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## Precipitation of dichloromethane as low-chlorine carbon nanoparticles from water by femtosecond laser pulses



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### ABSTRACT

We report on the transformation of dichloromethane to low-chlorine carbon nanoparticles by the exposure of aqueous dichloromethane solution and/or dichloromethane/water biphasic solution to femtosecond laser pulses. The pH of either solution immediately decreased due to the reduction of dichloromethane by hydrated electrons. The time evolution of transmittance revealed that particle formation was suppressed when the initial pH was low because protons scavenge hydrated electrons. The size and morphology of nanoparticles was independent of the initial pH and the reaction solution used. The analysis of the elemental composition of carbon particles showed that the Cl/C atomic ratio was, independent on the initial pH values, greatly reduced to 0.06. We propose that the violent destruction of dichloromethane and elimination of chlorine atoms not only as  $\text{Cl}^-$  but also  $\text{Cl}_2$  excludes chlorine atoms from the carbon network construction processes toward the formation of carbon nanoparticles.

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### 1. Introduction

Chlorohydrocarbons (CHCs), which are widely used in the chemical industry, are regarded as environmental pollutants due to their highly volatile nature and high solubility in water [1]. Emission of CHCs into the atmosphere and their discharge into water are known to harm the global environment. For the treatment of massive CHC fluid, combustion has practically been used. To remove CHCs from water, physical methods such as adsorption and membrane filtering have been used, as have biological [1] and catalytic treatments [2]. In addition, sonication [3], vacuum ultraviolet light irradiation [4], and radiolysis [5] have been examined to decompose CHCs in water. However, difficulties arise in those methods if the complete mineralization is not achieved. Once more volatile and soluble chlorine-containing organic fragments are formed from CHCs, it is difficult to separate them from water. For example, products originating in radical recombination, such as di-, tri-, and tetrachloroethane are found by VUV photolysis of aqueous dichloromethane (DCM) solution [4].  $\text{C}_2\text{H}_4\text{Cl}_2$ ,  $\text{HCOOH}$ , and  $\text{CH}_2\text{O}$  are obtained by  $\gamma$ -radiolysis of DCM in water [6]. The treatment of CHCs dissolved in water by above

mentioned methods is based on the production of reactive species such as hydrated electrons ( $e^-_{\text{aq}}$ ) and hydroxyl radicals ( $\bullet\text{OH}$ ) produced by high-energy deposition into water [2–6]. However, it seems that the conventional methods cannot produce enough density of reactive species to achieve complete decomposition of DCM. Herein, we suggest that the alternative way to remove CHCs from water is precipitation of the products of CHCs in water. If we obtain the resultant products as solid forms, the filtering of those products from water can be done easily. The formation of precipitates from aqueous DCM solution has only been reported in the case of high-dose radiolysis [5]. However, the resultant polymer contains a large amount of chlorine (Cl/C=0.34, stoichiometry was  $\text{C}_3\text{H}_3\text{OCl}$  [5].) The establishment of the simultaneous achievements of both dechlorination and solidification is expected to meet the requirement of the alternative methods for the treatment of CHCs.

It is well known that focusing intense femtosecond laser pulses onto water creates a high density of  $e^-_{\text{aq}}$  and  $\bullet\text{OH}$  in a well-confined volume [7]. Recently, we synthesized hydrophilic and hydrophobic carbon nanoparticles (CNPs) by femtosecond laser irradiation of the water phase of an aerated benzene/water biphasic solution as well as of the aqueous benzene solution [7,8]. We suggested that successive oxidations of benzene with  $\bullet\text{OH}$  finally lead to the formation of CNPs and their agglomerates [8]. In the case of benzene, the reaction rate of benzene with  $e^-_{\text{aq}}$  is much

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smaller than that with  $\cdot\text{OH}$ . On the contrary, we have shown that metal ions were reduced by a high density of  $e^-_{\text{aq}}$  generated from solvent by femtosecond laser ionization [9–12].

In this study, we report the significant reduction of Cl/C ratio from 2 (the reactant, DCM) to 0.06 (the products) are achieved by the transformation of DCM to carbon nanoparticles (CNPs) by femtosecond laser pulse irradiations. The relatively small Cl/C ratio and uniform element distributions in CNPs are explained by the violent fragmentation of DCM by high density  $e^-_{\text{aq}}$  followed by the elimination of chlorine atom not only as  $\text{Cl}^-$  but also  $\text{Cl}_2$ .

## 2. Materials and methods

Dichloromethane (DCM, Nacalai Tesque, 99.5%) and distilled water (Nacalai Tesque) was used without further purification. The saturated aqueous DCM solution ( $0.15 \text{ mol dm}^{-3}$ ) was prepared by separating the water phase one day after the mixing of DCM and water by shaking. The DCM/water biphasic solution was prepared by slowly adding 1 mL water to 1 mL of DCM in a quartz cuvette without disturbing the interface. Aqueous HCl (Nacalai Tesque) and NaOH (Nacalai Tesque) were used to prepare acidic (pH 2) and alkaline (pH 10) aqueous DCM solutions, respectively.

Femtosecond laser pulses ( $0.8 \mu\text{m}$ , 40 fs, 0.4 mJ, 1 kHz) were focused on a quartz cuvette with a 1-cm optical path length by using a plano-convex quartz lens with a focal length of 50 mm. The beam was focused on the center of the aqueous DCM solution (1 mL). In the case of the DCM/water biphasic solution, the beam was focused on the water phase 13 mm above the bottom of the cuvette (near the DCM/water interface).

