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Photochemical synthesis of ultrafine organosilicon particles from trimethyl(2-propynyloxy)silane and carbon disulfide

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Abstract

Under light irradiation at 313 nm with a medium-pressure mercury lamp, a gaseous mixture of trimethyl(2-propynyloxy)silane (TMPSi) and carbon disulfide (CS_2) produced sedimentary aerosol particles. From measurement of monitor (He–Ne laser) light intensity scattered by the aerosol particles, it was shown that the nucleation process of the aerosol particles was accelerated with increasing partial pressure of TMPSi. Analysis of FT-IR and X-ray photoelectron spectra (XPS) of the sedimentary aerosol particles revealed that excited CS_2 molecules reacted with TMPSi at $C{\equiv}C$ to initiate nucleation reaction of the particle formation. Several chemical species originated from CS_2 were incorporated into the polymerization reactions between TMPSi and CS_2 in forming $>C{=}S$ and $C{-}S$ chemical bonds.

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Keywords: Ultrafine particles; Photo-polymerization; Trimethyl(2-propynyloxy)silane; Carbon disulfide

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1. Introduction

Trimethyl(2-propynyloxy)silane (TMPSi) is a reactive organosilicon compound. ArF laser photolysis of gaseous TMPSi was dominated by polymerization at the triple bond and resulted in the chemical vapor deposition of polytrimethylsiloxy-substituted polyhydrocarbon [1], whereas the IR laser (TEA CO_2 laser)-photosensitized (SF_6) decomposition of TMPSi vapor produced transient $(CH_3)_2SiO$ species which subsequently polymerized into solid polydimethylsiloxane films [2]. Furthermore, aerosol particles were produced from a gaseous mixture of TMPSi and acrolein (2-propenal) (AC) upon exposure to N_2 laser light [3]. X-ray photoelectron spectra (XPS) analysis revealed that two kinds of Si atoms assignable to elemental silicon and silicon bonded in an organosilicon polymer were involved in the sedimentary aerosol particles, indicating that TMPSi was incorporated into the parent aerosol particles of polyacrolein, and cleavage of Si–C and Si–O bonds took place in the aerosol particles.

Besides AC molecules, carbon disulfide (CS_2) produces sedimentary aerosol particles [4–8], and can be used to synthesize composite aerosol particles [9,10]. In the present paper, aerosol particles have been synthesized from a gaseous mixture of TMPSi and CS_2 under light irradiation at 313 nm of a medium pressure mercury lamp and with N_2 laser light. Chemical structure of sedimentary aerosol particles was analyzed by FT-IR and X-ray photoelectron spectra and the nucleation process in aerosol particle formation from the gaseous mixture was studied by measuring monitor (He–Ne laser) light intensity scattered by the aerosol particles as formed in the irradiation cell. Photochemical reactions between TMPSi and CS_2 molecules were briefly discussed.

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2. Experimental

TMPSi was prepared by refluxing a mixture of 1,1,1,3,3,3-hexamethyldisilazane (Tokyo Kasei, GR grade, 96%) and 2-propyn-1-ol (Wako, EP grade, 98%) for 12 h under nitrogen atmosphere followed by fractional distillation. Fraction at 110 °C was used as a pure sample after checking its purity by gas chromatography. TMPSi was stored in a deaerated pyrex glass tube below 10 °C to prevent polymerization. The CS_2 and TMPSi liquids were degassed by freeze–pump–thaw cycles and purified by vacuum distillation immediately before use. To prepare a gaseous mixture, each vapor was introduced successively into a cross-shaped Pyrex cell (inner diameter (i.d.)) 35 mm, both arms 135 mm, volume 226 cm^3) or a small cylindrical Pyrex cell (inner diameter 20 mm, length 160 mm, volume 50 cm^3) equipped with a couple of quartz windows through a vacuum line equipped with a capacitance manometer (Edwards Barocel Type 600). The background pressure of the irradiation cell was $<5 \times 10^{-5}$ Torr (1 Torr = 133.3 Pa). The partial pressure of CS_2 in the irradiation cell was determined from its UV absorption in the 280–350 nm region. The gaseous samples were irradiated with a medium pressure mercury lamp (Ushio UM-452, 450 W) through a UV31 and a UVD33S filters (energy 3.5 mJ/(s cm^2)) to excite only CS_2 molecules at 313 nm or with nitrogen gas laser light (Lumonics HE-440, 337.1 nm, pulse width 10 ns) at an energy of 1.8 mJ/pulse effective on the area of 3 cm^2 at a repetition rate of 12 Hz. Laser power was measured with a pyroelectric joulemeter (Gentec ED-500) combined with a synchroscope (Iwatsu SS-7810). The aerosol particles were deposited on a glass and/or Cu substrates accommodated in the irradiation cell. Scanning electron microscopy (SEM) images were taken with a Topcon ABT-32 and a Philips XL30 CP scanning electron microscopes, and XPS of deposits were measured with a Gammadata Scienta ESCA 310 electron spectrometer using monochromatized Al Kα ($h\nu$ = 1486.6 eV) radiation for electron excitation. Sedimentary aerosol particles were mixed with KBr powder to prepare KBr pellets and FT-IR spectra of the sedimentary particles in the pellets were measured with a Nicolet Nexus 670 FT-IR spectrometer. Light intensity scattered perpendicularly to the incident monitor (He–Ne laser) light by the aerosol particles as formed in the irradiation cell under light irradiation was measured with a combination of a photomultiplier tube (Hamamatsu 1P28) and a lock-in amplifier (SRS SR-530) through a Y-52 filter.

