

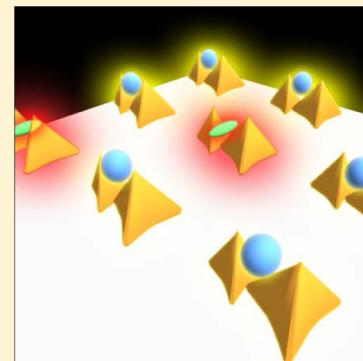
Plasmonic Optical Tweezers toward Molecular Manipulation: Tailoring Plasmonic Nanostructure, Light Source, and Resonant Trapping

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ABSTRACT: This Perspective describes recent progress in optical trappings of nanoparticles based on localized surface plasmon. This plasmonic optical trapping has great advantages over the conventional optical tweezers, being potentially applicable for a molecular manipulation technique. We review this novel trapping technique from the viewpoints of (i) plasmonic nanostructure, (ii) the light source for plasmon excitation, and (iii) the polarizability of the trapping target. These findings give us future outlook for plasmonic optical trapping. In addition to a brief review, recent developments on plasmonic optical trapping of soft nanomaterials such as proteins, polymer chains, and DNA will be discussed to point out the important issue for further development on this trapping method. Finally, we explore new directions of plasmonic optical trapping.



Radiation pressure, or radiation force, is theoretically derived on the basis of Maxwell's equations. It is produced simply by the electromagnetic interaction between light and a small particle, which is polarized by the light. This interaction is the driving force of the optical trapping of small particles. Tools based on optical trapping and manipulation are called "optical tweezers". Since the first successful experimental demonstration of optical trapping by Ashkin et al.,¹ the related science and technology have undergone enormous growth. Nowadays optical tweezers are a versatile tool and have reached the level of being of practical use, and several optical tweezers systems are now commercially available.

The basic set up of conventional optical tweezers is not quite complex. A single continuous-wave (cw) light beam from a solid-state-laser is introduced into an optical microscope and is focused by an objective lens with a high numerical aperture to generate radiation force on a small particle at the focal point. For a scanning trapping system, a Galvano-mirror system is built in the optical setup.^{2,3} Features of the optically trapped particle are monitored *in situ* with a video camera equipped with a microscope and sometimes the operator can manipulate and analyze the trapped particle by microspectroscopy (fluorescence, absorption, and Raman scattering).

Despite the simplicity of this optical scheme, optical tweezers have become a powerful tool mainly in the life and medical sciences, in which small biological materials such as living cells,⁴ bacteria,⁵ and microsphere-linked-DNA^{6,7} are optically manipulated. With the recent rapid progress that has taken place in these research fields, an urgent need has arisen to manipulate relatively smaller bioparticles such as fragmented-DNA, enzymes, oligopeptides, and so on. Also, in the field of

chemistry, the manipulation of molecules and catalytic nanoparticles would be a valuable technique. However, for conventional optical tweezers, it is rather difficult to perform stable optical trapping of small nanoparticles that have sizes of the order of nanometers (less than several tens of nanometers) because the radiation pressure decreases as the size of the particle gets smaller, and the pressure is too small to overcome the thermal fluctuation.

The novel trapping method is called plasmonic optical tweezers and utilizes localized surface plasmons to enhance the radiation force.

To overcome this limitation, new physical principles that radically reorganize optical tweezers need to be introduced. One such novel type of optical tweezers has recently been proposed and developed. The novel trapping method is called plasmonic optical tweezers and utilizes localized surface plasmons to enhance the radiation force. They can, potentially, overcome the limits and disadvantages of conventional optical tweezers. In this Perspective, we review the recent progress in plasmonic optical tweezers (that is, plasmonic optical trapping; POT) for manipulating nanoparticles and molecules and give

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an overview of the future for such plasmonic optical tweezers in physical chemistry and nanoscale chemistry. First, we carry out a theoretical treatment of the radiation force and the general features of POT. Then, the recent developments in POT are discussed from the viewpoints of the plasmonic nanostructure, the light source for plasmon excitation, and the polarizability of the trapping target. POT of biomolecules is also discussed and is presented as a future and application of POT. Furthermore, we refer to another significant force induced by photothermal effects that accompanies localized surface plasmon (LSP) excitation. It is never negligible and acts as a repulsive force in many cases. Finally, we discuss the future outlook for POT.

