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Nanosecond laser preparation of C_{60} aqueous nanocolloids

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ABSTRACT

C_{60} aqueous nanocolloids were prepared by irradiating a suspended aqueous solution of C_{60} with intense nanosecond 532 and 355 nm laser pulses. The initial submicron crystal of C_{60} was fragmented into nanoparticles, resulting in a transparent yellow solution which was followed by UV/vis absorption spectroscopy. The obtained absorption spectra were similar to those for C_{60} bulk film and its nanoparticles, which have a size on the order of 10 nm, and their formation had thresholds with respect to laser fluence. The nanoparticles were confirmed by their SEM observation and by examining the centrifuging effect on the colloids, while possible photochemical decomposition was excluded by ^{13}C NMR analysis of 1,2-dichlorobenzene-d_4 solution, where the possible products can be dissolved in addition to C_{60} nanoparticles. The present result is the first demonstration of the preparation of pure and very stable C_{60} aqueous nanocolloids without any additives. The formation mechanism and potential application to biological testing and toxicity are discussed.

1. Introduction

Fullerene C_{60} has been widely investigated and is now recognized to have great potential in the research fields of chemistry, physics, biology, applied sciences, and technical applications. Some of the more promising applications are medicinal and pharmaceutical. For example, C_{60} has been examined as a novel drug for photodynamic therapy [1,2] due to its high quantum yield of active oxygen and wide absorption band [3,4]. For such biological testing, the C_{60} molecules should be dissolved in water, although pristine C_{60} molecules are nearly water insoluble. Therefore, various water-soluble fullerene derivatives have been synthesized, although some of these derivatives have been reported to be highly toxic [5,6]. As a way alternative to such chemical synthesis, water dispersion of C_{60} itself has recently attracted increasing interest for biomedical applications. Some methods based on reprecipitation [7], solvent replacement [8], and ultrasonication [9] have been introduced to prepare the dispersion, and surfactant, polymer, or other detergents are often added. However, many of the incorporated ingredients and organic solvents are highly toxic to living cells and tissues, and this toxicity has become the most important factor limiting the biological applications of C_{60}. The toxicity of the water dispersions of C_{60} prepared by the above methods has been carefully investigated both in tissue culture and *in vivo*, and it is reported that the dispersion shows toxicity due to the contained impurities and used solvents [6,10]. Hand-grinding of C_{60} microcrystals can provide a water dispersion without the addition of many chemicals, but the resulting microcrystals usually have a wide size distribution and cannot simply be regarded as "nanocolloids," since C_{60} nanoparticles of less than 100 nm in size only make up 5 wt% of the prepared particles [11].

Over the past decade, we have developed a laser ablation method for preparing various organic dye nanoparticles in solution without any stabilizers or chemical modifiers [12–20]. In this method, organic crystalline powders of micrometer size are suspended in a poor solvent and exposed to laser pulses. Fragmentations of the initial crystals are induced and the ejected nanoparticles are efficiently collected by the poor solvent, resulting in a stable colloidal solution. Our method is being adopted by many researchers, such as for the preparation of various kinds of organic nanoparticles [21,22]. Most recently, Hayashi and co-workers used this method to prepare C_{60} nanoparticles suspended in ethanol [23], and demonstrated that the mean size and distribution of the nanoparticles were strongly dependent on the fluence and wavelength of the laser pulses. With regard to the use of C_{60} dispersion for possible biomedical applications, water should be chosen as a poor solvent, but to our knowledge there has been no report on the use of water in such cases.

In this paper, we present the preparation of C_{60} aqueous nanocolloids by the laser ablation method and their characteri-

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zation, examine the dispersibility of C_{60} nanoparticles in water, and discuss the ablation mechanism and its advantages for future applications.

