

Laser trapping dynamics of 200 nm-polystyrene particles at a solution surface

Ken-ichi Yuyama^a, Teruki Sugiyama^{*b}, Hiroshi Masuhara^{*a}

^aDepartment of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan; ^bInstrument Technology Research Center, National Applied Research Laboratories, Hsinchu 30076, Taiwan

ABSTRACT

We present laser trapping behaviors of 200 nm-polystyrene particles in D₂O solution and at its surface using a focused continuous-wave laser beam of 1064 nm. Upon focusing the laser beam into the solution surface, the particles are gathered at the focal spot, and their assembly is expanded to the outside and becomes much larger than the focal volume. The resultant assembly is observed colored under halogen lamp illumination, which is due to a periodic structure like a colloidal crystal. This trapping behavior is much different compared to the laser irradiation into the inside of the solution where a particle-like assembly with a size similar to that of the focal volume is prepared. These findings provide us new insights to consider how radiation pressure of a focused laser beam acts on nanoparticles at a solution surface.

Keywords: laser trapping, solution surface, polystyrene nanoparticle, colloidal crystal, structural color

1. INTRODUCTION

Laser trapping with a tightly focused single laser beam was firstly demonstrated using dielectric particles in 1986.¹ Ever since this innovative work was reported by Ashkin, the technique has been widely employed as optical tweezers to trap and manipulate micrometer-sized objects without mechanical contact in many fields of physics, optics, and biology.^{2,3} For nanometer-sized objects, this technique has been applied to J-aggregates⁴, polymers^{5,6}, liquid-like clusters of amino acids⁷, quantum dots⁸⁻¹⁰ as well as various nanoparticles¹¹⁻¹³. In dilute solution, a single nanometer-sized object is trapped at the focal spot and the trapped object can be analyzed individually and manipulated arbitrarily. Single J-aggregate spectroscopy, analysis of trap stiffness of an individual quantum dot, and patterning of single metal nanoparticles are representative results.^{4,9,11} On the other hand, in concentrated solution, numerous nanometer-sized objects are concurrently trapped in the focal volume, and eventually their assembly with a size similar to the focal volume is formed. Such laser trapping induced-assembly formation was demonstrated with long-chain polymers, liquid-like clusters of amino acids, quantum dots, and polystyrene nanoparticles.^{5-8,12,13} The formation dynamics was investigated by analyzing time evolution of emission or backscattered light intensity under their laser trapping.^{5,7,8,13} The intensity was increased with their trapping in the focal volume and finally saturated when the focal volume was fully occupied by the objects trapped.

The laser trapping technique enables us to confine, assemble, and manipulate target objects three-dimensionally in solution, so that most experiments have been conducted inside the solution. On the other hand, it is worth noting that numerous novel chemical phenomena have been developed at a solution surface. Since 2007, we have explored laser trapping-induced phenomena characteristic at an air/solution and a glass/solution interfaces and found that focusing a continuous-wave (CW) near-infrared (NIR) laser beam at the interfaces of a glycine solution film causes solid-liquid (crystallization) and liquid-liquid phase separations, respectively.¹⁴⁻¹⁶ Both phenomena are initiated by the increase in

Emails: sugiyama@narlabs.org.tw (TS), masuhara@masuhara.jp (HM)

Phone +886-3-577-9911, Fax +886-3-577-3947 (TS)

Phone +886-3-571-2121 ext. 56593, Fax +886-3-571-2121 ext. 56593 (HM)

Optical Trapping and Optical Micromanipulation X, edited by Kishan Dholakia, Gabriel C. Spalding,
Proc. of SPIE Vol. 8810, 88101V · © 2013 SPIE · CCC code: 0277-786X/13/\$18 · doi: 10.1117/12.2023020

local concentration due to laser trapping of glycine liquid-like clusters. The concentration increase is coupled with molecular alignment characteristic of a solution surface or a glass surface as well as surface deformation and convection, leading to the formation of a crystal or liquid nucleus. Once a nucleus for crystallization or liquid-liquid phase separation is formed, it spontaneously grows to bulk size through mutual molecular interactions.

