Photochemical Synthesis of Metal-Containing Ultrafine Particles Applicable to Nanolithography and Nanodevices

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From gaseous mixtures involving iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and carbon disulfide (CS_2), spherical ultrafine particles involving organometal compounds were synthesized under light irradiation at 313 nm. Chemical structure and chemical composition were changed by post-exposure with UV light and by the application of a magnetic field. By the post-exposure with 266 nm light upon the deposited particles, volatile fragments such as $\text{Fe}(\text{CO})_n$ ($n=1\sim3$) were evolved in addition to CO. The particle size was effectively diminished to as small as 58 nm by shortening the irradiation time up to 1 s. Upon exposure to intense laser light, photochemical reaction during aerosol particle formation changed dramatically and gaseous mixtures involving $\text{Fe}(\text{CO})_5$ produced magnetic particles. By controlling the convectional flow of the entire gaseous sample, linearly aggregated particles (i.e., particle-wires) were successfully produced. Potential applications of the particle-wires to nanolithography and in constructing nanodevices were discussed briefly. From solid materials such as poly(dimethylsilane), spherical particles were produced in the atmosphere of trimethylsilyl azide by the aid of laser ablation. Technical advantages in producing spherical particles from solid materials were also discussed.

Keywords: ultrafine particles, gas phase photochemical reaction, particle-wire, magnetic particle, iron pentacarbonyl, carbon disulfide, allyltrimethylsilane

1. Introduction

In order to synthesize fine and ultrafine particles from gaseous mixtures, a photochemical method has been developed by us [1] in which the nucleation and propagation reactions during aerosol particle formation are initiated via photochemical reactions of gaseous molecules. The gaseous mixtures involve reactive molecules such as carbon disulfide (CS_2) and 2-propenal (acrolein) (AC) to initiate nucleation reactions, and other gaseous component molecules such as organosilicon compounds (for examples, trimethylpropynyloxy-silane, allyltrimethylsilane (2-propenyltrimethylsilane) (ATMeSi), and trimethylsilyl azide (TMSAz)) which otherwise do not initiate chemical reactions under UV light irradiation participate to the nucleation and propagation reactions by reacting with reactive intermediate chemical species originating from CS_2 and/or AC [2-8]. The photochemical method has further been applied to gaseous mixtures involving organometal

compounds such as iron pentacarbonyl ($\text{Fe}(\text{CO})_5$) and cobalt tricarbonyl nitrosyl ($\text{Co}(\text{CO})_3\text{NO}$) [9-11]. These organometal compounds can initiate the nucleation reaction efficiently by themselves, but the participation of CS_2 and organosilicon compounds to the nucleation reaction changed the morphology of the deposit, and produced spherical particles [12].

In the present paper, sedimentary aerosol particles were produced from a gaseous mixtures of $\text{Fe}(\text{CO})_5$ and CS_2 , and the nucleation reactions during aerosol particle formation were studied from the analysis of FT-IR spectra. Diminution of the particle size is of our concern, and this was actually fulfilled by shortening the UV light irradiation time. The control of chemical structure of the aerosol particles is important to give some physical and chemical properties to the particles. In the particles involving organometal compounds, chemical compositions of aerosol particles were significantly changed by post-exposure with UV

light and by the application of a magnetic field. Moreover, upon exposure to intense laser light, magnetic particles were produced from the gaseous mixtures involving $\text{Fe}(\text{CO})_5$ and $\text{Co}(\text{CO})_3\text{NO}$ due to a drastic change of the chemical reactions. Furthermore, the photochemical method has further been developed to produce spherical particles from solid materials by the aid of laser ablation. This technique was applied to poly(dimethylsilane) (PDMS) powder, and some technical advantages were discussed. Finally, under specific experimental conditions, linearly aggregated particles (i.e., particle-wires) were successfully produced. The potential applications of the particle-wires were discussed briefly in relation to nanotechnology.

