SYNTHESIS OF ORGANIC HOLLOW GLOBULES BASED ON SINGULAR PHENOMENA OF NANOPARTICLES.
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Introduction: It has been recognized that carbonaceous chondrites may have supplied significant amounts of organics to the primordial Earth and contributed to the evolution of terrestrial life. Indeed, flyby missions to Comet P/Halley in 1986 showed that a significant amount of the mass of cometary dust is actually organics [1]. Although carbonaceous meteorites contain many kinds of amino acids, the dominant form of organics in meteorites is insoluble complex organic matter. Recently, it has been reported the existence of enigmatic organic grains in carbonaceous chondrites [2-5]. The organic grains, called organic globules, are a construction of shells with a cavity in their center and show via isotopic anomalies of nitrogen and hydrogen, that they are extraterrestrial products [3]. Then, a question "where and how were the primitive organic materials produced?" is fundamental to understand the evolutional history of carbon in space. Many kinds of organic molecules have been detected in interstellar space, in particular in molecular clouds, by astronomical observation. However, since insoluble organic matters usually do not detect by observation, to know the origin is very difficult.

At the time stars evolved, when the initial supply of organic material was introduced into space, astronomers have observed extinction features attributed to polycyclic aromatic hydrocarbons (PAHs), in the infrared region in many types of object [e.g., 6]. Since these features have been observed widely, PAHs must be abundant and ubiquitous in space. Here, we report a formation process of organic globules from PAHs based on laboratory synthesis experiment using "*singular phenomena of nanometer-sized particles*".

Singular Phenomena of Nanoparticles: It has been shown that nanometer-sized particles show unexpected singular phenomena. For example, the melting point of silver decreases from 1233 to 667 K as particle size decreases from macroscopic scale to 15 nm in diameter [7]. In addition, the diffusion coefficient changes to 8.3×10^{-19} from 2.4×10^{-28} ($m^2\cdot s^{-1}$) in the bulk material at 300 K (Cu atoms in Au nanoparticles) [8]. These phenomena induce an unexpected growth process of nanoparticles, which fused together and thus make a larger particle. When two different kinds of materials are mixed, an alloy particle is produced immediately. This is a characteristic growth process of nanoparticles. We believe significant phenomena of nanoparticles are important to elucidate the evolutional processes of materials in space. Present result is also result of peculiarity in nano-region, i.e., prodigious diffusion of vacancies produces the hollow center.

Experimental Methods: Globules were synthesized using benzene or anthracene, a PAH with three aromatic rings, introduced into He plasma generated between two stainless-steel electrode plates. He gas was introduced at a flow rate of 1000 sccm and maintained at a pressure of 10 Torr. Radio-frequency (frequency 13.56 MHz, output 200 W) discharge was used. The electron temperature and electron density are defined empirically as 10^4 K and 10^8–10^{10} cm^{-3}, respectively. When the benzene gas was introduced into the plasma field, the emission color of the plasma changed from pink to blue. During the experiment, the total gas pressure was maintained at 20 Torr. At the end of the experiment, brownish to yellowish or white deposits were visible on both electrodes. The deposited materials were observed using a JEOL 3200FS with a 300-kV electron beam.

For the anthracene experiments, this compound was introduced into the plasma field by evaporation of commercial anthracene powder charged in a tantalum heating boat, positioned just below the bottom center of the electrodes. Following a convection current of He gas at 20 Torr generated by the tantalum boat, anthracene gas was carried into the He plasma field.

