Laser fabrication and crystallization of nano materials

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ABSTRACT

We have prepared nanoparticles of five organic dye molecules by laser ablation of their microcrystals in poor solvents using the third harmonics of nanosecond Nd^{3+}:YAG laser as an excitation light source. Their colloidal solutions were stable for longer than 1 week without any surfactants. The mean size was almost common to all the dyes (about 50 nm) and its distribution was narrow, which was confirmed by SEM observation. By applying electrophoretic deposition, the homogeneous thin film of quinacridone nanoparticles was fabricated on an indium-tin-oxide electrode. It was demonstrated that the films with different grain size and crystalline phase can be fabricated arbitrarily by using different nanoparticles. Laser ablation is also useful for crystallization of organic molecules, which was demonstrated for a representative organic nonlinear optical material.

Keywords: Laser ablation, dye molecule, nano colloid, electrophoretic deposition, femtosecond laser, crystallization, nonlinear optical material, 4-(dimethylamino)-N-methyl-4-stilbazolium tosylate

1. INTRODUCTION

Laser fabrication is a fundamentally important phenomenon based on interactions between light and matters and has been utilized to prepare micro/nano structures of various materials. Particularly electronics engineers have paid much attention to laser fabrication for development of future electronic devices, while medical doctors have introduced lasers for microsurgery. Now no scientist and no engineer doubt high potential of lasers in material researches and their great contribution to the relevant technological developments. The laser fabrication studies have been conducted mostly for making fine structures on the material surface, cutting the substrates, and so on, and how to fabricate precisely and finely the micro/nano structures has been examined.

Now laser fabrication technique is coming to the next stage where laser could be used for forming new materials. Of course various kinds of thin film, metal nanoparticles, and so on have been designed and prepared by applying laser ablation, but organic and biological molecules, organic materials, and polymers have not received much attention as a target of laser fabrication. Laser-induced nucleation is another interesting topic, which has been limited to silicone and related materials, and has never been reported on soft matters. This is because laser fabrication usually needs high intensity irradiation, and as a result the organic, biological, and related systems can be easily decomposed, contaminating the products with chemical impurities. However our understandings of laser ablation dynamics and mechanism in the framework of molecular photophysics ad photochemistry is now being matured and we know in some cases how we can avoid chemical decomposition accompanying laser ablation and crystallization. Indeed we have developed some new methodologies for organic matters, some of which results are presented as representative examples.

The first result is on preparation of organic nanoparticles. The nanoparticles consisting of aromatic and dye molecules have attracted increasing attention, as they show interesting physical and chemical properties and are expected to be new materials for optical and electronic devices. Different from metals and semiconductors, however, it was recognized that preparing organic nanoparticles with the size less than 100 nm is difficult. For the past dedicate, however, several approaches based on reprecipitation of organic molecules in solvent with very low solubility (poor solvent) have been reported[1-8], and nanoparticles in the size range of less than 30 nm was prepared by applying micro-wave during reprecipitation processes[4]. In 2000 we proposed a novel method to prepare organic nanoparticles by ablating dispersed

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microcrystals in poor solvent[9]. This poor solvent is important, as it does not dissolve organic molecules but their nanocolloids formed upon laser ablation. Indeed we demonstrated nanoparticle preparation of some phthalocyanines and aromatic hydrocarbons in water and some other solvents[9-15]. In this preparation, microcrystalline powder suspended in a poor solvent is exposed to intense laser pulses, which leads to the fragmentation of the initial crystals, namely, the initial suspension is converted into a transparent colloidal solution. This method is simple compared with the reprecipitation method and will open a new door to control nanoparticle size and its molecular aggregation structure by adjusting laser parameters and chemical conditions. Here, we prepare nanoparticles of five dye compounds using nanosecond YAG laser as an excitation light source, and show that their mean size is always a few tens nm.