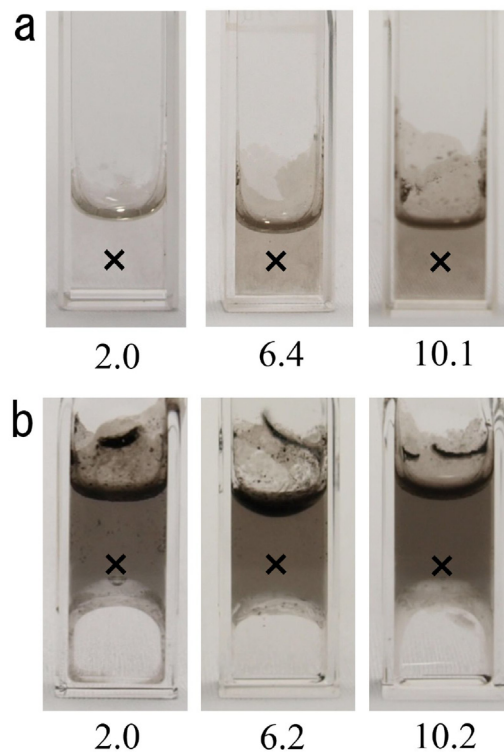
The time evolution of the transmittance was measured by using a diode laser (635 nm) and a calibrated Si pin-photodiode. A pin-hole ( $600 \mu\text{m}$  in diameter) was placed in both the front and back of the cuvette. The output signal from a Si pin-photo diode was collected by using a data logger (Graphtec, GL820). To avoid any disturbance caused by bubbles, the transmittance measurement was carried out 30 s after the beam was blocked. Batch-type pH measurements were carried out by using a calibrated pH meter (Horiba Scientific, B-712,  $12 > \text{pH} > 2$ ,  $\pm 0.1 \text{ pH}$ ).

After the 10-min laser irradiation,  $5 \mu\text{L}$  of aqueous DCM solution was dropped onto a copper grid covered with amorphous carbon film. The drop was allowed to dry in order to prepare specimens for transmission electron microscopic (TEM, JEOL, JEM-1010, 80 kV) observations.

In the case of the DCM/water biphasic solution, after the 10-min laser irradiation the solution was shaken to move the particles to the DCM phase. The DCM phase was then collected, centrifuged repeatedly (13,500 rpm, 90 min), and dried. Particles were washed with water in order to remove Na and Cl atoms physically deposited on the surface of particles. The particles were sonicated in distilled water and centrifuged repeatedly. The particles were then separated from water followed by drying in a vacuum. The precipitates suspended in acetone were dropped onto a silicon substrate. The drop was allowed to dry in order to prepare samples for observation under a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS, JEOL, JSM-6610LA, 15 kV) and a Raman spectrometer (JASCO, NRS-3100, 532 nm).

## 3. Results

Fig. 1 shows the aqueous DCM solution and the DCM/water biphasic solution after the 10-min laser irradiation. It should first be mentioned that visible particles were not observed when DCM was exposed to laser pulses under our experimental conditions. Therefore, it is suggested that the excitation and/or ionization of water is essential since the excitation and/or ionization of DCM



**Fig. 1.** The cuvette after the 10-min laser irradiation. (a) Aqueous DCM solution, (b) DCM/water biphasic solution. The values below the images indicate the pH before irradiation. Laser focusing position is indicated by  $\times$ .

does not lead to particle formation. It is also noted that the DCM/water biphasic solution contained more black particles than the aqueous DCM solution. This trend was similar to that observed in our previous study: more carbon particles were produced in the organic/water biphasic solution than in the aqueous organic solution [8,13]. As has been proposed in the case of the organic/water biphasic solution [8,13], the continuous supply of a carbon source (DCM in this study) through the DCM/water interface during the laser irradiation enhanced the production of particles. The black particles formed in the aqueous DCM solution moved to the DCM phase when DCM was added to the solution followed by shaking of the solution by hand. In the DCM/water biphasic solution, the black particles initially appeared in the water (upper) phase (Fig. 1b). However, these particles moved to the DCM (lower) layer when the DCM/water biphasic solution was shaken by hand. Therefore, it is reasonable to say that the black particles formed in both solutions were hydrophobic.

Laser irradiation was carried out for samples with different initial pH values. It was obvious that less amount of black particles were formed in the acidic than in the alkaline aqueous DCM solution (Fig. 1a). In the DCM/water biphasic solution, on the other hand, no initial pH effect was visible due to the high optical density of particles (Fig. 1b). The estimation of particle amount by weight is difficult because the 10-min laser irradiation gives less than 0.1 mg of particles although particles seem to be formed in high density. Therefore, we measured transmittance in order to trace the particle formation processes. Fig. 2 shows the time evolution of the transmittance measured at 635 nm. It should be noted that the condensation of black particles on the air–liquid interface (Fig. 1) prevents us from evaluating the actual amounts of black particles. The condensation behavior was observed after the 5-min (aqueous DCM solution) and the 3-min (DCM/water biphasic solution) laser irradiation. The transmittances of aqueous DCM solution after the 5-min laser irradiation were 69% (initial pH was 2.1), 40% (initial

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