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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 Cl^- but also Cl_2 excludes chlorine atoms from the carbon network construction processes toward the formation of carbon nanoparticles.

Keywords

ionization; hydrated electrons; filamentation, dechlorination, remote treatment

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]. $C_2H_4Cl_2$, HCOOH, and CH_2O are obtained by γ-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^-_{aq}) and hydroxyl radicals (•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 C_3H_3OCl [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^{-}_{aq} and •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 •OH finally lead to the formation of CNPs and their agglomerates [8]. In the case of benzene, the reaction rate of benzene with e^{-}_{aq} is much smaller than that with •OH. On the contrary, we have shown that metal ions were reduced by a high density of e^{-}_{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^{-}_{aq} followed by the elimination of chlorine atom not only as Cl^{-} but also 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 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 μm, 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 μm 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, $12 > \mathrm{pH} > 2$, ±0.1 pH).

After the 10-min laser irradiation, 5 μL 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

Figure 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 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.

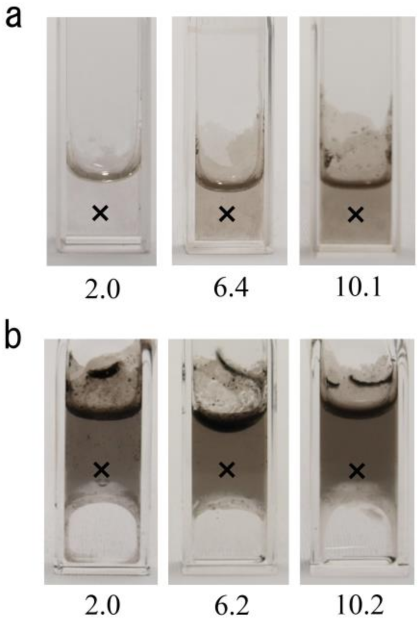

Figure 1. The cuvette after the 10-min laser irradiation. (a) Aqueous DCM solution, (b) DCM/water biphasic solution. The values below the images indicate the pH before irradiation. Laser focusing position is indicated by ×.

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. Figure 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 (DMC/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 pH was 6.2), and 38% (initial pH was 9.9). These results are consistent with what was observed by the eye (Fig. 1a). The transmittance seems to become constant by prolonged irradiation judging from the decay behavior in the cases of aqueous DCM solution.

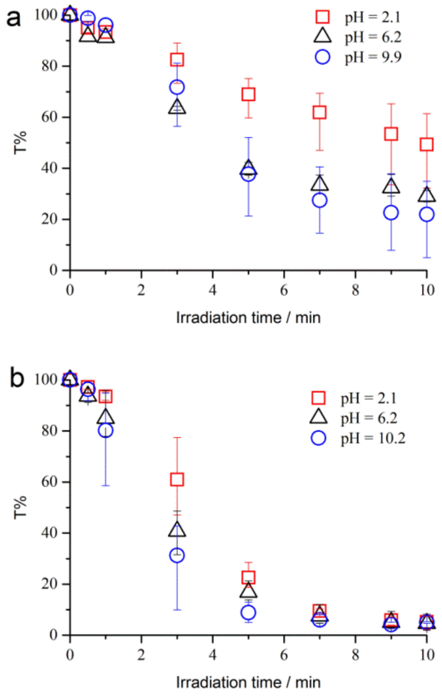

Figure 2. The time evolutions of the transmittance of (a) aqueous DCM solution and (b) the water phase of the DCM/water biphasic solution. The initial pH was adjusted to ca. 2, 6, or 10. The vertical bars show the maximum and minimum values obtained in the three measurements.

The decrease in the transmittance of the water phase was faster in the DCM/water biphasic solution than in the aqueous DCM solution. The transmittances of the water phase of the DMC/water biphasic solution after the 3-min laser irradiation, in which the condensation was not visible, were 61% (initial pH was 2.1), 41% (initial pH was 6.2), and 31% (initial pH was 10.2). The transmittance of the acidic solution was almost twice that of the alkaline solution. However, the transmittance became almost zero, independent on the initial pH value, after the 10-min laser irradiation, as confirmed by the eye (Fig. 1b). Although the quantitative analysis on reaction rates is hardly difficult by means of transmittance measurement, it takes longer time to reach 50% transmittance under acidic condition compared with that under alkaline condition. The times required to reach 50% transmittance of the aqueous DCM solution were 10 (pH 2.1), 4.1 (pH 6.2), and 4.3 min (pH 9.9). Those of the DCM/water biphasic solution were 3.3 (pH 2.1), 2.4 (pH 6.2), and 2.1 min (pH 10.2). Although there are some ambiguities in the transmittance measurements, it is concluded that the rate and yield of black particle formation is suppressed under acidic conditions.

