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Research paper

Nanoparticle formation by laser ablation of perylene microcrystals in an aqueous solution of Triton X-100

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ABSTRACT

Perylene microcrystals in aqueous solutions containing various concentration of Triton X-100, nonionic surfactant, were irradiated by a nanosecond laser under various irradiation conditions including the fluence and length of irradiation time. Perylene nanoparticles with diameters of several hundred nm were formed by the laser irradiation only when Triton X-100 was added in the solutions at sufficiently high concentrations of the surfactant. The transfer of perylene molecules into the micelles of Triton X-100 was avoided by optimizing the concentrations of the surfactant so that only perylene nanoparticles were obtained in the aqueous solutions.

1. Introduction

Nanoparticles have attracted much attention because of their unique properties. For instance, gold nanoparticles exhibit a lower melting temperature than the bulk crystal [1]. The absorption and emission spectra of perylene nanoparticles depend on the size of the nanoparticles [2–4]. The development of preparation methods for nanoparticles is important because size-controlled nanoparticles need to be prepared to study the size-dependent properties of the nanoparticles and to apply the nanoparticles in practical applications. Laser ablation of materials in poor solvents has been applied for the preparations of nanoparticles [5–21]. One technique used to prepare organic nanoparticles consisting of low-molecular-weight organic compounds is laser ablation of its microcrystals in poor solvents such as water. Organic microcrystals are suspended in a poor solvent and irradiated by pulsed-laser; the ablated materials form a colloidal solution of nanoparticles. Vanadyl phthalocyanine, quinacridone, fullerene, pentacene, diarylethene, and perylene nanoparticles have been prepared using the laser ablation technique [4–6,8–11,16–21]. Adding surfactants in poor solvents improves the production rate of organic nanoparticles and reduces the sizes of organic nanoparticles [10,18]. Li et al. proposed that the reason for the improvement of the production rate and reduction of the size was the inhibition of heat transfer from the excited crystals to water and the inhibition of the aggregation of the formed nanoparticles [10]. Köstler at al. reported that nanoparticles of some organic hydrocarbons could be prepared by the laser ablation technique only when surfactants were added to the solvents [18]. Accordingly, the use of surfactants can extend the applications of the laser ablation technique to various organic compounds.

Mafuné et al. prepared silver [12,14] and gold [13] nanoparticles by laser ablation of metal plates in aqueous solutions containing several surfactants. The effect of sodium dodecyl sulfate (SDS) on the size and abundance of the silver [14] and gold [13] nanoparticles in aqueous solutions was investigated by changing the fluence and irradiation time of the laser and the concentration of SDS. They proposed that SDS coats the embryonic metal nanoparticles produced by laser irradiation and terminates the growth of the nanoparticles. Usui et al. performed laser ablation of zinc metal plates in aqueous solutions of surfactants, resulting in the formation ZnO nanoparticles or $Zn(OH)_2$ sheets [15]. The sizes and optical properties of the ZnO nanoparticles depended on the structure and concentration of the surfactants. The formation of the ZnO nanoparticles was explained by considering the nature of the functional groups of the surfactants. The effect of surfactants on the characteristics of inorganic nanoparticles has been thoroughly studied; however, the effect of surfactants on the characteristics of organic nanoparticles has not been studied in detail. Organic nanoparticles are promising because of the possibility of designing organic compounds that can form organic nanoparticles. Therefore, it is important to study the effect of surfactants on organic nanoparticles produced by laser ablation of organic crystals in surfactant solutions.

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In cases of preparing nanoparticles by laser ablation of crystals of hydrophobic organic molecules in aqueous surfactant solutions, transfer of the molecules into the micelles of the surfactant and aggregation of prepared nanoparticles would occur spontaneously under certain conditions. The transfer of molecules into micelles and the aggregation of nanoparticles are adverse processes to preparation of nanoparticles. Insights into the transfers of the molecules and the aggregation of the nanoparticles will be useful for preparing organic nanoparticles by the laser ablation technique. In previous researches, transfer of hydrophobic organic molecules into micelles have not been discussed and aggregation processes of organic nanoparticles have not been observed experimentally.

Perylene is an aromatic hydrocarbon which is known as a fluorescence organic compound and forms into nanoparticles through reprecipitation method [2] or stratificational deposition method [3]. Laser ablation of perylene microcrystals in water has not accomplished preparations of size-controlled perylene nanoparticles [21]. Therefore, laser ablation of perylene microcrystals in surfactant solutions is challenging for preparing nanoaprticles.

In this study, perylene microcrystals suspended in an aqueous solution of Triton X-100, nonionic surfactant, were irradiated by a nanosecond laser. We examined the size and absorption spectra of the colloidal perylene nanoparticles obtained at various concentrations of Triton X-100 under various irradiation conditions. Dynamic light scattering (DLS) was employed to measure diameters of the nanoparticles that were dispersed in the aqueous solutions. The measurements of absorption spectra and DLS enabled us to examine transfer of perylene molecules into the micelle of Triton X-100 and aggregation processes of perylene nanoparticles in the aqueous solutions respectively. We investigated the formation process of the perylene nanoparticles by considering the ablation of the crystals, aggregation of the nanoparticles, and adsorption of Triton X-100 onto the nanoparticles. We discuss influence of the micelle of Triton X-100 on formation of the nanoparticles and a role of Triton X-100 in suppression of aggregation of the nanoparticles.