2. Experimental

C_{60} (>99.9% pure; Tokyo Kasei) was used without any further purification. A mixture of water and C_{60} microcrystalline powder (5.6×10^{-4} wt%, 0.40 mg/ml) was poured into a quartz cuvette of 1 cm × 1 cm × 5 cm with a small magnetic stirrer. The suspension was stirred vigorously and exposed to the second (532 nm, 14 ns, 10 Hz) or the third (355 nm, 8 ns, 10 Hz) harmonic of a Nd^{3+}:YAG pulsed laser under an aerated condition. All absorption spectra within a range of 200–800 nm were measured by a UV/vis spectrometer (Shimadzu; UV-3100PC) at room temperature. For the characterization of the initial dispersion before laser irradiation and the C_{60} water suspension after irradiation, both samples were dissolved in 1,2-dichlorobenzene-d_4 and analyzed using a 400 MHz NMR (JOEL; JNM-ECP400) with a broadband probe. The ^{13}C NMR experiment used a 30 degree ^{13}C pulse and 1-s relaxation delay with proton decoupling taking 25,666 scans. Proton decoupling was used to narrow and to detect any ^{13}C signals from proton-containing species that might be present. For examining the morphology of initial microcrystals and prepared nanoparticles, a drop of the suspensions before irradiation and one of the supernatant after laser irradiation were spread on a silicon substrate, which was cleaned using standard clean 1, then dried at 60 °C for 15 min and observed with a scanning electron microscope (SEM) (FEI Strata DB235-31). A solvent exchange experiment was performed in order to determine whether the photoproducts were formed by laser irradiation. After completely evaporating water from the samples under a vacuum for several days, toluene was poured into the cuvette, and the toluene solutions were examined by UV/vis spectrometry.

3. Results and discussion

3.1. Preparation of C_{60} aqueous nanocolloids by laser ablation at 532 and 355 nm excitation

First, C_{60} aqueous nanocolloids were prepared by laser ablation of C_{60} powder in water at 532 nm excitation. In order to elucidate the preparation process of the nanocolloids, the initial water suspensions were exposed to the 532 nm pulse with various fluences, and their absorption spectra were measured by a UV/vis spectrometer. Fig. 1(a) shows the absorption spectra of the supernatants before and after 10 min irradiation at fluences ranging from 10 to 200 mJ/cm^2; the absorption spectrum of molecularly dissolved C_{60} in toluene is given as a reference. Before irradiation no absorption band was observed, as most C_{60} microcrystals sank to the bottom of the cuvette and the supernatant had no color. This means that almost none of the C_{60} molecules were dissolved in water just by vigorous stirring. After irradiation, the absorbance of their dispersions increased as the laser fluences increased. This absorption increment of the irradiated suspension should depend on the number and size of the C_{60} crystals fragmented in water. After irradiation the dispersions changed into a transparent and pale yellow solution, and the color became deeper as the laser fluence increased. Their spectral shapes of the colloids were very different from that of toluene solution, but similar to that of C_{60} thin film with a face-centered cubic packing [24], suggesting that C_{60} is dispersed in water as small crystals. The difference between the spectral shape of the C_{60} molecular solution and that of the thin film of small C_{60} crystals can be explained generally in terms of Davydov splitting. Namely, mutual interaction between transition dipoles results in energy splitting of the excited electronic state, leading to a red shift of the absorption bands. Furthermore, these supernatants were almost transparent to the naked eye,