3. Results and discussion

Under light irradiation at 313 nm for 4 h, a gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr) deposited sedimentary aerosol particles of yellowish-brown color on a glass substrate (which was accommodated at the bottom of the irradiation cell in a way not to be directly exposed to the incident light) with a reproducible sedimentation pattern due to convection of the gaseous mixture (Fig. 1). The product yield of the sedimentary aerosol particles was ∼0.2 mg (∼0.3%). Under the same experimental conditions, pure CS_2 (50 Torr) produced the sedimentary aerosol particles of reddish-brown color with a product yield of ∼0.1 mg (∼0.2%). TMPSi has absorption peak at a wavelength shorter than 200 nm and does not absorb the light at 313 nm. Hence, slight color change of the sedimentary particles and the increase of the product yield deposited from the gaseous mixture strongly suggested that excited CS_2 molecules initiated the nucleation reaction involving TMPSi molecules. Fig. 2 shows a SEM image of the sedimentary aerosol particles deposited from the gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr). Aerosol particles were spherical and their particle sizes distributed over a wide range (0.2–1.0 μm) with a mean diameter of 0.61 μm. The value was almost identical to the one (0.6 μm) deposited from pure CS_2.

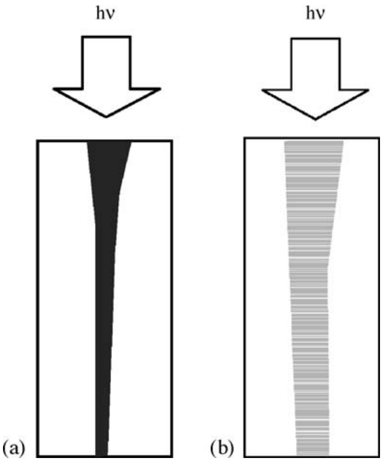


Fig. 1. Sedimentation pattern of ultrafine particles deposited from: (a) pure CS_2 vapor (50 Torr) and (b) a gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr) under light irradiation at 313 nm.

The nucleation and propagation processes in aerosol particle formation were monitored by measuring the He–Ne laser light intensity scattered by aerosol particles which were formed under UV light irradiation. The results are shown in Fig. 3. With increasing partial pressure of TMPSi from 0 to 15 Torr at a fixed partial pressure of CS_2 (50 Torr), the scattered light intensity increased and fluctuation of the scattered light intensity with an interval of ∼10 min was more pronounced. Note that in the present experimental set-up, scattered light from a fixed point with very small volume (i.e., only on ∼5 mm light path length of He–Ne laser) was detected. Hence, the measurement of scattered light intensity gave us the local information at a fixed small volume inside the irradiation cell. Fluctuations of the scattered light intensity with long and short periods were frequently observed in the nucleation processes involving CS_2 molecules [4–6]. The fluctuation of long period (∼10 min) is due to the convection of entire gaseous sample and the fluctuation of short period (∼2 min) is believed to be due to the temporal and local pressure change of reactant gaseous molecules caused

