J. Phys. Chem. 1993, 97, 8696–8700

Solar Generation of the Fullerenes

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Received: June 21, 1993

Fullerenes have been produced efficiently by direct vaporization of carbon in focused sunlight. Large-scale solar furnace implementations of this simple process may be uniquely capable of producing fullerenes and doped fullerenes in large amounts while avoiding the yield-limiting problems encountered with carbon arcs or plasmas. Evidence is presented that the worst of these problems is photochemical destruction of the fullerenes in the light from the arc. Solar furnaces can mitigate this problem both by avoiding the intense ultraviolet radiation associated with arcs and by preventing clustering of the carbon vapor until it passes into a relatively dark cluster formation and annealing zone.

Introduction

Since the original discovery in 1985 that fullerenes are produced spontaneously in laser-generated carbon vapors,[1] extensive research has been devoted to finding ways of making these species in large amounts at high yield. Triggered 5 years later by the success of Krätschmer et al.[2] in producing the first milligram amounts by resistive heating of graphite in an atmosphere of helium, the manufacture of these new nanoscale materials has now become something of a cottage industry. However, even with subsequent improvements using carbon arcs,[3] production of fullerenes has remained a highly expensive process which has resisted all attempts to scale past levels of several tens of grams per hour. This figure applies to the most abundant fullerenes, C_{60} and C_{70}. Higher fullerenes are produced by current techniques in such low amounts that they are effectively unavailable to all but a few very well funded or very determined groups. The problem is much worse with doped or otherwise modified fullerenes such as La@C_{82}, which are produced so inefficiently by carbon arc methods[4,5] that they are currently unavailable from any commercial supplier. Fullerene production has come a long way since 1985 but still not nearly far enough.

In the course of an extensive series of experiments aimed at increasing the production of both empty fullerenes and endohedrally doped metallofullerenes, we have discovered what may be the principal mechanism which prevents efficient scaling of the carbon arc technique to large rod sizes: photochemical destruction of the fullerenes by light from the arc. After considering ways this problem can be overcome in a fashion that scales well to large rod sizes, we propose that the best answer may also be the simplest: sunlight.

To understand the thinking and physical evidence which led to this conclusion, it is necessary to review in some detail the principal fullerene generation techniques as they have evolved over the past 8 years. Readers impatient to hear of the actual results of using direct sunlight may skip directly to end of the paper.

Existing Techniques

As is by now very well known, the original technique of pulsed laser vaporization of graphite in helium at room temperature that was used to discover C_{60} and the fullerenes is incapable of producing all but a microscopic amount of toluene-soluble small fullerenes. Subsequent experiments have revealed[6,7] that essentially all the carbon condensed in this fashion is actually composed of giant fullerenes, the vapor having condensed too rapidly at too low a temperature to have efficiently formed the most perfect fullerene, C_{60}. Heating the graphite target in an oven at 1200 °C was later found to dramatically improve the C_{60} yield.[7]

The resistive heating technique introduced by Krätschmer et al. was the first to produce visible amounts of fullerenes, and it also remains one of the highest yield methods yet known. Reports from most groups using some variant of this technique generally speak of yields of soluble fullerenes exceeding 20% and sometimes 30% or more of all the vaporized carbon. Unfortunately, this method turns out to be intrinsically limited to rod sizes of 3-mm o.d. or smaller. It is therefore capable of processing only small amounts of carbon and is unsuited to large-scale production of fullerenes.

The prime difficulty with evaporating carbon by resistive heating of a carbon rod is that the rod tends to become hottest in the middle. Evaporation proceeds fastest from this middle section, with the result that Ohmic heating becomes more concentrated. As a result, the center of the rod soon narrows and breaks, thereby shutting down effective operation. In addition, the temperatures required for evaporation at significant rates are so high (>3000 °C) that power loss through blackbody emission along the entire rod length becomes an economically prohibitive factor.

Krätschmer et al.[2] avoided this problem by using a technique first introduced by Bradley[8] in 1954 for production of amorphous carbon films in vacuum evaporators. Here a thin graphite rod is sharpened to a conical point and then forced with a spring so that it maintains direct Ohmic contact with a larger flat carbon electrode. Electrical current passing through the rod then dissipates most of its power in Ohmic (Joule) heating at the narrow point of contact, efficiently vaporizing the carbon at the sharpened end of the rod. As this point is increasingly blunted by the vaporization, it comes in better contact with the larger flat electrode, but only through a resistive layer of largely amorphous carbon deposited from a portion of the carbon vapor produced thus far. As long as this vapor-deposited boundary layer remains between the two electrodes in a sufficiently thick and resistive form, the electrical power continues to be dissipated just in this small zone, and carbon vaporization from the end of the thin graphite rod proceeds efficiently. Unfortunately, for graphite rods 6-mm diameter or greater, this layer does not remain sufficiently resistive and the entire length of the graphite rod soon begins to glow. Evaporation then proceeds very inefficiently from the center of the rod, quickly followed by breakage of the circuit.