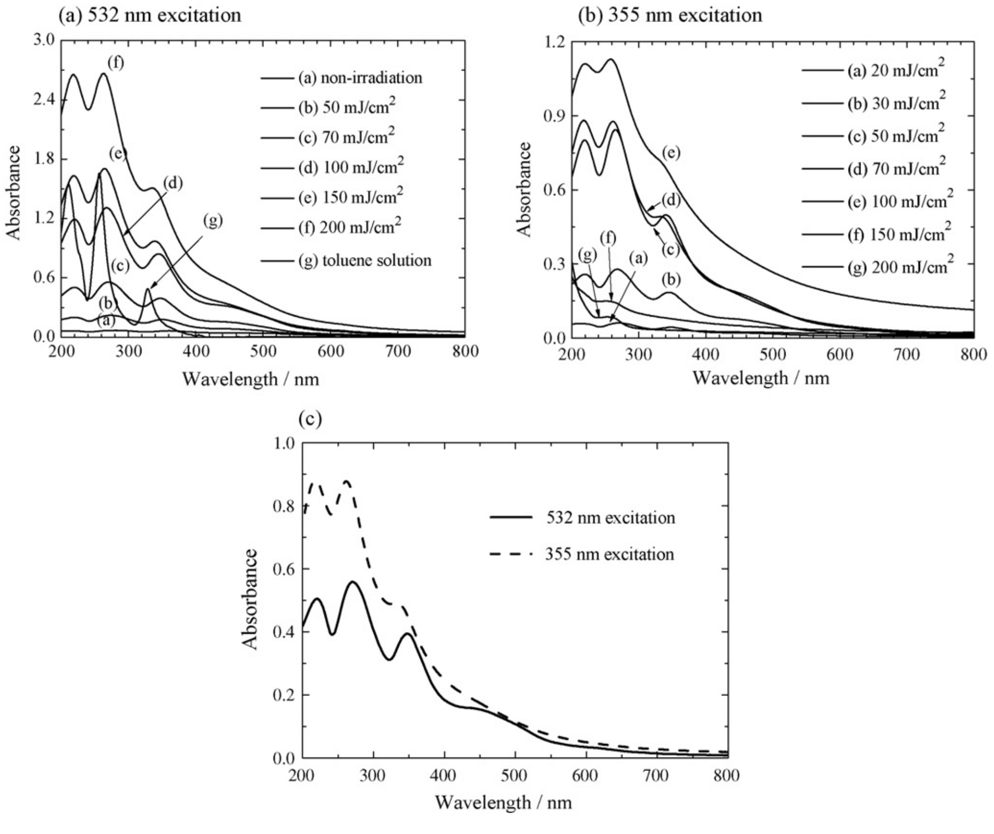

Fig. 1. (a and b) Absorption spectra of C_{60} aqueous nanocolloids after 10 min irradiation at various laser fluences. Absorption spectrum of C_{60} in toluene is given as a reference in (a). (c) Comparison of absorption spectra of C_{60} aqueous nanocolloids fabricated by 10 min irradiation at 50 mJ/cm^2.

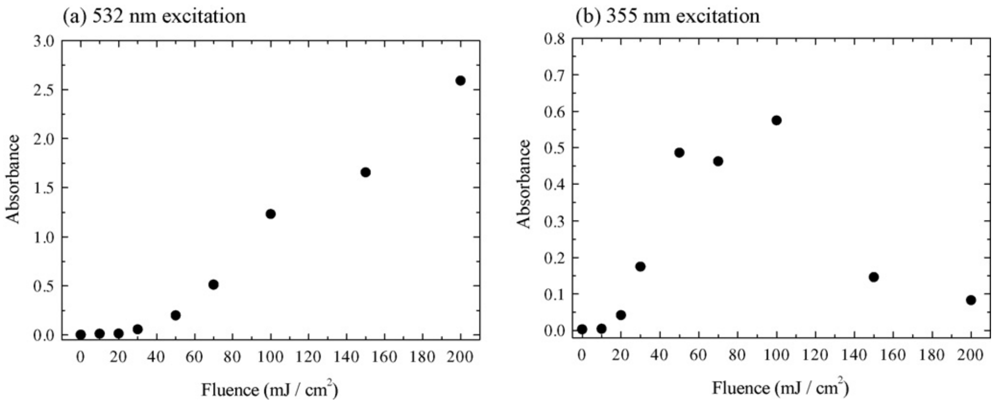

Fig. 2. Fluence dependence of the absorbance at 266 nm of C_{60} aqueous nanocolloids prepared by 10 min irradiation.

so that the size of the aggregates in water after laser irradiation was considered to be much smaller than the wavelength of visible light. These results indicate that C_{60} is dispersed in water as nanoparticles—that is, laser ablation of C_{60} microcrystalline powder results in the formation of C_{60} aqueous nanocolloids.

A similar preparation was made using 355 nm excitation, resulting in the absorption spectral data given in Fig. 1(b), where the laser intensity was changed from 10 to 200 mJ/cm^2. Up to the fluences of 50 mJ/cm^2, the spectral shapes continued to show their characteristic bands, but they were gradually modified as the fluence was increased further. Consequently, the high fluences around 150 mJ/cm^2 gave smaller absorption bands in the visible region. Indeed, the supernatants obtained at 200 mJ/cm^2 were colorless. This result is consistent with that by Tsuji et al., who reported that exposing C_{60} crystals in organic solvents to highly intense laser pulses induced the production of polyyne [25].