Theoretical Treatment of Radiation Force. Radiation force originates from a change in the momentum of light when it interacts (e.g., by scattering, absorption, and transmission) with a small particle on the basis of Newton's third law.⁸ When the radius (a) of the particle is much smaller than the wavelength (λ) of the light, the incident electromagnetic (EM) field is regarded as being uniformly distributed across the particle (long-wavelength approximation).^{9,10} Radiation force is described in the framework of the Rayleigh scattering theory where a particle is regarded as a point dipole. In this regime, the radiation force F exerted on the dipole is divided into three components: a scattering force F_{scat} , an absorption force F_{abs} , and a gradient force F_{grad} ; $F = F_{\text{scat}} + F_{\text{abs}} + F_{\text{grad}}$. The scattering and absorption forces are repulsive forces that push the particle away in the direction of light propagation.¹¹ The gradient force, F_{grad} , attracts the particle in the direction of the spatial gradient of the light intensity

$$F_{\text{grad}} = \frac{1}{2} |\alpha| \nabla \langle E^2 \rangle \quad (1)$$

$$\alpha = \alpha' + i\alpha'' = 3V \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \quad (2)$$

where $\langle E^2 \rangle$ is the time-averaged square of the electric field of the incident light (corresponding to the light intensity), α is the polarizability of the target particle, $V (= 4\pi a^3/3)$ is the volume of the particle, and ϵ_p and ϵ_m are the dielectric constants of the particle and the surrounding medium, respectively. In general, the scattering force, F_{scat} , exerted on the nanoparticle is proportional to a^6 , whereas the gradient force is proportional to a^3 .¹¹ Consequently, the gradient force becomes more dominant compared with the scattering force as the particle size decreases.

In this situation, nanoparticles can be trapped by the gradient force. However, simultaneously with F_{grad} , the particle undergoes Brownian motion with a thermal energy of $k_B T$ (k_B is the Boltzmann constant and T is the absolute temperature). Thus, for stable trapping of a nanoparticle, the trapping potential U created by the radiation force must overcome the thermal energy $k_B T$: $|U| \gg k_B T$.^{12,13} The potential energy U exerted on a nanoparticle is expressed as

$$U \approx - \int F_{\text{grad}} dr = - \frac{1}{2} |\alpha| \langle E^2 \rangle \quad (3)$$

The eq 3 tells us the general features of optical trapping: (i) the grip (trapping strength) becomes stronger as the laser intensity increases; (ii) stable trapping becomes harder as the size of the particle gets smaller. Using conventional optical tweezers, it is, in principle, possible to trap small molecular systems ($a \ll \lambda$). However, in reality, it is rather difficult due to the small polarizability and the spatial resolution.¹⁴ The

breakthrough needed in optical trapping that will enable us to overcome the disadvantages of conventional optical tweezers requires the introduction of some novel physics. Using LSP to enhance the power of optical tweezers is a promising solution. This technique is called plasmonic optical trapping (POT) and has the following advantages over conventional optical tweezers (Figure 1)

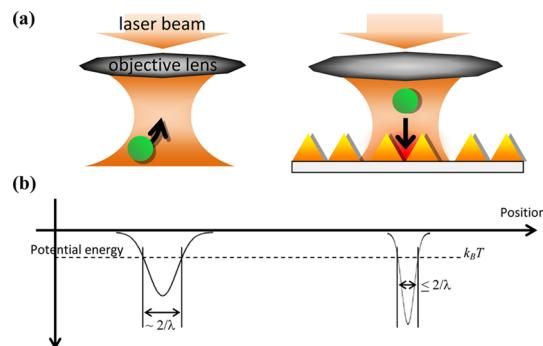


Figure 1. Schematic illustrations of optical tweezers and plasmonic optical tweezers. (a) (Left) Optical tweezers can trap a nanoparticle at the focal point of the laser beam, (Right) whereas plasmonic optical tweezers trap at the plasmonic active nanospace. (b) The depth of the potential energy of the radiation force corresponds to the probability distribution of the trapped particle. (Left) The distribution of the potential of optical tweezers generally forms a Gaussian profile. The trapping space is hardly smaller than the diffraction limit of the light. (Right) The potential energy profile of the plasmonic optical tweezers, on the other hand, strongly depends on the shape of the plasmonic nanostructure, being smaller than the diffraction limit.

- (i) The laser light intensity needed to achieve stable optical trapping is reduced due to the EM enhancement effect of plasmon in comparison with conventional optical tweezers.
- (ii) The motion of the trapped particle is tightly bound in the plasmonic nanospace, which is much smaller than the diffraction limit of light.
- (iii) POT can potentially be combined with conventional plasmonic applications such as the acceleration of photochemical reactions¹⁵ and highly sensitive chemical and biological sensors.¹⁶ These combinations would open new channels for novel plasmonic applications.