It was in just such an attempt to reproduce the Krätschmer–Huffman resistive evaporation technique with 6-mm-o.d. graphite rods that the "contact-arc" method was discovered.[3] The only way of localizing the heating to the ends of graphite electrodes of this larger diameter was found to be maintaining them in a

0022-3654/93/2097-8696$04.00/0

sort of near contact such that "the bulk of the power was dissipated in the arc and not in Ohmic heating of the rod".[3]

In fact, this turns out to be a distinctly new method which vaporizes the carbon electrodes very efficiently. In later work[7] it was determined that there is no necessity of actually maintaining any sort of contact between the rods, and in most current implementations a narrow gap generally exists, but the term "contact arc" has remained in the literature. The key feature of a contact arc as we use the term in this paper is that the rods are so close to each other compared to their diameters that the power dissipated in the plasma is not lost. Instead, the radiative power from the thin region of plasma between the two electrodes is mostly absorbed on the electrode surfaces themselves, producing a very power-efficient, localized evaporation of the electrode tips.

The yield of toluene-soluble fullerenes from such a contact arc using 6-mm-o.d. graphite rods was found to be about 15%. Because of the much more rapid vaporization of carbon and larger electrode sizes permitted, this method rapidly became the method of choice for commercial fullerene producers worldwide. This remains true in spite of the fact that the yield from this technique with 6-mm-o.d. rod sizes is generally found to be barely half that of the Krätschmer–Huffman resistive heating technique with 3-mm rods.

Extensive experiments in this laboratory at Rice University in early 1991 extended the contact arc method to 12.5-mm-o.d. rods.[9] Although the method at this scale was found to be successful, the yield of toluene-soluble fullerenes was found to be reduced to the range of 4–7%—roughly half that routinely obtainable with 6-mm-o.d. rods. This linear reduction of fullerene yield with rod diameter has never been adequately explained. A wide variety of designs have been attempted to improve the yield, including fast gas flow to quickly remove the fullerenes from the vicinity of the arc, and both preheater and postheater zones to either keep the gas hot enough to form fullerenes efficiently or cool it to minimize destruction of the fullerenes by reaction with other carbon species. Still the yield remained low, and this problem of low yield at large sizes is currently the single most controlling factor in the cost and availability of fullerenes worldwide. The contact-arc method simply does not scale well to large, industrially-relevant sizes of graphite rods.

Thus far, no other methods of fullerene production are known (at least to the authors) that are economically competitive with the contact arc. The extensive recent work of Howard et al.[10] has demonstrated that the fraction of C_{60} and C_{70} in soot produced in optimized sooting flames can be made impressively large, but the overall yield of fullerenes remains prohibitively low. Fullerenes have been produced by vaporization of carbon in an radiofrequency plasma torch,[11] but the radiative power loss from such a device makes it extremely inefficient, and the toluene-soluble fullerene yield is no better than that of the contact arc. Peters and Jansen have demonstrated that fullerenes can be produced by direct inductive heating of a carbon sample held in on a boron nitride support.[12] This technique is effectively a type of resistive heating which ought to be applicable to much larger sizes than the original Krätschmer–Huffman method, but again the radiative power loss and yield problems currently keep it from competing effectively with the contact arc.

Acute Contact Arcs and Photochemistry

Insight into what causes the reduction in yield of the contact arc method as the rod size increases has come from an unexpected direction. In the course of trying to make the yield better, we have found instead an amazingly effective way of making it worse, simply by bringing the rods together at an acute angle.