The second result is concerned with so-called particle film. The prepared nanoparticles can be regarded as an important building block to construct organic nanostructures for photonic and electronic devises. Usually organic molecules are building blocks and their self assembling structures, vacuum deposited thin films, and LB films were examined. These are now quite conventional, but the prepared films are always suffering from the intrinsic defects, distribution of grain size, and so on. If size-, shape-, and phase-controlled nanoparticles are used as a new building block, very homogeneous films are prepared and new functionality will be expected, which is here demonstrated by electrophoretic deposition of quinacridone nanoparticles.

As the third result we describe another contemporary laser fabrication method which is laser-induced crystallization. Particularly in the case of femtosecond irradiation, some proteins show highly efficient crystallization giving high quality crystal. This experiment was started by our pioneering trial in 2002, and dynamics and mechanism are being revealed by time-resolved imaging. Here we show a new laser-induced phenomenon of 4-(dimethylamino)-N-methyl-4-stilbazolium tosylate which forms a typical nonlinear optical material. From these experimental studies we consider that laser fabrication and crystallization are very promising as future methodology for organic photonic materials and devices.

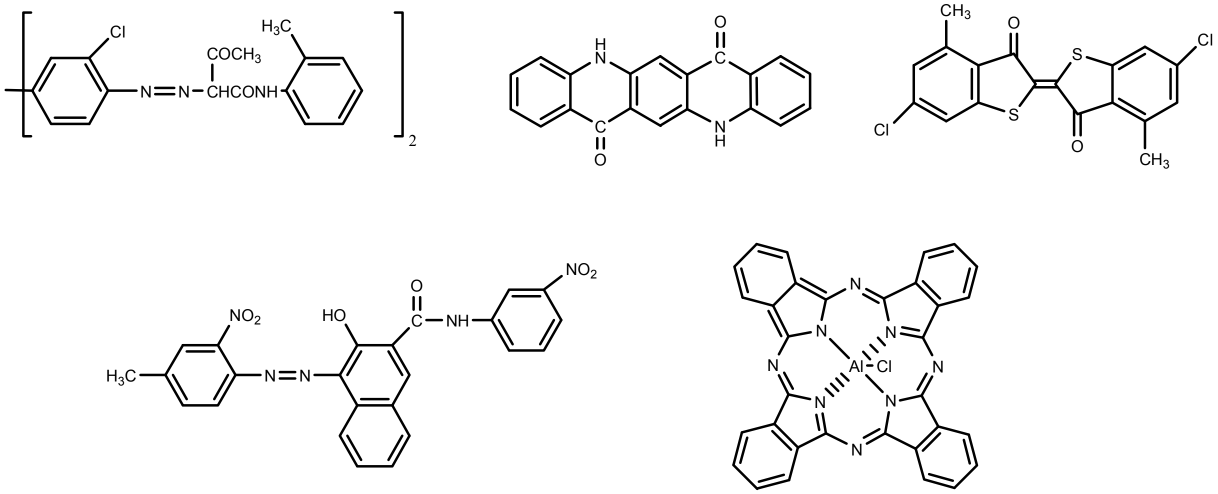

Fig. 1. Chemical structures of dye molecules used in this work: Upper from left to right; benzidine yellow (BY), quinacridone (QA), and oralith brilliant pink R (BP), lower from left to right; deep red (DR) and aluminum phthalocyanine chloride (AlPc).