Results: Figure 1 shows typical transmission electron microscope (TEM) image of synthesized organic grains produced from benzene. The high-resolution TEM

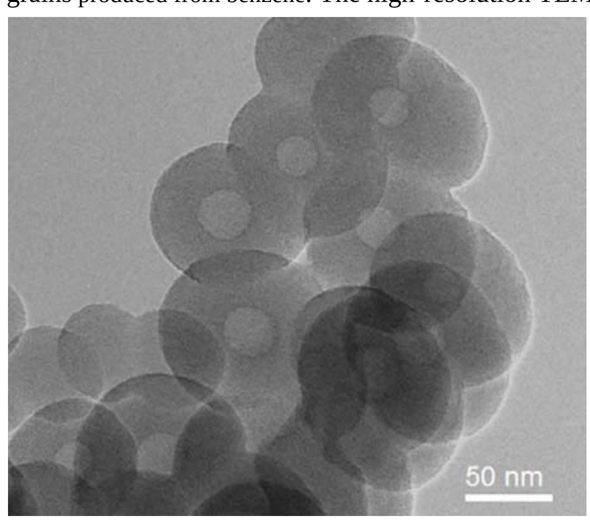

Figure 1. TEM image of laboratory organic globules with hollow center.

image and electron diffraction pattern indicated that the organic grains have a hollow center and an amorphous structure similar to natural globules.

In the case of anthracene, the same amorphous carbon particles were formed as expected. These experiments imply a trend whereby aromatic molecules are altered to amorphous carbon in a plasma field, in contrast to the formation of graphitic carbon from aliphatic molecules. We found globules were not produced from anthracene grains that had been deposited previously on the electrode plates and therefore must have been produced inside the plasma field. The spherical shape of the globules also suggested the globules were produced by the deposition of carbonaceous species in the plasma, rather than after condensation on the electrodes.

Formation mechanism of the hollow: Since the grains were irradiated by energetic plasma particles, primarily protons, they were altered markedly to form hydrogenated amorphous carbon. Vacancies can be formed by either electronic excitation and/or possibly by irradiation of protons [9]. There are numerous electrons and protons in experimental plasma, with energetic electrons causing elementary effects such as inner-shell, valence and plasmon excitations, while protons have the ability to knock carbon atoms directly out of the aggregate. Bonds are broken and the excess energy accumulated during relaxation converted directly into kinetic energy. As a result, excited carbon atoms may be displaced from the equilibrium to form vacancies [10]. This kind of effect occurs most efficiently with nanometer-sized particles. Although vacancies can be formed anywhere in the globules, vacancies at or near the surface should more easily vanish due to lattice softening and recombination with displaced carbon atoms from the interior. In addition, mobile carbon atoms can be segregated at the surface of the globules. On the other hand, interior vacancies can form clusters and grown into a void in order to minimize the surface area of defective sites like negative crystals.

This cavity formation mechanism must be size dependent, as all the vacancies will escape if the grain size is smaller than the size occurring at the surface. Indeed, only 2% of the laboratory globules with a diameter <30 nm had a hollow core, whereas ~50% of those with diameters >30 nm were hollow. In comparison, natural globules <100 nm diameter are not hollow.

During the TEM observation at an electron flux of 2×10^{18} cm^{-2} s^{-1}, the diameters of the synthesized globules decrease by approximately 10% upon electron irradiation with a total flux of ~4×10^{21} cm^{-2}. However, the diameter of the hollow center remains unchanged. A similar phenomenon has been observed with natural globules, whose diameters decrease approximately 5% after electron irradiation [11].

Formation route of globules: As hollow globules are never produced from the condensation of acetylene, methane, and atomic carbon in the same plasma, we believe the formation of PAH grains must therefore occur prior to the formation of hollow globules.

Initially, the PAH molecules can be produced from a single aromatic ring, benzene, which itself can be made from acetylene molecules in the gas ejected from evolved stars [12-13]. Benzene grows to larger PAHs by the abstraction of ring hydrogen and interaction with further acetylene [14-15]. During the growth of PAH molecules and as they move away from the central star, larger PAHs can coagulate to form PAH grains [16]. Then, the PAHs are polymerized to form amorphous organic particles by energetic plasma of the star, simultaneously. Energetic protons or electrons create vacancies in the organic globules. Finally, hollow organic globules are produced by coagulation of vacancies in circumstellar envelopes around evolved stars.

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