In this paper, we present laser trapping dynamics of 200 nm-polystyrene nanoparticles at a surface of the colloidal solution. Upon focusing a CW NIR laser beam at the solution surface, the particles are gathered and trapped at the focal spot, and a small assembly is formed. Further laser irradiation makes the assembly grow and expand outside the focal spot, despite no attractive interactions between the particles. Moreover, the central part of the resultant assembly is observed colored under halogen lamp illumination, which strongly supports that the assembly has a periodic structure like a colloidal crystal. On the other hand, laser trapping in the solution is much different from that at the solution surface, and just provides the particle-like assembly with a size similar to that of the focal spot. The laser trapping dynamics characteristic at the solution surface is discussed from the viewpoints of convection flow, thermophoresis, electric charge generation, and light scattering at assembly surface giving larger optical potential.

2. EXPERIMENTAL SECTION

An optical system based on an inverted microscope (Olympus, IX71) was used for experiments on laser trapping of 200 nm-polystyrene nanoparticles, as shown in Fig. 1a. A linearly polarized NIR laser beam from a CW Nd³⁺:YVO₄ laser (Coherent, Inc., MATRIX 1064-10-CW, $\lambda = 1064$ nm) was introduced into the inverted microscope through an objective lens (60 magnification, NA 0.90) as a light source for laser trapping. The laser power throughout the objective lens was set at 200–700 mW by combination of a half wave plate (HWP) and a polarizing beam splitter (PBS). A green laser (Laserglow technologies, LRS-0532-TFH-01, $\lambda = 532$ nm) was also introduced into the microscope in the same optical path as the trapping laser in order to adjust the focal position before starting irradiation of the trapping laser.

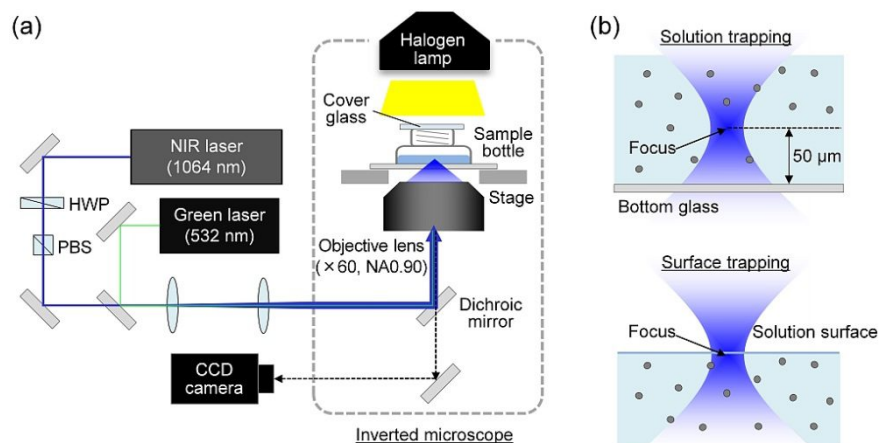


Figure 1. (a) A schematic illustration of the experimental setup. (b) The focal positions for laser trapping in this experiment.

The initial sample solution was prepared by diluting a 200 nm-polystyrene colloidal solution (Polysciences, Inc.) with D₂O (Aldrich, 99.9 %), and the final concentration of the sample was adjusted to be 3.8×10^{11} particles/ml (0.38 particles/ μm^3). We used D₂O, not H₂O, as solvent in order to minimize local temperature elevation during laser trapping due to light absorption by overtone vibration bands of OH. It is reported that the temperature elevation is 23 and 2.6 K/W in H₂O and D₂O, respectively, upon focusing a 1064 nm-laser beam by a high NA objective lens (NA=1.35, $\times 100$).¹⁷ The temperature elevation of the present sample solution is estimated to be 3.0 K/W under the 1064 nm-laser irradiation, since the commercial colloidal aqueous solution was diluted by 15 times with D₂O. A small amount (15 μL)