Fig. 2 shows the fluence dependence of the absorbance of supernatants at 266 nm for 532 and 355 nm excitation. The threshold of the coloration was clearly obtained, confirming that laser ablation was responsible for this phenomenon. The threshold at 532 excitation was estimated to be about 30 mJ/cm^2, which was almost twice that at 355 nm excitation. This result was considered to be due to the difference in the absorption coefficient of the initial crystals at excitation wavelength. The fluence dependence obtained at 532 nm excitation appeared to be a conventional laser ablation behavior. On the other hand, for 355 nm excitation, laser irradiation at high fluences dramatically altered the spectral shape—thus, for the excitation at a fluence higher than 150 mJ/cm^2, no appreciable absorption band was observed in the visible region, as described above.

It is important to point out that the spectral shapes of the nanocolloids obtained at 532 and 355 nm excitation were different from each other, even when the laser fluence was 50 mJ/cm^2. A comparison of the absorption spectral shapes is shown in Fig. 1(c). Under these experimental conditions, the ^{13}C NMR results, as described below, revealed that no photoproduct was formed by laser irradiation in either suspension. Thus, the difference in spectral shape should ascribable to the size of C_{60} nanoparticles in water. The most interesting point in Fig. 1(c) is the fact that the broad band in the range from 400 to 500 nm, which is a characteristic band of C_{60} bulk crystal, is not clear at 355 nm excitation, while the spectral shape at 355 nm excitation is almost the same as that of 10 nm-sized C_{60} aqueous nanocolloids in the presence of other chemicals [26]. Thus, it is suggested that the C_{60} nanoparticles dispersed in water

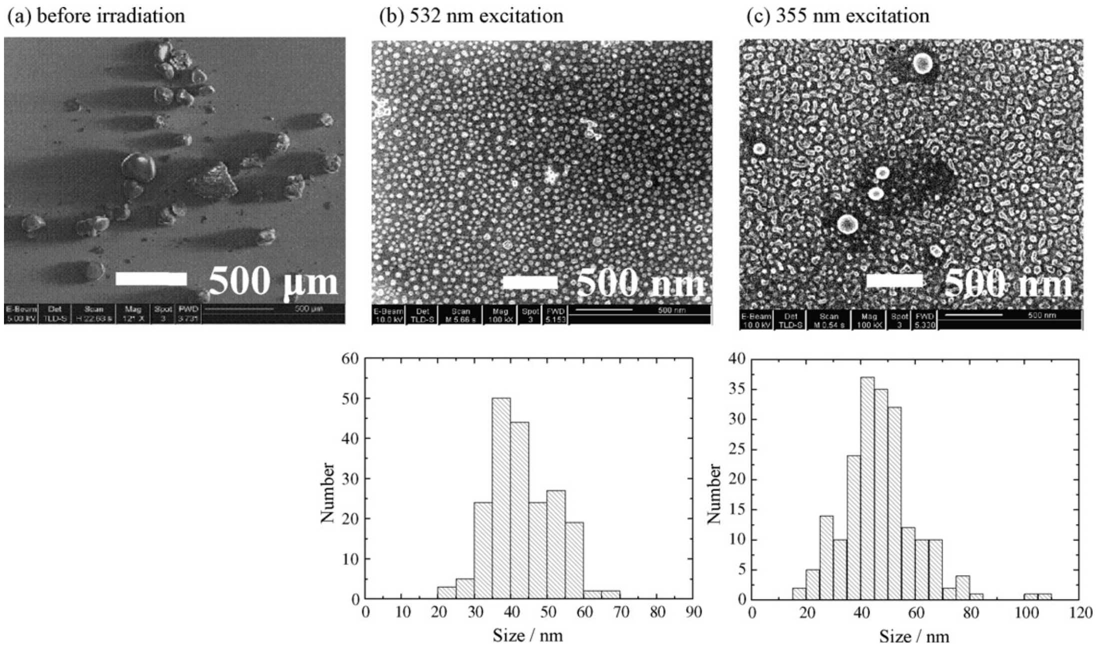

Fig. 3. SEM images of initial C_{60} microcrystals before irradiation and of C_{60} nanoparticle obtained after irradiation with the fluence of 50 mJ/cm^2 for 360 min. The corresponding size histograms estimated from SEM images are given below.

upon 355 nm excitation are smaller than those dispersed upon 532 nm excitation. And indeed, Hayashi and co-workers reported that 10 nm-sized C_{60} nanoparticles were dispersed in ethanol by laser ablation at 355 excitation, while larger ones were prepared at 532 nm excitation [23]. These results strongly support the idea that the suspension prepared at 355 nm excitation should contain smaller C_{60} nanoparticles compared to that prepared at 532 nm. It can be considered that 355 nm-laser irradiation is confined to a thinner surface layer than that by 532 nm excitation, causing fragmentation into smaller nanoparticles, since the initial C_{60} crystal has a larger absorption coefficient at 355 nm than at 532 nm. In Section 3.4, we discuss the particle size effect as it relates to the photo-thermal laser ablation mechanism.

