

Optical manipulation in conjunction with photochemical/photothermal responses of materials

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Abstract

This article reviews optical manipulation coupled with photochemical/photothermal responses of nanometer sized materials including molecular systems, polymers, and inorganic nanoparticles. After the introduction, section 2 overviews the optical trapping of nanometer sized molecular systems including early-stage studies, such as trapping of polymer chains, micelles, and molecular aggregates in solution at room temperatures. Then, the conformation control of macromolecule assemblies and gels by optical force are introduced, followed by micro-fabrications achieved by combining optical trapping and photochemical reactions. Section 3 summarizes studies on the evaluation of optical force acting on nanometric molecular systems using fluorescence correlation techniques.

Approaches to control optical force by using photochemical reactions are shown in section 4, where the absorption band of target materials are modified through photochromic reactions, leading to micromechanical motion of small particles synchronizing with the photochemical reactions. Section 5 overviews photothermal effect in optical manipulation such as natural convection, Marangoni convection and thermophoresis, and applications of the thermal effects to develop new methods of micromanipulation achieved by combining optical force and photothermal responses.

Keywords

Optical manipulation, Molecular system, Polymer system, Photochemical reaction, Photothermal conversion, Thermophoresis

Highlights

Trapping and assembling molecular systems by optical force.

Controlling the morphologies of molecular assemblies and polymer-gels by optical force.

Fabrications of polymeric microstructures by coupling optical force and photochemical reactions.

Switching optical force via photochromic reactions and its applications to micromechanical systems.

Photothermal conversion, fluid convection, and thermophoresis in optical manipulation: evaluation of the effects and useful applications.

1. Introduction

Phenomena originating from the interaction between photons and materials include absorption, scattering, reflection, refraction, and so forth. The photo-absorption by a molecule involves the transfer of energy from a photon to the molecule followed by the formation of its excited state. The deactivation of molecular excited state through photophysical/photochemical processes has been intensively studied as a main topic of the research field of photochemistry. On the other hand, the momentum is transferred from photons to materials through the absorption, scattering, reflection, and refraction, leading to the generation of optical force (radiation pressure) acting on the materials.[1,2] Since the invention of optical manipulation methods,[3,4] the technique using optical force have been attracting attention as a new tool of manipulation for small particles and applied to various researches, such as living-cell manipulation,[5] particle sorting,[6] analysis of micro-mechanical oscillator,[7] investigation on interparticle interaction,[8,9] control of DNA conformation,[10] and the detection of single motor proteins.[11]

Since the mid-1990s, the target size of the optical manipulation has been decreasing to nanometer scale; polymer[12] and metallic[13,14] particles ranging from few tens to few hundreds of nanometers were trapped and manipulated. The optical trapping was also applied molecular systems such as polymer chains, nanometer-sized gels, and molecular aggregates as summarized in Table 1. These achievements demonstrate that the optical force can be applied to the trapping and manipulation of molecular systems larger than ca. 10 nm in size in solution at room temperature. In addition to the aforementioned applications of optical force to molecular systems, trapping and assembling polymers and molecular aggregates, enhancement of crystallization, microscopic shape-changes of gels, optical manipulation coupled with photo-reactions have also been reported. Integrating

these studies, the research on optical force coupled with behaviors of molecules and nanomaterials are now entering a new phase. In this article, we will review studies on optical force in conjunction with chemical systems, which include trapping of polymer chains to form particles, morphology control of molecular assemblies, control of photopolymerization, photomechanical motions synchronizing photochemical reactions, and micromanipulation by combining optical force and photothermal responses.

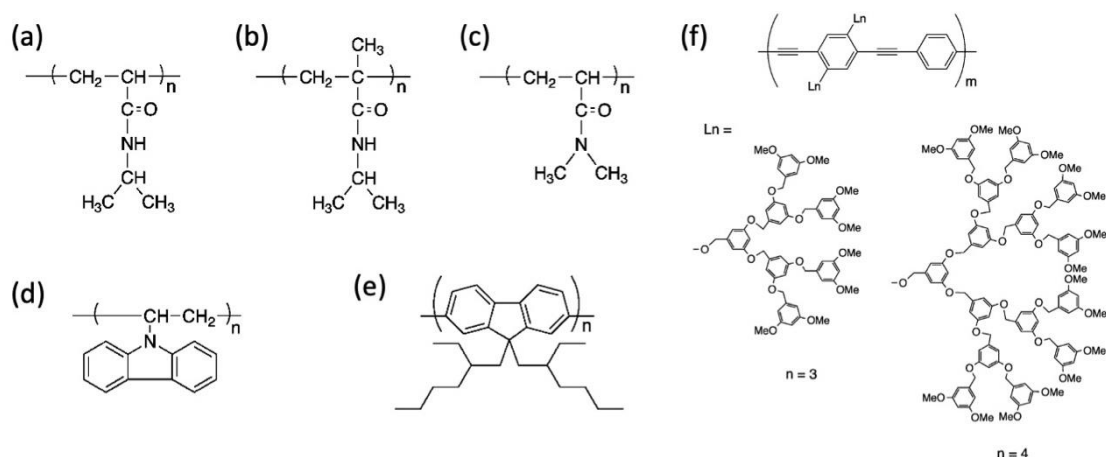
2. Optical force acting on molecular systems

2.1. Formation of a microparticle by trapping polymer chains and nanometric molecular aggregate in solution

Since the mid-1990s, studies on molecular systems as targets for optical tweezers have been reported (Table 1). One of the early studies is the collection of polymer chains using optical force. Scheme 1 shows several polymers successfully trapped in solution by optical force of 1064-nm laser at room temperature. For example, Ishikawa et al. have demonstrated a large number of poly (N-isopropylacrylamide) (PNIPAM) chains were optically trapped in water with a continuous wave (CW) 1064-nm laser to form single micrometer-sized particles at the focus of the trapping beam as shown in Fig. 1(a).[15] Water absorbs photons at 1064 nm owing to the overtones of the O-H stretching band, leading to the temperature elevation at and around the focal point of the 1064-nm laser. PNIPAM undergoes a volume phase transition in water from a coil structure to a globule one at 31 to 32 ° C; at a temperature > 32 ° C, the PNIPAMs with the globule structure aggregate with each other to form sub-micrometer sized particles. This aggregation is considered to help the trapping and formation of microparticle by optical force of the 1064-nm laser. To discuss the effect of optical force solely, the laser trapping experiment

of PNIPAM in deuterated water without absorption at 1064 nm was conducted by Hofkens et al., confirming the trapping of PNIPAM by optical force without the assist of the thermal phase transition.[16] Furthermore, poly(*N*-isopropylmethacrylamide) with a higher phase transition temperature of 46 ° C and poly(*N*, *N*-dimethylacrylamide) not showing phase transition were also successfully trapped by the focused CW 1064-nm laser.[17] In addition, trapping of polymer chains in organic solvents, such as poly(*N*-vinylcarbazole) and its derivatives, were demonstrated by using the optical force of CW 1064-nm laser.[18,19] A series of study on the assembling of polymer chains by optical force demonstrated that ca. 10-nm sized polymer chains can be trapped in solution at room temperature and they form aggregated structure beyond the electrostatic repulsive force of polymer electrolyte.[20] chromophoric side chains with high polarizabilities are preferentially trapped by optical force,[21] and so forth.

As is well known, molecules with small molecular weights are not trapped by optical force in solution at room temperature. While several studies have been demonstrated that optical force acting on molecular aggregates > ca. 10 nm is effective for the trapping and manipulation. Hotta et al. have optically trapped nanometer-sized swelled micelles in water, resulting in the coalescence to form a microparticle as shown in Fig. 1(b).[22] Patterning of orientation-controlled J-aggregate has been performed by Tanaka et al. using optical force.[23] Optical trapping of nanometer-sized clusters of egg-white lysozyme[24] and amino acids[25] have been demonstrated (Fig. 1(c)) by Tsuboi and co-workers. Sugiyama et al. have demonstrated rapid crystallization of glycine at the air/water interface using optical force.[26]



Scheme 1. Chemical structures of polymers successfully trapped in solutions by a focused near-infrared (1064 nm) laser beam: (a) poly(*N*-isopropylacrylamide), (b) poly(*N*-isopropylmethacrylamide), (c) poly(*N*, *N*-dimethylacrylamide), (d) poly(*N*-vinylcarbazole), (e) poly(fluorene), and (f) wire-type dendrimers.

Table 1. Target molecular systems of optical manipulation

Target system	Ref.	Research content
Polymer chain		
poly(<i>N</i> -isopropylacrylamide) and its derivatives	[15,16,19]	Assembling polymer chains to form microparticles with characteristic internal structures by optical force
poly(<i>N</i> -isopropylmethacrylamide)	[17]	
poly(<i>N</i> , <i>N</i> -dimethylacrylamide)	[17]	
poly(<i>N</i> -vinylcarbazole) and its derivatives	[17,18,21]	
amphiphilic random copolymer	[20]	
water-soluble carbazoly]- containing copolymer	[21]	
Molecular cluster/aggregate		
nanometer-sized micelles	[22]	Formation of micro-droplets by merging nanometer-sized micelles in water
<i>J</i> -aggregates	[23]	Patterning of J-aggregates on solid surface and the spectroscopic characterization of the single aggregates
Lysozyme	[24]	Aassembling molecular clusters by optical force
<i>L</i> -arginine, <i>DL</i> -proline, <i>DL</i> -serine, <i>L</i> -alanine, glycine	[25]	Nucleation for crystallization Aassembling molecular clusters by optical force
glycine	[26]	Rapid crystallization at air/water interfaces
Polymer assembly		
wire-type dendrimers	[27]	Optical force induced change in size and shape of polymer assembly formed through the evaporation process of solvents
poly(fluorene) and its derivatives	[28]	
Gel		
poly(<i>N</i> -isopropylacrylamide) hydrogel	[29]	Repetitive shrinking and expansion of rod-shaped microgels

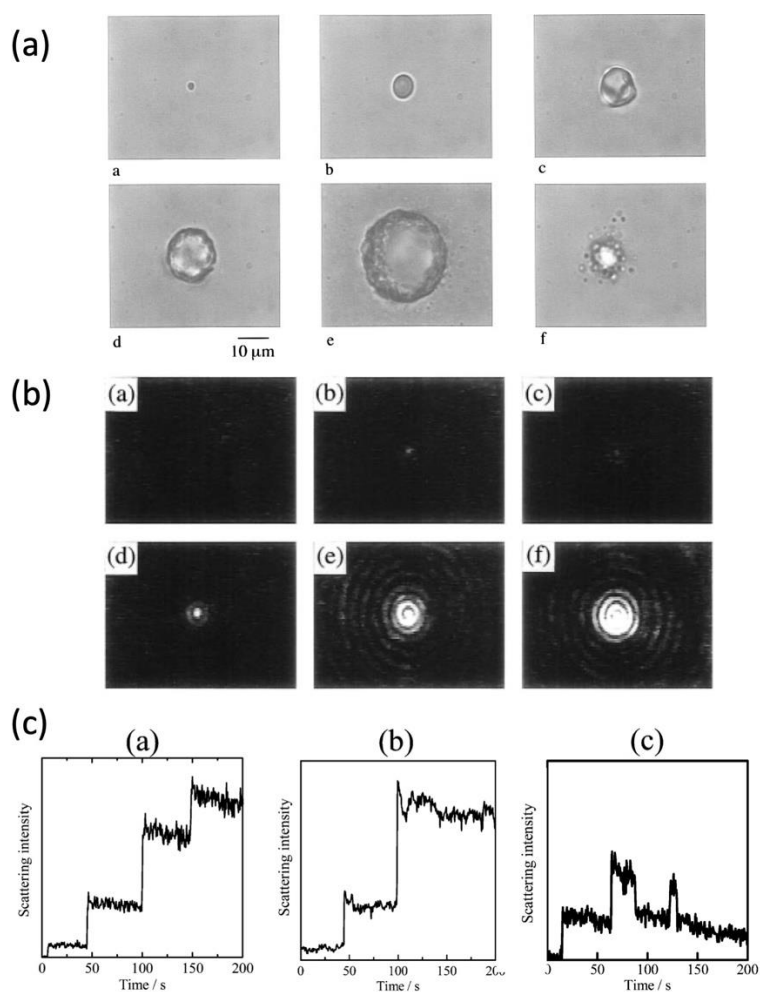


Fig. 1. (a) Trapping and assembling of chains of PNIPAM in D_2O at room temperature to form a microparticle by a focused CW 1064-nm laser. [16] (b) Optical dark-field (scattering) images of the time course of assembling and merging nanometer-sized swelled micelles of dodecyl sulfate in water by a focused CW 1064-nm laser. [22] (c) Time trajectory of backward scattering intensity of CW 488-nm laser used for monitoring optical trapping behavior and for Raman excitation during the trapping of the aggregates of *L*-arginine in water by a focused CW 1064-nm laser. [25] (a) was reprinted with permission from [16]. Copyright 1997 American Chemical Society. (b) was reprinted with permission from [22]. Copyright 1996 American Chemical Society. (c) was reprinted with permission from [25]. Copyright 2010 American Chemical Society.