2. NANOPARTICLE PREPARATION BY LASER ABLATION IN SOLUTION

For laser fabrication of dye compounds, we studied five molecules whose chemical structure and abbreviation are depicted in Fig. 1. BY, BP, DR, QA, and AlPc were purchased and used without further purification. Their micrometer-sized crystalline powders were added into a poor solvent where no appreciable dissolution of those molecules was detected, and QA and AlPc were sonicated for 30 min but the others were not. The dye concentration was about 5×10^{-3} wt%, and the composition of poor solvents were water/ethanol (7:1) for BY, water/ethanol (39:1) for BP and DR, and only distilled water for QA and AlPc. The mixture (3.0 ml) was put into a quartz cuvette of $1\times1\times5$ cm^3 with 1 cm optical path length. The microcrystals were dispersed in poor solvents by stirring the mixture vigorously with a magnetic stirrer, and then exposed to the third harmonic of nanosecond YAG laser (355 nm, 7 ns, 10 Hz). The spot size at the center of the cell was typically about 23 mm^2. The morphology of initial microcrystals and formed nanoparticles were examined with a scanning electron microscope (SEM) (FEI Strata DB235-31). Absorption spectra of the supernatants prior to irradiation and of the obtained colloidal solutions were measured with a spectrophotometer (Shimadzu, UV-3100PC). Absorption spectra were measured after standing the solution for 1 hr, which was necessary to exclude the contribution of the large crystals from the supernatant.

For all of the examined compounds, most of the initial microcrystalline powder sank on the bottom of a cuvette before laser irradiation, and its supernatant was almost colorless. This means that dye molecules are hardly dissolved in a poor solvent, since all compounds have strong absorption in the visible wavelength region. By irradiating the dispersed solution at a certain laser fluence above threshold values, the supernatant became colored and transparent by 10 min-laser irradiation. Figure 2 shows the absorption spectra at 1 hr after 5 min-laser excitation for QA, BY, DR, BP, and AlPc. The color solutions exhibited the characteristic absorption spectra of each parent pigment, although they are more or less modified compared with the molecular spectra in organic solvents. It is considered that dye compounds were dispersed in their poor solvents as their nanoparticles, because the solutions were transparent for visible light. The color of the colloidal solutions was observed for longer than a few weeks, while it gradually became pale due to their slow precipitation of nanoparticles.