2. Experimental

$\text{Fe}(\text{CO})_5$ (Kanto, 95%), ATMeSi (Tokyo Kasei, 98%), TMSAz (Tokyo Kasei, 96%), and CS_2 (Kanto, 98%) were degassed three times by freeze-pump-thaw cycles in the dark and purified by vacuum distillation immediately before use. PDMS (Wako, E.P. grade) was used as supplied. To prepare a gaseous mixture, each vapor was introduced successively into a cylindrical Pyrex cell (inner diameter 35 mm, length 160 mm or 200 mm) equipped with a couple of quartz windows or a cross-shaped Pyrex cell having a long (length 160 mm, inner diameter 35 mm) and short (length 80 mm, inner diameter 20 mm) arms equipped with a couple of quartz and KBr windows through a vacuum line equipped with a capacitance manometer (Edwards Barocel Type 600). The background pressure of the irradiation cell was less than 8×10^{-5} torr (1 torr = 133.3 Pa), and the leakage into the evacuated cell from the atmosphere was carefully controlled to be less than 1 Torr in a day. The partial pressures of $\text{Fe}(\text{CO})_5$, ATMeSi, and CS_2 in the irradiation cell were determined from the diagnostic band intensities of FT-IR spectra at 645 cm^{-1} for $\text{Fe}(\text{CO})_5$, 1259 and 854 cm^{-1} for ATMeSi, and 1530 cm^{-1} for CS_2 .

Gaseous samples were irradiated with a medium pressure mercury lamp (Ushio UM-452, 450 W) through UV29 and UVD33S filters (313 nm) (intensity $5.4\sim 8.8\text{ mJ/s}\cdot\text{cm}^2$) or with the third harmonic (355 nm) of a Nd:YAG laser (Continuum Surlite I-10, pulse width 6 ns, repetition rate 10 Hz, energy $32\sim 38\text{ mJ/pulse}$), resulting in the production of spherical aerosol particles. Absorbance of 1 torr of $\text{Fe}(\text{CO})_5$ and CS_2 vapors is 0.28 and 0.011, respectively, at 313 nm in 10 cm light path length. In a gaseous mixture of $\text{Fe}(\text{CO})_5$ and CS_2 , $\text{Fe}(\text{CO})_5$

was excited more (≈ 25 times) efficiently than CS_2 . ATMeSi has no absorption band longer than 220 nm.

Aerosol particles were deposited on a glass plate and/or Cu substrate placed at the bottom of the irradiation cell. In order to measure their chemical and physical properties, these samples had to be transported from the irradiation cell and exposed to ambient atmosphere. Scanning electron microscope (SEM) images were recorded with a JEOL JSM 6060 scanning electron microscope, and SEM-EDS analyses were performed using a Philips XL30 CP scanning electron microscope. The sedimentary aerosol particles were mixed with KBr powder to prepare KBr pellets and FT-IR spectra of the sedimentary particles embedded in the pellets were measured with a Nicolet NEXUS 470 FT-IR spectrometer.

3. Results and discussion

3-1. Chemical structure of sedimentary aerosol particles produced from $\text{Fe}(\text{CO})_5$ and CS_2

Under UV light irradiation at 313 nm for 10 min, pure $\text{Fe}(\text{CO})_5$ vapor (1.0 torr) produced two kinds of morphologically different deposits, i.e., hexagonal rod with a mean size of $2.8 \times 2.4\text{ }\mu\text{m}$ and crystalline particles with a mean size of $0.46\text{ }\mu\text{m}$ [12]. The major chemical species of the deposits was $\text{Fe}_2(\text{CO})_9$ [13, 14] in addition to a slight amount of $\text{Fe}_3(\text{CO})_{12}$ [15]. Although pure CS_2 vapor at a pressure of 2 torr did not produce any deposits because of its low partial pressure, a gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.1 torr) and CS_2 (1.9 torr) produced spherical sedimentary aerosol particles with a mean diameter of $0.31\text{ }\mu\text{m}$ [16]. FT-IR spectrum of the sedimentary aerosol particles (Fig. 1(a)) exhibited the $\text{C}\equiv\text{O}$ stretching bands at 2005 , 2037 , and 2080 cm^{-1} , but not the $\text{C}=\text{O}$ stretching band at 1825 cm^{-1} which was observed with $\text{Fe}_2(\text{CO})_9$ deposited from pure $\text{Fe}(\text{CO})_5$ vapor (Fig. 1(b)) [13, 14]. These results indicated that $\text{Fe}-\text{C}(=\text{O})-\text{Fe}$ chemical bond was not formed by the incorporation of CS_2 molecules, suggesting that the bond formation between $\text{Fe}(\text{CO})_4$ (originating from $\text{Fe}(\text{CO})_5$ [17]) and CS_2 was the primary chemical reaction of the gaseous mixture.