of the sample solution was poured into a hand-made glass sample bottle with a highly hydrophilic surface, and the solution thin film with 120–160 μm thickness was prepared. The sample bottle was covered with a glass substrate to suppress solvent evaporation and was set on the stage of an inverted microscope. After confirming the focal position of the green laser, the green laser was turned off, and the NIR laser was switched on. As shown in Fig. 1b, the laser beam was focused in the solution (the upper figure) or at the solution surface (the lower figure). Laser trapping behavior of polystyrene nanoparticles was observed with a charge-coupled device (CCD) video camera (WATEC, WAT-231S2) under halogen lamp illumination.

3. RESULTS AND DISCUSSION

The 200 nm-polystyrene nanoparticles were slightly visible with a CCD video camera under halogen lamp illumination, although their size is smaller than the resolution of the present optical system. The Brownian motion of the nanoparticles was observed everywhere in the solution before the laser was irradiated. Figures 2a and 2b show a series of CCD images under the NIR laser irradiation into the inside of the solution and the solution surface at 200 mW, respectively. When the focal position was set into the solution, the nanoparticles were instantly gathered, and one particle-like assembly with a size of several micrometers was formed within only 2 seconds and confined in the focal volume (Fig. 2a). The assembly size was larger compared to the previously reported results on molecular assemblies formed by laser trapping in solution.⁶ The present assembly might be observed as a larger transmittance image due to halogen lamp illumination. The temporal change in size of the particle-like assembly is shown in Fig. 2c. The assembly gradually became larger for 2 seconds, and then the growth was stopped with keeping the assembly size. This result means that the focal volume giving optical potential was fully occupied by the nanoparticles. Upon focusing the laser into the solution surface, the nanoparticles were gathered and confined in the focal volume at the early stage of the irradiation (Fig. 2b (1)–(2)), which is similar to the case of the irradiation inside the solution. However, further irradiation into the formed assembly caused its continuous growth (Fig. 2b (3)–(4)). The assembly expanded to the outside of the focal spot and eventually reached the size of 8 μm in diameter. The size of the assembly was almost saturated at 10 sec of the irradiation as shown in Fig. 2c. Still after that, the assembly size gradually became larger in little increments.

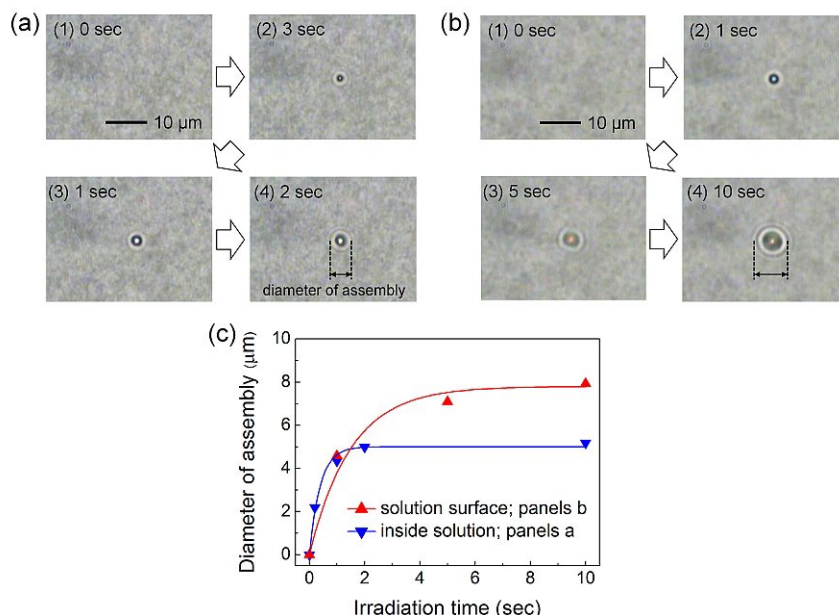


Figure 2. CCD images of the assembly formation induced by the laser irradiation into (a) the inside of the solution and (b) a solution surface. (c) Temporal change in assembly size under laser irradiation at each focal position.

