Laser Synthesis of Aerosol Particles from a Gaseous Mixture of Butyl Azide and Acrolein

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1. Introduction
Synthesis of ultrafine and nanometer-sized particles in the gas phase is of particular importance in the fields of microfabrication and nanotechnology. Collision of ultrafine and nanometer-sized particles on substrates under properly regulated conditions and fixation thereof can give a promising way to fabricate nonmeter-sized pattern and to modify the surface properties in very restricted tiny area.

Synthesis of organic materials in the gas phase and laser processing of organic materials were developed recently by using excimer laser light (ArF; 193 nm, KrF; 248 nm) which could induce photodecomposition, photopolymerization, and laser ablation for almost all organic substances [1-4]. Besides the use of excimer laser light, nitrogen gas laser light (337.1 nm) was recently applied to initiate polymerization reaction in the gas phase through two-photon process [5], and aerosol particles with a size of several tens of nm to 1 µm were successfully produced from gaseous acrolein (2-propanal) (AC) [6]. This technique was further developed to synthesize composite particles from gaseous mixtures of AC and some organosilicon compounds such as trimethyl(2-propynyloxy)silane (TMPSi) and vinyltrimethoxysilane [7,8]; chemical species of sedimentary aerosol particles were analyzed by X-ray photoelectron spectroscopy (XPS), and it was found that organosilicon compounds were incorporated into the polymerization reaction of AC molecules in aerosol particle formation, and that the chemical species of Si compounds in the sedimentary aerosol particles were largely dependent on chemical reactivity of the parent organosilicon compounds.

Under irradiation with N₂ laser light, nuclea-
tion process in aerosol particle formation from AC vapor is a two-photon process [8,9]. Utilization of a sensitization mechanism to the process has practical importance to improve the efficiency of nucleation reaction. Actually, this was successfully performed by using one-photon decomposition of formaldehyde (H$_2$CO) molecule in a gaseous mixture of H$_2$CO and AC [8].

Organic azide molecules are highly reactive, and photochemical reaction with AC molecule in the gas phase is of particular interest in improving the efficiency of nucleation reaction and in developing new chemical species in aerosol particles. In the present paper, butyl azide (BAz) was chosen as a representative of simple aliphatic azides, and from a gaseous mixture of BAz and AC, aerosol particles were produced under irradiation with N$_2$ laser light. To investigate the photochemical interaction between BAz and AC molecules, morphological characteristics of the sedimentary aerosol particles and the efficiency of aerosol particle formation were measured, and nucleation process and sensitization mechanism have been investigated by measuring monitor (He-Ne laser) light intensity scattered by the aerosol particles which were formed under irradiation with N$_2$ laser light.

2. Experimental

BAz was prepared from 1-bromobutane and sodium azide in aqueous methyl carbitol [2-(2-methoxyethoxy)ethanol] according to the method of Lieber el al [10]. BAz thus obtained was extracted by diethyl ether and was distilled under vacuum. AC (Merck, 95%, stabilized with 0.2% hydroquinone) was stored in a refrigerator below 10 °C to prevent polymerization, and was purified by distillation under vacuum. The BAz and AC liquids were degassed by freeze-pump-thaw cycles in the dark immediately before use. To prepare a gaseous mixture of BAz and AC, a fixed amount of AC vapor which was introduced into a specific region of a vacuum line with a mercury manometer was collected into a glass tube by freezing with liquid nitrogen, and another fixed amount of BAz vapor was introduced directly into a cylindrical cell (inner diameter: 35 mm, length: 200 mm) or a cross-shaped cell (inner diameter: 35 mm, long arm: 200 mm, short arm: 80 mm) furnished with quartz optical windows on each end. After AC liquid in the glass tube was vaporized, it was introduced into the cell (which was already filled with BAz) to prepare a gaseous mixture. The partial pressures of AC and BAz vapors in the cell were determined from the analysis of UV absorption spectrum. The background pressure of the vacuum system was 5 $\times$ 10$^{-5}$ Torr (1 Torr = 133.3 Pa). The gaseous samples were irradiated with a nitrogen gas laser (Molelectron UV24, 337.1 nm, repitition rate: 12 Hz). Laser power was measured with a pyroelectric joulemeter (Gentec ED-500) combined with a synchroscope (Iwatsu SS-7810). Scanning electron microscope (SEM) images were taken with a Topcon ABT-32 scanning electron microscope. Light intensity scattered by the aerosol particles was measured by the method described in a previous paper [11].