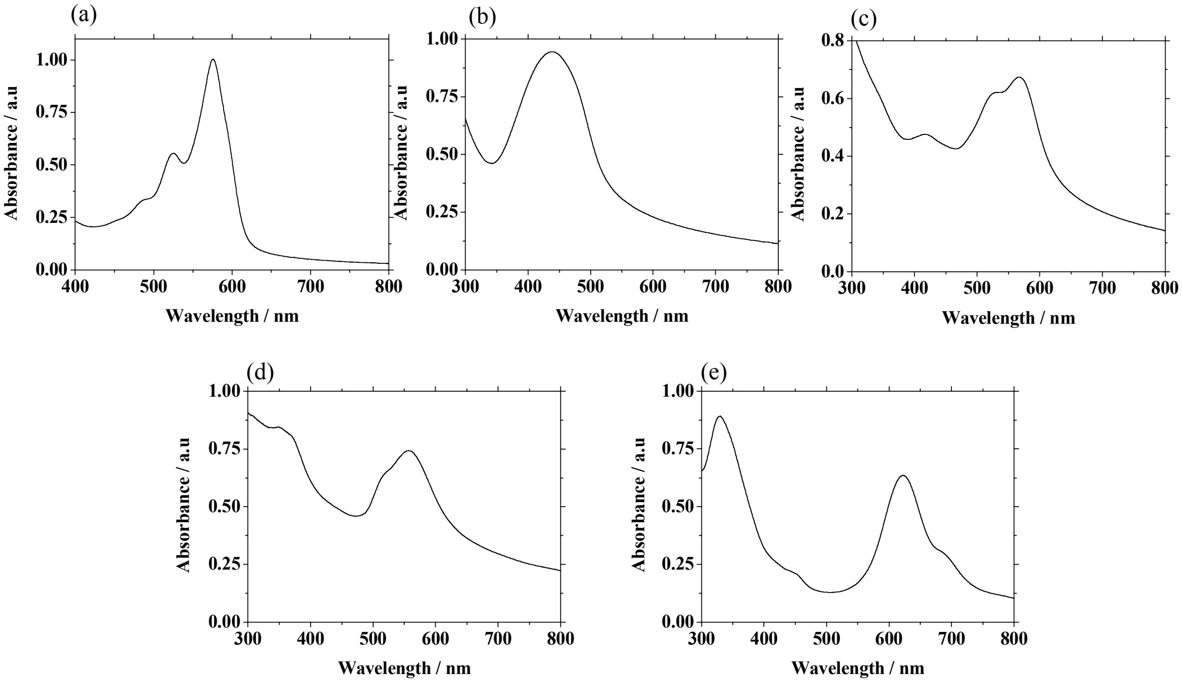

Fig. 2. Absorption spectra at 1 hr after 5 min-laser excitation for QA at 100 mJ/cm^2 (a), BY at 72 mJ/cm^2 (b), DR at 45 mJ/cm^2 (c), BP at 45 mJ/cm^2 (d), and AlPc at 54 mJ/cm^2 (e).

The laser fluence dependence of the absorption spectra of DR was demonstrated in Fig. 3, as a typical example. The flat spectrum of the initial supernatant can be mainly ascribed to scattering by micrometer-sized crystals. The spectral shape of the supernatants obtained above 19 mJ/cm^2 was almost independent on laser fluence. The absorbance increase with laser fluence was observed only above 11 mJ/cm^2, which means that the nanoparticle formation has a threshold with respect to laser fluence. The similar behavior of the laser fluence dependence was obtained for other dyes, while the threshold depended on each compound.

To confirm nanoparticle formation more directly, a drop of the supernatants of the colloidal solutions was spread on a surface-modified silicon substrate and dried in air at room temperature, and then nanoparticles on the substrate were observed with a SEM. Figure 4 shows SEM images of QA and AlPc as examples. Only small particles with their size of less than 100 nm were measured, although the size of initial crystal was ranged from a few micrometer to several hundreds nanometers. In order to compare the mean size of nanoparticles for each compound, the suspension was

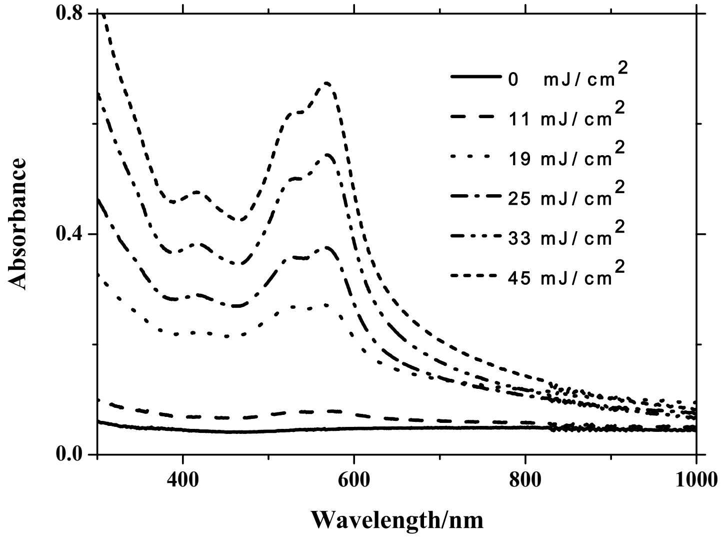

Fig. 3. The laser fluence dependence of the absorption spectra of DR.