The combination of optical trapping with plasmon was theoretically proposed in 1997.¹⁷ As described in the literature, the high EM field close to the surface of a metal tip can generate a strong radiation force on a dielectric nanoparticle. They theoretically suggest the efficient optical trapping of a nanoparticle close to the surface. Following this theoretical prediction, several research groups experimentally performed POT.^{18–21} Before describing their demonstrations, first, we outline the general features and characteristics of POT.

General Features and Characteristics of POT. It is widely and generally accepted that the EM field in the nanogap between adjacent metallic nanostructures is extremely high. The type of plasmon in the gap is called a “gap-mode” LSP, and this has an optical resonant band with longer wavelength than a LSP band of a single isolated metallic nanostructure. Such nanostructures are called “plasmonic nanoantennas” or “plasmonic nanojunctions”.

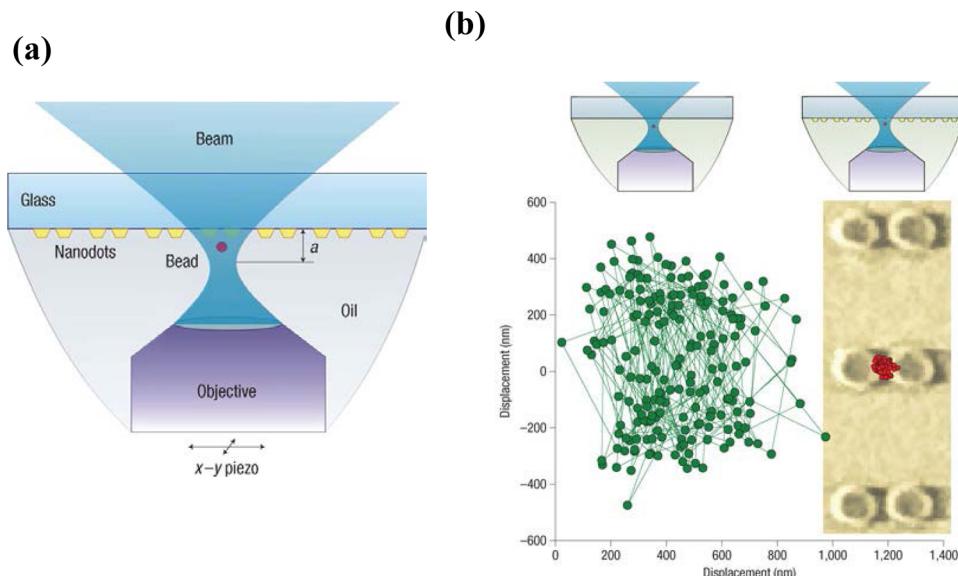


Figure 2. Plasmonic optical tweezers using double gold nanopillars. (a) Schematic illustration of the optical setup. In the article, the authors describe the fabrication of gold nanopillars with diameters of 100–140 nm, height of 90 nm, and pillar separations of 140–200 nm. (b) Temporal profiles of the positions of polystyrene nanospheres trapped by optical tweezers (left) and plasmonic optical tweezers (right) (time step 5 ms). Upper illustrations show relevant geometries of the experiment. The displacement of polystyrene trapped by optical tweezers was larger than that by plasmonic optical tweezers. Reprinted with permission from ref 22. Copyright 2008 Nature Publishing Group.

Table 1. POT of Nanoparticles on Plasmonic Gold Nanostructures Excited by Laser Light^a

plasmonic nanostructure		light source		trapped nanoparticle	
morphology	η^b	λ/nm	$I/\text{kW cm}^{-2}$	material	diameter/nm
nanopillar	20	974	1000	polystyrene ²³	110
double nanopillars	30	1064	5×10^{5c}	polystyrene ²²	200
four nanopillars	20	980	2.8	polystyrene ⁸⁵	100
					500
nanodiabolo	260	980	610	polystyrene ⁸⁶	350
nanohole	7	1064	200	polystyrene ²⁴	50
double nanoholes		975	500	polystyrene ⁶⁰	20
		820	720	silica ⁶⁰	12
			350	bovine serum albumin ⁵⁹	6.8
double nanorods	10	800	1.0	<i>E. coli</i> bacteria ¹⁸	2000
	30	808	200	gold ⁷¹	10
double nanopyramids	10^4	808	0.5	quantum dot ²⁵	10
			1.0	polymer chain ⁶⁵	100
			7.0	λ -DNA ⁶⁸	
double nanoblocks	6300	800	0.75	polystyrene ⁸⁷	350
		1064	60	polystyrene ²⁶	100
double nanotriangles	200	685	4.4	polystyrene ⁸⁴	500

^aWavelength λ , incident light intensity I . ^bThe enhancement factor η is defined as $|E_{\max}|^2/|E_i|^2$. ^cBecause the refractive index of the surrounding medium (oil, $n = 1.5$) was very close to that of the trapping target ($n = 1.6$), high light intensity was required in comparison with other types of POT (surrounding medium was water, $n = 1.33$).

