum STM and display a variety of structural habits depending on the metal and adlayer deposition conditions.[2,3] Recent advances in STM applied to electrode surfaces demonstrate that atomic resolution adlayer images can be obtained; Yau et al. have demonstrated the capability of imaging iodine on Pt(111) in air or electrochemical environment with atomic resolution, relying on nonvacuum preparation techniques.[4,5] Such progress has given much hope to investigators applying STM to electrochemical systems.

To further both the variety of substrate and the STM resolution on that substrate, we have begun using epitaxial films of Au(111) on mica[6,7] in our electrochemical and STM endeavors. Such Au substrates are relatively inexpensive to produce in large numbers and have atomically flat areas of up to 300 × 300 nm. Several investigators have implemented Au(111)/mica in the STM study of electrochemically induced processes, such as roughening and dissolution[8,9] of Au and metal deposition.[10] In addition, Widrig et al. have recently reported in air atomic resolution STM images of *n*-alkanethiols on Au(111)/mica substrates,[11] indicating that these substrates are ideal for the STM study of adsorbates.

Experimental Section

Preparation of Adsorbate Layers. Au(111) thin films (150 nm) were prepared by thermal evaporation of Au onto air-cleaved mica.[6] High-purity Au (99.99%) was evaporated at 0.2 nm/s in a Plasmatron P-30 thin film system operating at 2 × 10^{-6} Torr vacuum. The mica (Asheville-Schoonmaker, Newport News, VA) was heated to 310 °C and held there for 30 min before deposition was carried out at that temperature. Once the substrates had cooled to approximately 100 °C, the chamber was back-filled with N_2 and the Au/mica films were either placed in 10^{-2}–10^{-5} M aqueous KI (Johnson-Matthey Grade 1, Alfa, Danvers, MA) or

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