2.2. Conformation control of macromolecule assemblies and gels

The optical force was also applied to modify the formation process of microstructures through the evaporation of solvent. It is well known as dissipative structure that solutes form regular/periodic aggregates under some dewetting condition. The optical force of a focused CW 1064-nm laser was applied to systems under solvent-evaporation towards control of the structure. For instance, Masuo et al. have utilized the optical force of a focused CW 1064-nm laser to change morphology of gel-like assembly of wire-type dendrimers formed by concentration increase due to solvent evaporation.[27] They also demonstrated the selective formation of the wire-like aggregation of a conjugated polymer with optical force. Wire-like aggregation of poly(fluorene) is precipitated in its tetrahydrofuran (THF) solution drop-casted on a glass substrate during a slow solvent-evaporation under almost saturated vapor. The concentration of the poly(fluorene) gradually increased and finally reached a saturated one. Focusing a CW 1064-nm laser into the solution at a saturated concentration selectively induces the formation of the wire-like aggregation at the focal point as shown in Fig. 2(a).[28] In general, the shape and size of the dissipative structure depend on multiple conditions such as the evaporation rate of the solvent, the solute concentration, the solubility, the strength of the interaction between the substrate and the solute, and the strength of the interaction between the substrate and the solvent. In addition, optical force has been shown to be effective as a new controllable parameter.

The optical force of a focused CW 1064-nm laser can induce the volume phase transition of amphiphilic gel leading to microscopic mechanical motion. It is well known that PNIPAM hydrogel shows volume phase-transition at 31 - 32 ° C. At a temperature lower than the transition temperature, PNIPAM hydrogel is in the hydrated (swollen) state.

At the transition temperature, the gel drastically shrinks and keeps the shrunk state at temperatures higher than the transition temperature. Juodkazis et al. have successfully induced a local drastic volume change (shrinking) of a rod-shaped PNIPAM hydrogel around the focal spot of a CW 1064-nm laser beam owing to the optical force as shown in Fig. 2(b).[29] The shape of the gel was maintained in the shrunk state during the laser irradiation and swelled back to the original shape after the cease of the laser irradiation. This optical force induced volume change of the gel took place reversibly in millisecond time scale, which is much more rapid than volume change by temperature control.

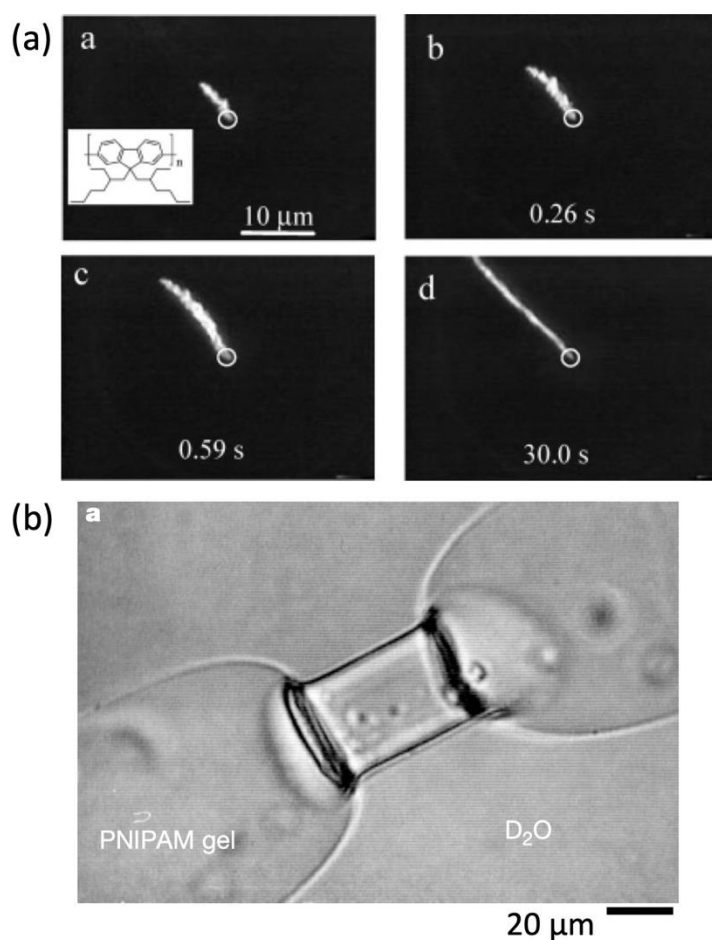


Fig. 2. (a) Time-course fluorescence images exhibiting the formation of fiber-like assembly of poly(2,7-(9,9-bis(2-ethylhexyl)fluorene)) (PEHF) in THF by focusing a CW 1064-nm laser beam with an objective (x100, NA 1.3). [28] (b) Volume phase transition (shrinking) of PNIPAM microgel induced by the optical force of a focused CW 1064-nm laser beam. [29] (a) was reprinted with permission from [28]. Copyright 2005 American Chemical Society. (b) was reprinted with permission from [29]. Copyright © 2000, Macmillan Magazines Ltd.

2.3. Fabrication of microstructures by using optical force and photochemical reactions

Optical manipulation in conjunction with photochemical reactions such as photopolymerization and photoisomerization permits the fabrication of microstructures. Using dual beam optical tweezers and photopolymerization, Misawa et al. have connected

polymer microparticles to form a linear structure as shown in Fig. 3(a).[30] First , two polymer microparticles were individually trapped with the two trapping beams and contacted each other in a solution containing acrylamide (monomer), crosslinker, and photo-initiator (Fig. 3(a), left top). Focusing ultraviolet (UV) laser light was focused to the contact point of the two particles to induce local photopolymerization, leading to the adhesion of the two particles. Then the bonded particle pair was trapped by one of the trapping beams under scanning for keeping the long axis of the particle pair parallel to the objective plane. Using the other trapping beam, another microparticle was trapped and contacted to the one end of the particle pair and the contact point was bonded by the photopolymerization. Repeating this process, the linear structure was fabricated as shown in Fig. 3(a).

Another photochemical reaction, photoisomerization, has been combined with optical manipulation by Dol et al. for the fabrication of microstructures through partial merging of spherically shaped multi-lamellar vesicles in water. A micrometer sized multi-lamellar vesicle of a dendrimer with azobenzene moieties in water was optically trapped by a 1064-nm laser. The trapped vesicle was attached to another vesicle adhered onto glass surface and, photoirradiation (at 420 nm) to the contact area between the two vesicles resulted in the bonding of the vesicles. [31] This bonding was attributed to the fusion of the outer bilayers of the two vesicles induced by the local disruption of the bilayers due to the conformational change of the azobenzene moieties through photoisomerization.

Although optical force is not effective for the trapping of small molecules at room temperature in solution, macromolecules can be trapped and, their local concentration can be increased by optical force as already shown above. Hence applying optical force to

polymer chains under polymerization, well-reacted polymer chains with enough molecular weight are selectively trapped and polymerization at the focal point of the trapping beam is enhanced. Based on this concept, efficient photopolymerization due to optical force has been demonstrated by focusing CW UV (355-nm) and near-infrared (NIR, 1064 nm) laser beams to the same point of photo-curable liquid resin.[32] Figure 3(c) shows microstructures of the resin solidified by irradiation with the UV laser (left) and with the UV and NIR lasers (right). These structures of columns and a gate were fabricated through point-by-point solidification by stage-scanning with fixed laser focuses. Comparing these polymer microstructures in the left and right of Fig. 3(c), the polymeric microstructures fabricated solely with the UV laser (Fig 3(c), left) are much larger due to excessive solidification around the focal point of the UV laser. On the other hand, the microstructures fabricated with the UV and NIR lasers, namely in the presence of the optical force, were much thinner, indicating higher precision of fabrication. The NIR laser trapped polymerized polymer chains, assisting the polymerization with a lower power of the UV laser. In addition, the trapping of polymer chains by the optical force led to efficient termination as well as efficient polymerization/crosslinking. As the result of these effects over-dose of UV laser was avoided and high-resolution fabrication was realized.

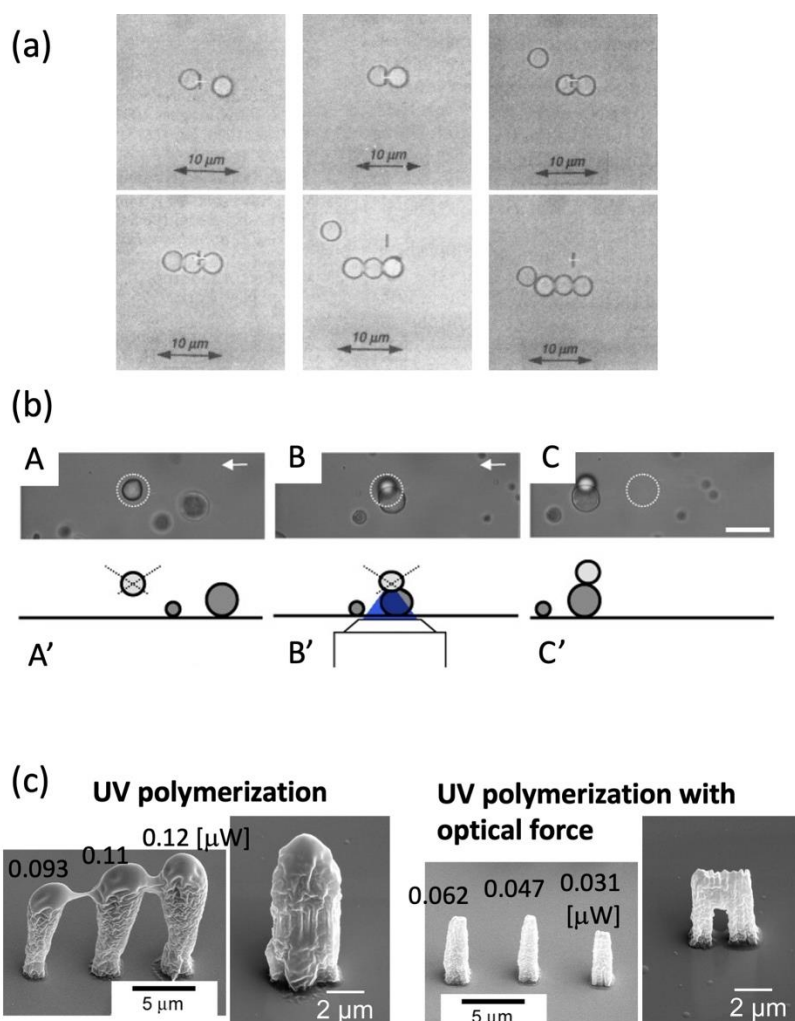


Fig. 3. Microfabrication enabled by combination of optical force and photochemical reactions. (a) Fabrication of a linear microstructure consisting of polymer microparticles.[30] These particles were linked using photopolymerization of the surrounding medium (solution containing acrylamide, crosslinker, and photoinitiator). (b) Bonding hard sphere multi-lamellar vesicles using laser tweezers and photoisomerization.[31] (A and A') A vesicle of a dendrimer with azobenzene moieties was optically trapped in water and contacted to another one fixed on glass surface. (B and B') The contacting point of the two vesicles was locally photoexcited, leading to disruption of the lamellar structure due to the conformational change (photoisomerization) of azobenzene units followed by the partial fusion of the vesicles. (C and C') The merged two vesicles were synchronically moved in accordance with the motion of the microscope stage. (c) Microstructures produced (left) only by UV irradiation and (right) by simultaneous irradiation by the UV and NIR lasers.[32] The column and gate shaped microstructures were produced via the same procedure with the same blueprint. Incident UV laser powers are shown in the figures. (a) was reprinted with permission from [30]. Copyright 1993 American Chemical Society. (b) was reprinted with permission from [31]. Copyright 2001 WILEY-VCH Verlag GmbH,

3. Diffusion behavior and concentration of molecules under optical trapping potential

3.1. Fluorescence correlation spectroscopy as a tool for measuring diffusion coefficient and molecular concentration in optical trap

The translational motion and concentration of polymer chains and molecular aggregates in solution are affected by optical force as shown in the previous sections. Therefore, in discussing the optical force effect in application to molecular systems, it is necessary to quantitatively evaluate the optical force acting on molecular systems and the molecular concentration within the trapping potential. For this purpose, fluorescence correlation spectroscopy (FCS) is an effective method.[33]

FCS measures the temporal fluctuation of fluorescence intensity emitted from the focal spot of a laser in a sample solution containing a very small amount of fluorescent molecule and calculate the autocorrelation function of the fluorescence fluctuation. Analyzing the autocorrelation function with a suitable model provides the information on the time scale of the fluorescence fluctuation. The measurement principle was proposed and demonstrated from 1972 to 1974,[34–36] and in 1993, a measurement system using a confocal laser scanning microscope, which is currently widely used for FCS measurement, was reported.[37] Several molecular processes cause the change in fluorescence intensity such as 1) increase/decrease in the number of fluorescent molecules in the detection volume of confocal microscope (confocal volume) due to Brown motion, 2) intersystem crossing from the S_1 excited singlet state to the T_1 excited

triplet state, and 3) fluorescence quenching due to excitation energy transfer and electron transfer. Hence the detailed analysis of the autocorrelation function provides several information on fluorescent molecule, such as the lateral diffusion coefficient, the lifetime of the triplet state, and the number of the molecules in the confocal volume. There have been numerous applications and derivative technologies in FCS, and a wide range of other information related with the fluorescence fluctuation can be obtained.[38–40]

By analyzing the autocorrelation function $G(\tau)$ of the time course of fluorescence intensity using a model suitable for the measurement target, the lateral diffusion coefficient and the concentration of fluorescent molecules in the confocal volume can be obtained. Equation (1) is the simplest analytical model of FCS that does not consider the contribution of the triplet-state formation via. the intersystem crossing.[39,40]

$$G(\tau) = 1 + \frac{1}{N} \left(1 + \frac{\tau}{\tau_D}\right)^{-1} \left(1 + \frac{\tau}{w^2 \tau_D}\right)^{-1/2} \quad (1)$$

Here, N is the average number of molecules in the confocal volume, and τ_D is the average time (average residence time) for the molecule to pass through the cofocal volume by Brownian motion. $w = w_z/w_{xy}$ is the shape parameter of the confocal volume; w_{xy} is the radius of the confocal volume approximated by the Gaussian function on the objective plane perpendicular to the optical axis, and w_z is the length of the confocal volume along the optical axis. The value of the confocal volume V is expressed by $V = \pi^{3/2} w_{xy}^2 w_z$.