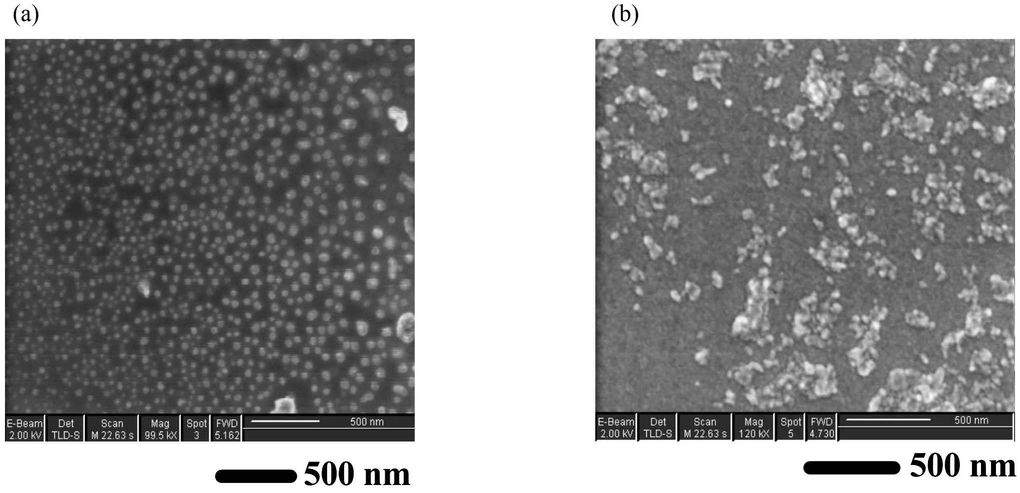

Fig. 4. SEM images of QA (a), and AlPc nanoparticles (b) formed by laser irradiation at the fluence of 98 mJ/cm^2 for 20 min and 45 mJ/cm^2 for 30 min, respectively.

irradiated at the fluences, which are larger by about 4 or 6 times than the threshold, until the absorption change of the supernatant was saturated with respect to irradiation period. With the supernatants of obtained colloidal solution, we carried out a SEM observation, and made the histograms of the particle size for each sample. The mean size and distribution for each compound are summarized in Table 1 where the thresholds of nanoparticle formation are listed. The mean size is ranged from 40 to 60 nm and independent of each dye, although their chemical structures and spectroscopic properties are quite different from each other.

The present results clearly demonstrate that the nanosecond laser ablation in a poor solvent is very useful for tailoring the nanoparticle of organic dyes. It should be noted that the mean size of prepared nanoparticles is about 50 nm for all dyes. Recently, we have reported that femtosecond laser excitation gives smaller nanoparticle than those by nanosecond laser one. The size was 13 and 17 nm for QA and VOPc, respectively, by using the femtosecond laser (780 nm, 200 fs FWHM) as an irradiation light source.[13] These experimental results indicate that the formed particle size is regulated by the pulse width of the excitation laser, but not so much changed for dye molecule.

The mechanism of laser induced fragmentation of microcrystals can be eventually described by photothermal laser ablation of organic solids. We have proposed and confirmed the photothermal mechanism for nanosecond and femtosecond laser ablation of copper phthalocyanine (CuPc) and its derivative films in atmosphere[16-18]. When organic solid is excited with an intense laser pulse, the electronically excited state is formed densely and relaxes quickly into the ground state through efficient nonradiative processes such as exciton-exciton annihilation. The time-constant of the non-radiative decay can be estimated to be in the order of 10 ps under the laser ablation condition. Therefore, in case of nanosecond laser excitation, a cyclic process of generation and relaxation of the excited state should occur during the temporal duration of the laser pulse. This photothermal conversion results in a rapid temperature jump, leading to fragmentation of bulk solids into small pieces. We considerer that similar photothermal ablation will respond to the nanoparticle formation by laser ablation in solvents. It should be noted, however, that in the solvent cooling process of heated materials due to thermal diffusion to the solvent takes place accompanying the laser heating. The cooling rate for small particles should be faster than for large one because of their larger specific surface. Indeed, it was reported that the rate constant was about 2 ns for polydiacetylene nanocrystal with the size of 150 nm, and faster for smaller nanocrystals[19]. Thus it is considered that transient temperature of particles during and just after irradiation with a 10-ns laser pulse decreases as decreasing particle size. Consequently, the temperature jump is expected to be not enough to induce fragmentation of particles smaller than a certain size, which should determine the particle size formed by the laser ablation.

Table 1. The threshold of nanoparticle formation for five dye molecules, and the mean size of nanoparticle and stability of the colloidal dispersion were obtained under the nanosecond YAG laser irradiation for BY at 35 mJ/cm^2 for 90 min, BP at 60 mJ/cm^2 for 90 min, DR at 60 mJ/cm^2 for 60 min, AlPc at 45 mJ/cm^2 for 30 min, and QA at 104 mJ/cm^2 for 10 min. *The half-decay time of the absorbance of the colloidal dispersion.