CS_2 molecules are known to be activated by transition metal complexes in the liquid phase [18, 19]. For iron carbonyls, π -coordination of CS_2 molecules and σ -coordination through a sulfur atom are reported [20]. Although the present experiment was done in the gaseous phase,

Fig. 1. FT-IR spectra of deposits produced from (a) a gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.1 torr) and CS_2 (1.9 torr) and (b) pure $\text{Fe}(\text{CO})_5$ vapor (1.0 Torr) under light irradiation at 313 nm for 10 min.

$\text{Fe}(\text{CO})_4$ species produced from excited $\text{Fe}(\text{CO})_5$ may react with CS_2 molecules through either π - or σ -coordination.

σ -Coordinated CS_2 can ligate another Fe atom to connect two Fe atoms as was observed for $\text{Co}_2(\text{CN})_{10}\text{CS}_2$ [18, 19].

For the above complex, $\nu(\text{C}=\text{S})$ and $\nu(\text{C-S})$ bands were expected to appear at $840\sim 980\text{ cm}^{-1}$ region [18].

Thiocarbonyl group can add to $\text{Fe}(\text{CO})_4$ to form $\text{Fe}(\text{CO})_4(\text{CS})$ [21-23], and combine two transition metal atoms by end-to-end bridging of a thiocarbonyl, $\text{M-C}\equiv\text{S-M}$ [24]. Considering that CS_2 molecules were polymerized in the gas phase mainly as $(\text{C-S})_n$ under UV light irradiation [25], photo-excited $\text{Fe}(\text{CO})_5$ may react with CS_2 to bridge two iron atoms through a thiocarbonyl group.

FT-IR band of an end-to-end bridging thiocarbonyl

Fig. 2. FT-IR spectra of sedimentary particles deposited from a gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.1 torr) and CS_2 (1.9 torr) under light irradiation at 313 nm for 10 min (a) before and (b) after post-exposure with a mercury lamp (313 nm) for 2 h.

has not yet been identified, although it was expected to appear near 1100 cm^{-1} [24]. Considering that the partial pressure of CS_2 in the present experiment is not high enough to induce efficiently the bimolecular reaction (5), two Fe atoms may possibly be connected by σ -coordinated CS_2 (reaction (3)) rather than by end-to-end bridging of a thiocarbonyl (reaction (6)).

3-2. Control of chemical composition by post exposure with UV light

Modification of chemical structure of aerosol particles is useful to give the particles some chemical and physical properties which are suitable for practical application in industry. Surface modification of AC particles which were synthesized by the photochemical method was successfully performed under UV light irradiation by introducing 1,3,5,7-tetramethylcyclotetrasiloxane vapor over the deposited particles [26]. The experimental result indicated that photochemical reactivity of the surface was maintained even after the sedimentation of the particles onto a substrate, and that the particles produced by the photochemical method were suitable for surface modification.

Organometal compounds can form a variety of chemical bonds with organic molecules [13]. For the particles involving metal carbonyl compounds, chemical structure can be changed by exposing UV light on the deposited particles without introducing

any reactive gaseous molecules (i.e., by post-exposure). The 313 nm light from a medium pressure mercury lamp was irradiated for 2 h on the deposited particles which were produced from a gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.1 torr) and CS_2 (1.9 torr) [16]. FT-IR spectra before and after the post-exposure are shown in Fig. 2. In Fig. 2(b), the $\approx 2000\text{ cm}^{-1}$ (2080, 2037, and 2005 cm^{-1}) bands assigned to $\nu(\text{C}\equiv\text{O})$ and the 607 and 576 cm^{-1} bands assigned to $\delta(\text{Fe-C-O})$ decreased their intensities compared to the intensities of ≈ 1650 and $\approx 1000\text{ cm}^{-1}$ bands originating from CS_2 . This showed that terminal $\text{C}\equiv\text{O}$ groups were evolved by the post-exposure, accompanying a slight change in chemical structure of the particles.