In 2008, Grigorenko et al. first demonstrated POT of polystyrene nanospheres (diameter, $d = 200$ nm) on the gap between two gold nanopads (Figure 2).²² Irradiation of near-infrared light ($\lambda = 1064$ nm) enhances the EM field in the 200 nm gap between the two gold nanopads. A nanoparticle in solution moving toward the nanogap by diffusion was trapped by the enhanced radiation force in the gap. The authors experimentally estimated the optical trap stiffness coefficient (spring constant), which is measured in terms of the force/displacement and expresses the strength of the radiation force, to be 1.3×10^{-2} fN nm⁻¹ mW⁻¹ (normalized by the incident laser power). This value is an order of magnitude higher than

that of conventional optical tweezers using the same laser power. Quidant's group also presented POT of *Escherichia coli* living bacteria (size $2 \times 0.8 \mu\text{m}$), suggesting that POT could become a powerful tool for manipulating biological micro-organisms.¹⁸

We summarize some recent experimental demonstrations of POT of micro- and nanoparticles (Table 1). POT has been explored using a variety of plasmonic nanostructures: nanopillars,^{22,23} nanoholes,²⁴ nanopyramids,²⁵ and so on. These structures were designed for the EM enhancement effect and the plasmon resonance band. In particular, Sasaki's group clearly showed theoretical and experimental results that a

strong trapping potential was formed on the plasmonic nanoscale.²⁶ They fabricated a finely shaped gold nanoblock dimer that had a 10 nm nanogap between the nanoblocks. Such a precise, well-defined nanostructure provided a further quantitative discussion on radiation force exerted on a polystyrene nanosphere. In addition, they found multiple potential wells on a single nanoblock pair separated by a distance smaller than the diffraction limit. In this Perspective, we focus on three novel trapping methods, (1) POT on chiral plasmonic nanostructures, (2) POT with femtosecond pulsed (fs) laser light, and (3) resonant plasmonic optical trapping, because these methods are promising approaches to the opening of new channels in designing the next generation of optical trapping tools.

POT on Chiral Plasmonic Nanostructures. The chirality of nanostructures is a hot topic in plasmonics.^{27,28} Plasmonic nanostructures with chirality would also enable novel insights into POT. For instance, Tsai et al. presented the selective trapping and rotation of microparticles using a chiral plasmonic structure and circularly polarized laser beams.²⁹ They fabricated a right-handed Archimedes microspiral using focused ion beam milling of a thermally evaporated gold film (thickness = 250 nm) (Figure 3a). The surface plasmon polariton of the structure was excited at 1545 nm. When they excited the structure with left-handed circularly polarized light, a dielectric microparticle was trapped at the center of the spiral due to the zero angular momentum (Top in Figure 3b). They showed optical micrographs (Top in Figure 3c) of the optically trapped polystyrene microparticle ($d = 1 \mu\text{m}$) with a left-handed circularly polarized laser beam. Stable optical trapping was achieved at 40 to 80 mW of laser power. Irradiation with right-handed circularly polarized light generated an optical vortex at the center, leading to rotation of the trapped microparticle (Bottom in Figure 3b and c). This means the angular momentum transfer from the light to the particle was mediated by a plasmonic nanostructure.

We expect that such selective optical manipulation techniques based on the chirality of the light and the plasmonic nanostructure will become useful as optical sorting systems for chiral nanoparticles and molecules. Toward other relevant applications of such chiral POT, we focus on recent applications of chiral plasmonic nanostructure for biosensing techniques.^{30,31} For instance, Ma et al. demonstrated DNA detection with a chiral plasmonic nanostructure by means of circular dichroism (CD) spectroscopy.³⁰ They fabricated the chiral assembly of gold nanorods bridged with DNA. CD signals from the DNA were detected at attomolar level of DNA concentration. Thus, by combining the chiral POT with such CD spectroscopies, the novel analytical tool will be demonstrated to detect the trapped biomolecules with high sensitive detection at single molecular level.