In order to examine laser power dependence of the assembly formation at the surface, we prepared the assembly with different laser intensities at a certain irradiation time. Figure 3a shows CCD images of the assembly formed by the 1 min-laser irradiation into a solution surface with three different laser powers of 300, 500, and 700 mW. Interestingly, the central part of each assembly was clearly observed colored in visible range under halogen lamp illumination, while the peripheral part showed almost no color. The polystyrene nanoparticles themselves have no absorption in visible range, so that it is reasonable to consider that the coloration is ascribed to structural color of the assembly. We suggest that the central part of the assembly has a periodic structure like a colloidal crystal. Thus, laser trapping of the nanoparticles clearly showed the focal position dependence. The particle-like assembly is formed inside the solution, while the crystal-like assembly is prepared at a solution surface. Considering that the formation of an ordered-structure is achieved only at the solution surface, the nanoparticles trapped at the surface are possibly governed by nature of the surface as well as their mutual interactions and rearranged to the most stable ordered-structure.

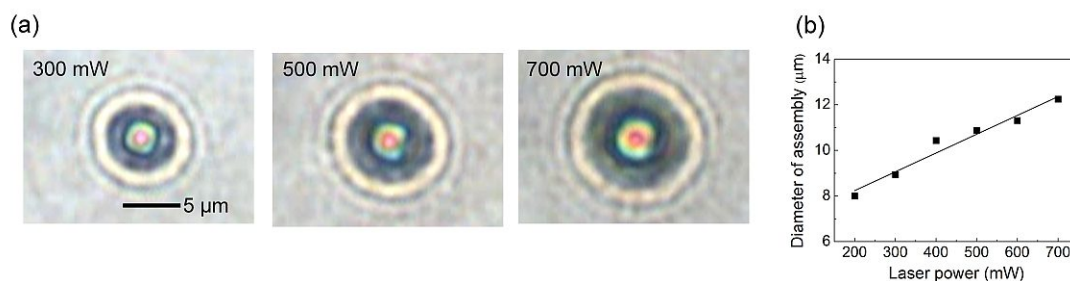


Figure 3. (a) CCD images and (b) size of the crystal-like assembly formed by the 1 min-laser irradiation into a solution surface with different laser powers.

Polystyrene nanoparticles under our experimental conditions are negatively-charged and have repulsive force with each other. Nevertheless, the crystal-like assembly of nanoparticles grew from the focal spot to its outside. It is of great interest and important to consider how the crystal-like assembly grows larger than the focal volume. One of the notable findings is that the size of the crystal-like assembly formed by the 1 min-laser irradiation became larger almost linearly with increase in laser power, which is shown in Figure 3b. According to this result, we propose the following possible mechanisms realized by laser irradiation for the unusual assembly growth.

The first possibility is heating and the accompanying convection flow due to change in density or surface tension (Heating Effect 1).^{18,19} Convection flow is collective movement of molecules in fluid, and solvent molecules and nanoparticles are transported together along the flow direction. If the convection directing to the focal spot is caused by the laser irradiation, the transported particles might be sequentially accumulated to a surface of the small crystal-like assembly. The second one is thermophoresis, in other word Soret effect (Heating Effect 2).^{20,21} Heating and generated temperature distribution can also induce thermophoretic force for nanoparticles in solution. When particles are located in a medium with temperature gradient, they receive the force, resulting in a concentration gradient of particles. Actually, these Heating Effects were occasionally pointed out for conventional laser trapping experiments.²²⁻²⁴