These experiments were guided by previous successes with laser vaporization. In our laboratory the best yield of fullerenes and metallofullerenes has been obtained by pulsed laser vaporization of appropriate carbon targets mounted in an quartz tube furnace heated to 1200 °C.[4] Here the key advantage is that there is a temporal separation between the vaporization event and the subsequent condensation. The short duration of the pulsed Nd:YAG laser (5–10 ns) naturally separates the extremely high-temperature laser-plasma episode necessary for vaporization from the subsequent cluster formation kinetics. The optimum temperature for fullerene formation is then set by the furnace. At 1200 °C the fullerenes remain in the vapor phase and are swept away from the laser vaporization region before the next laser pulse, moving down the quartz tube until they are deposited on cool surfaces at the end of the furnace. Fullerene yields of over 40% of the vaporized carbon are often achieved with this method, and doped fullerenes such as La@C_{60} and U@C_{28} are readily produced as well.[4,12] Unfortunately, while laser vaporization in an oven is efficient, it is not suited to large-scale production. Laser photons are simply too expensive.

It was while attempting to adapt carbon arc methods into quartz tube furnaces that we accidentally discovered what we now believe to be the principal factor limiting fullerene yields from carbon arcs in general. Figure 1 shows a schematic of the apparatus we constructed. In order to feed the carbon rods into the arcing zone within the tube furnace, we arranged to have them approach each other at a 30° angle. While earlier designs with 6-mm-o.d. carbon rods in the furnace in the normal straight-on contact arc mode had readily obtained the 15% yields normally expected, this design with rods meeting at 30° was stunningly bad. The fullerene yield was reduced to below 3%. This low yield remained poor regardless of adjustment of gas flow rates, oven temperature, and arcing current.

Compared with other designs we have tried, there is only one principal aspect that is different about this acute contact arc: ultraviolet radiation. Because of the acute angle, the intense UV radiation from the central portion of the arc plasma ($T \sim 10\,000$ K) is now fully exposed to the condensing carbon clusters as they flow downstream in the quartz tube. Considering the evidence recently found for photoinduced polymerization of fullerenes,[14–17] we now suspect that photochemical destruction of fullerenes may be the principal factor controlling yield in fullerene generators.

While the newly formed fullerenes are moving away from the region around the arc, they are exposed to intense light flux. Absorption of light efficiently produces an excited triplet state (T_1) which lives for a few microseconds[18] before the molecule relaxes back down to the ground electronic state, S_0.

$$C_{60}(S_0) + h\nu \rightarrow C_{60}{}^*(T_1)$$

Fullerenes such as C_{60} absorb at all wavelengths below about 7000 Å, but the absorption cross section in the ultraviolet below 3500 Å is 10–100 times stronger than in the visible. Ultraviolet light is therefore particularly effective, even though rapid internal conversion and intersystem crossing will produce the T_1 state regardless of the photon energy.

While the fullerene is in this T_1 state, it is an open-shell species, far more susceptible to reaction with other carbon species, C_x, than it was in the closed-shell S_0 state. The result of most such reactions will be to produce a nonvaporizable, insoluble product.

$$C_{60}{}^*(T_1) + C_x \rightarrow \text{insoluble carbon}$$

Since the rate of this bimolecular photochemistry increases linearly with photon flux and C_x concentration, it is a particularly significant problem within a few rod diameters of the electrode tips in the contact arc method. As the rod diameter is increased, this photochemically dangerous region becomes larger in direct proportion to the rod size, but the rate of migration of the fullerenes through this zone remains roughly constant. Therefore, the yield of fullerenes which make it through this zone without reacting will decrease linearly with rod diameter.

The central problem of forming fullerenes from a carbon vapor is that one must vaporize carbon at temperatures of over 3000