3.2. Evaluation of optical force and molecular concentration in optical trap with FCS

At the early stage of study on optical trapping at the molecular level, Chiu et al. employed single-photon counting of fluorescence with a confocal microscope to measure the trapping behavior as shown in Fig. 4(a), where the photon burst of 14-nm sized polymer particle was detected.[41] The histogram of single-molecule photon burst in the confocal microscopy is in general follows Poisson statistics, while the photon burst of molecules/nanoparticles exhibiting biased diffusion due to optical force deviates from the Poisson model. The 14-nm polymer particles showed deviated distribution of photon burst at short timescales.

By using fluorescence correlation technique, Chirico, et al. have reported more quantitative analysis on biased Brownian motion of dye molecules under focused laser irradiation.[42] Fluorescence autocorrelation curve for Rhodamine 6G under photoexcitation with a focused CW 532-nm laser was obtained and analyzed with a model taking into account the optical trapping potential due to the excitation laser (Fig. 4(b)), providing the optical trapping potential depth for the dye. The polarizability of the dye determined from the analysis was too much (almost 4 orders of magnitude) larger than that estimated using the Clausius-Mossotti relation. Although the quite large polarizability, namely very strong optical force, can possibly be ascribed to some resonant effect because of the photoexcitation at the resonance absorption band of the dye, the discrepancy is still controversial.

As already explained, FCS provides information on the concentration of molecules in the confocal volume. However, the applicability of a simple analytical model, such as eq. (1), in the presence of optical trap should be taken into consideration, because the lateral diffusion of molecules is affected by optical force and simple analytical models

are sometimes not applicable when the effect of the optical force is not negligible. For rational interpretation of FCS measurement in the presence of optical force, several approaches using computational simulations were reported.[43–45]

Figure 4(c) shows simulation results of the fluorescence autocorrelation functions for molecules in the presence of optical force. In the simulation, a laser beam for fluorescence excitation (spot diameter 500 nm) and a laser beam for trapping (spot diameter 1000 nm) coaxially focused to the same point. The three dimensional (3D) lateral diffusion and fluorescence emission of molecules in solution under the laser irradiation was simulated using Brownian dynamics method.[46,47] The simulation results for various optical trapping potential depths ($U_0 = 0$ to $4kT_R$ ($T_R = 293$ K)) and corresponding analytical results by Eq. (1) (solid black line) are shown together. In optical trapping under non-resonant conditions using a CW laser, the potential depth increases linearly with the incident light power and is expressed as $U_0(P) = \sigma P$. Here, σ is a parameter indicating the magnitude of induced polarization by the laser beam for trapping and P is incident light power (W). From Fig. 4(c), in the range of $U_0 < kT_R$, the conventional analytical model can be approximately applied even in the presence of optical force. In the case of $U_0 > kT_R$, however, Eq. (1) no longer reproduces the experimental results.

Figure 4(d) shows the dependence of N and τ_D on the trapping potential depth β standardized by kT_R ($\beta = U_0/kT_R$). Fig. 4(e) shows a plot of the increasing rate of N with respect to the unit trapping laser power, $\Delta N/\Delta P$, as a function of σ . From the relation plotted in Fig. 4(e) and a value of $\Delta N/\Delta P$ experimentally obtained thorough FCS measurement, it is possible to estimate the σ for nanoparticles and molecular systems with unknown polarizability, and therefore the potential depth.

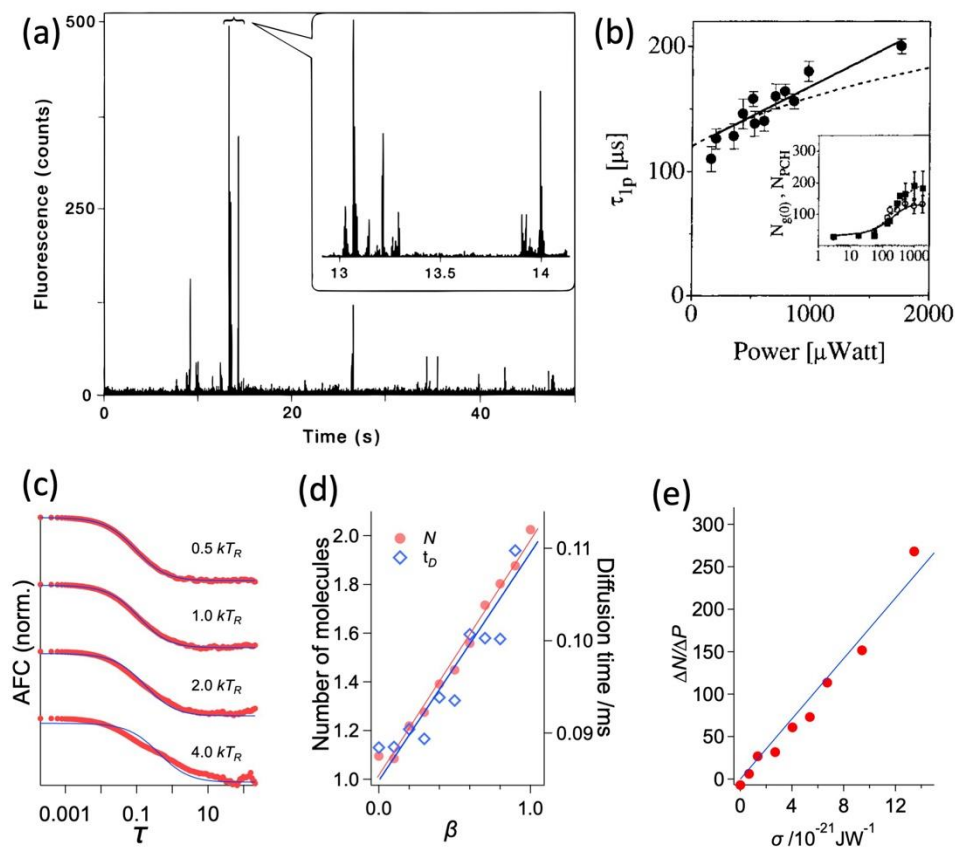


Fig. 4. (a) Time course of photon bursts of 14-nm sized polymer particle in water detected by a confocal microscope with a single-photon counting system.[41] (b) Diffusion time (mean residence time) of Rhodamine 6G in water, τ_{1p} , as a function of CW excitation power at 532 nm.[42] Inset: Average number of molecules in the confocal volume obtained from the $g(0)$ value of FCS analysis, $N_{g(0)}$ ($\circ$), and from the photon-counting histogram (PCH) analysis, N_{PCH} ($\blacksquare$). (c) Fluorescence autocorrelation curves (solid circles) in the presence of optical gradient field and their fitting results (solid lines).[47] (d) Plots of N and τ_D in the confocal volume as a function of optical trapping potential depth.[47] (e) Plot of $\Delta N / \Delta P$ as a function of σ obtained from the result shown in (c) [47] (a) was reprinted with permission from [41]. Copyright 1996 American Chemical Society. (b) was reprinted with permission from [42]. Copyright 2002 American Chemical Society. (c), (d) and (e) were reprinted with permission from [47]. Copyright 2010 American Physical Society.

4. Optical manipulation by switching optical force through photochemical reactions

As already shown above, the optical force is effective for the control of a photochemical

reaction (local photopolymerization). Conversely, photochemical reaction can be utilized for control of optical force. The optical force can be classified into three terms: scattering, absorption, and gradient forces. The scattering and absorption forces are due to the scattering and absorption of photons, respectively. Both forces push a photo-irradiated object towards the incident direction of photons. While the gradient force acts on a photo-irradiated object towards the spatial intensity gradient of light. Under a condition where the refractive index of a target particle is larger than that of the surrounding medium, the gradient force acts on the particle to a direction along which the light intensity increases.

To achieve optical manipulation, ordinary approach is the selection of photo-irradiation conditions for target objects such as incident power, wavelength, and intensity distribution of trapping laser. On the other hand, changing photo-response of target particles can also be effective for the manipulation of small objects. For instance, Smith et al. have examined optical trapping of two kinds of polymer chains with sizes of 10 to 20 nm in solution.[21] These polymers have pendant carbazolyl (Cz) groups attached to the polymer backbone, as shown in Fig. 5(a) and 5(b). They found that the polymer chains of (a) can be more efficiently trapped compared with (b) because of its larger polarizability at 1064 nm for the optical trapping. On one hand, Shoji et al. have performed optical trapping of myoglobin and apomyoglobin in aqueous solution.[48] At a trapping wavelength of 1064 nm, the myoglobin has optical absorption due to a heme cofactor, while the apomyoglobin is colorless because the heme has been removed. Fig. 5(c) shows successful optical trapping of the myoglobin at a laser power of 0.6 W. In contrast, the apomyoglobin was never be trapped under irradiation at the same laser power, as shown in Fig. 5(d). They concluded that the heme cofactor in the myoglobin enhances optical forces at 1064 nm, resulting in the efficient optical trapping. Thus, the photo-

responses of target particles greatly affect manipulation behavior in the optical trapping even at an equivalent particle volume.