These Heating Effects possibly become dominant with the increase in laser power, since local temperature becomes higher with the increase in the power. The direct observation of the trapping behavior with a CCD camera provided us a crucial insight to these Heating Effects. The motion of the nanoparticles around the crystal-like assembly under laser irradiation could be directly observed. It seemed that the nanoparticles at a solution surface layer were diffused from the assembly toward its outside, despite that the assembly continued to grow. The diffusion became vigorous with the increase in laser power. This particle motion can be explained from the viewpoint of Marangoni effect which generates the mass transfer along a solution surface due to surface tension distribution. A liquid with high surface tension pulls more strongly the surrounding medium, compared to a liquid with low one. Consequently, a gradient in surface tension causes liquid flow in a direction to regions with higher surface tension. Surface tension is a function of temperature, so that in the current trapping experiments the change in surface tension should be induced by laser heating. Light absorption by the colloidal solution at the focal point generates slight temperature elevation of 1–2 K. Even for this small

elevation the generated heat is meaningful and diffused from the focal spot to outside. The temperature at the solution surface layer becomes lower with distance from the spot, resulting in forming temperature distribution. Since higher temperature decreases surface tension, surface energy around the focal spot becomes lower compared to the surrounding area. The gradient of surface tension induces Marangoni convection flow with a direction from the focal spot to outside, possibly leading to the particle transportation in a direction away from assembly. The consideration supports that above two Heating Effects can be ruled out and other factors dominantly work.

We propose other two possibilities as follows. One is that, during the laser irradiation into the formed assembly, the assembly edge is locally charged plus, and negatively charged nanoparticles are attracted to the surface through electrostatic interaction (Electrostatic Effect). As the other possibility, laser light incident to the central part of the crystal-like assembly are efficiently scattered by the formed assembly itself and penetrates into the surrounding solution, and optical potential is formed at the assembly edge and surface (Optical Effect). Recently, we suggested this Optical Effect on basis of the results on laser trapping of L-phenylalanine at a surface of the unsaturated aqueous solution.²⁵ The laser irradiation led to laser trapping of liquid-like clusters of L-phenylalanine which consist of solute and solvent molecules weakly linked with each other, forming a plate-like crystal at the focal spot. Incidentally, the irradiation into the inside of the solution, a particle-like molecular assembly was prepared, but no crystallization was realized. For the point that an ordered-structure is formed only at the surface, the focal position dependence of laser trapping behaviors of the current nanoparticles is quite similar to that of L-phenylalanine. Interestingly, the laser irradiation into a central part of the formed plate-like crystal led to laser trapping at the crystal edge not only for L-phenylalanine molecules/clusters but also for 1 μm -sized polystyrene particles. Those microparticles were closely parked at edges of the crystal, where the periodical structure was formed. It can be considered that the molecules/clusters were also gathered and adsorbed to the crystal edge, leading to crystal growth. Their trapping at the crystal edge were achieved despite that the surface was not illuminated by the laser directly, and so we discussed the dynamics and mechanism in view of optical potential formed at the crystal edge by light propagation inside the crystal.

Based on the above consideration Figure 4 is proposed showing the possible formation mechanism for the crystal-like assembly of the nanoparticles at a solution surface. Upon the laser irradiation into a solution surface, gradient force toward the focal spot is exerted on the nanoparticles, and simultaneously temperature distribution is formed at the surface due to light absorption by the colloidal solution (Figure 4(1)). The former phenomenon causes laser trapping of the nanoparticles at the focal spot, while the latter induces outward mass transfer along the solution surface (Figure 4(2)). Nanoparticles trapped at the solution surface are rearranged to the most stable ordered-structure, which is possibly determined by the balance of trapping force, repulsion between the nanoparticles, and nature of the surface. Furthermore, the formed assembly itself acts as a scattering substance and diffuses the laser light to outside, giving optical potential at the assembly edge and surface (Figure 4(3)). Actually, we could observe the NIR laser extensively scattered by the formed assembly when the halogen lamp illumination was stopped. This result pushes us to consider that the scattered light generates optical potential at a surface of the crystal-like assembly and laser trapping of the nanoparticles is induced around the surface. The nanoparticles in the surrounding solution are trapped at the assembly surface by the extensively generated optical potential. The trapping at the surface will compete with the outward mass transfer. Consequently, the nanoparticles at the assembly surface are not tightly arranged, and no coloration is observed due to its non-periodic structure.

