

Spheres of Spheres of Azafullerene in the Solid State

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The isolation of fullerenes from arc-processed graphite has stimulated considerable interest in the formation and properties of other curved forms of carbon, including nanotubes¹ and buckyonions.² Such interest is directed both toward understanding the fundamental process of carbon nucleation and exploring the enhanced materials properties of such hierarchical structures. The introduction of heteroatoms into fullerene cages or graphitic networks is expected to fundamentally affect their structural and electronic properties, and for this reason it has been pursued vigorously in recent years. The chemical synthesis and purification in bulk quantities of the nitrogen-substituted fullerene, (C₅₉N)₂,³ afford an excellent opportunity to explore the properties of the condensed phases of heterofullerenes and their chemical derivatives. In this paper we report the first study of the structure and morphology of azafullerene in the solid state by electron microscopy and X-ray diffraction. The material shows an unprecedented self-organization among molecular fullerene solids on the mesoscopic length scale, as it is found to self-assemble, principally into large (>1 μm), poorly crystalline, hollow spherical particles which coexist with a minority hexagonal crystalline phase. Similar spherical morphology is also shown by an oxygenated derivative of the azafullerene (C₅₉N)₂O, which, however, shows a poorly ordered, cubic stacking sequence. Unlike the curling of extended graphitic networks, which occurs only under intense electron-beam irradiation, the mesoscopic spherical structures of azafullerene can be synthesized chemically under mild conditions.

The azafullerene dimer sample was prepared from a "holey bucky" as described previously,³ and was purified by HPLC on a Cosmosil "Buckyprep" column using toluene as eluent. Solid (C₅₉N)₂ was obtained from a solution in *o*-dichlorobenzene (ODCB), which was evaporated rapidly to dryness in a rotary evaporator. Heating the azafullerene dimer in ODCB in the presence of oxygen produced C₁₁₈N₂O, which was obtained as a solid in the same manner. Mass spectrometry and NMR showed it to be C₅₉N–C₅₉NO.⁴ The single-phase solid (C₅₉N)₂ and (C₅₉N)₂O samples were heated in vacuo at

140 °C overnight and kept under dry, anaerobic conditions before the performance of further measurements. Samples for electron microscopy were prepared by sonication in acetone and deposition on a holey carbon grid and were studied by both transmission (TEM) with JEOL 2010 and JEOL 2000FX microscopes, and scanning electron microscopy (SEM) with a JEOL 6300FEG microscope. X-ray powder diffraction measurements were made with a conventional X-ray source ($\lambda = 1.5406$ Å) on a Philips PW3040 ((C₅₉N)₂O, flat plate geometry; 2θ range, 5–40°; 2θ step, 0.02°; count time, 10 s) and a Siemens D5000 ((C₅₉N)₂, capillary mode; 2θ range, 5–40°; 2θ step, 0.02°; count time, 20 s) diffractometer.

The spherical morphology of the azafullerene sample, (C₅₉N)₂ is clearly evident in the scanning electron microscopy (SEM) picture (Figure 1a), which shows representative large particles with diameters in the range ~5–10 μm. Detailed insight into the constitution of the spherical shells is obtained by careful examination of a smaller particle (diameter ~2 μm) which is attached to the surface of one of the larger spheres (Figure 1b). This shows that the particles are made up of many microcrystals, while a hole of ~0.2 μm diameter reveals their hollow nature. Such holes are apparent in all of the particles that we have examined and may represent the signature of the escape of the solvent molecules at the final stages of particle formation. A similar picture emerges when the sample is viewed by transmission electron microscopy (TEM). The majority of the sample is in the form of essentially perfect spherical particles—Figure 2 shows a typical situation with many such particles of diameter ~1 μm clustering together into quasi-linear assemblies through interconnecting walls—but a smaller component is present as crystalline fragments. The oxygenated azafullerene sample, (C₅₉N)₂O appears to contain only the spherical particles (again with holes). Both materials are quite sensitive to electron irradiation, especially the pristine azafullerene, and show pronounced charging effects.