3.2. Characterization of C_{60} aqueous nanocolloids prepared by laser ablation

In order to measure the size of the C_{60} nanoparticles in water, SEM observation was carried out for the nanocolloids at each excitation with a fluence of 50 mJ/cm^2 for 360 min and for the nanocolloids following centrifuging at 2000 rpm for 30 min. Fig. 3 shows SEM images of the initial C_{60} crystals and C_{60} nanoparticles from the suspensions after laser irradiation. The irradiation time of 360 min gave saturated absorption spectra of the nanocolloids, which means that the irradiation yielded the maximum number of C_{60} nanoparticles under the experimental conditions used. In Fig. 3(a), the initial crystal consisted mainly of microcrystals with a size of several tens to several hundreds micrometers. Fig. 3(b and c) shows SEM images of C_{60} nanoparticles after laser irradiation at 532 and 355 nm excitation, respectively, from which their histograms were obtained. We confirmed that their average sizes were 44 and 42 nm, and that the coefficients of variation were 12% and 22% at 532 and 355 nm excitations, respectively. Thus, it is clearly demonstrated that laser irradiation of C_{60} bulk crystals in water gave nm-sized C_{60} particles dispersed into water. Surprisingly, the mean size at 355 nm excitation was almost the same as that at 532 nm excitation, which was not what we expected from the absorption spectral measurement. To understand this inconsistency, we have measured and compared the absorption spectra of both nanocolloids after centrifuging them at 2000 and 12,000 rpm for 10 min, with the results shown in Fig. 4. In the case of 532 nm excitation, the absorbance decreased slightly after the centrifuging at 2000 rpm, and no appreciable absorbance was observed after that at 12,000 rpm. On the other hand, in the case at 355 nm excitation, the absorbance showed almost no change after centrifuging at 2000 rpm, and it decreased only by half after centrifuging at 12,000 rpm. This result strongly supports our assumption that a number of smaller C_{60} nanoparticles were dispersed in water upon 355 nm excitation. The latter nanoparticles may be smaller than the size at which SEM observation is made possible under the present conditions.

In order to check whether photoproducts of C_{60} are involved in the nanocolloids, a solvent exchange experiment was conducted. As seen in Figs. 1 and 2, the spectral shape and absorbance at the fluence higher than 150 mJ/cm^2 at 532 nm excitation are slightly different from those at lower fluence. The aqueous nanocolloids prepared at 532 nm with the fluence of 70 and 200 mJ/cm^2 for 20 min were chosen as representative of this system. After water of both nanocolloids was exchanged for toluene, the absorption spectra of the nanocolloids were measured and normalized at 334 nm as shown in Fig. 5. The absorption spectrum at 200 mJ/cm^2 has a larger tail extending at the range from 350 to 600 nm compared to that of the non-irradiated sample, indicating that photodecomposition products are formed by laser irradiation and included in the aqueous nanocolloids. On the other hand, no absorption spectral change was observed at 70 mJ/cm^2. Indeed, in the case at 70 mJ/cm^2, the color of the toluene solution was violet, as a result of the pristine C_{60} being directly dissolved into toluene. In contrast, the toluene solution prepared from nanocolloids at 200 mJ/cm^2 was not violet, but obscure and brownish.