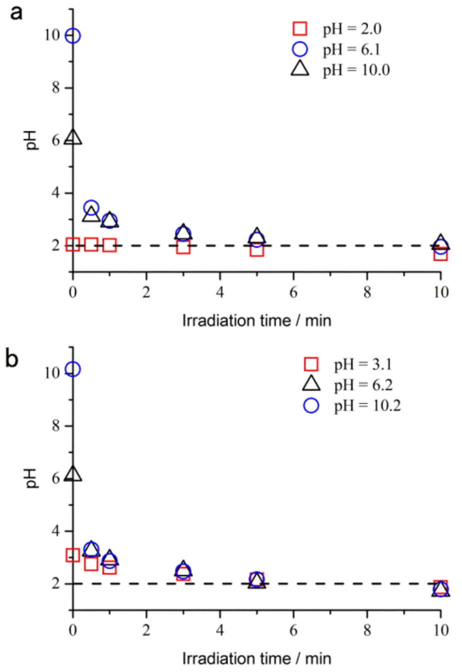

Figure 3. The time evolution of pH. (a) Aqueous DCM solution, (b) DCM/water biphasic solution. Broken lines indicate the lower limit of pH measurement.

The time evolution of pH upon laser irradiation is shown in Fig. 3. The pH dropped to around 3 by the 30-s irradiation. This sudden drop is independent on the initial pH in both the aqueous DCM solution and the DCM/water biphasic solution. In both cases, the pH became 2, which was the lower limit of our pH measurement, by the 5-min irradiation. The decrease in pH indicates the formation of Cl^- as the counter ion of H^+. The addition of silver nitrate aqueous solution to the DCM/water biphasic solution as well as to the aqueous DCM solution gave white precipitates after the 10-min laser irradiation. Furthermore, the coloration of the reaction solution occurred by adding a chlorine indicator such as 4,4'-diamino-3,3'-dimethylbiphenyl (or N,N-diethyl-p-phenylenediamine) aqueous solution. These results indicate that the reaction solution after laser irradiation contains Cl^- as well as Cl_2 and/or HClO.

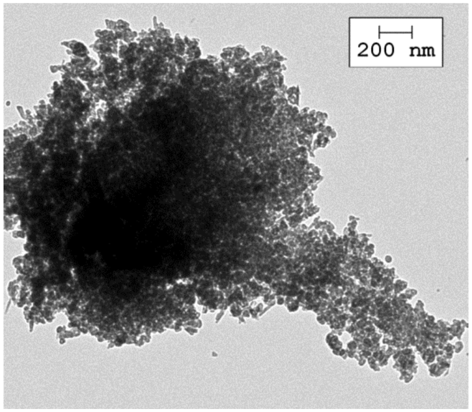

Figure 4. TEM image of the black particles collected from the aqueous DCM solution (initial pH = 6.0).

Figure 4 shows a typical transmission electron microscope (TEM) image of black particles produced by the 10-min irradiation to the aqueous DCM solution. Most of the particles were agglomerated, but the individual particles were less than 50 nm in diameter. The size and morphology seemed to be independent of the initial pH and the reaction solution used (aqueous DCM solution or DCM/water biphasic solution) although the size distribution was not obtained due to large agglomeration. Figure 5 shows the Raman spectra of the black particles. Two significant bands in the spectra were assigned as a D band (ca. 1340 cm^{-1}) and a G band (ca. 1580 cm^{-1}), respectively. It is clear that the particles show typical peculiarities of disordered structure of CNPs. The peak position and the ratio between the D band and G band intensities seemed to be independent of the initial pH.