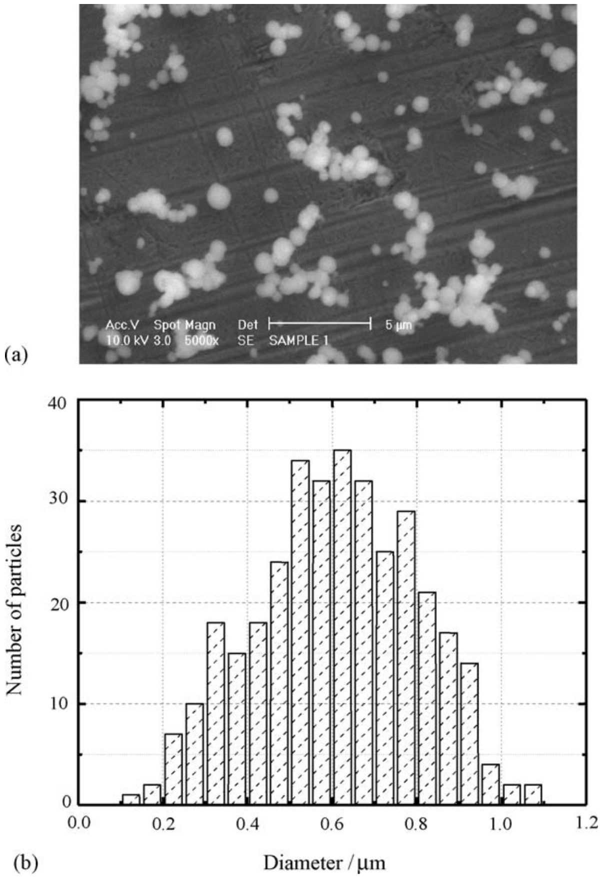


Fig. 2. (a) SEM image of sedimentary particles deposited from a gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr) under light irradiation at 313 nm, and (b) particle size distribution therefrom. Original magnification of SEM, 5000×.

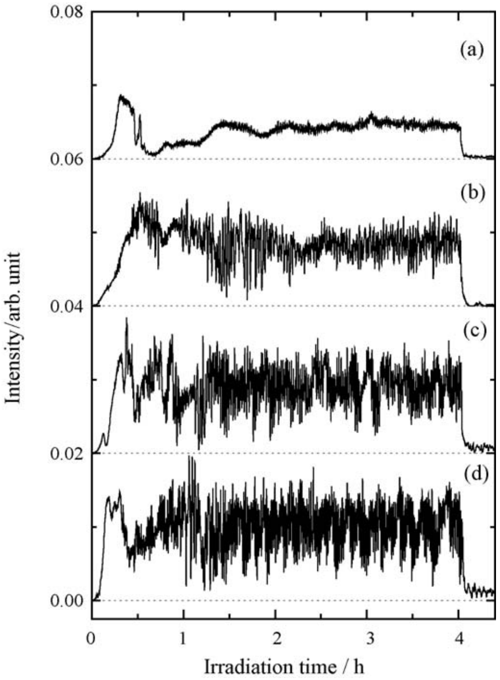


Fig. 3. He–Ne laser light intensity scattered by the aerosol particles produced from gaseous mixtures of CS_2 (50 Torr) and TMPSi under light irradiation at 313 nm. Respective partial pressures (in Torr) of TMPSi were: (a) 0, (b) 5, (c) 10, and (d) 15.

by the formation and sedimentation of the aerosol particles [4–6]. Scattered light intensity depends on the size of each aerosol particles and the number of particles of each size. In cases where the particle size distribution is not dependent on irradiation time of exciting light as in the present experimental conditions [11], scattered light intensity after reaching its maximum value is proportional to the number of aerosol particles with various particle sizes. In Fig. 3, with increasing partial pressure of TMPSi, the induction period to detect scattered light became shorter (from 200 to 100 s, and further to 75 s, and to 60 s at 0, 5, 10, and 15 Torr of TMPSi, respectively). During the induction period, nuclei of particles grow to a detectable size. Hence, the induction period is a measure of relative rate of nucleation and propagation reactions in aerosol particle formation. Shortening of the induction period and the stronger intensity of scattered light with increasing partial pressure of TMPSi clearly showed that both CS_2 and TMPSi molecules contributed to the nucleation and propagation processes in aerosol particle formation.