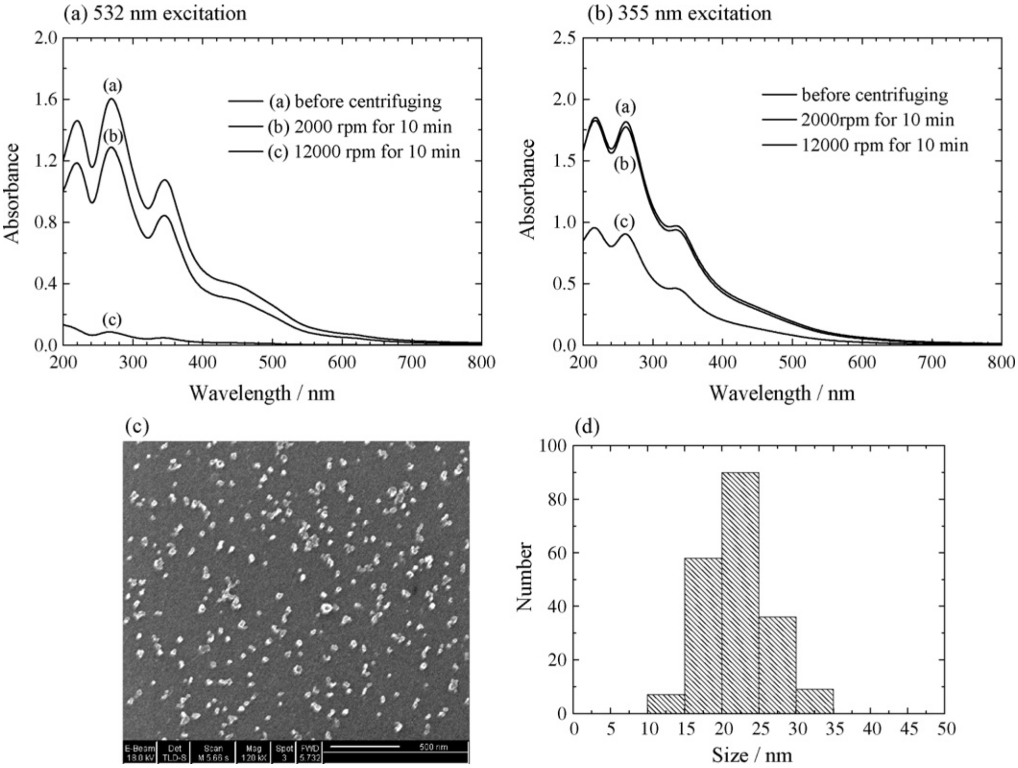

Fig. 4. (a and b) Absorption spectra of C_{60} aqueous nanocolloids processed by ultracentrifuge. The nanocolloids were obtained by irradiation with the fluence of 50 mJ/cm^2 for 360 min. (c) A SEM image of C_{60} nanoparticle obtained at 355 nm excitation after centrifuging at 12,000 rpm. (d) Its histogram estimated from (c).

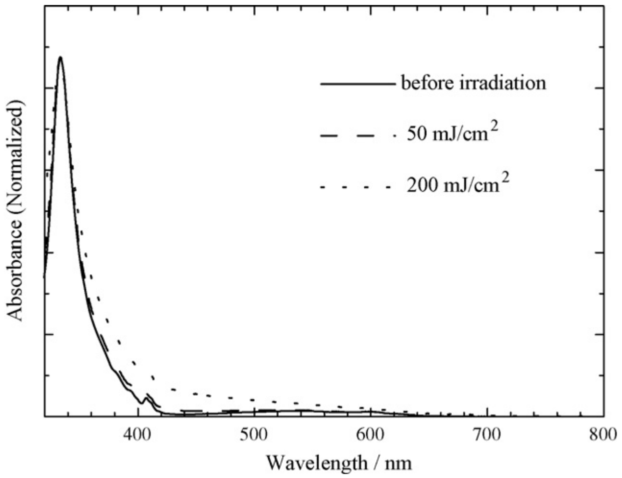

Fig. 5. Absorption spectra of C_{60} toluene solutions normalized at 334 nm for after the solvent exchange. These nanocolloids were fabricated at 70 and 200 mJ/cm^2 for 20 min.