2. Materials and methods

Perylene (Wako, purified by sublimation) and Triton X-100 (MP Biomedicals, molecular biology reagent grade, C_8H_{17}-C_6H_4-O-$(CH_2CH_2O)_n$-CH_2CH_2OH, n = 7-9) were used as received. Milli-Q water was used as a poor solvent. Microcrystals of perylene were suspended in water or aqueous solutions containing Triton X-100. The concentration of perylene in the suspensions was 0.0050 wt%. The concentrations of Triton X-100 were in the range from 0.0020 to 0.20 wt%, which were below or above the critical micelle concentration (cmc) of the surfactant [22]. However, the cmc could not be determined accurately because of the molecular weight distribution of the Triton X-100. The suspensions were ultrasonicated for 10 min to dissociate secondary particles of perylene microcrystals. The size of the crystals in the suspensions was from tens to hundreds of micrometers. The perylene crystals suspensions in a cuvette with and without Triton X-100 were exposed to the third harmonic of a Nd:YAG laser (Continuum, Surelite, 4–6 ns, 10 Hz, 355 nm). The suspensions were stirred during the laser irradiation. The suspensions were allowed to stand after irradiation to allow the non-ablated microcrystals and large aggregates of nanoparticles to sink to the bottom of the cuvette. The obtained supernatants were employed for measurement of the absorption spectra and the average diameter of the colloidal perylene nanoparticles dispersed in the supernatants. Allowing the irradiated suspensions to stand was needed to examine the dispersed nanoparticles that were formed by laser ablation. Absorption spectra of the supernatants were measured by a spectrophotometer (Shimadzu, UV-3600). The average diameters of the nanoparticles dispersed in the supernatants were measured by DLS (Malvern, Zetasizer Nano). Supernatants of perylene aqueous suspensions prior to laser irradiation also were examined by the spectrophotometer and DLS.

3. Results and discussion

Before irradiation, the supernatants of the aqueous perylene suspensions containing Triton X-100 at concentrations below 0.20 wt% and without Triton X-100 were colorless, indicating that perylene did not dissolve in the solutions. The color of the supernatant of the aqueous perylene suspension containing 0.20 wt% Triton X-100 was pale yellow before irradiation. The absorption spectrum of the supernatant containing 0.20 wt% Triton X-100 before irradiation is shown in Fig. 1 with absorption spectrum of perylene in ethanol. The absorption spectrum of the supernatant containing 0.20 wt% Triton X-100 before irradiation was very similar to that of perylene in ethanol in the visible region, indicating that some perylene molecules were stabilized in the micelles of Triton X-100 at 0.20 wt%. The high absorbance of the supernatant containing 0.20 wt% Triton X-100 at a wavelength region shorter than 300 nm is ascribed to photoabsorption of the surfactant. After irradiation for 10 min, the supernatants of the perylene suspensions with Triton X-100 at concentrations above 0.0020 wt% were transparent yellow, whereas the supernatants without Triton X-100 and with 0.0020 wt% Triton X-100 were colorless. The colors of the supernatants suggested that colloidal perylene nanoparticles were formed by the laser technique only when the concentrations of Triton X-100 was sufficiently high. The average diameters of the nanoparticles obtained in the supernatants are listed in Table 1, when the aqueous perylene suspensions were irradiated at 60 mJ/cm^2 for 10 min and the irradiated suspensions were allowed to stand for 1 day. The average diameters of the nanoparticles were approximately ten-fold larger than the semi-axes of the micelle models of Triton X-100 [23]. Colloidal particles were not detected in the supernatants without Triton X-100 and with 0.0020 wt% Triton X-100. Colloidal nanoparticles were detected in the supernatant containing 0.20 wt% Triton X-100 after irradiation, but not before irradiation. These results indicate that Triton X-100 at sufficiently high concentrations assists the formation of perylene nanoparticles in aqueous solutions for the laser ablation technique.

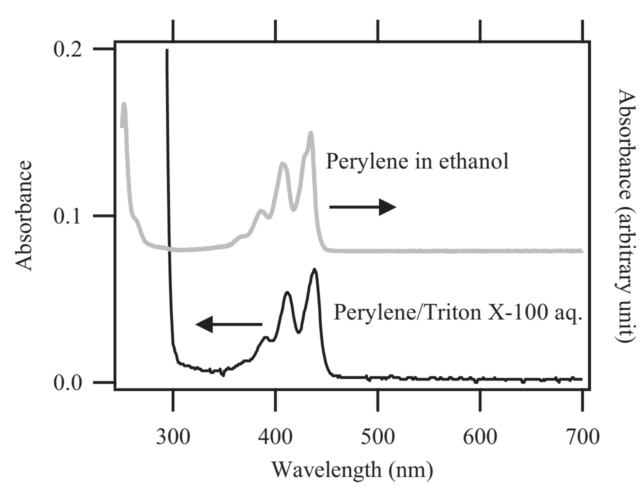

Fig. 1. Absorption spectra of the supernatant of the perylene aqueous suspension containing 0.20 wt% Triton X-100 before laser irradiation and a solution of perylene in ethanol.