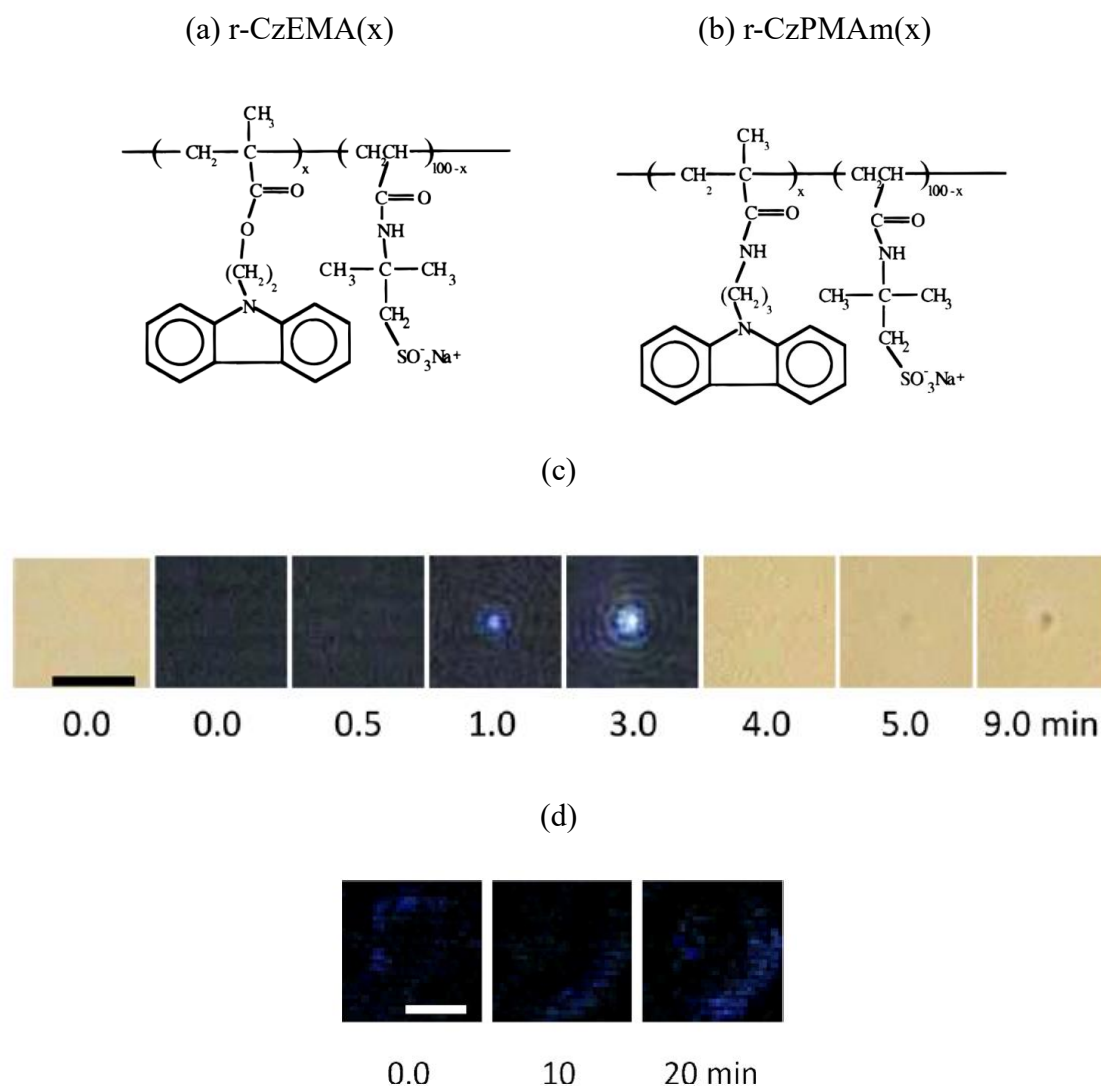


Fig. 5. Chemical structures and abbreviations of the random, water-soluble copolymers of (a) sodium 2-acrylamido-2-methylpropane-sulfonate (AMPS) and 2-(9-carbazoyl)-ethyl methacrylate (CzEMA), and (b) AMPS and [3-(9-carbazoyl)propyl]methacrylamide (CzPMAm). The carbazoyl content is given as x in mol %. (c) Optical observation during YAG laser irradiation of myoglobin (Mb) buffer solutions (pD 7.6): 0.2 mmol/L. 0.0 min corresponds to the time at which the YAG laser was switched on. Optical micrographs in (c) 0.0–3.0 min were obtained from backscattered Ar⁺ laser light. The other micrographs in (c) 0.0 and 4.0–9.0 min were obtained under bright-field illumination. (d) Optical micrographs of 0.3 mmol/L apomyoglobin (apoMb) buffer solution (pD 7.6) during YAG laser irradiation

under dark-field with backscattered light of an Ar⁺ laser; 0.0 min corresponds to the time at which the YAG laser was switched on. The scale bar shows 5 μm . (a) and (b) were reprinted with permission from [21]. Copyright 1999 American Chemical Society. (c) and (d) were reprinted with permission from [48]. Copyright 2013 American Chemical Society.

As shown above, there have been several studies which demonstrated selective trapping of organic nanomaterials on the basis of the difference in the photo-responses of target objects. These achievements imply that changing photo-responses of target materials using chemical reactions can modify optical forces acting on the materials. Indeed, in recent years, photomechanical micromotions of small particles were demonstrated by modifying optical forces using photoinduced change in spectroscopic properties of molecules contained in the particles. In the following, such new series of optical manipulation will be shown, in which P-type[49] and T-type[50] photochromic reactions are utilized to modulate photon forces by light irradiation.

4.1. Switching of optical force using P-type photochromic reaction

The momentum of a photon is resonantly transferred to an object through photo-absorption by the object, resulting in the generation of absorption force pushing the object towards the light propagation. Therefore, changing the color (absorption spectrum) of target objects using photochromic reaction (color change of molecules by photoinduced isomerization) can be effective for regulating optical force acting on the objects through the appearance and disappearance of absorption force.

Figure 6(a) shows the structures of the open-ring and closed-ring isomers of a diarylethene (DAE) derivative used for the photochromic optical manipulation.[51] DAE is a well-known P-type photochromic molecule; the colorless open-ring isomer (open form) absorbs UV light to isomerize to the closed-ring isomer (closed form), while the

closed form undergoes back isomerization to the open form under visible (VIS) light irradiation. This reciprocal color change due to the photoinduced isomerization can be induced many times. Figure 6(b) shows absorption and fluorescence spectra of the DAE in 1,4-dioxane. Note that the closed form of the DAE shows bright fluorescence and it was used for monitoring the position of particle containing the DAE under optical trap.

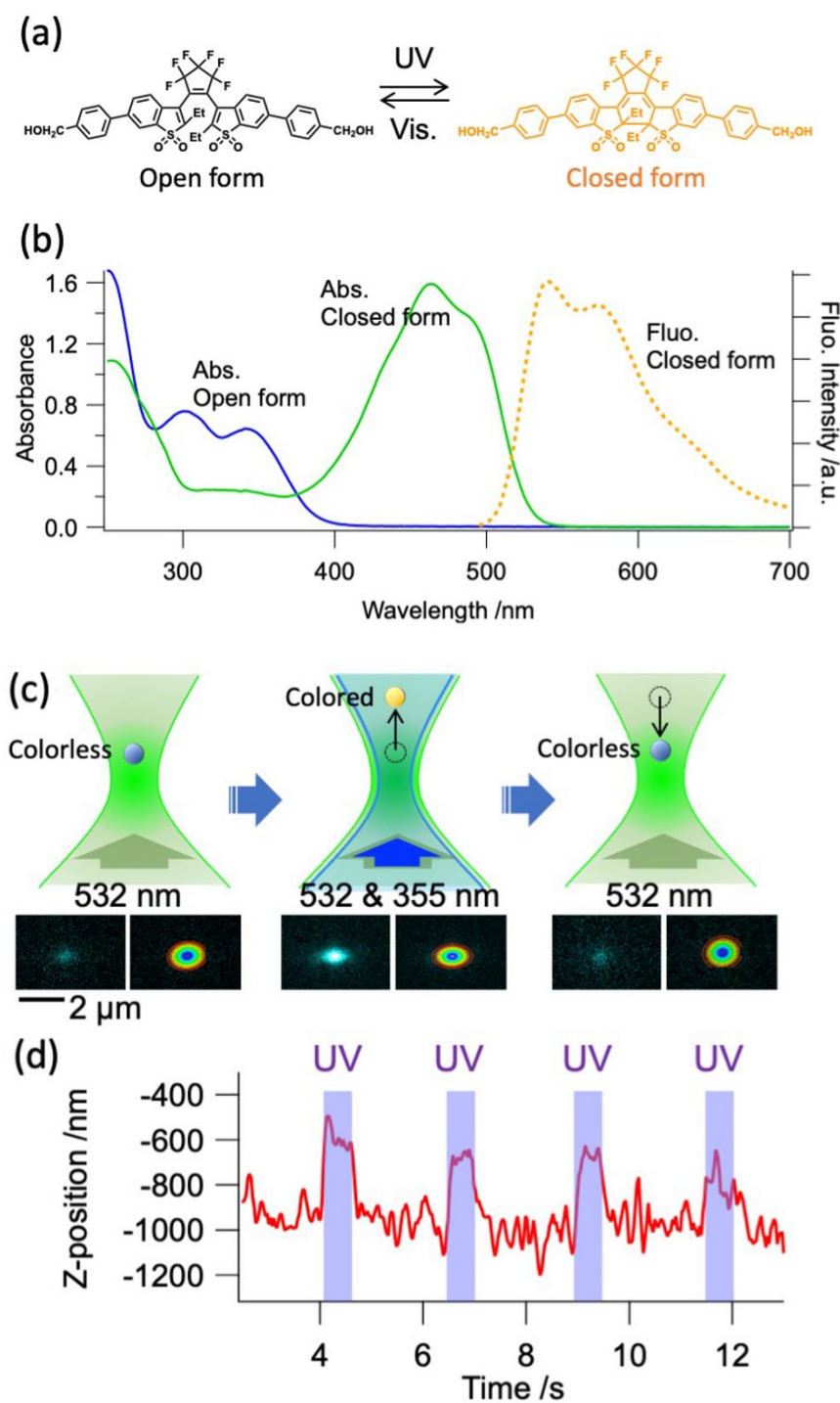


Fig. 6. (a) Chemical structures of the open and closed-rig isomers of the DAE used for the photochromic optical manipulation. (b) Steady-state absorption and fluorescence spectra of the DAE in 1,4-dioxane. (c) Illustration of micro-mechanical motion of an optically trapped PMMA particle containing DAEs regulated by the photochromic reaction of the DAE. Actual fluorescence images of a trapped PMMA particle with the DAEs (left) before, (middle) during, and (right) after UV irradiation are shown in the bottom; the particle was trapped with 532-nm

laser at 6 mW and the photoisomerization was induced with 355-nm (29 W cm^{-2}) laser. (d) Time course of the Z-position of a trapped PMMA particle with DAEs by 532-nm laser at 6 mW. The trapped particle was periodically photo-irradiated with the 355-nm laser with an irradiation time of 0.5 s.

Figure 6(c) shows a micromechanical motion of one of the PMMA particles triggered by the photochromic reaction of the DAE. At the initial stage, the PMMA particle was optically trapped with a CW 532-nm laser, where almost DAEs in the particle were in the open form and the fluorescence intensity of the particle is very weak (Fig. 6(c), left). The particle was trapped at a point on the optical axis of the 532-nm laser where the scattering force balanced with the gradient force. UV excitation of the open forms in the particle induced the isomerization (coloration) of the DAEs and the number of the closed forms increased. The particle thus efficiently absorbed the 532-nm light, leading to the increase in mainly the absorption force pushing the particle towards light propagation. As a result, the particle moved along the optical (Z) axis of the 532-nm laser to a point where the gradient force balances with the sum of the scattering and absorption forces (Fig. 6(c), middle). It should be noted that once the closed form was produced, the absorption of the 532-nm laser by the closed form induces the back isomerization (ring-opening reaction). Because of the low quantum yield of the back isomerization, relatively large number of the closed forms was kept during the UV irradiation. After turning the UV laser off, the ring-opening (de-coloration) reaction solely took place and the number of the closed-ring isomers decreased. Then the particle returned to the initial position as the absorption force decreased with decreasing number of closed forms (Fig. 6(c), right).

The positional shift along the optical (Z-) axis of the trapping laser was detected by astigmatism imaging method.[52,53] Fig. 6(d) shows a time course of the Z-position of a trapped PMMA particle containing DAEs under periodic UV exposure; nanoscopic

reciprocal motion of the trapped particle synchronized with the photochromic reaction of the DAEs was successfully induced. The amplitude of the positional shift along the Z-axis was in a range from 50 - 1000 nm depending on experimental condition.

4.2. Switching of optical force using T-type photochromic reaction

Microscopic mechanical motion synchronizing a T-type photochromic reaction of a pyranoquinazoline (PQ) derivative has been also reported.[50] Fig. 7(a) shows chemical structures of closed form (CF) and transoid-cis (TC) isomers of the PQ derivative used in the report. The corresponding absorption spectra are shown in Fig. 7(b). The CF isomer has absorption band only in the UV region, hence the isomer is colorless. On the other hand, the TC isomer has remarkable absorption bands over visible wavelength range from 450 - 700 nm. UV irradiation to the CF isomer induces isomerization to TC isomer along with color change. The CF isomer is the most stable form and the back reaction from the TC isomer to the CF one (decoloration process) can take place thermally at a room temperature ca. 296 K.

Figure 7(c) shows optical transmission images of a polyacrylic ester (PAE) microparticle containing PQs before, during, and after CW UV (355 nm) laser irradiation. The UV exposure induced ring-opening reaction of CF isomers to TS forms in the particle and the transmittance of the illumination light of the microscope decreased due to this coloration. After cutting the UV laser off, the transmittance recovered to the initial value owing to the thermal back reaction from TC to CF. This transmittance change triggered by the UV irradiation indicates that the coloration and decoloration reaction of the PQ could be induced in the PAE microparticles.

Figure 7(d) shows a time trajectory of the Z-position of an optically trapped PAE

microparticle with PQs before, during, and after 355-nm UV laser irradiation. The UV laser irradiation started at 4 sec and finished at 6 sec. During the UV irradiation the Z-position of the microparticle gradually shifted from 0 to ca. 350 nm synchronizing with the coloration of the PQs. After cutting the UV light off, the Z-position gradually decreased back to the initial value owing to the thermal back reaction from TC to CF. The time scale of the backward motion is 1-2 s, which is comparable to the time constant of the thermal back reaction of PQ in PAE microparticles. The speed of the positional shift along the Z-axis depended on the intensity of the UV laser. The photochromic optical manipulation also demonstrated lateral motion of a microparticle on the XY plane perpendicular to the optical (Z) axis, by irradiating a part of an optically trapped microparticle containing PQ with the focused UV laser at 355 nm. Thus, the three-dimensional microscopic mechanical motion of optically trapped single polymer particle was demonstrated using the T-type photochromic reactions.