Here, we should more carefully examine possible photoproducts of laser irradiation, since it is well known that fullerene derivatives such as C_{120} [27] and C_{180} [28] are synthesized by exposing C_{60} ethanol solution to visible light. We therefore performed ^{13}C NMR analysis, which gives multiple peaks and often a broadened band for chemically altered fullerene derivatives. As a typical example for this analysis, a nanocolloid prepared under the same laser irradiation conditions as used in the solvent exchange experiment was chosen. Water of the nanocolloid was completely evaporated under a vacuum, and the residue at the bottom of the cuvette was dissolved by 1,2-dichlorobenzen-d_4, by which possible photoproducts can also be dissolved. Fig. 6 shows the ^{13}C NMR spectra of C_{60} dissolved in 1,2-dichlorobenzen-d_4. The multiple peaks around 130 ppm are ascribed to the solvent, while the single peak at 143 ppm is quite similar to that of solid-state ^{13}C NMR of bulk C_{60} crystal [29]. Note that it was reported that the chemical shift of the C_{60} water dispersion prepared by another method was 146 ppm [30]. The difference was ascribed to be the intercalation of the used solvent into the C_{60} crystal lattice, which is a well known phenomenon [31]. Thus, ^{13}C NMR analysis revealed that no appreciable photoproduct is formed under these laser irradiation conditions. Of course, decomposition of C_{60} is surely induced above 150 mJ/cm^2 at 532 nm excitation, although no detailed assignment of photoproducts has been made. A similar result was obtained at 355 nm excitation, and at less than 50 mJ/cm^2 no photoproducts were observed by ^{13}C NMR analysis. Thus we can conclude that photodecomposition can be well suppressed by selecting the laser wavelength and tuning the laser fluence properly, under which conditions only C_{60} nanoparticles are dispersed in water.

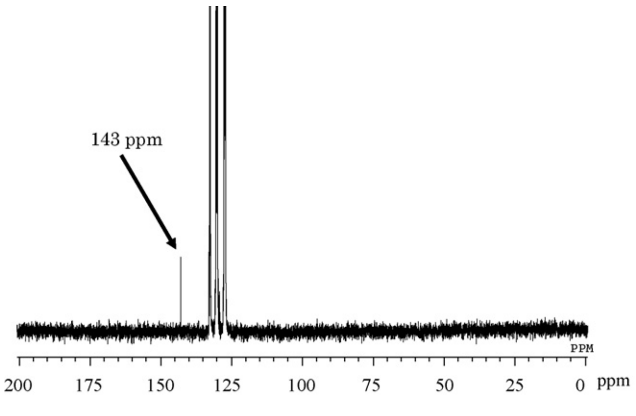

Fig. 6. ^{13}C NMR spectrum of 1,2-dichlorobenzene-d_4 solution dissolving both fabricated C_{60} nanoparticle.

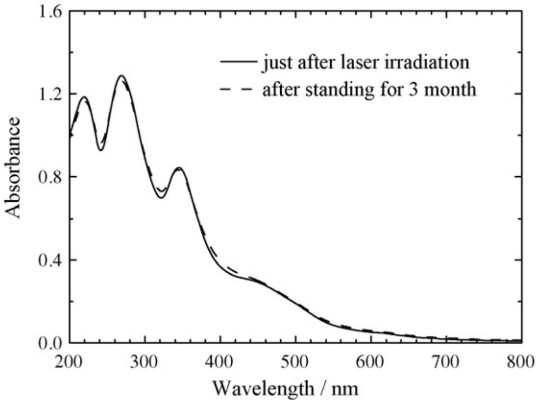

Fig. 7. Absorption spectra of C_{60} aqueous nanocolloids before and after standing at room temperature. The nanocolloid was fabricated by 532 nm irradiation at 70 mJ/cm^2 for 20 min.

3.3. *High dispersibility of C_{60} aqueous nanocolloids by laser ablation*

One of the most important issues in regard to the preparation of nanocolloids is their dispersibility. Not only biological testing but also all other applications require nanocolloids with high stability. Tracing the decay of the absorption spectrum of the nanocolloids is a useful and easy way to estimate the dispersibility, since the decay is due to aggregation of nanoparticles followed by sedimentation. Fig. 7 shows the absorption spectral decay of aqueous nanocolloids prepared under the same laser irradiation conditions as used for the SEM observation. It can be clearly seen that the absorption spectra remain basically constant even after the nanocolloids have stood for three months at room temperature. This result indicates that C_{60} nanoparticles formed by the present laser ablation method remain stably dispersed in water for a long period. It is worth noting that no chemical reagents are added in this method. The surface condition of the C_{60} nanoparticles, which may be responsible for the long stabilization, is interesting from the standpoint of how a hydrophobic fullerene changes into a hydrophilic one. It is considered that the surface molecules of C_{60} nanoparticles are partly changed into hydroxided molecules, since the laser beam is irradiated into the C_{60} water suspension without de-aeration. Alternatively, the nanoparticles may be charged to some extent due to the ionization of the surface molecules as a result of the high intensity laser excitation. However, since no chemically modified and/or ionized C_{60} was detected by NMR analysis, we consider at the present stage of investigation that such minor changes in the chemical and physical properties of the surface of C_{60} nanoparticles would not be sufficient to attain the present high dispersibility.