This result was compared to the case of particle formation from a gaseous mixture of TMPSi and AC under N_2 laser light irradiation [3]. In the latter case, two-photon excited AC molecules initiated nucleation reaction with TMPSi molecules. Due to low efficiency of photo-excitation of AC by two-photon and low quantum-efficiency in polymerization reaction of resulting excited AC ($\phi < 6.2 \times 10^{-3}$) [12,13], the induction period to detect scattered light became longer (15 min under N_2 laser irradiation at 2.7 mJ/pulse) compared to the present result (60 s) of TMPSi/CS_2 gaseous mixture. Efficiency of nucleation reaction is improved in TMPSi/CS_2 gaseous mixture, because CS_2 molecules are very efficient in aerosol particle formation and are reactive to the other gaseous component.

Furthermore, in the present experiment, it was found that the particle size distribution of sedimentary particles did not depend on the partial pressure of TMPSi. This means that the integration of the scattered light intensity against irradiation time gives a relative measure of the product yield of the sedimentary particles deposited from gaseous mixtures with various partial pressure of TMPSi. The scattered light intensity integrated to the irradiation time of exciting light is plotted in Fig. 4. The integrated scattered light intensities of the gaseous mixtures were two times larger than that of pure CS_2, in agreement with the product yield obtained by weighing.

Chemical processes in the gaseous phase were investigated by measuring FT-IR spectra of a gaseous mixture of CS_2 (10 Torr) and TMPSi (5 Torr). The spectrum of the mixture before the light irradiation (Fig. 5) coincided with the superimposed spectra of the individual CS_2 and TMPSi, showing the absence of chemical reaction and complex formation between the components. Upon UV light exposure,

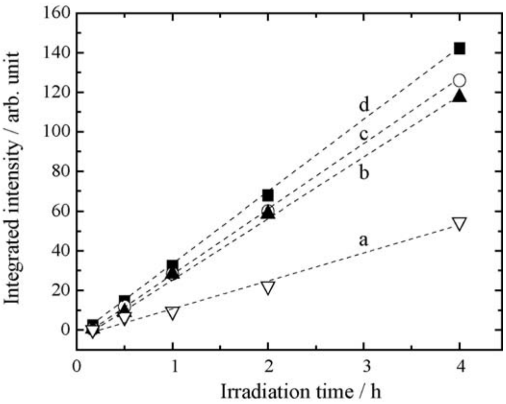


Fig. 4. Scattered light intensity integrated to the irradiation time of exciting light for gaseous mixtures of CS_2 (50 Torr) and TMPSi. Respective partial pressures (in Torr) of TMPSi were: (a) 0, (b) 5, (c) 10, and (d) 15.

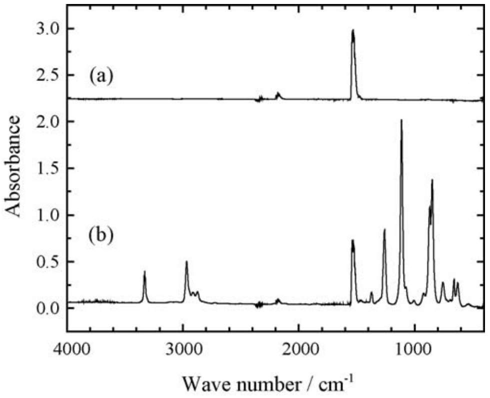


Fig. 5. FT-IR spectra of (a) pure CS_2 vapor (10 Torr), and (b) a gaseous mixture of CS_2 (10 Torr) and TMPSi (5 Torr).

the spectra of the gaseous mixture were measured after allowing for complete sedimentation of the formed aerosol particles. Depletion of ν(C=S) band at 1521 cm^{-1} of CS_2 was compared in pure CS_2 and in the gaseous mixture. The value ($-\ln(A/A_0)$) was plotted against cumulative irradiation time (Fig. 6), and the depletion rate of CS_2 (assuming the pseudo first order decay) was determined to be $2.1 \times 10^{-4}\,s^{-1}$ in the gaseous mixture and $9.7 \times 10^{-6}\,s^{-1}$ for pure CS_2. CS_2 depletion was accelerated by ≈20 times due to the presence of TMPSi. For a gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr), the depletion of TMPSi bands (3324, 2968, and 1260 cm^{-1} bands) was also measured. In a typical experiment under 4 h irradiation, TMPSi and CS_2, respectively, depleted by ∼6% (0.6 Torr) and ∼1.2% (0.6 Torr), i.e., almost equal amount in each other. This strongly suggested that TMPSi was incorporated significantly into the sedimentary particles.