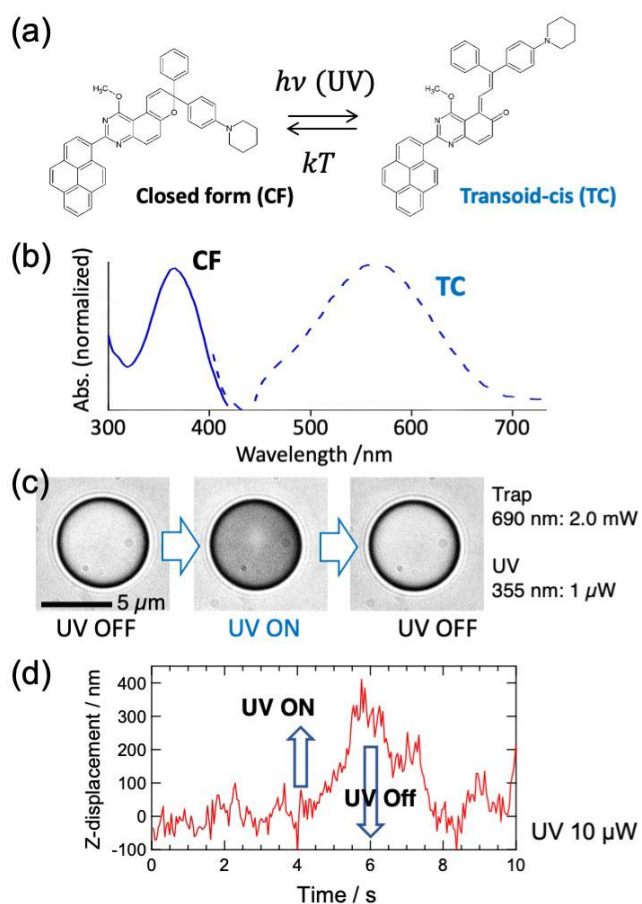


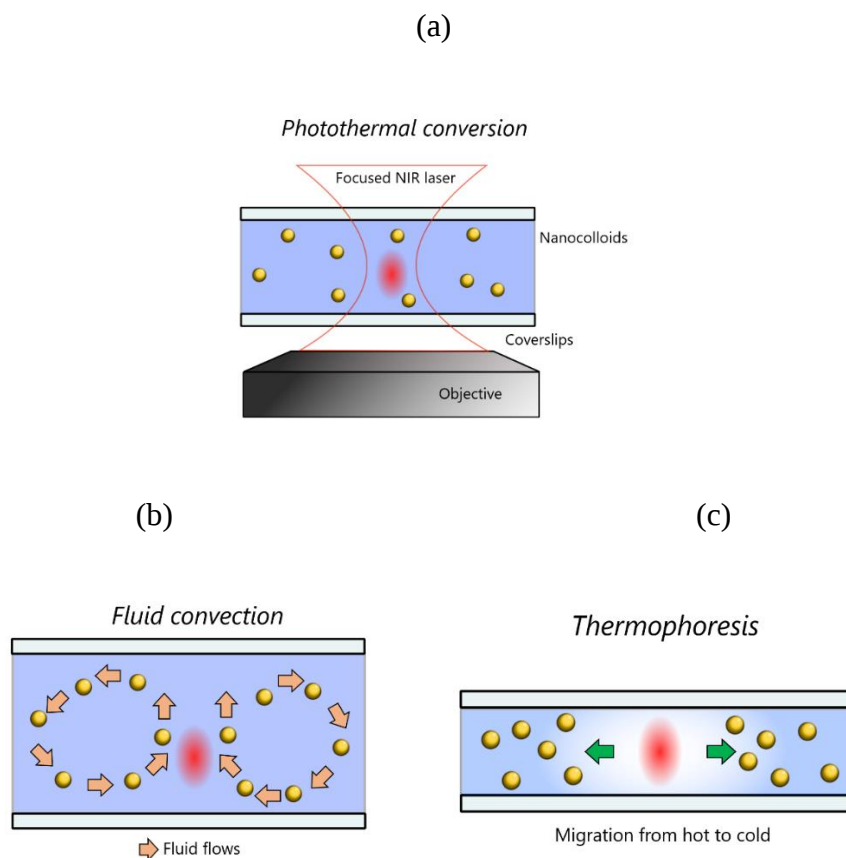
Fig. 7. (a) Structures of the closed form (CF) and transoid-cis (TC) isomers of PQ used for photochromic optical manipulation. (b) Absorption spectra of the PQ in toluene before and after UV irradiation. (c) Sequential optical transmission images of an optically trapped PAE microparticle in water with CW 690-nm laser (left) before, (middle) during, and (right) after UV irradiation with a 355-nm CW laser. (d) Time course of the Z-position of an optically trapped PAE microparticle by a CW 690-nm laser; the positional shift along the optical axis was induced by the irradiation of UV (355 nm) laser.

5. Photothermal effects in optical manipulation

Optical manipulation requires intense laser lights because momentum of individual photons is essentially small. In condensed phase, heat generation due to the intense laser irradiation give rise to additional thermal forces on targets of the optical manipulation; fluid convection and thermophoresis are major ones that exerts the forces. Thus, optical manipulation in condensed phase should be treated as a multiphysics problem consisting of electromagnetism, heat transfer, and fluid dynamics. At the early stage of the development of optical manipulation techniques, the heat generation under laser irradiation was considered as an undesired side effect that disturbs the optical manipulation because physical aspects of the fluid convection and the thermophoresis in the small volume were unclear. However, the thermal forces in optical manipulation have gained much attention and their positive aspects are now largely accepted, because researchers have realized that the thermal effects can greatly assist the optical manipulation by suitably designing the microsystems.

In this section, the main topic can be divided into the following three: i) laser-induced local temperature increase (i.e., photothermal conversion), ii) fluid convection, and iii) thermophoresis. Please note that the thermophoresis differs from the fluid convection; it is the temperature-induced migration of tiny objects without macroscopic fluid flows. In general solution systems, laser irradiation leads to an increase in local temperature due to photothermal conversion (Scheme 2a). The size of sample chambers determines which of the fluid convection or the thermophoresis is dominant. The fluid convection is observed in larger chambers (Scheme 2b), while the thermophoresis occurs in thinner film-like samples chambers (Scheme 2c). In sample chambers with intermediate sizes, both of the convection and thermophoresis could occur simultaneously.

The photothermal conversion, the fluid convection, and the thermophoresis will be individually summarized in the following sub-sections.



Scheme 2. (a) Photothermal heating of aqueous solution by the focused NIR laser. (b) Fluid convection induced by the laser heating. (c) Thermophoresis induced by the laser heating.

5.1. Photothermal conversion: bulk solution and nanoparticles

Here we consider a typical case of optical manipulation where small particles dispersed in an aqueous solution are irradiated with a focused laser beam as shown in Scheme 2a. In such a case, both the liquid medium itself and the nanoparticles can act as heat sources, depending on laser wavelength and material of the particles. First, we describe the case

of laser heating of the solution without particles. Second, we will introduce the laser-heating of nanoparticles.

5.1.1. Laser heating of aqueous solution

In most cases of optical manipulation in solution phase, water is used as solvent. The heating due to the photo-absorption by water is essentially small, but it is not negligible when NIR lasers are employed as trapping light sources. Water absorbs photons in the NIR wavelength region owing to the overtone vibrational transitions of the O-H bond of water molecule and the absorbed photon energy is converted into heat. Since Ashkin invented the optical tweezers in 1986 [4], a NIR laser at a wavelength of 1064 nm has been widely used for optical manipulation because of its availability and the high transmittance of water at this wavelength [54]. In 1980s, heat generation in optical tweezers with the 1064 nm laser has not been discussed in literatures. Thereafter, Ishikawa et al. reported a first experimental result on thermally-assisted optical trapping of molecular objects in 1993 [15]; they succeeded in trapping of thermo-responsive polymers by optical force together with the laser heating of water. On the other hand, Liu et al. reported the first quantitative estimations of the local temperature under optical trapping condition with the focused 1064 nm laser based on phase transition of lipid bilayers in 1995 [55]; they observed a temperature increase rate of 11.5 deg K/W. Thus, we could find a few pioneering works on the heat generation under optical trapping condition in 1990s.

In 2000s, several methods for measuring the local temperature under optical trapping conditions are developed. For instance, Fischer et al. have reported the temperature increase, ΔT , versus the incident laser power of at 1064 nm, ΔP , as $\Delta T/\Delta P \approx$

5 deg K/W by observing thermal phase transitions of a Langmuir monolayer [56]. Conia et al. have estimated a transient temperature elevation of ~ 40 deg K/W induced by laser irradiation at a wavelength of 980 nm for 250 ms using the interferometric technique [57]. Schmidt et al. have reported an ~ 8 deg K/W temperature increase by analyzing thermal motions of an optically-trapped microbead [58]. On one hand, we have developed a method for the temperature estimation based on fluorescence correlation spectroscopy.

5.1.2. FCS thermometry for the evaluation of laser heating

As mentioned above, the values of $\Delta T/\Delta P$ are different within an order of magnitude depending on the sample and measurement method. The difference is probably due to different monitoring targets for temperature estimation, Langmuir membrane, the lipid membrane, and optically trapped small particles. To directly observe the temperature elevation due to the absorption of NIR laser light by solvent itself, a new method has been proposed in which small amount of fluorescent molecule is used as a probe and the diffusion behavior of the probe molecules depending on the temperature is precisely measured by FCS.[59]

The value of τ_D experimentally obtained by FCS is related to translational diffusion coefficient D by the following equation: $\tau_D = w_{xy}^2/4D$. Here, w_{xy} is the radius of the focal spot of the excitation laser of confocal microscope. The translational diffusion coefficient D is related to the viscosity $\eta(T)$ of the solvent by the Stokes-Einstein equation: $D = kT/6\pi a\eta(T)$. Here, a is the hydrodynamic radius of the probe molecule. By eliminating D from these two equations and summarizing them, the following expression can be obtained.[39]

$$\frac{\rho}{\tau_D} = \frac{T}{\eta(T)} \quad \left(\rho = \frac{6\pi a w_{xy}^2}{4k} \right) \quad (2)$$

The right-hand side of equation (2) is the temperature/viscosity, which is a function of the absolute temperature T . The denominator on the left-hand side is the average residence time, which is a value experimentally obtained by FCS. Considering ρ as a temperature-independent constant, the value of $T/\eta(T)$ can be obtained from the measurement of the average residence time τ_D by FCS. Since the relationship between $T/\eta(T)$ and T can be obtained from the measurement of the viscosity of solvent with a viscometer, the temperature T within the focal volume can be determined from the measurement of τ_D . Figure 8(a)-(d) show the temperature at the focal point of CW near-infrared laser light with a wavelength of 1064 nm for water, heavy water, ethanol, and ethylene glycol. The slope of the plot, that is the temperature rise per unit incident light power $\Delta T/\Delta P$, depends on the solvent, and the values of $\Delta T/\Delta P$ for water, ethanol, and ethylene glycol are 22-24, 42-56, and 56-63 K/W, respectively.

The light power P in the solvent after traveling by a distance x is expressed as $P = P_0 e^{-\varphi x}$ from Lambert's law. Here, P_0 and φ are the incident light power and the absorption coefficient of the solvent, respectively. While the amount of heat Q_{abs} generated at the focal point can be proportional to the product of φ of the solvent and the incident light power P ; $Q_{abs} \propto \varphi P$. Assuming that the focal volume is a spherical (radius, r_1) heat source which generates a constant amount of heat Q_{abs} per unit time and the surrounding medium is a uniform heat conductor, the temperature T at a distance r from the center of the heat source can be described by one-dimensional heat conduction equation. Solving it under the boundary conditions of $T = T_1$ at $r = r_1$ and $T = T_r$

(room temperature) at $r = \infty$ gives the following relationship.

$$\frac{\Delta T}{\Delta P} \propto \frac{\phi}{\gamma} \frac{1}{r_1} \quad (3)$$

Here, γ is the thermal conductivity of solvent.

From equation (3), $\Delta T/\Delta P$ is expected to be proportional to ϕ/γ , the ratio of the light absorption coefficient and thermal conductivity of the solvent. As shown in Fig. 8(e), $\Delta T/\Delta P$ plotted against ϕ/γ for the three solvents, water, ethanol, and ethylene glycol, is approximately a straight line, demonstrating the validity of this simple model. Furthermore, measurements for other alcohols have also confirmed that $\Delta T/\Delta P$ is proportional to ϕ/γ [60]. From the relationship in eq. (3), it is possible to predict how much the temperature will rise under an optical trapping condition when the light absorption coefficient and thermal conductivity of a solvent used are known. Therefore, it is useful for interpreting various experimental results and designing new experimental systems.