3.4. *Ablation mechanism and excitation wavelength dependence of C_{60} nanoparticle size*

We have previously studied the laser ablation mechanism of polymer films, aromatic hydrocarbon-doped polymer films, organic amorphous films, and organic crystals, and elucidated how electronic excitation evolves to ablation [32–35]. For nanosecond and femtosecond laser ablation, photothermal and photomechanical processes are critical, as shown by our direct observation of these processes using time-resolved absorption and emission spectroscopies and dynamic imaging [36,37]. In the present ablation, nanosecond excitation energy of 532 and 355 nm photons should be efficiently converted to thermal energy, inducing fragmentation into nanoparticles. In the case of 355 nm-laser irradiation, the penetration depth of laser light is short because the absorption coefficient is relatively large, so the energy density should be higher and heated up to greater extent compared to that by 532 nm excitation. Thus smaller nanoparticles should be prepared for 355 nm excitation, which is confirmed by the centrifuging experiments.

On the other hand, the size distribution before the centrifuging looks similar for both excitations, as shown in Fig. 3. It is important to note that the present experiment was performed in water, which afforded cooling. The cooling process due to thermal diffusion to solvent takes place competitively with fragmentation [14]. The cooling rate for smaller particles should be faster due to their larger surface to volume ratio. Consequently, when the particle size is smaller, the temperature elevation is not fast enough to induce further fragmentation. On the other hand, the size of the initially prepared nanoparticles is relatively large for 532 nm excitation, and thus the cooling is slower and further fragmentation will be possible. We therefore consider that the size distribution of C_{60} by 532 and 355 nm excitation becomes similar, although the absorption coefficients at the two wavelengths are different. Of course, we should note that additional smaller nanoparticles are formed, as shown by the centrifuge experiment, and this is a problem that remains to be addressed. A time-resolved spectroscopic approach might be able to confirm whole our explanation if the effective temperature is reflected in the absorption and/or Rayleigh light scattering spectroscopy.

4. Summary

We have succeeded in preparing C_{60} aqueous nanocolloids by nanosecond laser ablation in solution. No detergent and no organic solvent were added during the process, so that it is pure in principle. Possible photoproduct formation was carefully checked and surely denied at relatively less fluence on the bases of ^{13}C NMR analysis of 1,2-dichlorobenzene-d_4 solution dissolving C_{60} nanoparticles and of UV/vis abruption measurement after the solvent exchange, although decomposition was occurred due to the high laser fluence. The particles were characterized by SEM observation and their size was estimated to be around 40 nm. When centrifuging was applied for the nanocolloids obtained at 355 nm excitation, smaller particles of about 23 nm were prepared. Both nanocolloids were very stable and their absorption spectra did not change for three months. At the present stage, we consider that the SEM observations were identical between the two excitation wavelengths because the water dispersion prepared by 355 nm excitation included small nanoparticles beyond the measurement limit of SEM. Therefore, further detailed study by transmission electron microscope will be needed to characterize the smaller nanoparticles, while the surface properties should be considered to explain the high stability. Plans for both such studies are currently underway in our laboratory.

Reprecipitation, solvent exchange, and ultrasonication methods have often been applied for preparing organic nanoparticles, but when using these methods, there remains the possibility that some amount of solvent will be left in the dispersion. This is very critical for applying C_{60} nanoparticles to biological testing, photodynamic therapy, and so on, as organic solvents are usually toxic for living cells and tissues. The other preparation method involves mechanical grinding, but it is well known that most of the nanoparticles remain larger than 100 nm by this method. This is often too large for efficient endocytosis of living cells. Laser ablation in solution is a powerful method to overcome these problems, and Hayashi et al. applied this method to C_{60} [23]. They used ethanol as a poor solvent and gave no detailed examination of its dispersibility, so that direct extension to biological application was not possible. In the present study we have successfully prepared very stable C_{60} aqueous nanocolloids with a size of several tens nm. We believe our approach will contribute to biomedical applications in addition to materials research, and will help to realize the high potential of the laser ablation method.

Acknowledgements

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