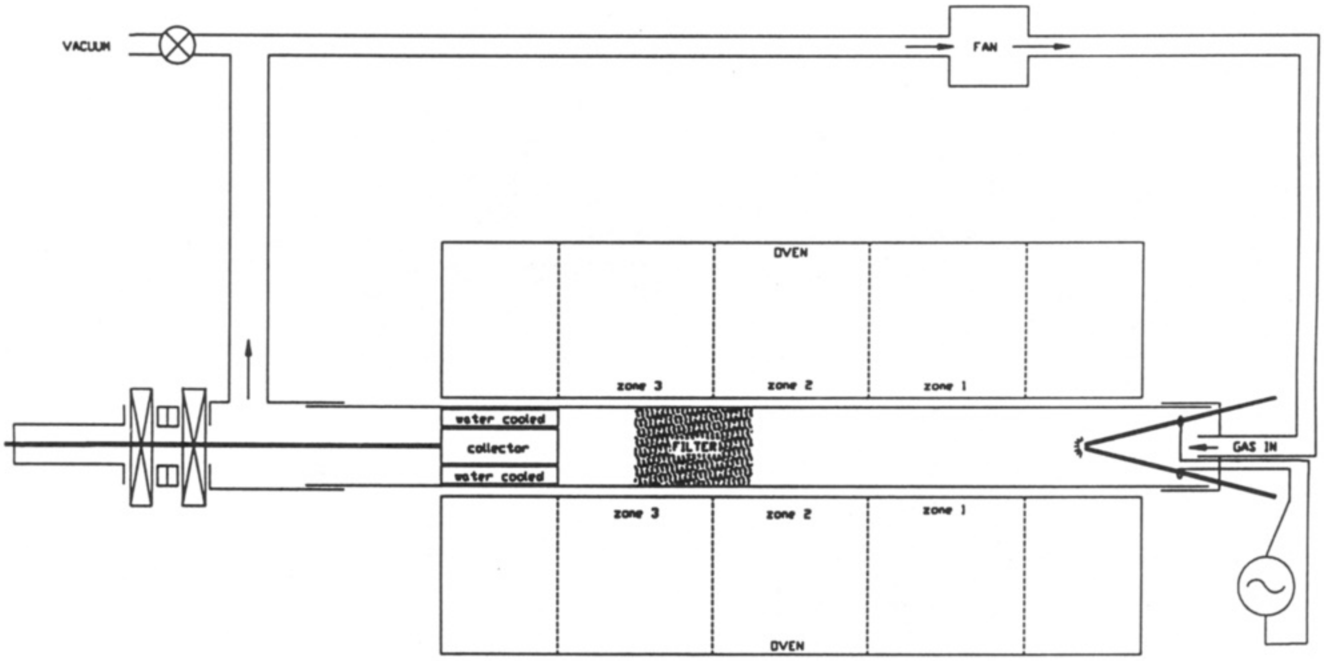

Figure 1. Schematic of carbon arc/oven apparatus having 30° angle between the carbon rod electrode.

°C to achieve adequate rates. At such temperatures blackbody emission is highly intense. With very small carbon rods the fullerenes are exposed to this radiation only briefly, and if the rods are heated resistively there is not much ultraviolet radiation flux. For larger-diameter carbon rods one must use an arc to localize the heating to the tips of the rods. Now the photochemical destruction mechanism is aggravated by the UV radiation from the 10 000 K plasma at the core of the arc. If the two electrodes are directly opposed to each other and the gap is kept much smaller than the rod diameters, most of this ultraviolet light is blocked. Even so, as the graphite rod diameters increase, it is progressively less likely that the fullerenes drift away from the formation zone without reaction.

In a carbon arc when the gap between the two rods is increased, more ultraviolet light escapes but the rate of carbon evaporation from the electrode tips also decreases sharply, and there is only a small decrease in fullerene yield.[7] However, if the gap is kept small but the angle between the rods is made acute, the rate of vaporization remains very high and both the ultraviolet light flux and the concentration of reactive, C_x, species are very high. The result is the dramatic reduction in fullerene yield observed for the acute contact arc.

The pulse laser vaporization in an oven method avoids this photochemistry problem by fortuitous timing. During the laser pulse a super-hot plasma is generated with copious UV production, but by the time the fullerenes begin to self-assemble from the vapor, the laser pulse is over and the hot plasma has recombined. If the gas flow rate is sufficient, the fullerenes produced by pulse *n* are far down the quartz tube in a region out of view from the laser target area before pulse *n* + 1 arrives. Photochemistry is simply not a factor with pulsed laser vaporization. But it will be with continuous lasers or with *any* method of continuously vaporizing carbon.

The chief problem for large-scale production of fullerenes therefore appears to be how one can minimize photochemical destruction of the fullerenes emerging from a vaporization region that is always hot and—more problematically—always BRIGHT.

A Solar Solution

In order to minimize the photochemistry, it appears necessary to transport the carbon vapor into a relatively dark zone before the fullerenes have begun to form. Furthermore, it will be helpful to allow the carbon vapor to expand so that the concentration of reactive C_x species is so low that it is very unlikely that a fullerene excited to the T_1 state will suffer a reactive collision within its lifetime. This expansion will happen naturally as the carbon vapor is drawn away from the vaporization source by the inert carrier gas, if somehow the condensation process can be postponed. But the clustering rate of carbon is the highest of any element in the periodic table. Large clusters of carbon are found in vapor at equilibrium with solid graphite even at 3000 °C.[19] To minimize photochemical destruction of the fullerene clusters, we must first keep carbon from clustering until we are ready. But, how does one keep carbon from clustering?