POT with a Femtosecond-Pulsed Laser. The study of conventional optical tweezers using femtosecond-pulsed (fs) laser light is still an active research area because fs laser irradiation frequently results in efficient trapping and the discovery of novel physical phenomena.^{32–35} Okamoto's group recently found nonlinear behavior of a "trap split",³² Dholakia's group controlled the two-photon luminescence of trapped nanoparticles,³³ and recently Masuhara's group found that trapped nanoparticles spread out from the focal spot of the laser beam in two opposite directions.³⁴ All this research was performed using fs laser beams and can potentially be extended to POT. Roxworthy and Toussaint first reported POT with a fs

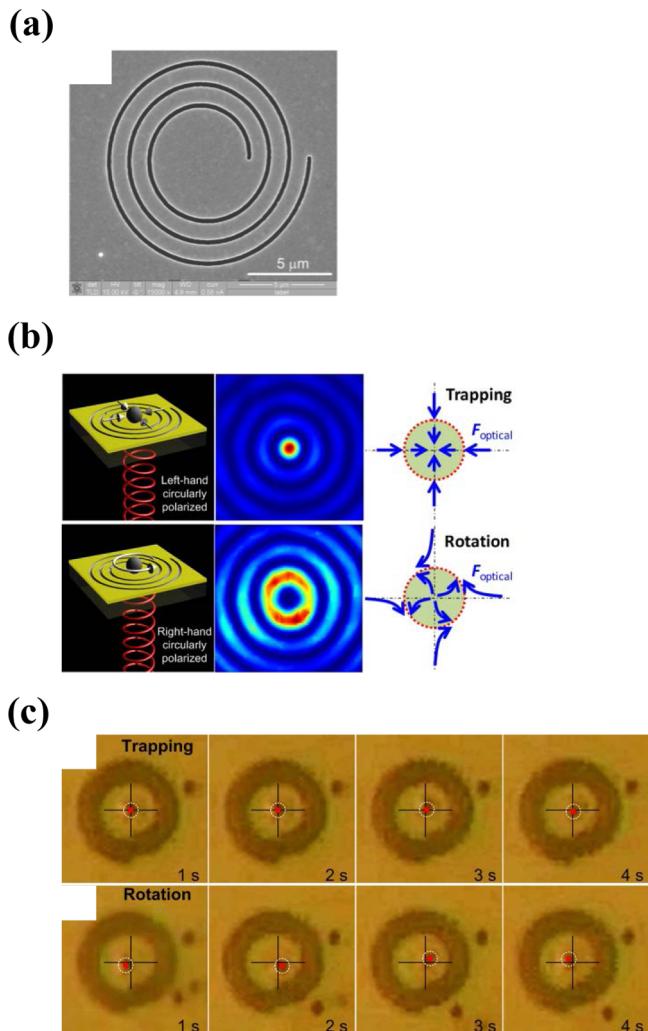


Figure 3. Selective trapping and rotation of a single microsphere on a plasmonic Archimedes spiral excited by circularly polarized laser beams.(a) Geometry of the nanostructure and the surface plasmon intensity profiles. (b) (Top) Left-handed circularly polarized plane wave excitation leads to trapping of a microparticle. (Bottom) Right-handed circularly polarized plane wave excitation can be used to trap and rotate a microparticle. (c) Optical micrographs of a trapped microsphere on a plasmonic nanostructure under (top) left-handed and (bottom) right-handed circularly polarized plane wave excitation. Reprinted with permission from 29. Copyright 2014 American Chemical Society.

laser.³⁶ Enhanced EM fields were generated at nanogaps in gold bowtie nanostructures by irradiation with a 100 fs pulsed Ti:sapphire laser (80 MHz repetition rate, $\lambda = 800 \text{ nm}$). Comparing the fluorescence intensity from trapped fluorescent polystyrene microspheres ($d = 1.2 \mu\text{m}$) using a fs laser with that using a cw laser, the fs laser excitation led to an increase in fluorescence intensity due to the increase in radiation force. The authors claimed that the trap stiffness of POT with a fs laser ($14 \text{ fN nm}^{-1} \text{ mW}^{-1}$) was 2-fold higher than that of POT with a cw laser and five times more than that of conventional optical tweezers with a fs laser. They also trapped Ag nanoparticles ($d = 80 \text{ nm}$) at the nanogap under fs laser light irradiation. In addition to increment of trapping efficiency by using fs laser, they observed adhesion of these trapped nanoparticles to plasmonic active sites. Such behavior has never been observed for POT with cw lasers. The theoretical

treatment of POT with a fs laser is the next challenging task for a further understanding of the mechanism. The characteristic behavior peculiar to POT with a fs laser is applicable for trapping DNA, as described below.