We attempted to obtain electron diffraction patterns from both the spherical particles and the small fragments. We were unable to find crystalline regions in any of the spherical particles for (C₅₉N)₂ but obtained diffraction patterns consisting of broad concentric rings, signifying poorly ordered, microcrystalline structures in both cases (Figure 3). On the other hand, the small fragments evident in the TEM images of the pristine azafullerene sample (Figure 2) gave reasonable diffraction patterns, consistent with crystalline character. However, the sensitivity to electron irradiation and the specimen drift during the experiments make recording of the electron diffraction patterns difficult. For the oxygenated azafullerene sample, the diffraction patterns again consisted of well-developed, broad concentric rings, consistent with a poorly crystalline nature and/or a distribution of lattice spacings (similar to that shown in Figure 3).

With this background in mind, it was not surprising to find that the powder X-ray diffraction profile of the azafullerene sample, after degassing at 140 °C under vacuum, was dominated by a large background contribution reflecting its poorly crystalline nature. However, superposed on this we find a well-developed series of Bragg lines (Figure 4a), which presumably arise from

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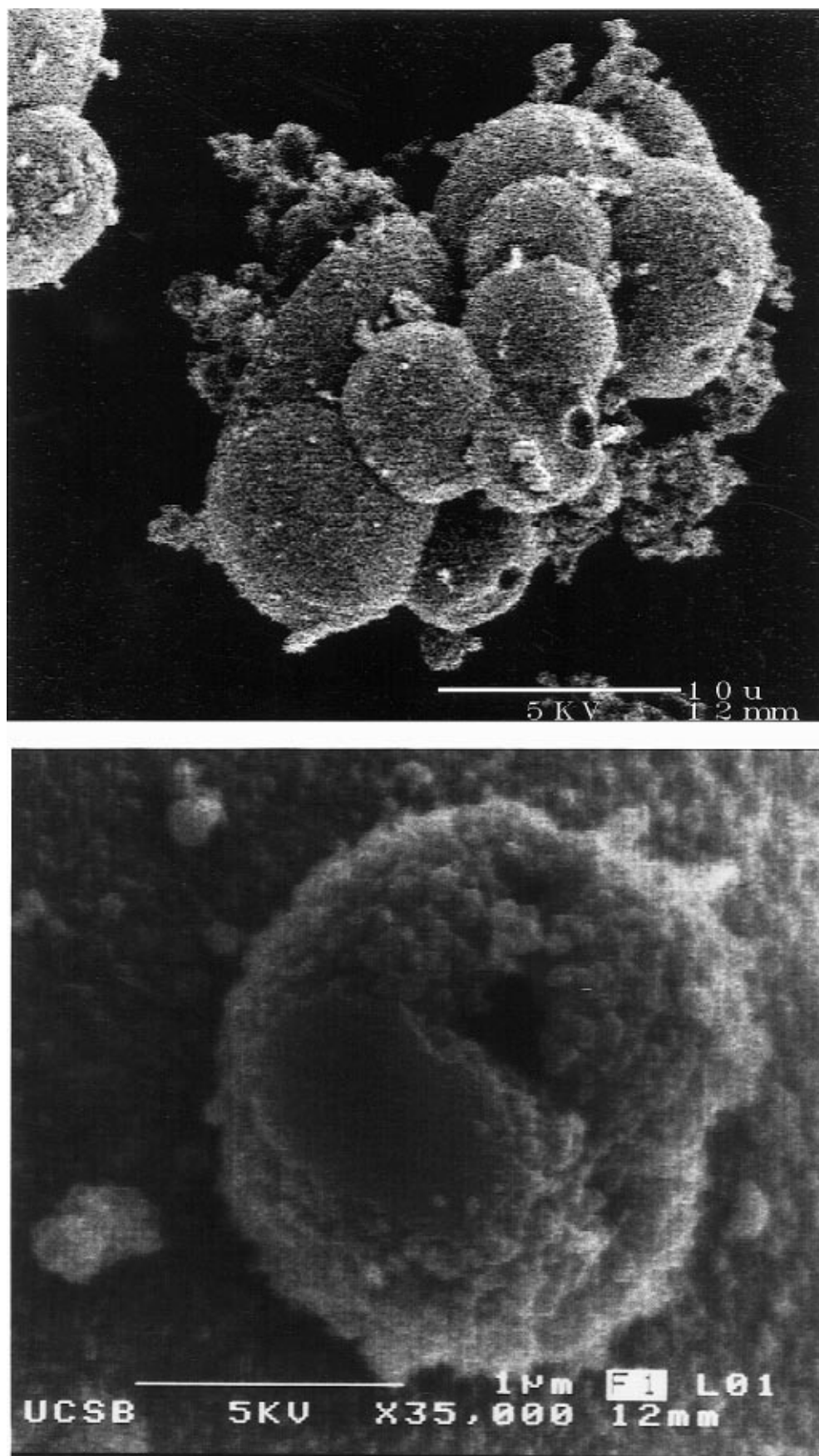