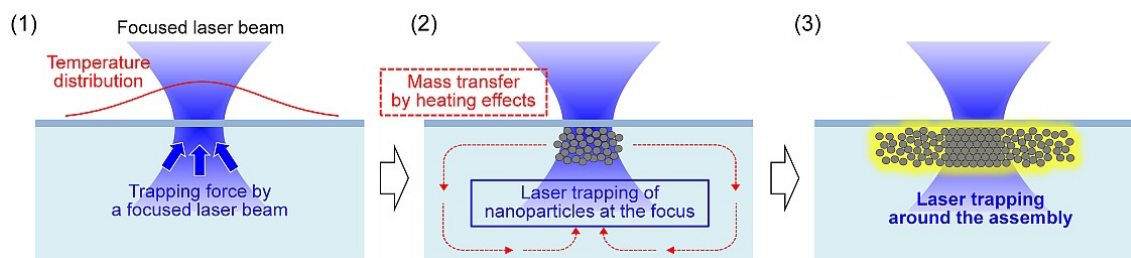


Figure 4. Possible formation mechanism of the crystal-like assembly of nanoparticles under laser irradiation at a solution surface.

4. SUMMARY

We performed a comparison of laser trapping of 200 nm-polystyrene particles in D₂O solution and at its surface using a focused laser beam of 1064 nm. Upon focusing the CW laser beam into a solution surface, the particles were gathered at the focal spot, and the assembly was extended to the outside and becomes much larger than the focal volume despite that they have less attractive interactions with each other. The central part of the formed assembly is observed colored in visible range under halogen lamp illumination due to a periodic structure like a colloidal crystal, being governed by nature of the surface. The assembly dynamics at the solution surface is much different compared to the laser irradiation into inside of the solution giving the particle-like assembly. These findings enable us to consider how radiation pressure of a focused laser beam acts on nanoparticles at a solution surface and will also lead to deep understanding of the mechanism for laser trapping-induced formation of molecular crystals at a solution surface.

ACKNOWLEDGEMENT

The present work is supported by the MOE-ATU Project (National Chiao Tung University) of the Ministry of Education, Taiwan, to H.M., and the National Science Council of Taiwan to T.S. (NSC 102-2113-M-492-001-MY2) and to H.M. (NSC 100-2113-M-009-001).

REFERENCES

- [1] Ashkin, A., Dziedzic, J. M., Bjorkholm, J. E. and Chu, S., "Observation of a single-beam gradient force optical trap for dielectric particles," *Opt. Lett.* 11, 288–290 (1986).
- [2] Ashkin, A., "Optical trapping and manipulation of neutral particles using lasers," *Proc. Natl. Acad. Sci. USA* 94, 4853–4860 (1997).
- [3] Ashkin, A., "History of optical trapping and manipulation of small-neutral particle, atoms, and molecules," *IEEE J. Sel. Top. Quant. Electron.* 6, 841–856 (2000).
- [4] Tanaka, Y., Yoshikawa, H. and Masuhara, H., "Two-photon fluorescence spectroscopy of individually trapped pseudoisocyanine J-aggregates in aqueous solution," *J. Phys. Chem. B* 110, 17906–17911 (2006).
- [5] Singer, W., Nieminen, T. A., Heckenberg, N. R. and Rubinsztein-Dunlop, H., "Collecting single molecules with conventional optical tweezers," *Phys. Rev. E* 75, 011916-1–011916-5 (2007).
- [6] Borowicz, P., Hotta, J., Sasaki, K. and Masuhara, H., "Laser-controlled association of poly(*N*-vinylcarbazole) in organic solvents: radiation pressure effect of a focused near-infrared laser beam," *J. Phys. Chem. B* 101, 5900–5904 (1997).
- [7] Tsuboi, Y., Shoji, T. and Kitamura, N., "Optical trapping of amino acids in aqueous solutions," *J. Phys. Chem. C* 114, 5589–5593 (2010).
- [8] Pan, L., Ishikawa, A. and Tamai, N., "Detection of optical trapping of CdTe quantum dots by two-photon-induced luminescence," *Phys. Rev. B* 75, 161305-1–161305-4 (2007).
- [9] Jauffred, L., Richardson, A. C. and Oddershede, L. B., "Three-dimensional optical control of individual quantum dots," *Nano Lett.* 8, 3376–3380 (2008).
- [10] Jauffred, L. and Oddershede, L. B., "Two-photon quantum dot excitation during optical trapping," *Nano Lett.* 10, 1927–1930 (2010).
- [11] Ito, S., Yoshikawa, H. and Masuhara, H., "Laser manipulation and fixation of single gold nanoparticles in solution at room temperature," *Appl. Phys. Lett.* 80, 482–484 (2002).
- [12] Magome, N., Kitahara, H., Ichikawa, M., Nomura, S. M. and Yoshikawa, K., "Rhythmic bursting in a cluster of microbeads driven by a continuous-wave laser beam," *Phys. Rev. E* 65, 045202-1–045202-4 (2002).
- [13] Hosokawa, C., Yoshikawa, H. and Masuhara, H., "Optical assembling dynamics of individual polymer nanospheres investigated by single-particle fluorescence detection," *Phys. Rev. E* 70, 061410-1–061410-7 (2004).
- [14] Sugiyama, T., Adachi, T. and Masuhara, H., "Crystallization of glycine by photon pressure of a focused CW laser beam," *Chem. Lett.* 36, 1480–1481 (2007).