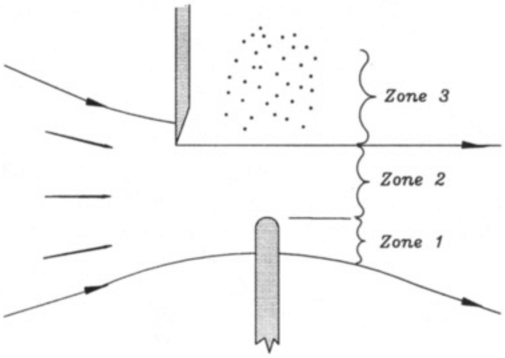

Figure 2. Conceptual sketch of a solar furnace designed to produce fullerenes. Carbon is vaporized by solar heating in zone 1, maintained as a vapor in the intense solar flux of zone 2, and then permitted to condense in relative darkness in the shadowed zone 3 where the carrier gas temperature is maintained high enough to allow the clusters to anneal as they grow to become fullerenes.

Ironically, the answer to how to minimize cluster photochemistry may involve more light. Imagine simply overwhelming the clustering by photolysis (and concomitant thermolysis) induced by intense sunlight. Figure 2 shows a conceptual sketch of a fullerene generator which utilizes focused sunlight both to vaporize a carbon target (in zone 1 as labeled in the Figure 3) and to maintain the carbon as an essentially atomic vapor (through zone 2), until it passes into the shadow where clustering is finally permitted to occur (zone 3). There are many aspects of such a design that are appealing and many that require detailed thought, experimentation, and analysis. For example, what is the solar flux necessary to effectively bleach away the clusters in zone 2?

These detailed considerations are complicated and well beyond the scope of this initial paper. However, realizing that the solar

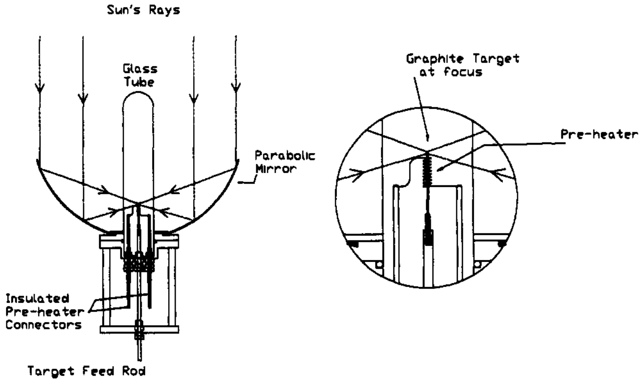

Figure 3. Schematic of "Solar1" fullerene generator. In operation the assembly shown in this figure is mounted on an equitorial telescope mount with motorized drive so that the parabolic mirror continually tracks the sun.

flux at the surface of the earth is sufficient with readily obtainable collection optics[20] to attain well over 1500 W/cm^2, which is equivalent to the rate of emission from a perfect blackbody at 4000 K where the vapor pressure of carbon is nearly 1 atm, we decided the concept of Figure 2 was reasonable, and a simple first experiment was in order.

Solar1: A Small-Scale Demonstration

As an initial demonstration that fullerenes can in fact be produced by direct sunlight, we assembled the apparatus shown schematically in Figure 3. Sunlight was collected by the parabolic mirror (Melles Griot, electroformed nickel with rhodium finish, 35.6-cm o.d., 6-cm focal length) and focused onto the tip of a 0.4-mm-diameter graphite rod (Poco Graphite AXM-5Q). As shown in the figure, this rod was mounted inside a 58-mm-i.d., 2-mm-wall, 30-cm-long Pyrex tube and arranged such that it could be translated along the optic axis of the paraboloid. To minimize the extent of conductive heat loss and to help anneal the carbon clusters as they grew from the vapor, the graphite rod was enclosed by a helical tungsten preheater (8 turns on 3-mm-diameter cylinder, 10-mm length, 0.25-mm-diameter tungsten wire) mounted 3 mm below the tip of the target rod as shown in the figure. In practice, the system was evacuated to <30 mTorr and degassed with the preheater for several hours to remove absorbed gases from the graphite rod, purged, and then back-filled with 50 Torr of argon and sealed off. The apparatus was then mounted on the yoke of an 8-in. equitorial telescope mount (Celestron Pacific) and adjusted so that the sunlight was focused directly on the tip of the graphite target. With careful alignment of the equitorial axis to the earth's rotation, the motorized telescope mount was easily able to track the sun for several hours without need for further adjustment.