3. Results and Discussion

Upon exposure to N$_2$ laser light at an energy of 3.9 mJ/pulse for 2.5 h, a gaseous mixture of BAz (18 Torr) and AC (41 Torr) deposited sedimentary aerosol particles of yellowish brown color on a glass plate (which was placed at the bottom of the irradiation cell in order not to be directly exposed to the incident laser light) (yield; 0.3mg) in addition to an opaque thin film which deposited all over the side wall inside the cell (yield; 0.5 mg). The opaque film was not produced from pure AC vapor as was reported previously [6]. Aerosol particles fell down on the glass plate with a reproducible sedimentary pattern due to convection of the gaseous mixture. Analysis of SEM images of the sedimentary aerosol particles showed that aerosol particles were spherical with a mean diameter of $\approx$0.6 μm regardless of the partial pressure of BAz between 5 and 20 Torr. The mean diameter of the aerosol particles was not sensitive
to the molar ratio of the gaseous mixture of AC and BAz and also to the incident laser intensity. Aerosol particles deposited from AC vapor were white and the diameter was ~0.9 μm [8]. Both the color and the particle size of the aerosol particles deposited from the gaseous mixture of BAz and AC showed that BAz participated in aerosol particle formation process.

The dependence of the yield of sedimentary aerosol particles on irradiation time of laser light (using Molecron UV24) at an energy of 3.9 mJ/pulse was measured with a gaseous mixture of BAz (18 Torr) and AC (41 Torr). The result is shown in Fig. 1. The yield increased linearly with irradiation time up to 5 h. Under irradiation longer than 5 h, a thin polymer (polyacrolein) film was formed on the surface of the optical quartz window as was observed with a gaseous mixture of AC and carbon disulfide [9].

The laser intensity dependence (1.0 - 4.6 mJ/pulse) of the yield of sedimentary aerosol particles was also measured with a gaseous mixture of BAz (18 Torr) and AC (41 Torr) under irradiation for 5h. The result is shown in Fig. 2. Above a threshold energy (~0.6 mJ/pulse), the yield increased almost linearly with increasing laser intensity. This result suggested that the aerosol particle formation process was initiated by one-photon process. From the UV absorption spectra in Fig. 3, BAz has an absorption band at 285 nm, and its long wavelength tail extends to 350 nm. Absorbance of 18 Torr of BAz at 337.1 nm is 0.012 for optical light path length of 20 cm in this experiment. Although AC molecule absorbs N2 laser light more efficiently (absorbance at 337.1 nm is 0.63 for light path length of 20 cm) than BAz molecule, AC molecules needed two-photons to initiate aerosol particle formation [8,9]. Hence, the result in Fig. 2 strongly suggested that photochemical reaction of BAz initiated the aerosol particle formation by one-photon process. This conclusion was further supported from the fact that the yield of the sedimentary aerosol particles increased with increasing the partial pressure of BAz as is shown in Fig. 4.

When AC liquid was mixed with BAz liquid at room temperature, chemical reaction was induced thermally to result in producing a polymerized material. To decide whether thermal chemical reaction took place in the gas phase, FT-IR spectrum was measured with a gaseous mixture of BAz (5 Torr) and AC (38 Torr); the spectrum is shown.
in Fig. 5. The spectrum of the gaseous mixture was composed of the spectrum of pure AC vapor and that of pure BAz vapor, and showed no new band ascribed to a new chemical species. Moreover, UV absorption spectrum of the gaseous mixture which were kept still in the dark for 5 h did not change from the spectrum measured immediately after preparing the gaseous sample. These results strongly suggested that thermal chemical reaction of the gaseous mixture did not take place under the present experimental conditions, and aerosol particles was actually produced photochemically.