- [15] Yuyama, K., Sugiyama, T. and Masuhara, H., "Millimeter-scale dense liquid droplet formation and crystallization in glycine solution induced by photon pressure," *J. Phys. Chem. Lett.* 1, 1321–1325 (2010).
- [16] Sugiyama, T., Yuyama, K. and Masuhara, H., "Laser trapping chemistry: From polymer assembly to amino acid crystallization," *Acc. Chem. Res.* 45, 1946–1954 (2012).
- [17] Ito, S., Sugiyama, T., Toitani, N., Katayama, G. and Miyasaka, H., "Application of fluorescence correlation spectroscopy to the measurement of local temperature in solutions under optical trapping condition," *J. Phys. Chem. B* 111, 2365–2371 (2007).
- [18] Da Costa, G., "Optical visualization of the velocity distribution in a laser-induced thermocapillary liquid flow," *App. Opt.* 32, 2143–2151 (1993).
- [19] Rybalko, S., Magome, N. and Yoshikawa, K., "Forward and backward laser-guided motion of an oil droplet," *Phys. Rev. E* 70, 046301-1–046301-4 (2004).
- [20] Braun, D. and Libchaber, A., "Trapping of DNA by thermophoretic depletion and convection," *Phys. Rev. Lett.* 89, 188103-1–188103-4 (2002).
- [21] Duhr, S. and Braun, D., "Two-dimensional colloidal crystals formed by thermophoresis and convection," *Appl. Phys. Lett.* 86, 131921-1–131921-3 (2005).
- [22] Dasgupta, R., Ahlawat, S. and Gupta, P. K., "Trapping of micron-sized objects at a liquid-air interface," *J. Opt. A: Pure Appl. Opt.* 9, S189–S195 (2007).
- [23] Louchev, O. A., Juodkazis, S., Murazawa, N., Wada, S. and Misawa, H., "Coupled laser molecular trapping, cluster assembly, and deposition fed by laser-induced Marangoni convection," *Opt. Exp.* 16, 5673–5680 (2008).
- [24] Uwada, T., Sugiyama, T. and Masuhara, H., "Wide-field Rayleigh scattering imaging and spectroscopy of gold nanoparticles in heavy water under laser irradiation," *J. Photochem. Photobio. A: Chem.* 221, 187–193 (2011).
- [25] Yuyama, K., Sugiyama, T. and Masuhara, H., "Laser trapping and crystallization dynamics of L-phenylalanine at solution surface," *J. Phys. Chem. Lett.* 4, 2436–2440 (2013).