Resonant POT. In the above, we have discussed the uses of POT with the focus on the plasmon excitation light source and the plasmonic nanostructure. To enable molecular manipulation based on POT, we introduce a new physical feature to POT, which is electronic resonant excitation of the target particle. According to eq 1, the radiation force is proportional to both ∇E^2 and the electric polarizability α of the target particle. The basic concept of resonant optical trapping is that the electric polarizability should be enhanced under resonant excitation conditions. Resonant optical manipulation has been theoretically proposed by our co-workers in Ishihara's group.^{37–39} Since the first experimental demonstration of resonant optical manipulation of dye-doped polystyrene nanospheres,⁴⁰ similar resonant effects have been suggested using Au,^{41–43} Ag,⁴⁴ CuCl nanoparticles,⁴⁵ and fluorophore-labeled antibodies as trapping targets.⁴⁶ In particular, resonant optical trappings of metallic nanoparticles have great potential for applications such as photothermal therapy and ultrasensitive sound detection in microscale (nanoear).^{47,48} We have recently reported the resonant optical trapping of small proteins by conventional optical tweezers.^{49,50} Because heme proteins (e.g., cytochrome c and myoglobin) have an absorption band in the near-infrared region, resonant optical trapping of these proteins was observed by tuning the laser light to be resonant with the electronic transition. The combination of such resonant optical trapping with POT, called resonant plasmonic optical tweezers (RPOT), will permit researchers to manipulate small molecules.

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We first experimentally and theoretically demonstrated RPOT using dye-doped polystyrene nanospheres as trapping targets.⁵¹ Our plasmon nanostructure was a nanopyratidal dimer array (Figure 4a), which has an extinction band at $\lambda \geq 650$ nm corresponding to a gap-mode localized surface plasmon. Near-infrared laser light ($\lambda = 690$ nm) excites the plasmon, resulting in an enhanced EM field in close proximity to the gap between the nanopramids. As a trapping target, we used two kinds of dye-doped polystyrene nanospheres ($d = 100$ nm): one was resonant with the near-infrared laser light (resonant condition) and the other nonresonant (Figure 4b). We experimentally compared the trapping efficiency for these two different kinds of nanospheres: POT under the resonant conditions was at least five times higher than that under the nonresonant conditions (Figure 4c). Furthermore, theoretical calculations on the basis of the discrete dipole approximation (DDA) also reinforced our observations: the enhancement factor of the radiation force was predicted to be 5–10 (Figure 4d).⁵¹ These results strongly suggest that this methodology will provide a novel approach for the efficient trapping of small molecules.

Recent POT Demonstrations toward Molecular Manipulation; POT of Soft Nanomaterials (Protein, Artificial Polymer Chains, and DNA). Using conventional optical tweezers, some researchers were able to trap biological nanomaterials such as proteins,^{49,50,52} DNA^{53,54} and smaller molecules.^{14,55,56} Such trapping of biomolecules still presents a challenge because the radiation force dramatically decreases as the size of the molecule gets smaller. Accordingly, optical trapping of these smaller molecules requires high intensity light (a few tens of MW/cm²). By using POT, trapping can be achieved with a weak incident light intensity due to the EM enhancement effect of plasmons. Such POT of molecules is significant from the viewpoint of analytical chemistry and photochemistry. One of the major plasmonic applications in analytical chemistry is molecular spectroscopy with ultrahigh sensitivity. A representative example is surface-enhanced Raman spectroscopy.⁵⁷ Another application is enhancement of photochemical reaction yields.^{15,58} Such enhancements of the spectroscopic signals and reaction yields should take place at a plasmonic hot site, that is, a plasmonic nanogap. In the solution phase, in which molecules dissipate by diffusion, one must bring the molecules to an active nanogap site. Consequently, POT also plays an important role in transporting molecules to the gap site.

Gordon's group claimed that a double nanohole (a dumbbell-shaped nanohole) in a thin gold film was capable of generating a strong radiation force on a single protein molecule (bovine serum albumin, BSA), resulting in optical trapping of the single BSA molecule at the edge of the hole.⁵⁹ Such optical trapping with a plasmonic nanohole is called self-induced back action (SIBA) trapping.^{24,59–64} A great advantage of SIBA trapping is the highly sensitive detection of trapping events at the single molecule level by means of a change in transmission intensity. By using such SIBA trapping, they carried out optical trapping of a single BSA molecule. Furthermore, they claimed that the radiation force induced the folding–unfolding transition in a trapped protein. We consider highly sensitive spectroscopies such as surface-enhanced Raman and fluorescence spectroscopy should be combined with SIBA trapping, providing new possibilities for novel plasmonic sensors with high efficiency.