	BY	AlPc	BP	DR	QA
mean size / nm (standard deviation /nm)	59 (±16)	56 (±28)	40 (±9)	43 (±10)	50 (±10)
threshold / mJ cm^{-2}	8	6	10	7	30
stability of colloidal dispersion*	1 month	>3 months	1 week	1 week	> 1 month

3. ELECTROPHORETIC DEPOSITION OF DYE NANOPARTICLES

Electrophoretic deposition is now one of well known methods to construct colloidal films and has been used in various systems. This is based on the fact that charged colloidal particles move toward an oppositely charged electrode under an applied DC electric field and are deposited on it. As nanoparticles prepared by laser ablation in solution are positively charged, which may be due to surface ionization due to high intensity excitation, they are assembled on the anode forming homogeneous film. This behavior is dependent on pH of the solution, applied electric field, concentration of the nanoparticles in mother solution, and so on. Furthermore the prepared film preserves the structural, physical, and chemical properties of the component nanoparticles, so that we can control the properties of the film by choosing different kinds of nanoparticles.

QA nanoparticle was prepared by the above laser ablation and electrophoretic deposition method was applied. In its colloidal solution indium- tin-oxide (ITO) coated glass substrate and stainless plate were immersed and the constant DC voltage was supplied for a few tens min. When the electrodes were taken out from the solution, the particles were only weakly attached on the ITO electrode, while they were packed with each other and bounded to the substrate strongly after being dried. It was confirmed that the prepared film was very homogeneous over a millimeter scale and had a porous structure. When the nanoparticles with smaller size were used, the porous part was not major. On the other hand, the film fabricated with larger particles gave more porous film. Here we present how photoconductivity of the nanoparticle film depends on the component nanoparticles.

It was already reported that QA nanoparticles had different phase depending on the excitation wavelength of lasers for inducing ablation. In the case of 355 nm excitation, the third harmonic of ns Nd^{+3}:YAG, the formed nanoparticles had always β-phase independent on the laser fluence. On the other hand, the phase changed form β to γ in the case of 532 nm excitation by increasing the laser fluence. When the nanoparticles with different size and phase were used, the prepared films had different properties. The photoconductivities of some QA particle films are shown as a representative example in Fig. 5. The sizes of component particles are 110, 55, 35, and 25 nm for #1, #2, #3, and #4, respectively. The phases of #1 and #4 are β and γ, respectively, while that of #1 and #4 is their mixture. It is noteworthy that the phase of QA nanoparticle is controlled by laser wavelength and that of the electrophoretically fabricated films from these particles are exactly the same to that of component particles. This is indeed a new possibility to obtain the films with different photonic properties.

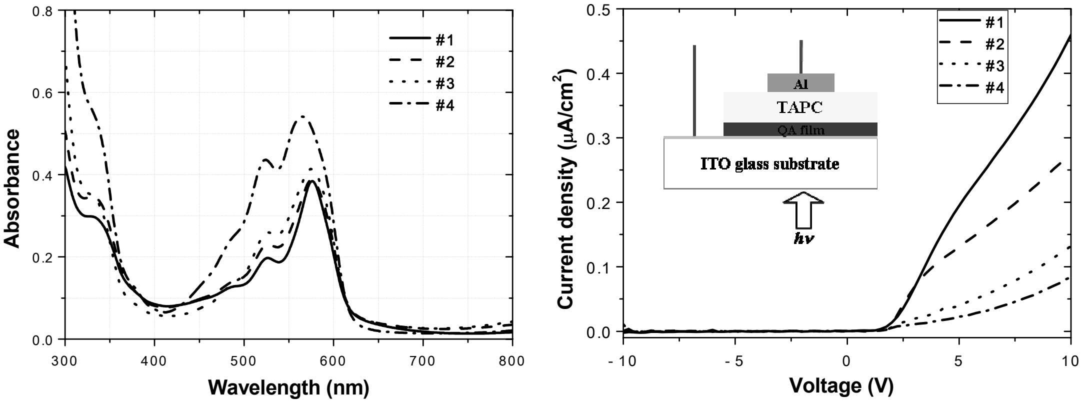

Fig. 5. Absorption spectra and photoconductivity of QA nanoparticle films with different size and phase.