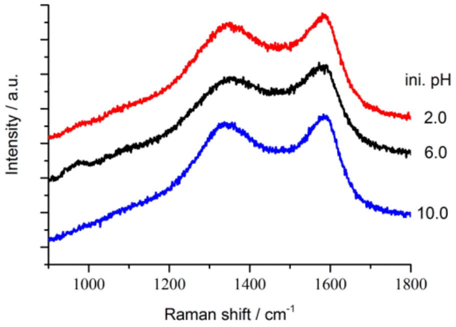

Figure 5. Raman spectra of black particles.

Table 1 shows the atomic composition as well as the Cl/C and O/C atomic ratios of CNPs obtained by a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (SEM-EDS). Due to the deep penetration of high-energy electrons, the SEM-EDS measurements can be used to investigate the atomic composition of agglomerated whole particles. In addition, the irradiation area of electrons (100×100 μm^2) was large enough to allow us to obtain the averaged atomic composition of the CNPs. It was found that both the Cl/C and O/C atomic ratios were independent of the initial pH. We emphasize that the Cl/C atomic ratio is reduced from 2 (CH_2Cl_2) to 0.05−0.06 (products). The obtained atomic compositions correspond to a particle with an approximate $C_{35}O_3Cl_2$ stoichiometry. Furthermore, the elemental mapping analysis using SEM-EDS showed the uniform distribution of each element in the particles (Fig. 6).

Table 1. Atomic compositions (atom%) and their relative ratios of carbon nanoparticles

pH	C[a]	O[a]	Cl[a]	O/C	Cl/C
2	88.1±0.7	6.7±0.6	5.0±0.3	0.076	0.057
6	88.3±1.0	7.2±0.9	4.4±0.3	0.081	0.050
10	88.3±1.0	6.8±1.4	4.8±1.0	0.077	0.054

[a] Average of six (pH = 2, 6) and four (pH = 10) measurements.

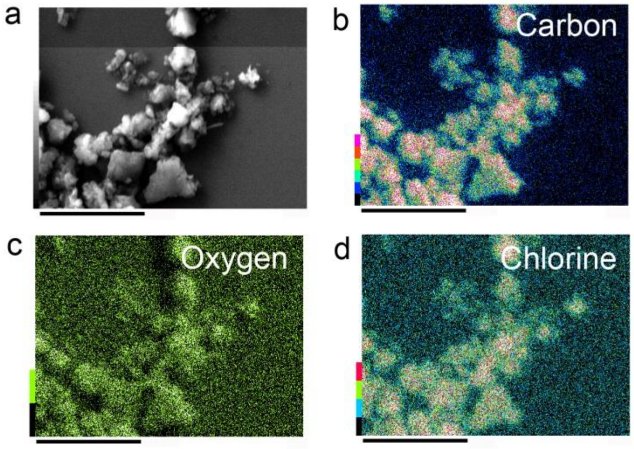

Figure 6. (a) SEM-image and (b-d) EDS mappings of carbon particles collected from the aqueous DCM solution (initial pH = 6.0). Scale bar, 20 μm.

4. Discussion

We demonstrated the transformation of DCM dissolved in water to low-chlorine CNPs by femtosecond laser irradiation. In order to clarify the plausibility of the femtosecond laser pulses in the production of low-chlorine CNPs from DCM, we need to consider 1) what was the reactive species and primary reaction, 2) why did the suppression of CNP production occur under acidic conditions, 3) why did Cl_2 (or HClO) exist in the reaction solution, 4) why did CNPs contain small amounts of chlorine, 5) why was each element uniformly distributed in particles, and 6) how we could improve the treatment efficiency?

