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著者	Mieno Tetsu, Hasegawa Sunao, Mitsuishi Kazutaka
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Production of Various Carbon Nanoclusters by Impact Reaction Using Light-Gas Gun as Simulation of Asteroid Collisions in Space

Tetsu Mieno*, Sunao Hasegawa¹, and Kazutaka Mitsuishi ²

Department of Physics, Shizuoka University, Shizuoka 422-8529, Japan

¹ Institute of Space and Astronautical Science, Japan Aerospace Exploration Agency, Sagami-hara 229-8510, Japan

² National Institute of Materials Science, Tsukuba, Ibaraki 305-0003, Japan

Abstract

An impact production of carbon nanoclusters is carried out in nitrogen gas using a two-stage light-gas gun. A small polycarbonate ball (or a stainless steel ball) is injected at about 6.5 km/s into a pressurized target chamber to collide with an aluminum target (or a hexane + aluminum target) in 1 atm of nitrogen gas. We can confirm the production of many types of carbon nanoclusters such as aluminum-encapsulated carbon nanoparticles, carbon nanotubes, and balloonlike nanocarbons. Therefore, it is expected that many types of carbon nanoclusters are produced by impact reactions of asteroids in space, when such reactions take place in a carbon-rich atmosphere. Particularly on Titan satellite, a large number of carbon clusters produced by impacts of asteroids are expected to be stored.

*E-mail address: sptmien@ipc.shizuoka.ac.jp

1. Introduction

A huge number of carbon atoms are produced by the nuclear fusion of stars in space. As carbon atoms constitute many types of molecules such as organic molecules on Earth, they are stored in various ways in space.¹⁻⁴⁾ Therefore, it is desirable to know what types of carbon molecules and clusters are stored in space, even if the tools for detecting carbons in space are insufficient. Recently, a Cassini-Huygens explorer developed by the National Aeronautical and Space Administration (NASA)/European Space Agency (ESA) has investigated the surface of Titan (one of Saturn's moons) and revealed Titan's surfaces for the first time, where many large methane seas exist and methane circulation occurs in a nitrogen gas atmosphere.^{5, 6)} From the images and data obtained by the Titan exploration, it can be expected that many types of carbon clusters and hydrocarbon molecules are stored in these cold methane seas. It has been reported that, in a nitrogen atmosphere, there are many types of organic molecules such as methane, ethane, propane, acetylene, and benzene, which are produced by UV light reactions in the upper atmosphere.⁷⁻⁹⁾

Here, we suggest that repeated asteroid impact on the surface of Titan over a long period in a nitrogen atmosphere produced many types of carbon clusters, which are stored on Titan's surface. Following impact, carbon materials were quickly heated and ablated from the surface, reacted with each other in nitrogen gas, and became carbon clusters and hydrocarbon molecules, many of which fell into the methane seas by gravity and remained there under a low-temperature, UV-shielded condition. However, some of the products would have diffused into space. Therefore, we expect that many types of carbon clusters are stored on Titan's surface at present. High-energy impact, not only on Titan's surface, but also in space, could create carbon clusters from any carbon material. In the history of solar planets, the impact of asteroids has played important roles.^{10, 11)}

To prove the possibility of producing of carbon clusters in space, a model experiment is carried out using a two-stage light-gas gun.¹²⁻¹⁵⁾ A projectile with a velocity of about 6.5 km/s collides with a target in nitrogen gas, causing an impact reaction in a hot gas phase. The samples produced are carefully analyzed by transmission electron microscopes (TEM). In the last paper, the production of C₆₀ and higher fullerenes was reported following the measurement using a laser desorption mass spectrometer and a high-performance liquid chromatograph.^{12, 13)} Here, other types of carbon clusters, which are the major components of the product obtained by the impact

reaction other than fullerenes, are investigated.