Figure 1. Representative SEM images of azafullerene spherical particles. (a, top) Aggregates of large particles with diameters in the range of $\sim 5\text{--}10\ \mu\text{m}$ diameter are shown under magnification. (b, bottom) Expanded view of a smaller particle attached on the surface of a particle in (a); its hollow nature is clearly discernible in this image.

the minority crystalline fragments observed by electron microscopy. The X-ray powder pattern at ambient

temperature indexes readily on a hexagonal lattice (space group $P6_3/mmc$ or one of its subgroups) with $a =$

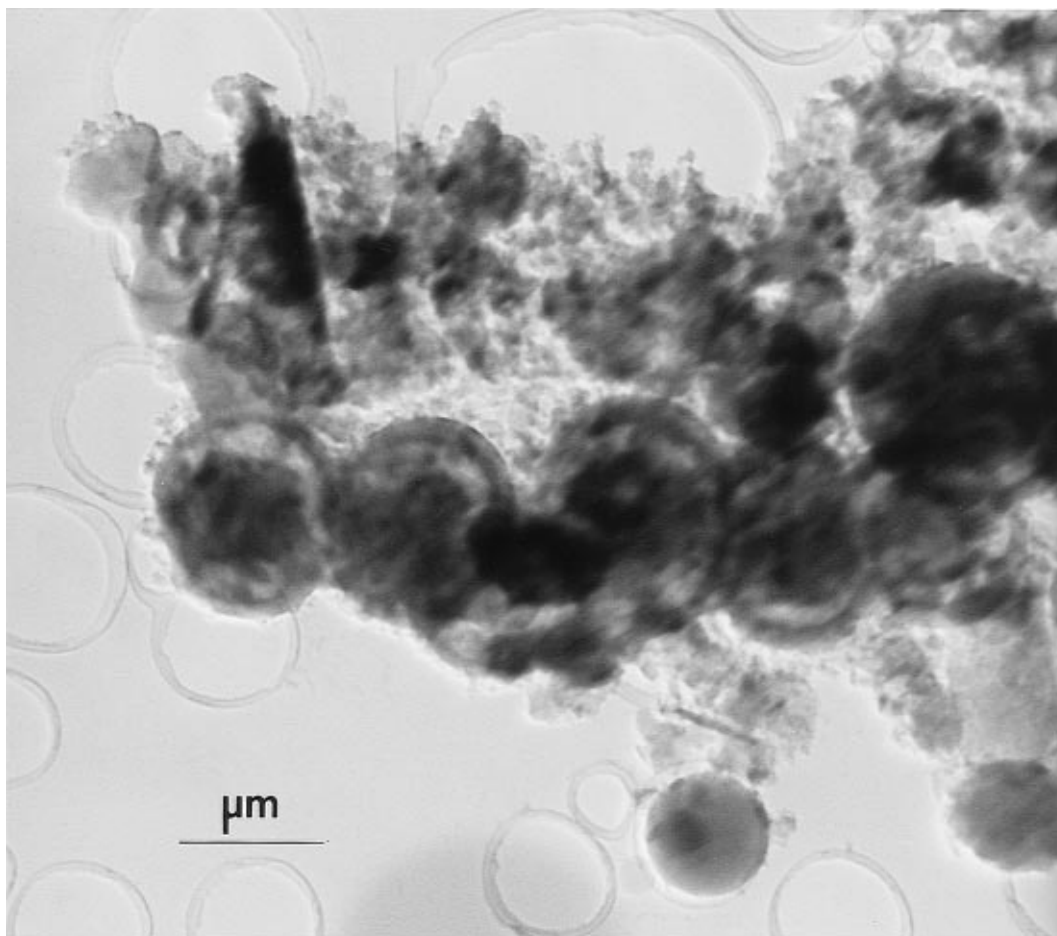


Figure 2. Representative TEM image of azafullerene solid showing a large collection of poorly ordered spherical particles together with crystalline microfragments.

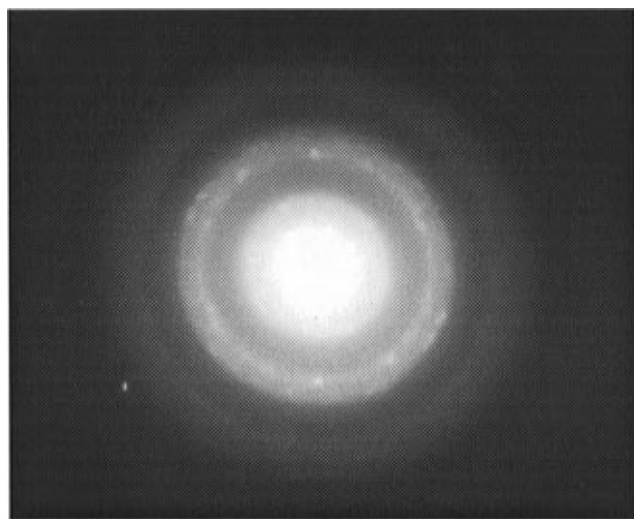


Figure 3. Electron diffraction patterns arising from the poorly crystalline spherical particles of the $(C_{59}N)_2$ solid.

9.97 Å and $c = 16.18$ Å. What is noteworthy is that the c/a ratio is equal to 1.623, only marginally smaller than the ideal ratio of 1.633 expected in the case of spheres packed in a hexagonal close-packed (hcp) lattice. Indeed C_{60} has been also reported to exist in a hcp form with lattice dimensions $a = 9.98$ Å and $c = 16.30$ Å ($c/a = 1.633$)⁵ besides the more stable face-centered-cubic structure in which the interball distance is 10.02 Å. The stability of the hcp form in both C_{60} and $(C_{59}N)_2$ is evidently driven by the presence of residual solvent

molecules in the lattice. Monomeric azafullerene, $C_{59}N$, is expected to be either a cationic or an open-shell molecule because a trivalent atom replaces a tetravalent atom of C_{60} . As isolated, it is not ionic and there is only a weak electron spin resonance signal, indicating the presence of one unpaired electron for roughly every 250 molecules; this result is consistent with the molecular dimerization.³ However, it is remarkable that the results described above reveal that the position of the X-ray powder diffraction lines of the minority component of the solid as well as the TEM diffraction spots are in accord with an almost ideal hcp lattice. However, the broad peaks resulting from the poor crystallinity of the $(C_{59}N)_2$ solid may obscure additional subtle details arising from dimerization of the azafullerene. Further work is currently underway to unravel this complex issue.⁶⁻⁸ The X-ray diffraction pattern of the oxygenated azafullerene, $(C_{59}N)_2O$, is also consistent with the TEM measurements in that a sample with extremely

