Nanoparticle preparation of quinacridone and *β*-carotene using near-infrared laser ablation of their crystals

K. Yuyama · T. Sugiyama · T. Asahi · S. Ryo · I. Oh · H. Masuhara

Abstract Quinacridone nanoparticles with a mean size of about 200 nm are successfully prepared using nanosecond near-infrared (NIR) laser ablation of its microcrystalline powders in heavy water. The absorption spectra of the formed colloidal solutions depend on the excitation wavelengths, which is eventually ascribed to number and energy of absorbed photons. *β*-carotene has low photostability and is easily decomposed upon UV/VIS laser ablation of its solid, while its nanoparticles are prepared utilizing this NIR laser ablation technique. The advantage of nanoparticle preparation by NIR laser ablation is discussed.

1 Introduction

Recently, much attention has been focused on organic nanoparticles because of their unique optical properties and potential applications in pigments, cosmetics, and drugs [1–3]. Conventionally grinding method has been applied, but the size of prepared nanoparticles is around 100 nm, and smaller size has been requested. An approach based on reprecipitation of organic molecules has been reported, where an organic molecule solution is quickly injected into a poor solvent with or without a surfactant, forming nm-sized precipitates of the molecule [4–6]. Furthermore, the shape and size of the precipitates can be controlled by microwave irradiation during the reprecipitation processes [7]. This method is simple and useful for various kinds of organic compounds, while the selection of good and poor solvents for each molecule is sometimes an arduous task.

Over the past decade, we have applied a laser ablation technique to the formation of organic nanoparticles and succeeded in the nanoparticle preparation of fullerene, dye molecules, and other compounds [8–14]. For quinacridone (QA), we have succeeded in forming 10-nm-order nanoparticles using femtosecond laser pulse as an irradiation light source [11]. It is worth noting that this size of organic nanoparticle has never been fabricated by other methods. Control of size and phase of the nanoparticles was also achieved by adjusting experimental parameters such as the laser wavelength, pulse width, and solvent [12, 13]. Furthermore, we found that some nanoparticles prepared using this method were well dispersed in a poor solvent as a colloidal solution without surfactants [14]. In this ablation method, microcrystalline powders suspended in a poor solvent are exposed to an intense UV/VIS pulsed laser beam, inducing the fragmentation of the initial crystals into their nanoparticles via a top-down process. Consequently, the solutions that are opaque before laser irradiation become transparent and colored with the characteristic absorption band of their nanoparticles.

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Upon exposing organic solids to a nanosecond UV/VIS laser beam, an electronically excited state is formed densely in the surface layer and quickly relaxes into the ground state through efficient nonradiative processes in the order of 10 ps [15–17]. The photothermal conversion in the surface layer is efficiently induced during the temporal pulse duration of the laser beam, leading vigorous lattice motion and the following fragmentation from the surface. Hence, this ablation method still faces a serious problem, namely, some organic molecules which undergo photodecomposition by UV/VIS light irradiation cannot be fabricated well.

In this study, we propose a novel preparation method of organic nanoparticles in which NIR pulsed laser is used as an excitation light source for laser ablation. The fragmentation is caused directly via the vibrationally excited state, not an electronically excited one, and thus we expect that the photodecomposition can be avoided enough. In general, organic molecules show their characteristic absorption bands in NIR region, which correspond to the overtones or Fermi resonances of the fundamental vibrational frequencies. It is well known that a CO_2 laser with a wavelength of about 10 μm can induce the etching of various kinds of materials in air [18]. However, IR lasers are not suitable as an excitation light source for laser ablation method in a poor solvent, since photons are mostly absorbed by the solvent molecules, not by target crystals. Thus we consider NIR laser as suitable to induce ablation due to vibrational excitation. As the first demonstration of organic nanoparticle formation using a NIR laser ablation technique in a poor solvent, we present the preparation of QA nanoparticles depending on the laser wavelength, intensity, and solvent. Furthermore we show that this method is useful for fabricating nanoparticles of β-carotene which has low UV/VIS photostability.