4. CRYSTALLIZATION OF ORGANIC MOLECULES BY FEMTOSECOND LASER IRRADIATION

When intense femtosecond laser pulse is focused in transparent solution, its multiphoton absorption takes place very efficiently and induces some nonlinear phenomena leading to an impulsive force. Above a certain laser fluence shockwave generation and cavitation bubbling were commonly observed and followed local convection. When the laser is focused with high-numerical aperture objective lens, these phenomena are confined in the small volume around the laser focal point with size less than μm, we have named the dynamics “Laser Micro/nano Tsunami”. When the femtosecond laser is focused on supersaturated solution of organic molecule or protein, a local concentration of the solute is locally and temporally increased around the focal point and sometime leads to a nucleation of the solute.

The representative demonstration is shown in Figure 6. As the sample, we used supersaturated solution of 4-(dimethylamino)-N-methyl-4-stilbazolium tosylate (DAST), whose crystal has be expected as a promising nonlinear optical material. A regenaratively amplified Ti:sapphire laser (800 nm, 120 fs, 1 kHz, 30 μJ/pulse) was focused through a convex lens with focal length of 150 mm in the center of a vessel containing the supersaturated solution, whose diameter and height are 26.5 and 21 mm, respectively. When the laser pulse train with energy of 30 μJ/pulse was introduced at 7 mm away from the surface of the solution, objects with metallic gloss were generated around the laser focal point with strong fluorescence and rose up to the surface of the solution as shown in the figure. The objects would be attributed to polycrystal of DAST. Here we used supersaturated solution with extremely high concentration (35 g/l) in order to demonstrate obvious crystallization immediately after the laser irradiation, so that rapid polycrystallization was induced. On the other hand, when we used the solution with low concentration, crystal growth was slow and takes a time; 1 day, 1 week or several months[20]. Under this condition, we could get single crystals with size larger than mm.

Such laser-induced crystallization now receives much attention in the relevant fields, above which the crystallization of protein is one of the interesting contemporary topics[21-24]. The nucleation dynamics relating with the concentration processes has been investigated on means of phenomenological experiments by us[25-28]. Also glycine and urea crystallizations by ns laser irradiation were reported by Garetz *et al.*[29-30], while we have recently succeeded in demonstrating laser trapping crystallization of glycine[31].

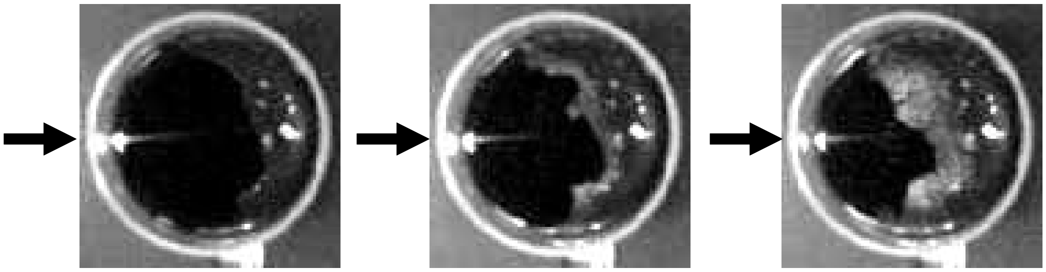

Figure 6. Femtosecond laser-induced crystallization of 4-(dimethylamino)-N-methyl-4-stilbazolium tosylate (DAST). The images from the top of the sample vessel were captured with interval of 15 sec from the left to the right. Arrows indicate direction of the laser irradiation. The diameter of the vessel is 26.5 mm.

5. ACKNOWLEDGEMENT

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