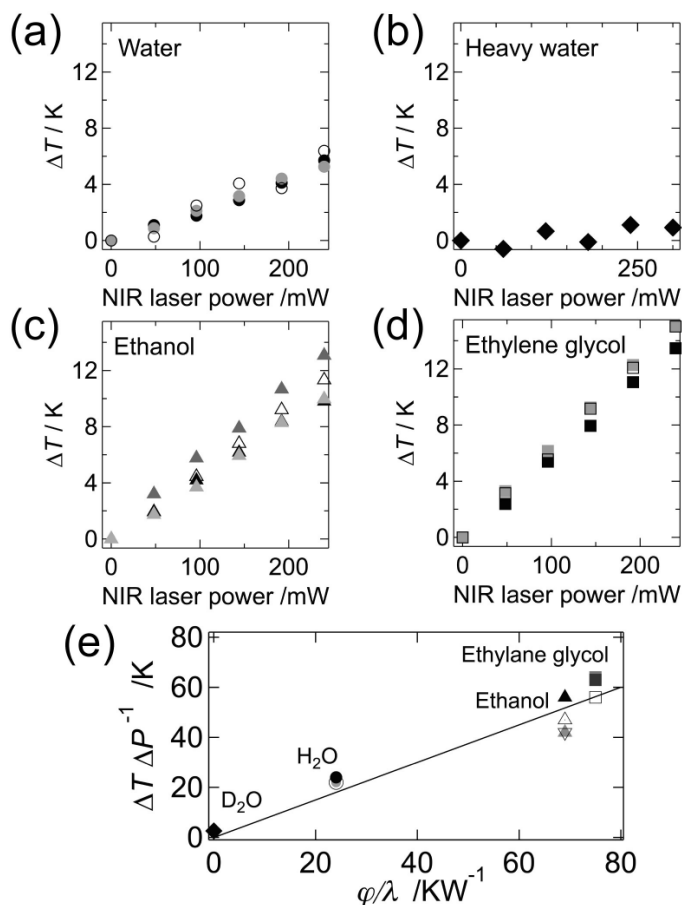


Fig. 8. (a-d) Temperature at the focal point of the NIR laser estimated by using FCS as a function of the incident laser power. Solvents used are (a) water, (b) heavy water, (c) ethanol, and (d) ethylene glycol. (e) Plot of $\Delta T / \Delta P$ as a function of the ratio of extinction coefficient of solvents ϕ to the thermal conductivity λ . Reprinted with permission from [59]. Copyright 2007 American Chemical Society.

5.1.2. Laser heating of nanoparticles

When the target of optical manipulation is a nanoparticle with a large absorption cross-section, such as noble metal nanoparticles (plasmonic nanoparticles), heat generation due to photothermal conversion is more pronounced. The plasmonic nanoparticles have been used as *plasmonic optical tweezers* in recent years. [61,62] In the plasmonic tweezers, localized surface plasmon resonance (LSPR) band is excited to generate enhanced optical

near-fields for induction of the gradient force. Subsequently, the photoexcitation of LSPR band results in a significant temperature increase in the metal nanoparticle due to the photothermal conversion. For detailed mechanisms on the photothermal conversion of the plasmonic nanoparticles, readers can refer several review articles.[63–66]

In this section, we will focus on thermometric methods for the temperature of single nanoparticles under laser illumination. Probing the temperature of nanoparticle is inherently difficult. Although some conventional optical methods can give information on the temperature around a single nanoparticle, [59,67,68] direct measurement of the nanoparticle temperature is hardly achieved due to the diffraction limit. To overcome such limitation, we have developed a method for direct temperature measurement of the single nanoparticle on the basis of plasmonic spectroscopy. [69,70] In general, the plasmonic spectrum of single nanoparticle is determined by the following parameters at a constant temperature: the dielectric function of metal, the size and the shape of the nanoparticle, and the refractive index of the surrounding medium. [71] Therefore, one can expect spectral changes of the nanoparticle by taking temperature dependence of these parameters into account. We calculated the temperature-dependent dielectric function of gold, and the decrease in refractive index of the surrounding medium due to the temperature increase; the size and the shape of the nanoparticle were assumed to be independent of temperature. With these parameters, we calculated the temperature dependent plasmonic spectra of single gold nanoparticle as shown in Fig. 9(a). To measure the nanoparticle temperature with the numerical results, we performed single-nanoparticle experiments on the CW laser heating under optical microscope (Fig. 9(b)). By comparing the numerical and the experimental scattering spectra, we successfully evaluated the static nanoparticle temperature in the temperature range from 300 to 600 K

with an accuracy of ± 20 K. [69] In addition, this spectroscopic thermometry was in agreement with numerical temperature simulations based on the finite element method. [70] On the other hand, for the temperature measurement of colloidal nanoparticles, small angle X-ray scattering (SAXS) is one of the most powerful tools. Siems et al. have reported that the SAXS could precisely probe lattice expansion of colloidal gold nanoparticles induced by pulsed-laser heating. [72] Their experimental results on the transient temperature changes of the gold nanoparticles were well reproduced by the numerical solutions of the general heat diffusion equations. Therefore, for both the pulsed-laser and the CW laser heating, the numerical temperature simulations of the metal nanoparticles are valid and can provide reliable expectations of the temperature of nanoparticles under photoexcitation.

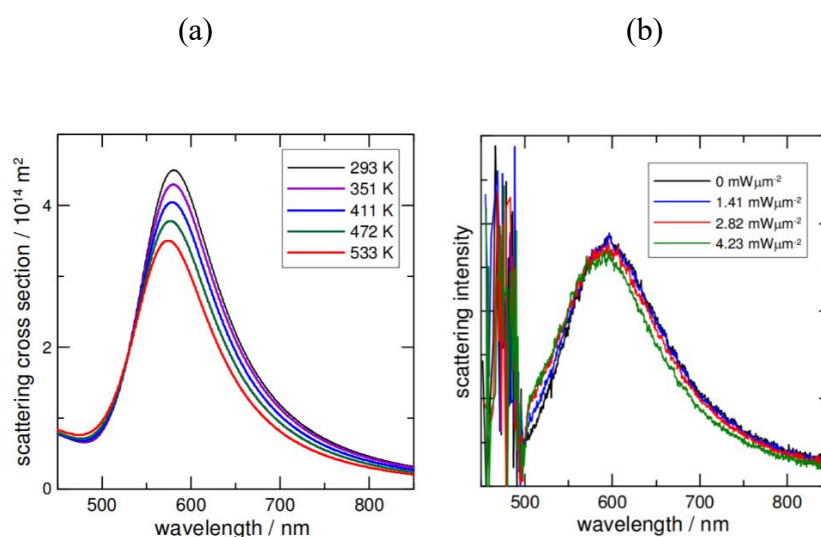


Fig. 9. (a) Calculated scattering spectra of a single gold nanoparticle at various temperatures. (b) Scattering spectral changes of a single gold nanoparticles induced by the laser heating at 488 nm. For both (a) and (b), the single nanoparticle with a diameter of 100 nm was placed on a glass substrate and immersed in water. Reprinted with permission from [69]. Copyright 2012 American Chemical Society.

5.2. Fluid convection

In the present section, we describe fluid convection in solution induced by the laser heating in optical manipulation. In general, the fluid convection can be divided into two types: i) natural convection driven by a buoyancy force, ii) Marangoni convection driven by a surface tension. Both two convections can be induced by the laser heating and can be coupled with the optical manipulation.

5.2.1. Natural Convection.

Here, we introduce a typical case of the natural convection in water in the conventional optical tweezers. Now we consider the laser heating of water by the optical tweezers with a focused 1064 nm laser as shown in Fig. 10(a) [60]. The laser is tightly focused through an oil-immersion microscope objective ($NA = 1.3$), and the spot diameter was assumed to be $0.48 \mu\text{m}$ in FWHM in the focal plane (x - y plane). The sample chamber consists of two glass cover slips. The thickness of water layer is $300 \mu\text{m}$. The focal spot of the laser is $30 \mu\text{m}$ away from the glass surface. We numerically calculated the temperature distribution and the subsequent natural convection in this system in the steady-state. As already introduced in the previous section, the temperature field can be calculated with the heat conduction equations (Fig. 10b). To calculate the fluid flows, Navier-Stokes equations should be solved together with the heat conduction equations. Detailed description of the heat and mass transfer equations can be found in elsewhere [73]. Here, we introduce the buoyancy force as a representative equation of the natural convection, as follows [60]:

$$F = \begin{pmatrix} F_{x,y} \\ F_z \end{pmatrix} = \begin{Bmatrix} 0 \\ \alpha g \rho (T - T_\infty) \end{Bmatrix} \quad (4)$$

where α [K^{-1}] is the thermal expansion coefficient of water, g [m s^{-2}] is the gravitational acceleration, ρ [kg m^{-3}] is the density of water, and T_∞ is the room temperature of 293 K in the present case. Figure 10c shows the computational 2D velocity distribution at an NIR laser power of 220 mW [60]; note that the temperature increase at the focal point is 5 K at this laser power, and the laser power is a net value at the sample position. Because the sample chamber is a closed system, the water flows form circulating patterns from bottom to top. At the focal point of the laser ($x = 0 \text{ }\mu\text{m}$ and $z = 30 \text{ }\mu\text{m}$), the velocity is at most 500 nm s^{-1} ; we defined the velocity at this point as v_{source} . The highest velocity (v_{max}) is observed at the position of $x = 0 \text{ }\mu\text{m}$ and $z = 100 \text{ }\mu\text{m}$. To evaluate the flow velocity quantitatively, we calculated the v_{source} and the v_{max} as a function of the NIR laser power. As shown in Fig. 10d, the v_{source} and the v_{max} linearly increased with the NIR laser power. From these results, we could devise the following two conclusions on the natural convection. (i) Although the natural convection occurs under the optical trapping condition, its contribution in the optical manipulation is less significant because of its slow velocity ($v_{source} < 500 \text{ nm s}^{-1}$). (ii) At the center of the sample chamber, the flow velocity (v_{max}) exceeded $1.8 \text{ }\mu\text{m s}^{-1}$. This suggests that the natural convection might be used as a mild stirrer of the sample solution to transport the target objects into the focal spot of the laser. Please note that the flow velocity strongly depends on the height of the sample chamber (i.e. thickness of the water layer). This is because the buoyancy force is accelerated along the direction of the gravitational acceleration. In the sample chambers thinner than a few tens of micrometers, the natural convection can be suppressed [74,75].