2. Experimental Procedure

The experiment is carried out using a two-stage light-gas gun^{12, 14)} available at the Institute of Astronautical Science (ISAS), Japan Aerospace Exploration Agency (JAXA), photographs of which are shown in Fig. 1. This gas gun can accelerate a polycarbonate ball 7.1 mm in diameter (or a stainless steel ball 3.2 mm in diameter with a sabot^{12, 14)}) using compressed hydrogen gas to about 6.5 km/s under a vacuum of 0.1 Pa. The weights of the polycarbonate ball and the stainless-steel ball are 0.228 and 0.128 g, respectively. Their impact energies at a velocity of 6.5 km/s are 9.6 and 5.4 kJ, respectively. To accelerate a smaller projectile less than the diameter of the gun barrel, a sabot is usually used. Here, the sabot has a cylindrical shape 7.1 mm in diameter, 6.5 mm in height, 0.280 g in weight, is made of nylon, and has a cross-shaped slit. The metal ball is embedded on the front side of the sabot. After ejection from the barrel, the sabot is separated from the metal ball by centrifugal force, and only the metal ball hits a target.¹⁴⁾ The ball collides with an aluminum target (or a hexane + aluminum target) in a pressurized chamber, where 1 atm of nitrogen gas is present. The pressurized chamber is located in the target chamber. A schematic of the pressurized chamber made of stainless steel is shown in Fig. 2; the chamber is 255 mm in diameter and 250 mm in length. To collect the carbon samples produced, the inside walls of the chamber are covered with clean aluminum sheets, from which deposited samples on the mg order are carefully collected. The pressurized chamber is first evacuated using a rotary pump and then filled with 1 atm of nitrogen gas. An accelerated ball penetrates the aperture of the pressurized chamber, 65 mm in diameter, covered with a 0.1-mm-thick aluminum film, and hits an aluminum target 76 mm in diameter and 30 mm in thickness. The target can be cooled to between - 60 and - 70 °C from the back side by the thermal conduction of a copper rod, which is cooled by liquid nitrogen. A thin hexane layer about 2 mm thick can be retained in a shallow sink in front of the aluminum target, which is covered with a thin aluminum film, as shown in Figs. 2 and 3(a). After the impact, a metal shutter immediately closes the aperture to protect impurity inflow from the gun region.

3. Results and Discussion

In this experiment, six types of experimental conditions are used and shots are successfully fired. The target temperature is set at - 60 to -70 or 20 °C. The projectile is of the polycarbonate or stainless-steel type. The target is a pure aluminum disk or a hexane + aluminum disk. We defined the six types as follows. Types A and B: The polycarbonate ball hits the aluminum target at - 62 and 20 °C, respectively. Types C and D: The stainless-steel ball hits the hexane + aluminum target at -62 and 20 °C, respectively. Types E and F: The polycarbonate ball hits the hexane + aluminum target at -70 and 20 °C, respectively.

After the impact, the pressurized chamber is carefully removed from the target chamber and opened. A crater on the aluminum target made by the impact is shown in Fig. 3(b), which is about 10 mm in diameter and about 7 mm in depth. The samples produced are carefully collected from the chamber wall. Some of the samples collected are dispersed in propanol, placed on a collodion-film-coated copper grid, and observed by TEM (Hitachi High Technology H-7650, acceleration voltage of 100 kV).

From the observed images, many carbon and aluminum particles of several tens of nm size are confirmed. Figure 4 shows a typical image of an aggregate of the clusters produced, where a polycarbonate ball hits an aluminum target at - 62 °C (Type A condition). Many aluminum nanoparticles (dark gray) and carbon nanoparticles (light gray) are observed. Almost all the aluminum nanoparticles are covered with graphite and amorphous carbon layers. In the series of experiments, aluminum nanoparticles are usually observed, because the impact ablates the target surface and the aluminum vapor cools under the nitrogen gas to become nanoparticles. Typical examples of the aluminum-encapsulated carbon nanoparticles are shown in Fig. 5, where a polycarbonate ball hits an aluminum target at - 62 °C (a) (Type A condition), and a stainless-steel ball hits a hexane + aluminum target at - 62 °C (b) (Type C condition). Graphite layers covering the aluminum particles are clearly observed, which suppress the chemical reactivity of the aluminum particles. The majority of the aluminum-encapsulated carbon nanoparticles have a spherical shape and are 10 ~ 100 nm in diameter. On average, we could not find a clear difference between these particles in Figs. 5(a) and (b). As aluminum does not absorb carbon atoms, it is conjectured that carbon atoms deposit on the surface of aluminum particles and cover them during the reaction process.