The fourth harmonic (266 nm) of pulsed Nd:YAG laser light was also used for the post-exposure [16]. To escape from the effect of laser ablation, laser light was defocused using a concave lens to reduce the energy to $5\text{ mJ/pulse}\cdot\text{cm}^2$ and was irradiated on the particles. Analysis by SEM-EDS showed that population of Fe, S, C, and O atoms in the particles after the post-exposure was 21.0, 5.0, 38.2, and 35.8 At.%, respectively, and that before the post-exposure was 15.9, 2.4, 39.0, and 42.7 At.%, respectively. Before the post-exposure, atomic ratio of C (and O) to Fe atom was roughly 2.5 : 1, but it reduced to 1.7 : 1 after the post-exposure, indicating that CO groups were evolved by the post-exposure. Furthermore, atomic ratio of Fe to S reduced to 4.2 : 1 (from 6.5 : 1) after the post-exposure. This strongly suggested that upon exposure to 266 nm light, volatile fragments such as $\text{Fe}(\text{CO})_n$ ($n = 1\text{--}3$) were produced and evolved in addition to CO species.

3-3. Control of chemical composition by an external magnetic field

Magnetic field has recently been found to influence the chemical reactions during aerosol particle formation, resulting in a change in the particle size and chemical composition of the sedimentary particles [27, 28]. In a gaseous mixture of glyoxal and CS_2 , aerosol particle formation processes changed depending on the excitation wavelength. This was clearly demonstrated by observing different magnetic field dependence of the nucleation reaction rate during aerosol particle formation [29, 30].

For a gaseous mixture of $\text{Fe}(\text{CO})_5$ (0.9 torr) and CS_2 (21 torr), magnetic field effect on the chemical structure of the sedimentary aerosol particles was studied using a superconducting magnet

Fig. 3. FT-IR spectra of sedimentary particles produced from a gaseous mixture of $\text{Fe}(\text{CO})_5$ (0.9 torr) and CS_2 (21 torr) under light irradiation at 313 nm for 2 h in the presence of magnetic fields of (a) 0, (b) 3, and (c) 5 T.

under light irradiation at 313 nm [12]. FT-IR spectra of the sedimentary aerosol particles are shown in Fig. 3. Compared to the spectrum in Fig. 2(a), band intensities in the $800\text{--}1700\text{ cm}^{-1}$ region increased due to the increased partial pressure of CS_2 , showing that a larger amount of CS_2 molecules were incorporated into the aerosol particles. With increasing magnetic field up to 5 T, the $\text{C}\equiv\text{O}$ stretching band intensity in the 2000 cm^{-1} region increased, indicating that chemical reactivity of $\text{Fe}(\text{CO})_5$ was promoted under a magnetic field, resulting in the increase in the amount of chemical species originating from $\text{Fe}(\text{CO})_5$. However, we could not detect any band ascribed to bridging $\text{C}=\text{O}$ bond. This indicated that incorporation of a larger amount of CS_2 molecules was enough to interrupt the formation of $\text{Fe}(\text{C}=\text{O})\text{--Fe}$ chemical bond and the reaction (3) took place efficiently even in the presence of a high magnetic field where the chemical reactivity of $\text{Fe}(\text{CO})_5$ was promoted.

During aerosol particle formation processes, several chemical reactions take place concurrently. Among these reactions, some are accelerated or decelerated by the application of a magnetic field. Due to this, a change in chemical structure and chemical composition of the particles is induced.

Thus, a magnetic field can be utilized to control the chemical properties of the sedimentary particles.

3-4. Synthesis of magnetic particles

Upon exposure to intense laser light, some gaseous mixtures change photochemical processes dramatically. Under intense light irradiation with the third harmonic (355 nm) of a Nd:YAG laser at an energy of 35 mJ/pulse, gaseous mixtures of $\text{Fe}(\text{CO})_5$ and TMSAz and of $\text{Fe}(\text{CO})_5$ and CS_2 produced ultrafine particles with a diameter of 50 ~ 100 nm. The particles were aggregated in each other, and were attracted towards a permanent magnet. Thus, we have succeeded in producing magnetic particles using the photochemical method. In a preliminary HRTEM analysis, crystalline nanodomain of metals was detected inside the particles. Further study is now in progress.

3-5. Control of particle size

In the synthesis of ultrafine particles in the gas phase, light irradiation induces the convection of entire gaseous sample. The aerosol particles produced under light irradiation travel along the cylindrical cell wall due to convection. Throughout the entire travel period, aerosol particles continue to grow by colliding with excited molecules (gas-to-particle conversion) during nucleation mode and then by colliding with other particles (coagulation) during accumulation mode, and finally collide with the substrate at the bottom of the irradiation cell within one convection cycle. Hence, the particle size is expected to change by varying the exciting light intensity, light irradiation time, and ambient temperature which regulate the reaction rate and the reaction time.