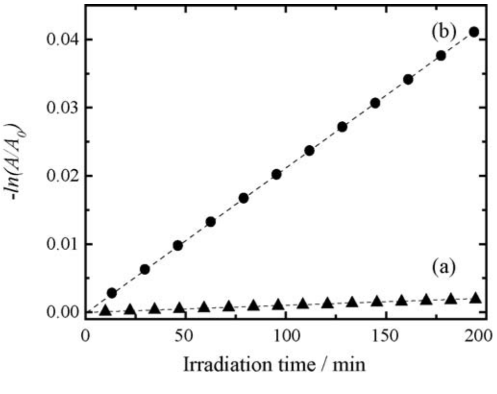


Fig. 6. Depletion ($-\ln(A/A_0)$) of CS_2 molecules against irradiation time for (a) pure CS_2 vapor (10 Torr), and (b) a gaseous mixture of CS_2 (10 Torr) and TMPSi (5 Torr).

FT-IR spectra of sedimentary aerosol particles deposited from the gaseous mixtures of TMPSi (5, 10, or 15 Torr) and CS_2 (50 Torr) are shown in Fig. 7. When TMPSi was mixed with CS_2 vapor, strong bands characteristic of trimethylsilyl group such as $\delta(SiCH_3)$ band at 1250 cm^{-1} and $\rho(SiCH_3)$ band at 845 and 865 cm^{-1} and of ν(Si–O) band at 1100 cm^{-1} appeared, whereas the bands of polymeric CS_2 at 1443 and 1508 cm^{-1} disappeared and ν(C=S) band at 1060 cm^{-1} became weak. The ν(C=S) band was obscured by the overlapping ν(Si–O) band with increasing partial pressure of TMPSi. FT-IR spectra measured with both the gaseous mixtures and the sedimentary aerosol particles clearly indicated that TMPSi was incorporated into the nucleation and propagation reactions in aerosol particle formation.

The XPS analysis was performed on the sedimentary aerosol particles deposited on a Cu substrate from a

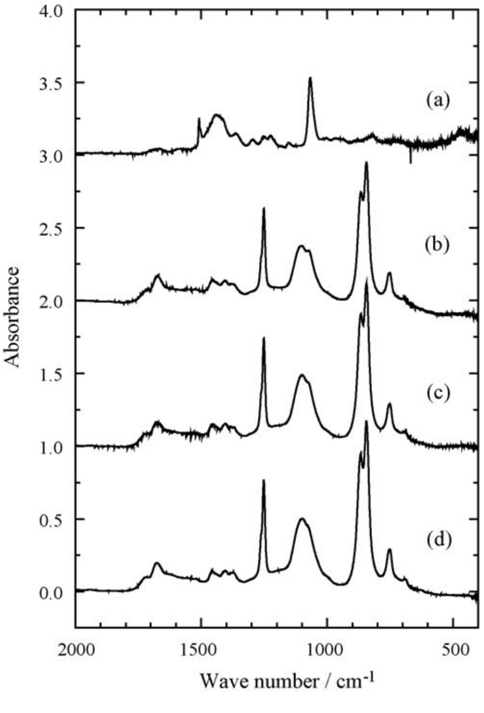


Fig. 7. FT-IR spectra of sedimentary particles deposited from gaseous mixtures of CS_2 (50 Torr) and TMPSi under light irradiation at 313 nm for 4 h. Respective partial pressures (in Torr) of TMPSi were: (a) 0, (b) 5, (c) 10, and (d) 15.

gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr). To check the homogeneity over the substrate, the spectra were measured at two different spots on the substrate. The Stoichiometry of atoms was $S_{1.0}C_{8.2}O_{3.4}Si_{0.57}(Cu_{1.8})$, and $S_{1.0}C_{7.1}O_{2.6}Si_{0.26}(Cu_{1.4})$ in each spot. Cu signal came from the uncovered substrate, and the analysis of the signal indicated that some fraction of the O and also of the C signals could originate from oxidation of the substrate and the surface contamination with hydrocarbons present prior to particle deposition. The population of atoms measured at two different spots indicated that the sample may not be homogeneous. Stoichiometry of atoms clearly showed that Si (i.e., TMPSi molecule) was involved efficiently in the sedimentary particles with molar ratio of 1:1–1:2 to CS_2 molecule, in agreement with the result obtained from the depletion of the gaseous molecules. Si 2p spectra at two different spots showed a major band at 101.6 eV, which was assigned to silicon atoms in trimethylsilyl group bonded to oxygen atom. Fig. 8 shows the S 2p spectra measured at two different spots. Considering the splitting due to spin-orbit coupling of S 2p band, the spectra were resolved into four bands. The results are summarized in Table 1, together with the results of C 1s spectra. The particles contain sulfur atoms in a C—S bonding (and partly in elemental sulfur) as a major (~40%) contribution. About 40% of sulfur can be assigned to sulfur in >C=S or Cu—S bonding, and remaining ~13% to sulfidic and/or S—O moiety [14–16]. These latter two contributions likely result from reactions of S with Cu substrate and with atmospheric oxygen. In the C 1s spectra of the sedimentary aerosol particles, carbon belonging to the C—S bonding was detected at 285.5 eV. The binding energies (284.5 and 287.7 eV) of components of the C 1s spectra are compatible with carbon contained in C—C and C—H bonds (major components) and C—O and C=O bonds (minor components). The atomic ratio of S and C atoms pertinent to the C—S bonding was evaluated to be ~1:3. For the particles deposited from pure CS_2, the value is very close to unity [17]. This implies that contribution from carbon contained in $-CH_2-CH_2-$ and $-CH_2-CH=CH-CH_2-$ bonds is significant to the band at 285.5 eV.

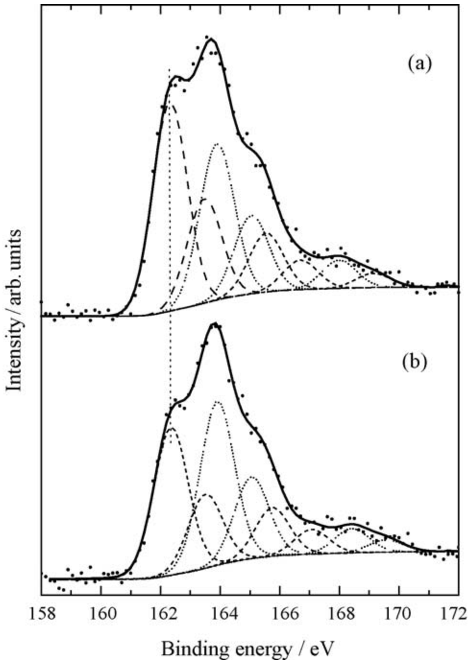


Fig. 8. Fitted spectra of S 2p electrons of the sedimentary particles produced from a gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr) measured at two different spots: (a) and (b).

As revealed from the XPS analysis, the particles deposited from the gaseous mixture of TMPSi and CS_2 contain sulfur atoms in >C=S bonding as well as in C—S bonding. The sedimentary particles deposited from pure CS_2 contain sulfur atoms predominantly in C—S bonding [17]. Formation of >C=S bonding are clearly due to the interaction of CS_2 with TMPSi molecule. Under UV light irradiation at 313 nm, excited CS_2 molecules react with both CS_2 [4,5,18–23] and TMPSi molecules in the ground electronic state.

$$CS_2 + h\nu \rightarrow CS_2^* \tag{1}$$

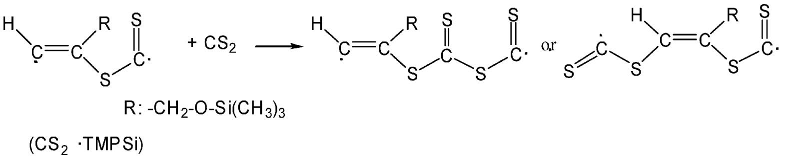
$$CS_2^* + CS_2 \rightarrow (CS_2)_2^* \rightarrow (CS)_2 + S_2 \tag{2}$$

$$CS_2^* + \text{TMPSi} \rightarrow (CS_2 \cdot \text{TMPSi}) \tag{3}$$

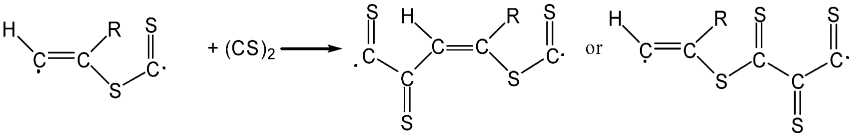
Table 1
XPS characterization of aerosol particles deposited from a gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr)