2 Experimental

QA (>99.0% pure; Tokyo Kasei) and β-carotene (>97.0% pure; Tokyo Kasei) were used without any further purification. Microcrystalline powders of QA were put into D_2O (3.3 wt%), and the suspension was then sonicated for 30 min. The mixture (6.0×10^{-2} ml) was added into a 5.0 cm × 1.0 cm × 0.10 cm quartz cuvette, into which D_2O was poured carefully (0.40 ml) in order to prevent the initial crystals from floating. On the other hand, microcrystalline powders of β-carotene were directly added into a cuvette, and then a 0.40 ml portion of D_2O was poured into the cuvette, since β-carotene is easily trapped at the solution surface due to its high hydrophobicity. For QA nanoparticle preparation, NIR nanosecond laser pulses with wavelengths of 1528, 1607, 1688, and 1754 nm were used as excitation light sources. For β-carotene, only a 1706-nm-laser beam was used. The tunable optical parametric oscillator (OPO) systems pumped by the third harmonic (355 nm, 8 ns, 10 Hz) of Nd^{3+}:YAG laser (Continuum, Surelite I) was used in order to generate all NIR laser pulses ranging from 1528 to 1754 nm. The laser pulses were directly exposed to the crystals sunk on the bottom for 30 min to suppress the absorption by the surrounding solvent molecules. For QA nanoparticle preparation, the same experiment described above was carried out with using H_2O as a solvent.

The absorption spectra of the colloidal solutions formed by NIR laser irradiation were measured one day after the irradiation using a spectrometer (Ocean optics, USB-2000) for a range of 400–800 nm. In the case of β-carotene, the solvent exchange experiment was carried out in order to confirm whether or not the photoproducts were formed during the irradiation. Specifically, after evaporating D_2O completely from the colloidal solutions under a vacuum for several days, the residual nanoparticle powders were dissolved in dichloromethane. The absorption spectra of the solutions were measured by a UV/VIS spectrometer (Shimadzu, UV-3100PC) and compared with that of β-carotene dichloromethane solution for a range of 300–800 nm. For the supernatants of the colloidal solutions after centrifuging (3000 rpm, 5 min), the prepared nanoparticles were observed by a scanning electron microscope (SEM; FEI, Strada DB235-31), and the mean size was estimated by dynamic light scattering (DLS) measurement (Ohtsuka-denshi, ELSZ-2).

3 Results and discussion

3.1 QA nanoparticle preparation

For the nanoparticle preparation by the NIR laser ablation method, the most important process is to select the wavelength of an excitation light source. The wavelength should be chosen on the basis of the absorption spectrum in the NIR region, rather than the IR region. However, since it is quite difficult to measure the NIR absorption spectrum of QA solids, overtones of molecular vibrations presumed from the IR spectrum were chosen as excitation wavelengths in this work. Figure 1(a) shows the FT-IR spectrum of QA solids. The broad absorption band ranged from 2800 to 3300 cm^{-1} is assigned to the mixture of the C–H and N–H stretching modes of QA, so that their overtone vibrations are estimated to be from 5600 to 6600 cm^{-1}, or 1515 to 1785 nm. In this range, laser beams with 1528, 1607, 1688, and 1754 nm were chosen as excitation light sources. Absorption spectra of D_2O and H_2O are shown in Fig. 1(b) with each excitation wavelength.

First, QA colloidal solution was prepared at each excitation wavelength by exposing D_2O suspensions of QA to the laser pulses at the fluence of 730 mJ/cm^2 for 30 min.