The effect of these experimental parameters was evaluated on the aerosol particles produced from a gaseous mixture of $\text{Fe}(\text{CO})_5$ and CS_2 [16]. The experimental results showed that in order to diminish the particle size, the decrease in the light irradiation time was most effective. This is due to the fact that in the nucleation mode during aerosol particle formation, the gas-to-particle conversion takes place only when the gaseous molecules are irradiated with UV light. Hence, the propagation time of the nucleation mode can be controlled directly by changing the irradiation time of UV light. In order to decrease the particle size, UV light was irradiated for a short period (1~10 s) on a gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.1 torr) and CS_2 (1.9 torr) [16]. The particle size distributions of the deposited particles are shown in Fig. 4, compared to the results

Fig. 4. Particle size distributions of sedimentary particles deposited from a gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.1 torr) and CS_2 (1.9 torr) under light irradiation at 313 nm for (a) 120, (b) 60, (c) 10, (d) 5, (e) 2.5, and (f) 1 s.

Fig. 5. Mean diameters of the sedimentary particles as a function of the cube root of the irradiation time.

under light irradiation for 60 and 120 s. The mean diameter of the particles was 220, 190, 130, 97, 77, and 58 nm under light irradiation for 120, 60, 10, 5, 2.5, and 1 s, respectively. With shorter irradiation time, the mean diameter of the sedimentary particles became smaller until to 58 nm. In Fig. 5, the mean diameter is plotted as a function of the cube

root of the irradiation time. A good linear relationship holds for the particles with mean diameters of less than 100 nm, to which the nucleation mode of particle growth dominates. The linear relationship showed that the number of molecules incorporated into the particles was roughly proportional to the reaction time. These results demonstrated that in the photochemical method, the size of aerosol particles was effectively controlled by changing the irradiation time. This is a technical advantage of the photochemical method.

3-6. Spherical particle formation from solid materials

In order to synthesize various kinds of spherical particles, it is preferable to utilize solid materials as photochemical reagents in addition to gaseous molecules. Synthesis of ultrafine and fine particles from solid materials generally needs the melting and/or vaporization of solid materials. To do this, laser ablation of solid materials has frequently been used as a convenient and powerful method [31-36], but it has been realized that simple use of laser ablation did not produce spherical particles efficiently.

Now, we have developed a synthetic method to produce spherical particles from solid materials by the aid of laser ablation and photochemical reaction to ambient gaseous molecules. The method was applied to poly(dimethylsilane) (PDMS) in the atmosphere of trimethylsilyl azide (TMSAz) [37]. Chemical reactivity of TMSAz towards PDMS was utilized to produce spherical fine particles [8].

The third harmonic (355 nm) of pulsed Nd:YAG laser light at an energy of 32~36 mJ/pulse was irradiated on the PDMS powder vertically across the aperture of a small aluminum chamber. The laser-ablated PDMS escaped from the chamber across the aperture and scattered over a glass plate. Without filling TMSAz vapor, the PDMS powder produced crystalline deposits as the major product (Fig. 6(a)) together with a small amount of spherical particles with a diameter of $\sim 1 \mu\text{m}$ as a minor product (Fig. 6(b)). Although TMSAz (20 torr) did not absorb light at 355 nm and did not produce any solid material under laser light irradiation for 5 min, laser-ablated PDMS in the presence of TMSAz vapor (20 torr) produced only spherical particles over the whole glass plate with a mean diameter of $1.3 \mu\text{m}$ (Fig. 7). FT-IR spectrum of the particles is shown in Fig. 8, together with the spectra of PDMS powder without laser ablation and of TMSAz vapor. In addition to the bands at

Fig. 6. SEM images of laser-ablated PDMS; (a) crystalline deposit, (b) spherical particle. Original magnification of SEM, (a) 6,000 $\times$, and (b) 23,000 $\times$.

Fig. 7. (a) SEM image of laser-ablated PDMS particles produced in the presence of TMSAz vapor (20 torr), and (b) particle size distribution therefrom. Original magnification of SEM, 6,000 $\times$.