Using confocal fluorescence microscopy, we examined the conformational changes to flexible polymer chains trapped at a plasmonic nanostructure (Figure 5).⁶⁵ We used a fluorescence-labeled poly(*N*-isopropylacrylamide) as a trapping target, which is a representative water-soluble thermoresponsive polymer ($d \sim 11$ nm) (Figure 5a). Upon elevating the temperature, ΔT , by ~ 10 K above room temperature, aggregates ($d \sim 100$ nm) of polymer chains were formed in the aqueous solution accompanied by phase separation into polymer-rich and water-rich domains.^{66,67} In addition, the fluorescent probe exhibited fluorescence behavior in response to the polarity around the probe (i.e., the fluorescence was blue-shifted upon phase separation). Consequently, POT of such thermoresponsive polymer chains would provide insights into the microenvironments around trapped polymer chains. Upon plasmon excitation, microassembly of the polymers in the excitation area was clearly observed (Figure 5b). Stopping the plasmon excitation led to the release of the trapped polymer chains that became polymer chains dissolved in water. In order to gain an insight into this, we conducted fluorescence microscopy during POT of the polymer chains (Figure 5c). The fluorescence from the area clearly increased, indicating an increase in the number of polymer chains in the area due to

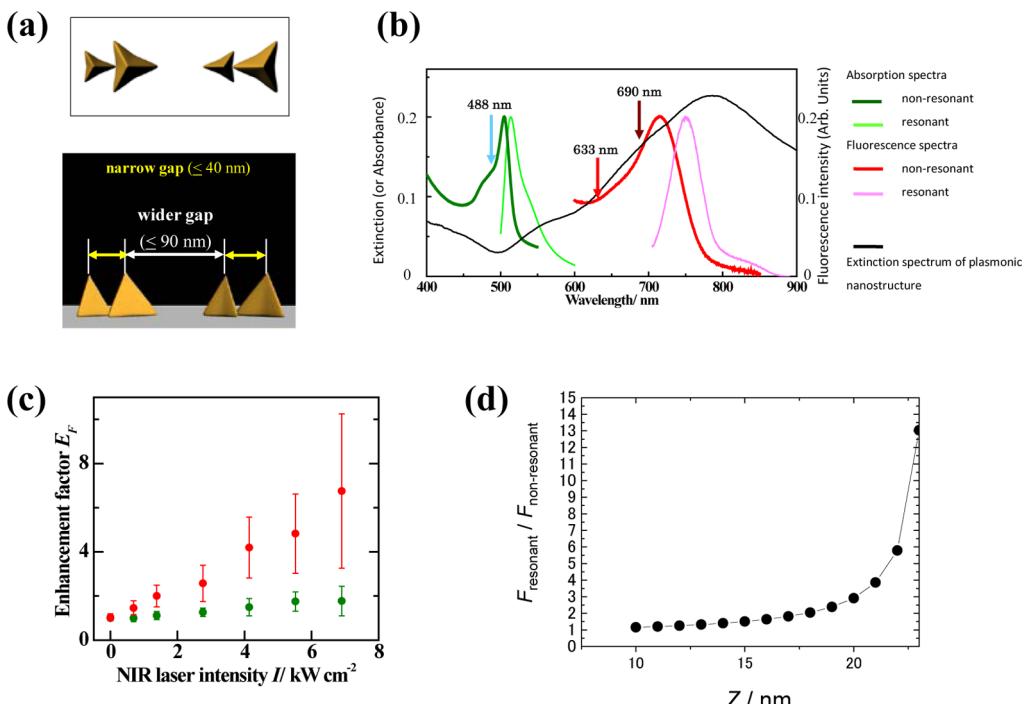


Figure 4. Resonant plasmonic optical trapping of 100 nm diameter polystyrene nanospheres. (a) Schematic illustrations of gold nanopiramidal dimer array. (b) Absorption and fluorescence spectra of the nonresonant nanospheres (green/light-green lines) and resonant nanospheres (red/pink lines) dispersed in water. The extinction spectrum of the gold nanopiramidal dimer array is also shown (black line). The cw laser light at 690 nm was used for plasmon excitation. (c) Plasmon excitation intensity dependences of the fluorescence enhancement factors for nonresonant (green circle) and resonant (red circles) nanospheres. The enhancement factor is proportional to the number of trapped particles. (d) Calculated radiation force exerted on the resonant nanospheres divided by that on the nonresonant nanospheres in the z direction. Reprinted with permission from 51. Copyright 2012 The Japan Society of Applied Physics.