Fig. 1 (**a**) IR spectrum of QA crystal. Inset shows the spectrum in the range of 2800 to 3400 cm^{-1}, in which overtones of the vibrational band indicated by *arrows* correspond to the excitation laser wavelengths. (**b**) Absorption spectra of D$_2$O and H$_2$O measured in the cuvette with 1-mm optical pass length. The excitation wavelengths are indicated by *arrows*
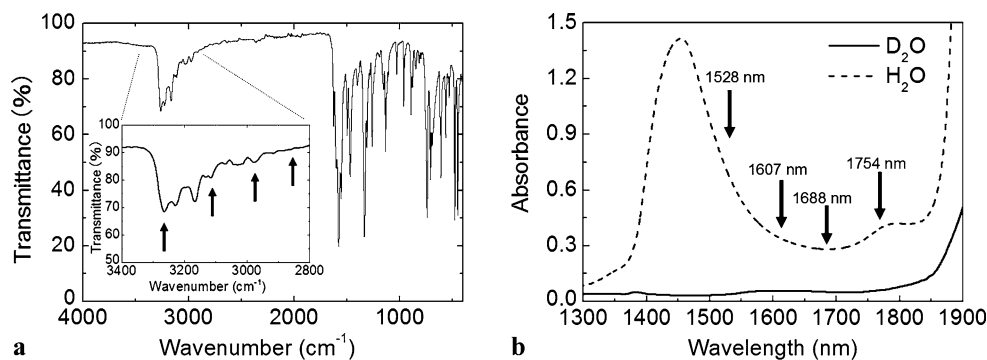
Fig. 2 (**a**) Absorption spectra of D$_2$O suspensions of QA with and without nanosecond NIR laser pulses of four different excitation wavelengths at the fluence of 730 mJ/cm^2 for 30 min. (**b**) Excitation wavelength dependence of the peak absorbance of the QA colloidal D$_2$O solutions
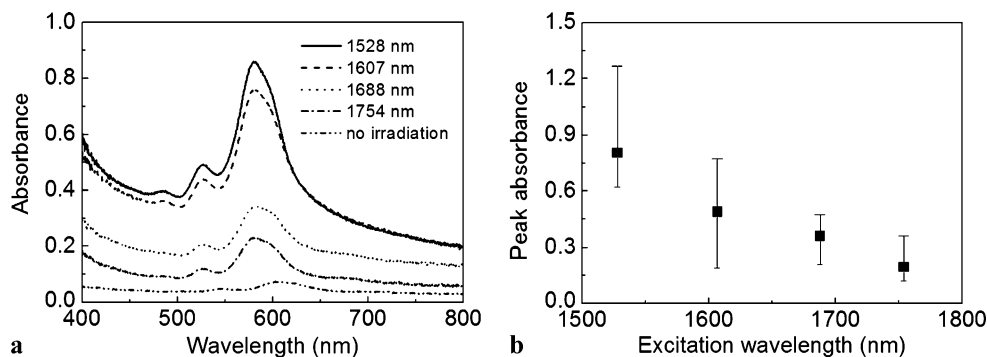
Fig. 3 (**a**) Laser fluence dependence of the peak absorbance of QA colloidal D$_2$O solutions at 1528-nm excitation. (**b**) Histogram of the nanoparticle size obtained from DLS measurement
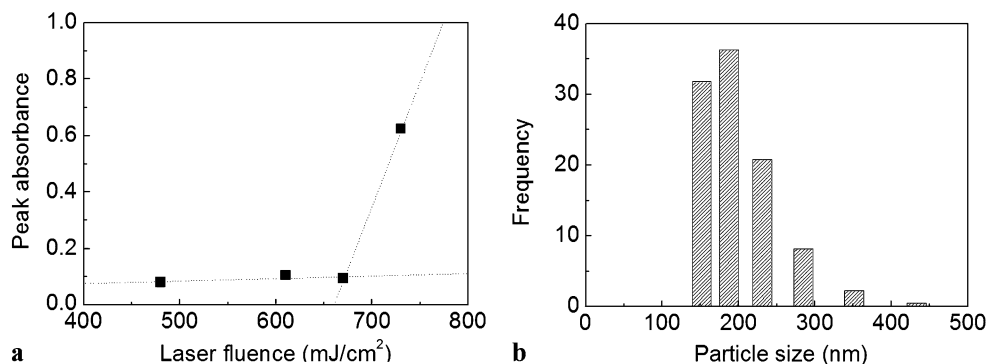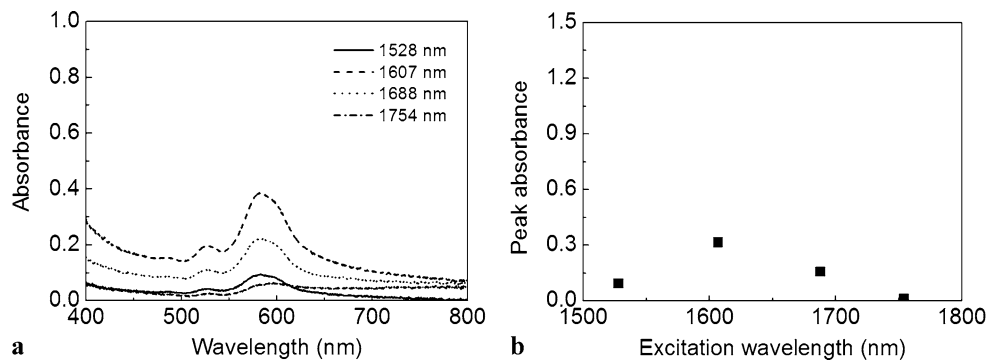
Compared with the case of laser ablation using UV/VIS laser pulses, the laser intensity used in this experiment was much higher, since in general the absorption coefficients in NIR region are much smaller than those in UV/VIS region. The absorption spectra before and after laser irradiation are shown in Fig. 2(a). Before laser irradiation, the absorption spectrum was almost flat without the specific absorption band. Actually, the initial μm-sized crystals sank down to the bottom of the cuvette, and its supernatant was almost colorless. After laser irradiation, all supernatants became red-purple color and showed absorption bands at around 580 nm. All of their spectral shapes were quite similar to that of QA colloidal solution prepared by UV laser irradiation in a previous report [12]. The peak absorbance at each wavelength, which is normalized subtracting the absorbance at 800 nm as the scattering of large particles, is plotted in Fig. 2(b). We found that the absorbance decreases as the
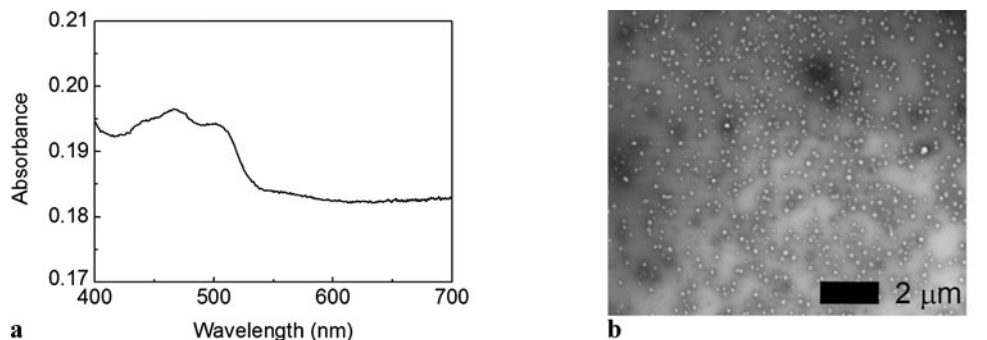
wavelength becomes longer, namely the fragmentation of the crystals occurred most efficiently at 1528 nm excitation. We suspect that NIR photons are absorbed by QA and efficiently converted into the molecular vibration, since D$_2$O has very small absorption coefficient at each wavelength in Fig. 1(b).