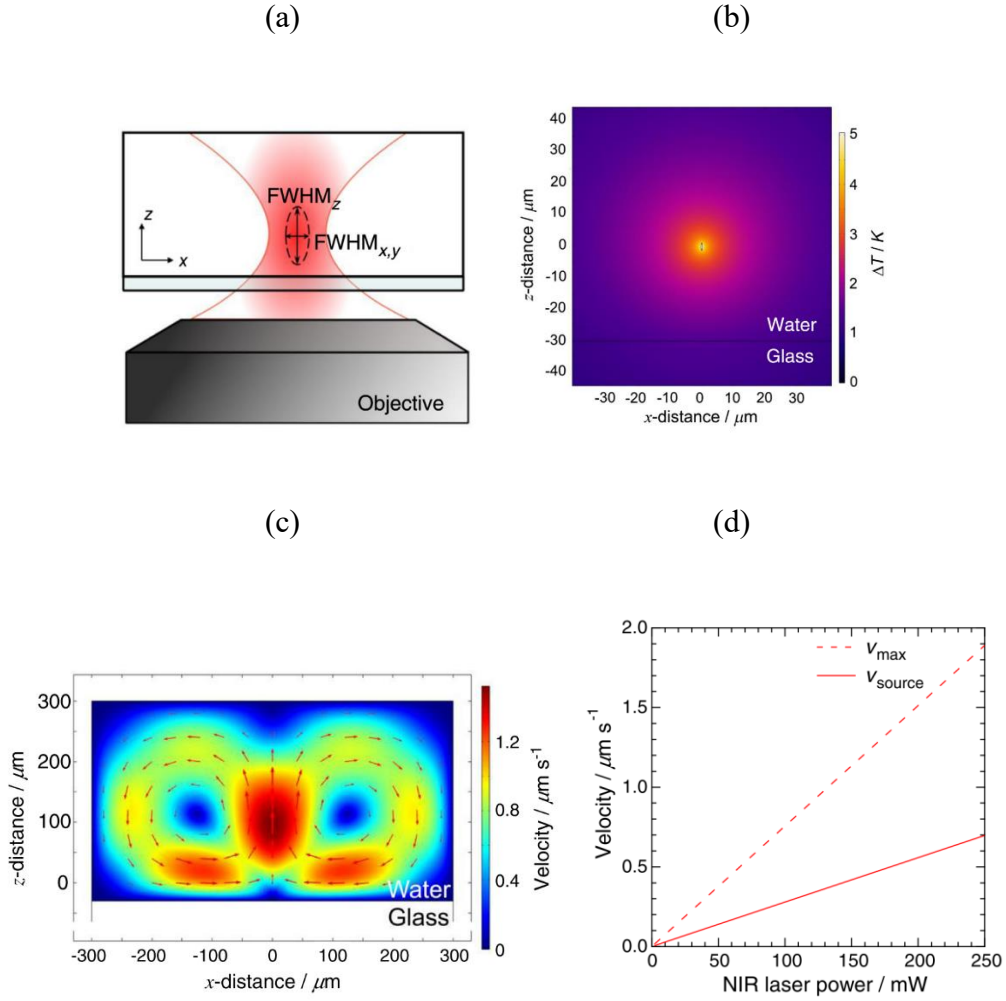


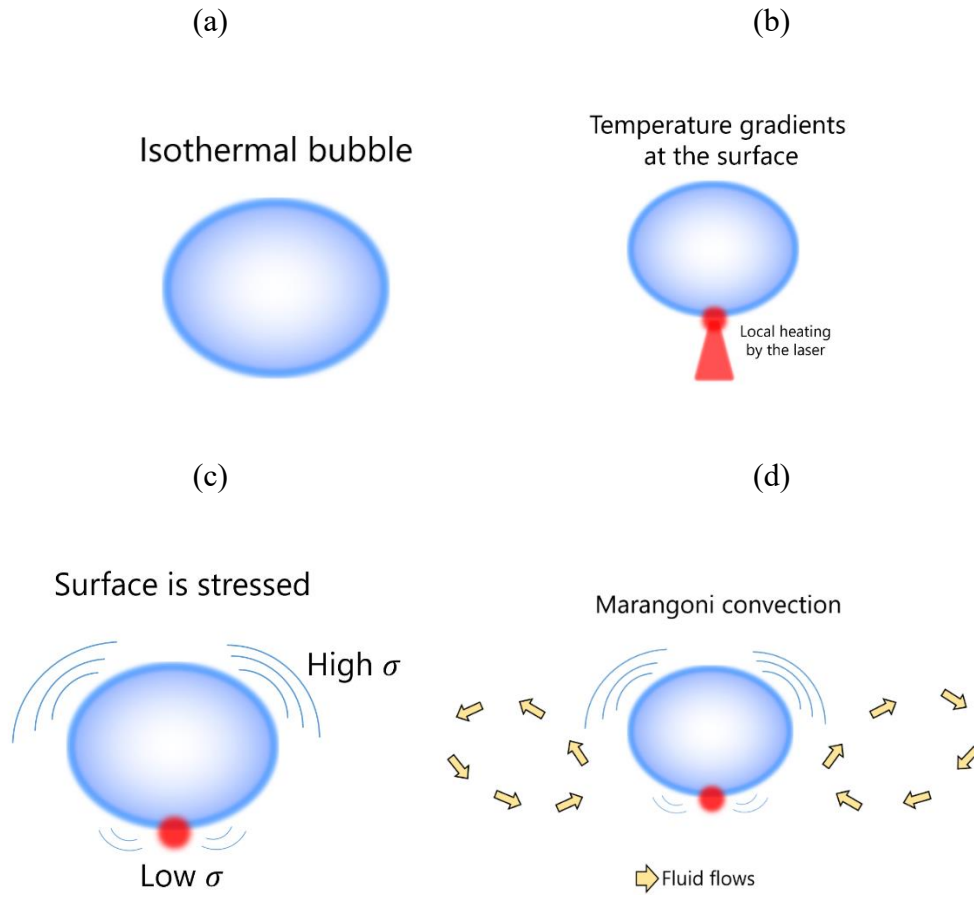
Fig. 10. (a) Computational modeling of 2-D heat conduction and the subsequent natural convection at the steady state. (b) Calculated 2-D temperature distribution for the system consisting of water and glass substrate at a NIR laser power of 220 mW. (c) Computational 2-D velocity distribution for the system consisting of water and glass substrate at an NIR laser power of 220 mW. (d) Calculated convective velocity as a function of NIR laser power at the center of the heat source (v_{source}) and the center of the sample chamber (v_{max}). Reproduced from [60] with permission from the SPIE.

Next, we introduce the natural convection in plasmonic tweezers. In the plasmonic tweezers using an isolated single metal nanostructure (including individual dimers and trimers), the natural convection is negligible because the heating volume is too small to

induce the buoyancy force, even if the water layer is thick [73]. In contrast, the natural convection plays a role on the mass transport when multiple nanostructures are irradiated for the plasmonic trapping. Roxworthy et al. have reported that the natural convection driven by the collective heating of gold nanodimers can transport polystyrene particles at a velocity about $2.0 \mu\text{m s}^{-1}$ [76]. Thus, the thickness of the sample chamber and the heating volume are the two major parameters to control the natural convection in the optical manipulation.

5.2.2. Marangoni convection

Marangoni convection occurs near interfaces because its driving force is surface tension. In research fields related to nanotechnology, Marangoni convection induced by the plasmonic bubbles (photothermally generated tiny bubbles around plasmonic nanoparticles) has been attracting growing interest because of its excellent ability to transport and collect small objects. The mechanistic aspects of the Marangoni convection are summarized in Scheme 3. First, we consider a tiny air bubble in water. If temperatures of the bubble surface are entirely isothermal, no convection could occur (Scheme 3a). Local photo-irradiation to a part of the interface with a focused laser at 1064 nm produces local temperature gradient at the interface (Scheme 3b). Under the temperature gradient, the interface is locally stressed because the surface tension (σ) is temperature dependent (Scheme 3c). Then, fluid flows are induced to get rid of the interfacial stress (Scheme 3d); this stress is called as *shear stress*. Under continuous laser heating that keeps the bubble size constant, static Marangoni flows is observed around the bubble. Readers can refer the physical aspects and numerical simulations of the Marangoni convection driven by the plasmonic bubble in our previous work [77].



Scheme 3. (a) Isothermal bubble with no fluid convection. (b) Local temperature gradients formed by the laser heating. (c) Surface tension (σ) is distorted by the temperature gradient. (d) Marangoni flows around the bubble under steady-state laser heating.

The key features of the bubble-induced convection are fast convection velocity and long-range attraction.[78] The bubble-induced Marangoni convection affects an entire region of a sub-mm sized sample chamber as typically shown in Fig. 11, where the corresponding flow transports colloidal particles or molecules to the bubble-substrate interface [79]. Although optical trapping can assemble small objects, it takes relatively long time in a diluted solution because the optical tweezers are essentially diffusion-

limited processes [80]. Therefore, both the natural and the Marangoni convection are expected to assist and boost the optical trapping/assembling.

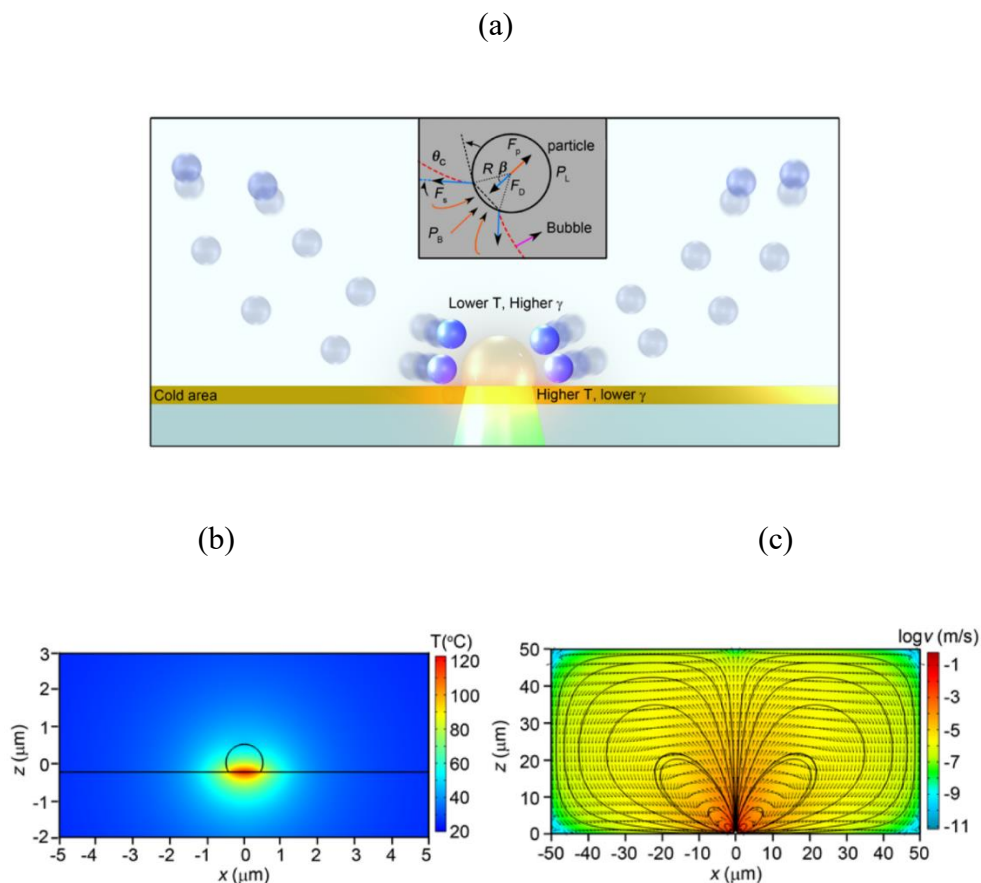


Fig. 11. Particle trapping on the surface of a microbubble generated through the plasmon-enhanced photothermal effects. (a) Schematic illustration (in a cross-sectional view) of the particle-trapping mechanism by a single microbubble. The blue spheres indicate the suspended particles in the deionized water. (b) Simulated temperature distribution around a 1- μm bubble in a cross-sectional view. (c) Simulated flow velocity distribution around a 1- μm bubble with logarithmic scale in a cross-sectional view. The black lines indicate streamlines of the convective flow. Reprinted with permission from [79]. Copyright 2016 American Chemical Society.

5.3. Thermophoresis

5.3.1. Physical aspects

As already mentioned in the beginning of this section, thermophoresis is the temperature-induced migration of small objects, and it differs from the fluid convection. In the most cases of the thermophoresis, the small objects move from hot to cold. The thermophoresis is often referred to as *thermodiffusion*, *Soret effect*, and *Ludwig–Soret effect*. In general, the thermophoresis occurs both in gas and solution. First, the thermophoresis was discovered in the 19th century for aerosol particles.[81] Developments of physical models and historical aspects of the thermophoresis can be found in the literature.[82] In actuality, the thermophoresis is better known in the fields of combustion engineering and aerosol technology [83]: for instance, soot exhibits thermophoretic motions. Here, we deal with the thermophoresis in solution because of its importance and a potential applicability in the optical manipulation. In 2002, Braun et al. demonstrated that the laser-heating-induced thermophoresis can be used to transport DNA.[84] Since this pioneering work by Braun, the laser-heating-induced thermophoresis in solution has been attracting growing interest in recent years; these modern studies on the thermophoresis are called as *microscale thermophoresis (MST)*. Here, we review the mechanistic aspects of the microscale thermophoresis.

First, we need to recognize that the thermophoresis in solution phase is a complicated phenomenon. No theoretical formula has been proposed that can explain all the experimental results without inconsistency, although the entire picture is getting to be understood. For readers unfamiliar with the thermophoresis, the following phenomenological description is somewhat understandable [84]:

$$j = j_D + j_T = -D\nabla c - D_T\nabla T \quad (5)$$

where j is the diffusion flux, D is the diffusion coefficient, c is the concentration, D_T is the thermodiffusion coefficient, and ∇T is the temperature gradient. Obviously, this is a phenomenological formula based on the Fick's first law. In this equation, the whole diffusion flux is divided into the ordinary diffusion term and the thermodiffusion (i.e. thermophoresis), as j_D and j_T . We can expect that the thermodiffusion occurs along the temperature gradient (∇T) from this equation. However, the D_T hinders intuitive understanding of the thermophoresis because this is a phenomenological/empirical value estimated from experimental results. The direction of the thermophoresis, whether *hot to cold* (thermophobic motion) or *cold to hot* (thermophilic motion), can be determined by the Soret coefficient (S_T) [K^{-1}] as follows:

$$S_T = \frac{D_T}{D} \quad (6)$$

The thermophoretic motion from hot to cold is observed with the positive Soret coefficient, while the direction is reversed when the Soret coefficient is negative. Figure 12 shows the thermophoresis of fluorescent polystyrene nanoparticles with a diameter of 100 nm in aqueous solution [85]. As shown in Fig. 12a, a thin Cr film is irradiated with a focused NIR laser. In Fig. 12b, the fluorescent nanoparticles escaped from the laser spot due to the thermophoresis. One can clearly see that the thermophoresis can be described as a diffusive phenomenon from a macroscopic viewpoint as represented in the above equations.