By the exposure of water to femtosecond laser pulses, reactive species such as e^{-}_{aq}, •OH, and H• are generated. They react with DCM as described in Scheme 1. The reaction rate of DCM with e^{-}_{aq} (1), •OH (2), and H• (3) are 6.3×10^{9} [14], 6.6×10^{7} [15], and 4.0×10^{6} dm^{3} mol^{-1} s^{-1} [14], respectively. Femtosecond laser irradiation produces significantly high density of electrons, which is estimated to be from 10^{18} (1.7×10^{-3} mol dm^{-3} [16]) to 7.3×10^{19} cm^{-3} (0.12 mol dm^{-3} [17]). The highest value is presumably incorrect because the annihilation before hydration is not considered [17], however, even the lowest value is far exceed the concentration of e^{-}_{aq} (on the order of μmol dm^{-3} [18], < 4 μmol dm^{-3} at 7 Gy [5]) that obtained by radiolysis. Based on the rate constants of DCM mentioned above and the expected electron density, the reaction between DCM and e^{-}_{aq} would be the most probable primary reaction. Unfortunately, the chemistry beyond the primary reactions between DCM and e^{-}_{aq} is uncertain due to its complexity. It is noted that e^{-}_{aq} also attacks hexafluorobenzene dissolved in water to form CNPs [19].

$$\mathrm{DCM} + e^{-}_{aq} \longrightarrow \cdot CH_2Cl + Cl^{-} \tag{1}$$

$$\mathrm{DCM} + \cdot OH \longrightarrow \cdot CHCl_2 + H_2O \tag{2}$$

$$\mathrm{DCM} + \cdot H \longrightarrow \cdot CHCl_2 + H_2, \cdot CH_2Cl + HCl \tag{3}$$

$$e^{-}_{aq} + e^{-}_{aq} \xrightarrow[H_2O]{} H_2 + 2\,OH^{-} \tag{4}$$

$$e^{-}_{aq} + \cdot H \xrightarrow[H_2O]{} H_2 + OH^{-} \tag{5}$$

$$e^{-}_{aq} + \cdot OH \longrightarrow OH^{-} \tag{6}$$

$$e^{-}_{aq} + O_2 \longrightarrow \cdot O_2^{-} \tag{7}$$

$$e^{-}_{aq} + H^{+} \longrightarrow \cdot H \tag{8}$$

$$Cl^{-} \longrightarrow \cdot Cl + e^{-}_{aq} \tag{9}$$

$$\cdot Cl + \cdot Cl \longrightarrow Cl_2 \tag{10}$$

$$\cdot Cl + Cl^{-} \longrightarrow \cdot Cl_2^{-} \tag{11}$$

Scheme 1. Possible Reactions in Aqueous DCM.

In order to clarify the pH effect on the production of CNPs, we consider the quenching reactions of e^{-}_{aq} competitive with the primary reaction between DCM and e^{-}_{aq}. The rate of DCM disappearance by e^{-}_{aq} is 9.5×10^{8} s^{-1} (1.1 ns) based on the saturated concentration of DCM in water (0.15 mol dm^{-3}). The quenching reaction rate constants of e^{-}_{aq} with e^{-}_{aq} (4), H• (5), •OH (6), O_2 (7), and H^{+} (8) are 0.55×10^{10}, 2.5×10^{10}, 3.0×10^{10}, 1.9×10^{10}, and 2.3×10^{10} $dm^{3}mol^{-1}s^{-1}$, respectively [20]. The reactions (4)-(6) would influence the pH of the solution because OH^{-} is formed in these reactions. However, the pH of the solution fell from 6 or 10 to 3 with the 30-s laser irradiation, as shown in Fig. 3. The degree of pH drop indicates that the solution is not neutralized efficiently by OH^{-}. Therefore, the annihilation (4) and scavenging process of e^{-}_{aq} by H• (5) and/or •OH (6) are expected to be minor processes. The concentration of O_2 in water is 2.7×10^{-4} mol dm^{-3}, thus the rate of e^{-}_{aq} disappearance and the formation of O_2^{-}• under aerated conditions is 5.1×10^{6} s^{-1} (0.19 μs). Though O_2 is evolved from water by a prolonged femtosecond laser irradiation [21], the quenching of e^-_{aq} by oxygen (7) would not be important. The rate of e^-_{aq} disappearance by H^+ is calculated to be 2.3×10^8 s^{-1} (4.3 ns) when pH is 2. Thus, this reaction (8) is competitive with the disappearance of e^-_{aq} by DCM (1.1 ns). In addition, the resultant H• is inactive toward DCM. Based on the kinetics of e^-_{aq}, it is concluded that the suppression of CNP formation under acidic conditions is attributable to the loss of e^-_{aq} by H^+.