Figure 3(a) shows the fluence dependence of the peak absorbance of the colloidal solutions prepared by using a laser beam at 1528 nm. The threshold of the coloration was clearly obtained, confirming that laser ablation was responsible for this phenomenon [8–14]. The threshold was estimated to be about 670 mJ/cm^2, which was more than 20 times higher than that at UV/VIS excitation reflecting the lower absorption coefficient in the NIR region [12]. In order to estimate the mean size of the prepared nanoparticles, DLS measurement was carried out after centrifuging the solution prepared at the 1528-nm excitation for 5 min at 3000 rpm.
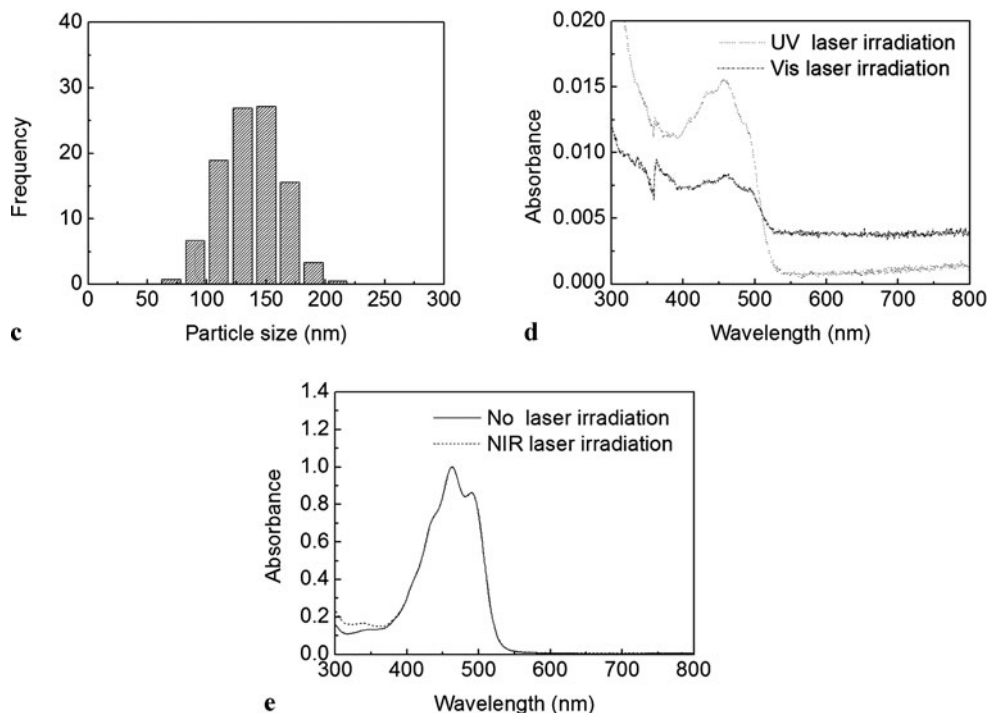
The result in Fig. 3(b) showed that the mean size was about 200 nm and that the coefficient of variation was 25. Hence, we found that QA nm-sized particles were prepared in D_2O as the colloidal solution via the fragmentation of the initial μm-sized crystals. The mean size and distribution were larger compared with the result of UV/VIS laser ablation. This result is consistent with the lower absorption coefficient in the NIR region, since laser ablation at the wavelength at which the crystals have a lower absorption coefficient induces larger nanoparticles [12].