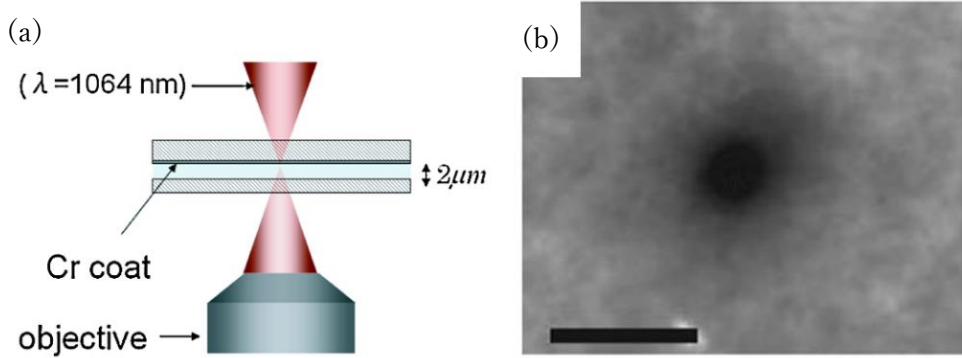


Fig. 12. (a) Experimental setup for the thermophoresis. The laser fed into a thin glass chamber (2 μm) is focused on the top surface coated by a thin Cr layer for light absorption. (b) Fluorescence intensity of 100 nm beads under temperature gradient. The laser is focused at the center. The scale bar: 10 μm . Reproduced from [85] with permission from the American Physical Society.

Although the above expressions give us qualitative information on the thermophoresis, we need a more detailed picture. In the followings, we introduce a microscopic model of the thermophoresis proposed by Würger [86]. Figure 13 shows this model. Here, we consider a charged small particle in solution surrounded by counterions which forms electric double layers around the particle surface. These counterions give rise to excess pressure to the particle in the Debye length, as follows:

$$P = (n_+ + n_-)kT$$

where P is the excess pressure, $n_{\pm}$ is the excess ions, k is the Boltzmann constant, and T is the temperature. At a constant temperature, the excess pressure acting on the particle is in equilibrium. However, once the particle is exposed to a temperature gradient, a slight

temperature difference between the hot side to the cold side of the particle can result in pressure difference. This pressure difference is one of the causes of osmotic flows at the particle surface. Finally, the particle moves along the temperature gradient due to the osmotic flows. The above is one of the most plausible explanations of the microscale thermophoresis at the present stage. Jiang et al. has successfully visualized the thermo-osmotic flows around a microparticle [87]. Very recently, Baffou's group has developed a comprehensive method for quantitative measurement of the Soret coefficient.[88] This method is expected to greatly assist further understanding of the physical aspects of the thermophoresis.

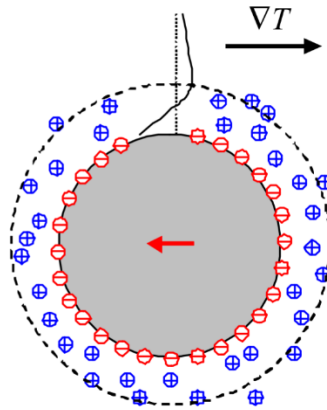


Fig. 13. A charged bead with its diffuse layer in a temperature gradient. The solid line indicates the fluid velocity profile in the laboratory frame. The particle moves to the left, the flow changes sign within the boundary layer and reaches its maximum velocity beyond the screening length, before slowly decaying at larger distance. Reproduced from [86] with permission from the IOP Science.

The induction of the thermophoresis in solution requires temperature gradients in the order of 10^5 to 10^6 [K m⁻¹]. Such temperature gradients can be easily obtained with the focused laser irradiation under optical microscope. In addition, using individual

plasmonic nanoparticles as heat sources leads to much enhanced temperature gradients in the order of 10^8 [K m⁻¹], resulting in much stronger thermophoretic forces.

Typically, the thermophoretic forces acting on small particles are in the order of femtonewtons [89]. In practice, the thermophoresis is sometimes hidden by the fluid convection because the thermophoretic force is essentially small. As already shown in scheme 2, the use of a thinner sample chamber can suppress the natural convection. The Marangoni convection can be eliminated by avoiding the formation of the laser-induced bubbles. In addition to the spatial temperature gradient, the magnitude of thermophoretic forces acting on nanoparticles strongly depend on their materials. For metal nanoparticles, the thermophoretic forces are expected to be very small because of their high thermal conductivities [74]. This is because the temperature difference at the particle surface would be minimized due to the higher thermal conductivity. Therefore, using nanoparticles with anisotropic thermal conductivity, e.g. Janus particles introduced in the next subsection, leads to remarkable thermophoretic behaviors.

5.3.2. Thermophoretic forces in the optical manipulation

In this sub-section, we introduce some recent papers reporting on interplay of the thermophoretic force and the optical force in the laser manipulation. In 2015, Nedev et al. reported that the thermophoresis can act as a counterbalancing force to optical dissipative forces (i.e. scattering and absorption forces) to control the position of an optically-trapped microparticle [90]. They performed optical trapping experiments for individual Janus microspheres in water with a focused 1064 nm laser beam. At the lowest laser power, they observed ordinary trapping behavior at the focal plane. Surprisingly, when increasing the laser power, the trapped Janus particle moved against the direction of the

laser propagation; with decreasing the laser power, Janus particle returned to the original position. In other words, they observed the laser-power-dependent hysteresis motions of the Janus particle along the propagation axis of the laser. These results are summarized in Fig. 14. They concluded that the thermophoretic force arising from the heating of one side of the Janus particle is the cause of the hysteresis motions.

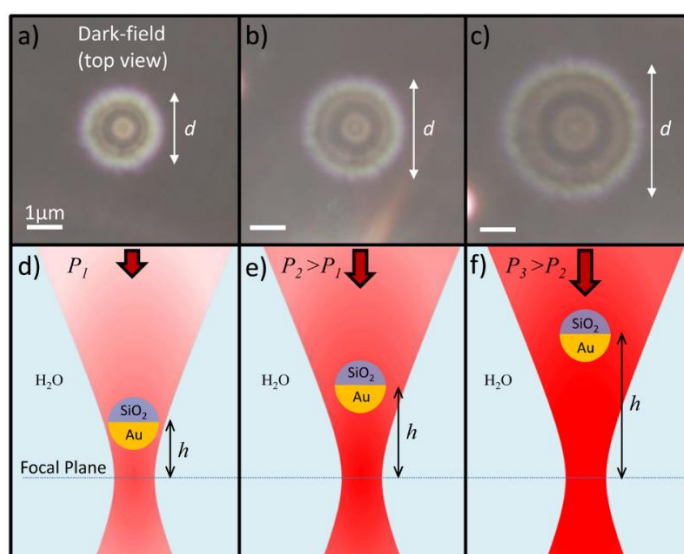


Fig. 14. (a–c) Dark-field images of a Janus particle in an optical trap for increasing laser powers (left to right). (d–f) Schematics of the experimental situations of (a)–(c) with the incident illumination from above. Increasing the laser power causes a reversible axial displacement in a direction opposite the beam propagation. Reprinted with permission from [90] (<https://pubs.acs.org/doi/10.1021/ph500371z>). Copyright 2015 American Chemical Society.

In 2016, Stefani's group reported that the thermophoresis plays a major role in optical printing of plasmonic nanoparticles onto substrates [91]. The optical trapping and the printing of plasmonic nanoparticles is one of the popular applications of optical manipulation [14,92]. In this application, fabrication of nanodimers with a controlled spacing at the nanometer scale has been a difficult process because of repulsive

interactions between the two nanoparticles. Although the electrostatic repulsion has been considered to be a major repulsive interaction, Stefani and colleagues figured out that heat generation and subsequent thermophoresis around the already printed single nanoparticle prevent the printing of another nanoparticle next to the first one, as shown in Fig. 15. In 2017, the same group reported more detailed reports on the role of the thermophoresis in the optical printing, and proposed a few ideas to minimize the thermophoretic force using the substrate with high thermal conductivities. [93]

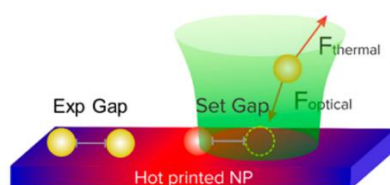


Fig. 15. Schematic of the Au–Au dimers printing experiment and its relevant parameters and forces. As the laser beam illuminates the nanoparticles on the surface, the local temperature increases. Reprinted with permission from [93]. Copyright 2017 American Chemical Society.

In 2019, we developed a method to utilize the thermophoresis in the optical tweezers for selective trapping and analyzing of a single nano-object [75]. In general, the optical tweezers are powerful tools to analyze single small objects in liquids. However, for these analytical purposes, a dilute concentration of solutes is necessary because the gradient force indiscriminately attracts any small objects with enough polarizabilities. To overcome this limitation, we introduced the thermophoretic force counterbalancing to the gradient force in the optical tweezers (Fig. 16a). For this purpose, we used a NIR CW laser at a wavelength of 1475 nm. This laser strikes the absorption band of water in the

NIR regions, therefore, this has not been used in the optical tweezers. However, we demonstrated that this laser wavelength is effective for simultaneous induction of the optical trapping and the thermophoresis. By changing the laser spot diameter, we can tune the ratio of the thermophoretic force and the gradient force acting on the nanoparticle. We demonstrated simultaneous selective trapping of a single nanoparticle and sweeping others out from the laser spot (Fig. 16b). This method paved a way for manipulating single nano-objects in dense environments with various kinds of materials.

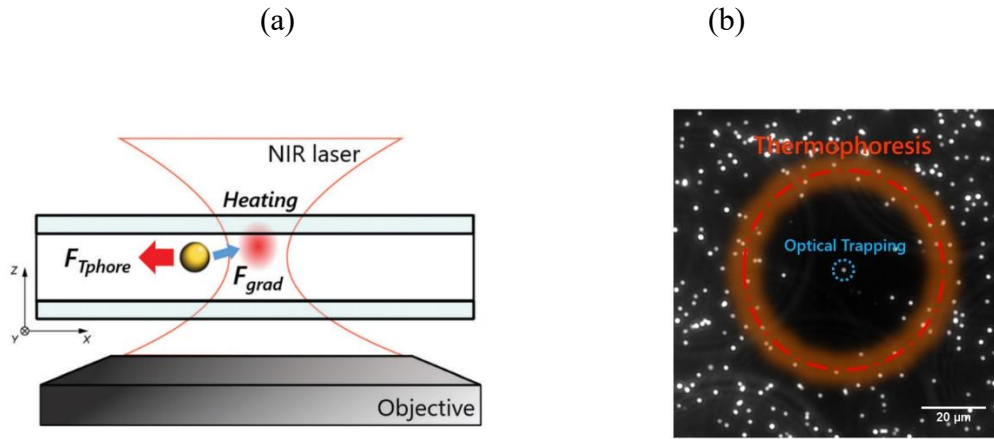


Fig. 16. (a) Schematic illustration of optical gradient- and thermophoretic forces (F_{grad} and F_{Tphore}) acting on a plasmonic nanoparticle under irradiation of a focused NIR laser. (b) Dark field image of simultaneous trapping and separation of the plasmonic nanoparticles by the optical trapping and the thermophoresis. Reproduced from [75] with permission from the Royal Society of Chemistry.

In 2020, Wenger's group proposed to utilize the thermophoresis in the plasmonic tweezers by adding surfactants [94]. They conducted systematic experiments on the concentration of sodium dodecyl sulfate (SDS) and Triton X-100 in the plasmonic trapping of polystyrene nanoparticles. As a result, they observed that the trapping

efficiency is enhanced for 20-folds with the SDS compared to that without surfactants. In contrast, adding the Triton X-100 resulted in a decrease in the trapping stiffness. Therefore, the authors clarified that trapping potentials of the optical tweezers can be deepened or shallowed with the thermophoresis of the surfactants, although the mechanism is still unclear at the present stage. Thus, the thermophoresis has been accepted and utilized in the optical manipulation in the last decade.

6. Summary and outlook

In this review article, optical manipulation of nanometer-sized materials using photochemical reactions and photothermal conversion was described. First, we reviewed pioneering works on optical manipulation of polymer chains and molecular aggregates in 1990s in the section 2; some researchers already found that optical forces on the nano materials can be modified through photoresponses of materials in these studies. Along this line, it was demonstrated that photochromic reactions of diarylethene derivatives and pyranoquinazoline derivatives can switch the optical forces on nanomaterials in recent years as described in the section 4. In the section 3, we summarized evaluation methods of molecular objects and nanoparticles under optical trap using fluorescence correlation spectroscopy (FCS); the FCS is one of the most powerful tools to estimate potentials of the optical trap. On the other hand, one sometimes observes significant photothermal effects such as fluid convection and thermophoresis because intense laser light is required for optical manipulation. These temperature-induced migrations of nanomaterials are reviewed in the section 5; physical aspects of the fluid convection and the thermophoresis, and recent progresses of optical manipulation combined with these photothermal effects were described.

Summarizing the above, photochemical and photothermal responses can greatly assist optical manipulation of nanomaterials. Although parameters of light as an external field for optical manipulation are essentially limited (e.g. wavelength, phase, polarization, etc.), using the photochemical and the photothermal responses of materials for modifying and/or assisting optical forces can potentially provide a wide variety of optical manipulations thanks to the diversity of photo-responses of materials. We foresee such approaches can pave the way to new methodologies for science and technology, for

instance, condensation and extraction of chemical products, nanofabrications, new micro-spectroscopy based on the detection of optical forces, microscopic thermal control systems, chemo/thermo-responsive photo-mechano-devices, and so forth.

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Declaration of Competing Interest

The authors declare no conflict of interest.

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