Although neither Cl_2 nor HClO was detected in high-dose radiolysis [5], we detected Cl_2 (or HClO) as well as Cl^- in the reaction solution after the 10-min laser irradiation. The detection of Cl_2 (or HClO) in this study indicates that it is necessary to consider the transformation of Cl^- to Cl_2 (or HClO). However, Cl^- does not transform to Cl_2 without strong oxidizing reagents. The possible process by which to change the valence of Cl^- may be the multiphoton ionization of Cl^- to Cl• (9) by femtosecond laser pulses. Once Cl• is formed, Cl_2 may presumably be formed by the recombination of two Cl• (10). However, Cl• probably reacts with Cl^-, forming $•Cl_2^-$ (11, 8.5×10^9 $dm^3mol^{-1}s^{-1}$ [22]), because the self-recombination of Cl• would be a minor process [22]. Once $•Cl_2^-$ is formed, Cl_2 is produced from Cl• and $•Cl_2^-$, and also from two $•Cl_2^-$ [22]. More probably, multiphoton ionization of $•Cl_2^-$ forms Cl_2 since $•Cl_2^-$ has absorption maximum at 340 nm, which is accessible by three 0.8-μm photons. The pK ($[Cl_2]/[HClO] = 1$) varies from 1.25 to 2.11, depending on the concentration of chlorine [23]. In addition, the solubility of Cl_2 in water is high (≈ 0.08 mol dm^{-3} at pH = 2) even in the presence of HCl [24]. Thus Cl^- as well as Cl_2 was the dominant form of chlorine after the 5-min laser irradiation, as the pH of the reaction solution became 2. Although we cannot evaluate the concentration of Cl_2 by absorption spectroscopy due to the dense formation of CNPs, it is suggested that the elimination of chlorine atom not only as Cl^- but also Cl_2 would presumably be one of the important factor in low-chlorine products formation. The efficient elimination of chlorine atoms baring carbon skeleton of DCM helps carbon network constructions and finally leads to CNP formation.

The partial fragmentation of DCM would leave chlorine atoms in the fragments. Thus, the recombination of these fragments results in dimeric compounds such as $C_2H_4Cl_2$ [6] as well as a chlorine-incorporated polymer found in radiolysis [5]. If the CNPs are formed by femtosecond laser irradiation via the partial fragmentation processes, the resultant CNPs should contain large amounts of chlorine. The elemental analysis, however, showed that only a small portion of chlorine was incorporated into the resultant CNPs ($Cl/C = 0.06$, $C_{35}O_3Cl_2$). In addition, each element was uniformly distributed in CNP agglomerates. Therefore, it is suggested that the low-chlorine CNP formation is explained in terms of the violent fragmentation of DCM and/or its fragments by femtosecond laser pulses.

The precipitation of DCM as low-chlorine CNPs in water is demonstrated by femtosecond laser irradiation. This evidence reveals the potential ability of femtosecond laser processing of organic wastes dissolved in water. However, our proposed method has many difficulties for the engineering applications (productivity, high investment cost, and scalability). The low production yield is originated in the very small reaction volume (in a few tens of micrometers in diameter [12]) although the electron density achieved in this study reaches 10^{18} cm^{-3} (1.7×10^{-3} mol dm^{-3}.) In addition, laser pulses cannot penetrate due to the high optical density when the black CNPs are formed. These disadvantages could be overcome by producing several hundreds of focusing spots using a fly's-eye lens array as well as by using a flow reactor [25,26]. More cost effective and high productivity approach may be the replacement of femtosecond laser to the combination of other plasma sources and VUV light if high density electron generation as well as successive photoreactions are possible.

5. Conclusions

The precipitation of DCM as low-chlorine CNPs in water is demonstrated for the first time by femtosecond laser irradiation. The production of the agglomerates of CNPs was suppressed under low pH conditions owing to the quenching of the primary reduction reaction between DCM and e^{-}_{aq} by protons. The complete destruction of the DCM skeleton excluding chlorine atom from the CNPs construction process enables us to produce low-chlorine CNPs. We propose that the generation of high density of electron as well as successive multiphoton reactions only achievable by femtosecond laser pulses is a useful and alternative way to remove CHCs from water.

Acknowledgements

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