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(6) Azafullerene, $(C_{59}N)_2$, recrystallized from CS_2 solution retains its ambient pressure hexagonal structure to 200 kbar,⁷ while solvent-free sublimed $(C_{59}N)_2$ adopts at ambient temperature and pressure a monoclinic structure comprised of dimeric $(C_{59}N)_2$ units.⁸

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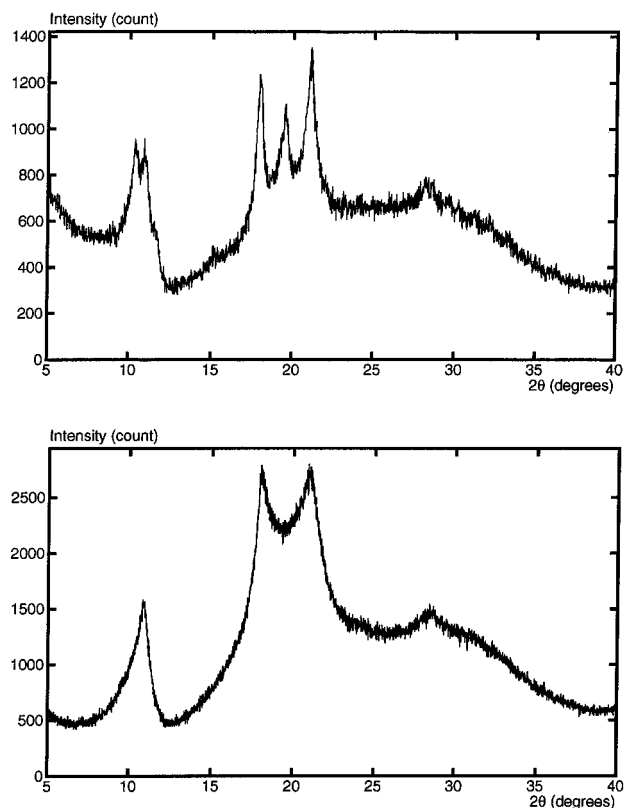


Figure 4. Observed laboratory X-ray diffraction profile of (a, top) $(C_{59}N)_2$ and (b, bottom) $(C_{59}N)_2O$ solid at ambient temperature ($\lambda = 1.5406 \text{ \AA}$). The observed reflections index in (a) on a hexagonal unit cell with $a = 9.97 \text{ \AA}$ and $c = 16.18 \text{ \AA}$ and in (b) on a pseudocubic unit cell with $a = 13.9 \text{ \AA}$.

poor crystallinity is evident. Four very broad Bragg peaks are observed, superimposed on a background of amorphous origin (Figure 4b). The reflections index on

a pseudocubic unit cell with size 13.9 \AA , corresponding to a reduced interball spacing of $\sim 9.8 \text{ \AA}$ with respect to both the pristine C_{60} and azafullerene solids.

The origin of the spherical, hollow particle morphology, not to be confused with that of soot particles, is of great interest, as, to the best of our knowledge, it has no precedent among other all-carbon molecular fullerene solids. One can speculate that this arises from the self-assembly of smaller spherical particles as a result of rapid solvent evaporation, analogous to spherical particles resulting in spray-drying procedures or from flash-evaporation of foams.⁹ It is clearly remarkable that the small azafullerene balls form a hierarchical mesoscopic structure that is, itself, spherical, and even more tantalizing to contemplate the possibility that the holey nature of the balls is a consequence of the aspherical nature of the polar molecule, itself. The ability to prepare novel macroscopic forms of fullerene-based solids could lead to important materials applications, based on the porous nature of the present solid. Finally, equally exciting is the discovery that azafullerene gives rise to a series of alkali-metal intercalates¹⁰ with electronic properties potentially as rich as those of their fullerene antecedents.

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