When a polycarbonate ball is injected onto an aluminum target at $T \sim - 62$ °C (Type A condition),

we can confirm the presence of bundles of carbon nanotubes grown from aluminum particles, which resemble sea urchins, as shown in Fig. 6. The nanotubes are observed to be single-walled, and they appear to have the same diameter of about 2 nm and the lengths of 10 ~ 70 nm. Except under this condition, no production of such sea-urchin-type nanotubes is observed. It is conjectured that the hot surface of the aluminum particles serves as a catalyst of nanotube growth, but its mechanism was not elucidated. The production process can be compared with the laser-ablation production of carbon molecules and carbon clusters.¹⁶⁻¹⁸⁾

More often, the production of balloonlike carbon nanoparticles (shell-like nanocarbons) is observed under carbon-rich conditions. Typical images of the balloonlike nanoparticles are shown in Fig. 7, where (a) a polycarbonate ball hits a hexane + aluminum target at - 70 °C (Type E condition), and (b) a polycarbonate ball hits a hexane + aluminum target at 20 °C (Type F condition). As the products are collected using propanol, they coagulate in propanol, and thus it is difficult to observe separated clusters. In Fig. 7(a), there are many balloonlike carbon nanoparticles of about 20 nm diameter. The figure is obtained by TEM (Hitachi High-Technology H-9000NAR, acceleration voltage of 200 kV) to record a clearer image. Figure 7(b) shows an edge of the coagulates, where balloonlike carbon nanoparticles of various sizes are observed, and they have several graphite layers and facet structures. In the case of the polycarbonate ball hitting the hexane + aluminum target, we could observe many balloonlike carbon nanoparticles. Usually, these particles have a diameter range of 10 ~ 20 nm. On average, we find no clear difference between the two target temperatures (- 70 and 20 °C), as shown in Figs. 7(a) and (b), respectively.

To confirm the chemical composition and crystal structure of the nanoclusters produced, a higher-performance TEM system (JEOL JEM-3000F, acceleration voltage of 300 kV) with an electron energy-loss spectroscopy (EELS) analyzer is used.¹⁹⁾ By EELS, the carbon atom (or aluminum atom) distribution in the sample is visualized. Figure 8(a) shows an image of the balloonlike particles measured by this TEM, where a polycarbonate ball hits a hexane + aluminum target at 20 °C (Type F condition). At the edge of the coagulates of carbon nanoparticles, many empty balloonlike nanoparticles are observed. By magnifying the central part of this figure, many balloonlike nanoparticles of about 10 nm diameter with several shell-like crystal layers are observed, as shown in Fig. 8(b). As the particles coagulate and the TEM image becomes not so clear, the positions of several balloonlike nanoparticles in Fig. 8(b) are indicated by solid lines in Fig. 8(d).

They are not perfect spheres and often have facet structures. The arrows in Fig. 8(b) show the distance between the layers, which is about 0.3 nm, almost the same as the interplanar distance of graphite (0.335 nm). The carbon mapping of Fig. 8(a) by EELS is shown in Fig. 8(c), where the brightness increases with carbon atom density. The distribution of balloonlike nanoparticles in Fig. 8(a) is almost consistent with the carbon atom distribution in Fig. 8(c). Therefore, it can be confirmed that these balloonlike nanoparticles are made of graphite layers.

By EELS, aluminum atom distributions are also observed, by which many nanosized aluminum particles are confirmed. Although we attempted to detect nanoparticles including nitrogen atoms by EELS, no signals of nitrogen atoms are detected. It is conjectured that the sensitivity of EELS is still low. Therefore, we will seek hydrocarbon molecules including nitrogen atoms in the samples produced by other methods.

In all the cases, when a polycarbonate (or stainless steel) ball hits an aluminum (or hexane + aluminum) target under the low-temperature (or the normal-temperature) condition, carbon and aluminum nanoparticles are produced. However, the polycarbonate ball creates more carbon clusters than the stainless steel ball. Even under the low-target-temperature condition, many types of carbon clusters are produced. In particular, the production of single-walled nanotubes is confirmed under this condition. Under the above conditions, no production of onionlike carbon nanoparticles (bucky onions)^{20, 21)} is confirmed. Onionlike nanocarbon particles are made by encapsulation of smaller fullerenes, and the center of the particles is considered to be a C₆₀ molecule. As these molecules are usually made by the electron-beam-heating method, their production by impact was also expected.

By using a high-speed camera, which is set at a viewing window of the target chamber, a short strong optical emission inside the pressurized chamber is recorded. This strong emission remains for about 10 μ s and then a long weak emission from the target occurs. The gas temperature of the plume after the impact has been measured by other groups^{15, 22)} and estimated to be 5000 K, which is sufficient to atomize carbon-source materials.