This "Solar1" fullerene generation apparatus was operated for 3 h (11 A.M.–2 P.M.) on a day when the direct solar flux at the test site (at 1400-m elevation in the Franklin Mountains near El Paso, TX) was measured to be 800–900 W/m^2. During operation the central axis of the evaporator made an angle of 10–25° from vertical while tracking the sun. As a result, the argon gas heated by the tungsten preheater was efficiently carried up over the solar-irradiated carbon tip by convection, and the condensing carbon vapor was quickly swept out of the intense sunlight, cooled in the upper regions of the pyrex tube, and subsequently deposited on the upper walls.

The fullerene content of the soot deposits collected on the inside of the Pyrex tube was analyzed by extraction with toluene followed by detection of the fullerene content by high-pressure liquid chromatography, HPLC (Waters 510 pump, 996 photodiode array), on a reversed phase column (Waters Nova-pak C-18, 3.9 × 300 mm) with toluene/methanol (50:50 at 2 mL/min) as the eluant. With the photodiode array fullerenes were identified by their characteristic UV/vis spectra. Fullerene yields in the solar-vaporized carbon extract were estimated by comparison with calibrated standards at 306 nm. The toluene extract had the wine-red color characteristic of high-yield fullerene soots. Over the 3-h experiment 5 mg of carbon was evaporated from the target. Most of this was found to dissolve in toluene at room temperature. Figure 4 shows the HPLC analysis of this soluble fraction, demonstrating that its fullerene content was predominantly C_{60} and C_{70}.

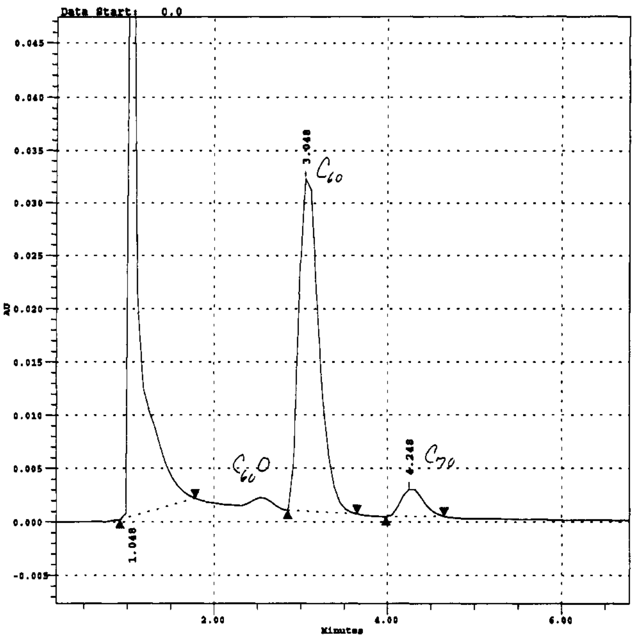

Figure 4. HPLC analysis of the toluene soluble extract produced by solar vaporization of a graphitic carbon rod in the Solar1 apparatus of Figure 3.

While this result is impressive, a much larger scale test will be necessary before it is clear whether the advantages of solar furnace generation of the fullerenes are as substantial as envisioned above.[21] In particular, there is no way with this small Solar1 apparatus to verify that focused sunlight can be used effectively to prevent condensation of the carbon vapor until it passes into a dark cluster formation and annealing zone. That question among others such as how to incorporate dopants and how to collect large amounts of fullerene soot while keeping the input windows clean will have to wait for ... Solar2.

Acknowledgment. The authors are indebted to W. Herndon and the Department of Chemistry at University of Texas at El Paso for help in carrying out these experiments, to R. Dufour of the Rice University Space Physics and Astronomy Department for encouragement and loan of the telescope mounts used in this experiment, and to R. Cruse of Skywatcher Inc., Conroe, TX, for advice and loan of parabolic reflectors. This research was funded for production and study of metal clusters in fullerenes by the U.S. Department of Energy, Office Basic Energy Research, Division of Chemical Sciences, for boron-doped fullerenes by the Office of Naval Research, and for pure and metal-doped fullerenes by the National Science Foundation, the Robert A. Welch Foundation, and the Texas Advanced Technology Program.

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(21) While we were preparing this manuscript, we learned that A. Lewandowski and co-workers at the National Renewable Energy Laboratory (NREL) High Flux Solar Furnace in Golden, CO, had independently produced fullerenes by solar evaporation of carbon within the past week. See: Fields, C. L.; Pitts, J. R.; Hale, M. J.; Bingham, C.; Lewandowski, A.; King, D. E. *J. Phys. Chem.*, following paper in this issue.