Line designation	Measuring spot (a)		Measuring spot (b)		Assignment [14–17]
	Binding energy (eV)	Population	Binding energy (eV)	Population	
S $2p_{3/2}$	162.0	0.46	162.0	0.39	>C=S, Cu—S
	163.6	0.35	163.6	0.43	C—S
	165.2	0.13	165.4	0.13	R—S—O
	168.1	0.06	168.4	0.06	R—SO_2
C 1s	284.5	5.53	284.5	4.00	C—C, C—H
	285.5	0.91	285.5	1.32	C—S
	286.4	0.49	286.4	0.86	C—OH
	287.7	0.74	287.7	0.63	C=O
	288.2	0.53	288.2	0.28	C—O—C
Si 2p	101.6	0.57	101.4	0.16	Si—C
	–	–	102.8	0.06	Si—O

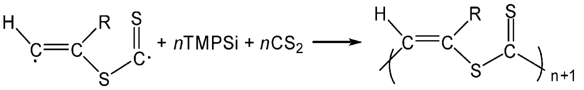
Considering the acceleration of nucleation reaction with increasing partial pressure of TMPSi, reaction (3) is more efficient than reaction (2) in the gaseous mixture. Transient species ($CS_2 \cdot$TMPSi), can react with CS_2, $(CS)_2$, and TMPSi (reactions (4)–(6)) to initiate polymerization reactions.



(4)



(5)



(6)

These reactions may compete with each other to produce complex chemical structures of the aerosol particles. Thus, the C–S and C=S structures are involved in the sedimentary aerosol particles, and TMPSi molecules can accelerate the nucleation reaction in aerosol particle formation through polymerization reaction at the C≡C bond, resulting in the formation of ultrafine particles which are rich in organosilicon compounds.

Upon exposure to N_2 laser light, a gaseous mixture of TMPSi and CS_2 produced sedimentary aerosol particles. FT-IR spectrum of the deposited particles is shown in Fig. 9. Compared to the spectrum of the sedimentary particles produced under light irradiation at 313 nm (Fig. 7), ν(C=S) band at 1066 cm^{-1} and ν(C=C) band at 1672 cm^{-1} became prominent. This may suggest that strong laser light favors formation of $(CS)_2$ species, resulting in more abundance of >C=S (and possibly C=C) chemical bonds in the aerosol particles [22]. In TMPSi/CS_2 gaseous mixture, one-photon process of CS_2 is very efficient to produce ($CS_2 \cdot$TMPSi) species (Eq. (3)). Hence, two-photon excitation of TMPSi molecules which may be followed by C=C bond formation from the C≡C bond of TMPSi molecules [1] does not contribute significantly. This is in contrast to the case of TMPSi/AC gaseous mixture [3] where AC initiated nucleation reaction by a two-photon process with much lower efficiency than CS_2. Thus, in TMPSi/AC gaseous mixture, two-photon process of TMPSi molecules contributed effectively to the particle formation, resulting in Si–C bond cleavage of trimethylsilyl group followed by the production of elemental silicon in the particles.

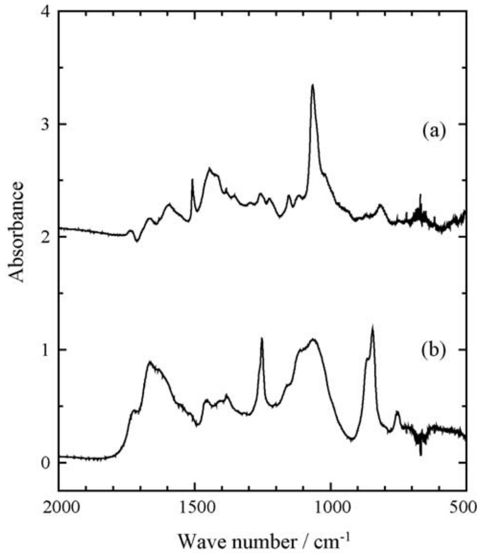


Fig. 9. FT-IR spectra of sedimentary particles deposited from (a) pure CS_2 (50 Torr) and (b) a gaseous mixture of CS_2 (50 Torr) and TMPSi (10 Torr) under N_2 laser light irradiation for 3 h.

4. Conclusions

Ultrafine particles being rich in organosilicon compounds were synthesized from the gaseous mixture of TMPSi and CS_2. TMPSi molecules accelerated the nucleation and propagation reactions in aerosol particle formation, and the chemical interaction with CS_2 molecules and possibly with $(CS)_2$ species produced >C=S chemical bond in addition to C–S chemical bond in the sedimentary particles.

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