From the experimental results, we can create a scenario of the production process of carbon nanoparticles in this experiment. Following the impact of a high-speed projectile in nitrogen gas, the ablation of the source material and target material takes place. In the ejected plume, as the temperature is about 5000 K, most of the carbon material is in gaseous state. In a nitrogen gas

atmosphere, carbon atoms frequently collide with each other, expand and cool before arriving at the chamber wall. In the gas phase or on the wall surface, they self-organize to carbon nanoparticles, metal-encapsulated nanocarbons, nanotubes or balloonlike nanocarbons, depending on the local reaction conditions. The exact production processes of these clusters are still unclear, but the laser ablation and the arc discharge methods for the production of carbon clusters have similar production processes. We speculate that many aluminum-encapsulated nanocarbons are produced when there are many aluminum particles ablated from the target, on which carbon atoms deposit, being not absorbed, thereby covering the aluminum particles. We also speculate that many balloonlike nanocarbons are produced when there are many carbon atoms in the high-temperature plume, which frequently collide with each other and cool down in the gas phase without any catalyst. By this process, carbon atoms bind to each other to make graphene layers, in which defect sites form 5-membered rings, and graphene layers become three-dimensional. As the positions of the 5-membered rings are not controlled, the graphene layers form imperfect carbon spheres, which can become the observed balloonlike carbon nanoparticles with multilayers and facet structures. However, as the impact plume is nonuniform and time-varying, a wider range of reaction conditions are included in one impact reaction. The production process is not simple. In this experiment, there is a good probability to produce fullerenes in the reaction,¹²⁾ but almost zero probability to produce bucky onions. Theoretical investigation to clarify the production processes of these carbon clusters is necessary and will be attempted in the future.

4. Conclusions

Nanoscale carbon clusters such as aluminum-encapsulated carbon nanoparticles, carbon nanotubes and balloonlike nanocarbons are successfully produced by impact reactions in 1 atm of nitrogen gas. Depending on the projectile material, target material, and target temperature, the composition of the species produced changes. As the parameter dependence of this reaction is not clarified, a continuous study of the impact reaction is now under way.

Although the impact energy density for Titan would be much higher, we consider that many types of carbon clusters were produced by the impact of asteroids and stored in the methane seas of Titan, which are stable under a low-temperature, UV-shielded condition brought about by the atmosphere. When carbon material is included in impact in space, there is a possibility of carbon cluster

formation.

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Figure captions

Fig. 1. (Color online) Photographs of gas gun: (a) gun-barrel part and (b) target chamber of gas gun.

Fig. 2. (Color online) Schematic of pressurized impact chamber located in target chamber.

Fig. 3. (Color online) Photographs of (a) inside of pressurized chamber and (b) metal target with crater after impact.

Fig. 4. Typical TEM image of clusters collected in pressured chamber. A polycarbonate ball hits an aluminum target at - 62 °C (Type A condition).

Fig. 5. TEM images of carbon nanocapsules collected in pressured chamber, where aluminum nanoparticles are coated with graphite layers. (a) A polycarbonate ball hits an aluminum target at - 62 °C (Type A condition). (b) A stainless steel ball hits a hexane + aluminum target at - 62 °C (Type C condition).

Fig. 6. TEM images of sea-urchin-type single-walled carbon nanotubes (SWNTs) collected in pressured chamber, where many SWNTs grow radially from aluminum particle. A polycarbonate ball hits an aluminum target at - 62 °C (Type A condition).

Fig. 7. TEM images of balloonlike nanocarbons collected in the pressured chamber, where graphite layers form the balloon's walls. (a) A polycarbonate ball hits a hexane + aluminum target at - 70 °C (Type E condition). (b) A polycarbonate ball hits a hexane + aluminum target at 20 °C (Type F condition).

Fig. 8. (Color online) (a) TEM image of balloonlike nanocarbons collected in pressured chamber, where polycarbonate ball hits hexane + aluminum target at 20 °C (Type F condition). (b) Magnified image of (a), where graphite layers of balloons are observed. These layers have a layer distance of about 0.3 nm. (c) Carbon mapping of image (a) obtained by EELS, where higher carbon atom-density forms brighter image. (d) Positions of several balloonlike nanocarbons in (b) are indicated by solid lines.

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