Nucleation process of the gaseous mixture of BAz and AC was studied by measuring the intensity of He-Ne laser light scattered perpendicularly by the aerosol particles being formed under irradiation with N2 laser light. The result for a gaseous mixture of BAz (18 Torr) and AC (41 Torr) under irradiation with N2 laser light at an energy of 2.2 mJ/pulse is shown in Fig. 6A. Under irradiation for 23 min, scattered light intensity began to increase, and reached to its first maximum at \( \approx 52 \) min. Between 20 and 200 min, scattered light intensity slowly fluctuated at an interval of \( \approx 50 \) min, and then at \( \approx 200 \) min, it increased again rapidly until reaching to a maximum at 220 min, followed by a fluctuation with an interval of \( \approx 25 \) min. In this experiment, N2 laser light was shut down at 300 min. Without the exciting laser light, scattered light intensity increased for 3 min, accompanied with intensity fluctuation due to continued propagation and sedimentation of the aerosol particles, and then decayed rapidly (see the insert in Fig. 6A). The behavior of the scattered light intensity suggested that the aerosol particles were produced under two kinds of chemical processes. For the purpose of comparison, scattered light intensity was also measured with pure AC and pure BAz vapors under the same experimental conditions; scattered light was not detected for 60 min for pure AC and for 170 min for pure BAz during which the measurement was actually done. From this result, it is clear that a sensitization mechanism is operative in the gaseous mixture.

Laser power dependence of the scattered light intensity was further measured with the gaseous mixture (Fig. 6B). Aerosol particles was produced with the laser power as low as 1.5 mJ/pulse at which pure AC vapor did not produce any aerosol particles even under prolonged irradiation [8]. At the energy of 1.5 mJ/pulse, only the first process in the particle formation was observed within 300 min. Increasing the laser intensity to 1.9 and to 2.5 mJ/pulse, induction period during which the nucleation propagates to form aerosol particles became shorter, and the second process in the particle formation started earlier.

AC molecule needs two photons to produce HCO and \( \text{C}_2\text{H}_3 \) radicals which can initiate polymerization reaction under irradiation with \( \text{N}_2 \) laser light [8,9]. In the gaseous mixture of BAz and AC, \( \text{N}_2 \) laser light is absorbed by BAz and excited BAz...
molecules can decompose into reactive species, i.e., the nitrene. The nitrene can initiate a collision-induced chemical reaction with AC molecules in the gas phase eventually resulting in aerosol particle formation. Thus, the primary role of BAz in the gaseous mixture is to increase the efficiency of nucleation reaction in aerosol particle formation through one-photon process. This process may correspond to the first phase in the light scattering experiments observed at low laser energy, and the second phase which was easily observed at the laser intensity higher than 1.9 mJ/pulse may correspond to the nucleation due to photopolymerization of AC molecules.

Elucidation of chemical reactions which took place in the gas phase between photoexcited BAz and AC molecules is important in view of synthesizing new chemical materials. Preliminary experiment to characterize the chemical structure of the sedimentary aerosol particles deposited from the gaseous mixture of BAz and AC was done by measuring FT-IR spectrum. The spectrum indicated that the main component of the aerosol particles was polyacrolein, but the spectrum showed several bands which were not assigned to polyacrolein at 1056, 1116, 1235, 1376, and 1658 cm\(^{-1}\), indicating that BAz was incorporated into the aerosol particles. Detailed analysis of the chemical structure of the sedimentary aerosol particles is now under study.

4. Conclusions

Under irradiation with N\(_2\) laser light, sedimentary aerosol particles with a mean diameter of \(\sim 0.6 \mu m\) were synthesized from a gaseous mixture of BAz and AC. Although the light absorbptivity of gaseous BAz was very small at 337.1 nm compared to that of gaseous AC, BAz significantly increased the efficiency of aerosol particle formation. The measurement of monitor light intensity scattered by the aerosol particles as formed under irradiation with N\(_2\) laser light indicated that at low N\(_2\) laser intensity (1.5 mJ/pulse), nucleation proceeded only through the photochemical reaction of BAz, but at higher laser intensity (\(\geq 1.9 \) mJ/pulse), nucleation through chemical reaction of AC by two-photon process became effective. From the fact that BAz sensitized the nucleation reaction of the aerosol particles, it was strongly suggested that reactive...
species, i.e., the nitrene induced a chemical reaction with AC in the gaseous mixture.

References