Although, as described above, D_2O has very small absorption coefficients at these wavelengths, the light absorption may not be ignored since the QA suspension includes a large amount of D_2O molecules. Some researchers could

doubt that nanoparticles were formed via fragmentation by laser ablation of D_2O [19–21]. In order to exclude the possibility of the induced ablation, the same experiment was carried out with a substituted solvent, H_2O, which has a higher absorption coefficient at each wavelength than D_2O as shown in Fig. 1(b). After laser irradiation, all suspensions became colored as described above. The absorption spectra and the peak absorbance at each excitation wavelength are shown in Fig. 4. We found that the shapes of the absorption spectra were quite similar to those of the D_2O colloidal solutions, while the absorbance change, on the whole, was clearly suppressed compared with that of D_2O in Fig. 2(b). If the nanoparticles were prepared via the laser ablation of H_2O, the induced fragmentation of QA should have occurred more efficiently, since the absorption coefficients of H_2O are much higher than those of D_2O at the region. Therefore, we suspect that the suppression of nanoparticle preparation was just due to the light absorption of H_2O. These results indicate that QA nanoparticles were prepared by NIR laser ablation of the bulk solids, not by the laser ablation of the solvent. As far as we know, this is the first report of organic nanoparticle preparation utilizing NIR laser ablation in a poor solvent.

3.2 Preparation of β-carotene nanoparticles

Next, NIR laser ablation method was applied to nanoparticle preparation of β-carotene with low UV/VIS photostability. Actually, we have already found that β-carotene/D_2O suspension became colorless and its characteristic absorption band disappeared because of its photodecomposition even when the solution was exposed to UV (355 nm) or visible (532 nm) nanosecond laser pulses at a lower fluence for a short time. In this work, the laser beam at 1706 nm was chosen as an excitation light source, as this wavelength corresponds to the C–H stretching mode of β-carotene [22]. The NIR laser beam was irradiated into β-carotene suspension at the fluence of 730 mJ/cm^2 for 30 min. Figure 5(a) shows the absorption spectrum of the colloidal solution after laser irradiation, which has a band in the range from 420 to 520 nm in addition to the flat band due to scattering. Actually, the supernatant became slightly orange. The characteristic band in that region was consistent with that of the colloidal solution of β-carotene prepared by precipitation method [5]. This result suggests that initial β-carotene crystals were fragmented in D_2O into small particles. In order to estimate the size of fragmented particles, after the colloidal solution was centrifuged for 5 min at 3000 rpm, a portion of the supernatant was put on a silicon substrate with a hydrophobic surface, and SEM observation was carried out. Figures 5(b) and (c) show the image and the histogram of β-carotene nanoparticles, respectively. We confirmed that the mean size was 138 nm and that the coefficient of variation was 28.

To verify molecular decomposition, we conducted the solvent exchange experiment described in the experimental section. Figures 5(d) and (e) show the absorption spectra of dichloromethane solutions obtained by resolving the prepared nanoparticles by irradiation with UV, visible and NIR laser pulses. In the case of UV and visible laser irradiation, the absorption spectra are quite different from that of a β-carotene solution, which is a signal of photodecomposition. On the other hand, the sample prepared by the NIR laser irradiation shows a similar absorption band of the β-carotene solution. The results demonstrate that photodecomposition was suppressed by NIR laser irradiation in the nanoparticle formation process. Thus, we have succeeded in the preparation of β-carotene nanoparticles by suppressing photodecomposition using NIR laser ablation method.

4 Conclusion

We have successfully prepared QA and β-carotene nanoparticles in D_2O with the mean size of 200 and 150 nm, respectively, using NIR laser ablation technique. We found that QA nanoparticle formation depended on the excitation wavelength, which is ascribed to the number and energy of absorbed photons. For nanoparticle preparation of β-carotene with low UV/VIS photostability, the photodecomposition was suppressed by this NIR laser ablation method. This example indicates a high potential of the laser ablation method for fabricating various kinds of organic compounds including some molecules with low UV/VIS photostability like drugs.

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