Fig. 8. FT-IR spectra of (a) laser-ablated PDMS particles produced in the presence of TMSAz vapor (20 torr), (b) PDMS powder, and (c) TMSAz vapor (5 torr).

1250, 832, 743, 691, and 630 cm^{-1} ascribed to PDMS and the bands at 1259 and 834 cm^{-1} ascribed to TMSAz [38], a new band was observed at 1036 cm^{-1} , assignable to $\nu(\text{C-N})$. Considering that antisymmetric stretching band of the azido group, $\nu_a(\text{N}_3)$ at 2153 cm^{-1} became very weak, it was strongly suggested that TMSAz reacted with PDMS, accompanying the decomposition of the azido group to produce the trimethylsilyl nitrene intermediate. Through chemical reaction between the nitrene and laser-ablated PDMS, spherical particles were efficiently produced.

The PDMS powder emits fluorescence at 362 nm. The PDMS/TMSAz particles thus obtained showed a fluorescence peak at 344 nm, being shifted to shorter wavelength by 18 nm than that of PDMS powder (Fig. 9). Thus, fluorescent spherical fine particles were successfully produced. This technique may be applied for various solid polymer materials to produce spherical particles.

3-7. Formation of linearly aggregated fine particles

UV light at 313 nm was irradiated on a gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.1 torr) and CS_2 (2.0 torr)

Fig. 9. Fluorescence spectra of (a) laser-ablated PDMS particles produced in the presence of TMSAz vapor (20 torr) and (b) PDMS powder.

Fig. 10. SEM images of linearly aggregated particles produced from a gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.7 Torr), CS_2 (9.5 torr), and ATMeSi (16 torr) under light irradiation at 313 nm for 12 min. Original magnification of SEM, (a) 850 $\times$, and (b) 10,000 $\times$.

only for a short time (2.5 s) repeatedly (20 times). This intermittent light irradiation induced a modulated convectonal flow of the entire gaseous sample to result in a deposition of linearly aggregated particles. Linearly aggregated particles (i.e., particle-wires) were more easily formed by involving ATMeSi in the gaseous mixture. From a

ternary gaseous mixture of $\text{Fe}(\text{CO})_5$ (1.7 torr), CS_2 (9.5 torr), and ATMeSi (16 torr), particle-wires as long as 850 μm (with a mean diameter of 0.4 μm) were produced under light irradiation for 12 min (Fig. 10). Particle-wires as long as 250 μm with a mean diameter of 0.2 μm were also produced from a gaseous mixture of $\text{Co}(\text{CO})_3\text{NO}$ and ATMeSi [11]. The formation of particle-wires is characteristic of the sedimentary particles produced by the photochemical method. This is due to the fact that the sedimentary particles maintain the photochemical reactivity even after depositing on a substrate [8, 26]. Hence, two neighboring particles on the substrate can be connected in each other via chemical reaction. The particle-wire is flexible, and can be connected to another particle-wire so as to form a longer wire in any shape.

Particle-wires may be used as thin conductive wires when each constituent particle has electric conductivity or when the surface of the entire particle-wire is modified with any conductive materials. Two-dimensional deposition or arrangement of the particle-wires forming a specific pattern may be used as a resist pattern in lithography with a resolution equal to the diameter of constituent particles as small as several tens of nm. For the arrangement of the particle-wires, a technical development in manipulating particles and particle-wires is required. Together with this development, production of particle-wires with specific properties opens a way to constructing nano-devices.

4. Conclusions

Under UV light irradiation, spherical fine and ultrafine particles involving organometal compounds were synthesized from gaseous mixtures involving $\text{Fe}(\text{CO})_5$ and $\text{Co}(\text{CO})_3\text{NO}$. By applying a magnetic field, chemical reaction of the gaseous molecules, hence the chemical structure of the sedimentary particles was significantly changed. The particle size was effectively controlled by changing the irradiation time of UV light. To diminish the particle size, the decrease in the irradiation time was the most effective. Furthermore, by controlling the convectional flow of the entire gaseous sample, particle-wires were produced. The practical application of the particle-wires to lithography and in constructing nano-devices is expected. The photochemical method was further developed to produce spherical particles from solid PDMS powder with the aid of laser ablation. This technique is useful to produce a

variety of spherical particles from solid materials.

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