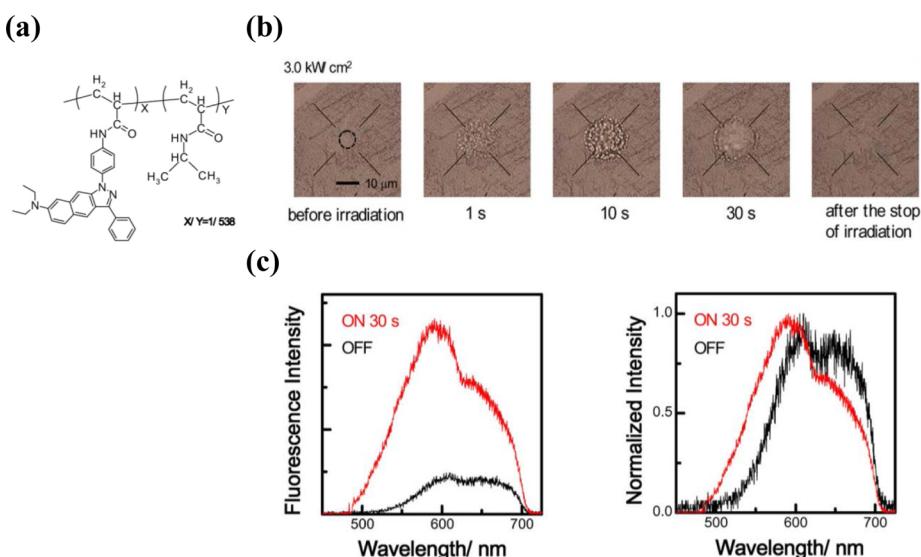


Figure 5. (a) Chemical structure of the polymer chain used as a trapping target. (b) Optical micrographs of the polymer assembly trapped using plasmon excitation (3.0 kW/cm^2). The circles shown by dotted lines correspond to the plasmon excitation area. (c) Spectral changes in the fluorescence upon plasmon excitation (3.0 kW/cm^2). The right-hand panel shows the normalized spectra of those shown in the left-hand panel (black and red lines show spectra before and upon plasmon excitation, respectively). Reprinted with permission from 65. Copyright 2013 American Chemical Society.

optical trapping (left panel in the figure). In the normalized spectra (right panel), we noticed the blue-shift of the fluorescence upon POT with plasmon excitation at 3.0 kW/cm^2 . It should be noted here that such a blue shift was not observed during POT at 1.0 kW/cm^2 (see the literature in detail⁶⁵), implying that plasmon excitation at 3.0 kW/cm^2 gives

rise to thermoresponsive phase separation. This phase separation is due to the photothermal effect, which is an important issue currently for POT, which we discuss below in more detail. These results strongly suggest that aggregates of the polymer from the phase separation are optically trapped

with great efficiency because the radiation force is proportional to the size of the target particle (eq 1).

On the other hand, the characteristic trapping behavior of DNA clearly differs from that of polymer chains (Figure 6a).⁶⁸

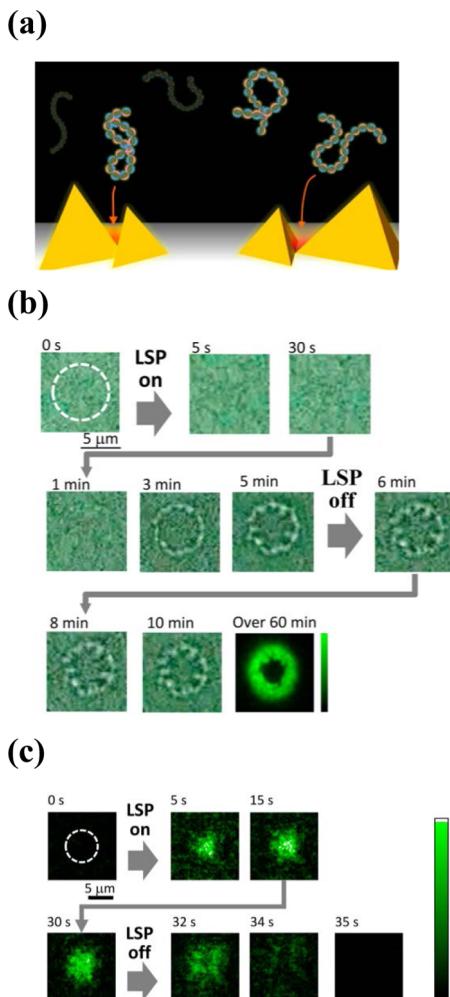


Figure 6. (a) Schematic illustration of plasmonic optical tweezers for DNA. (b) Micrographs of fixed micropatterns of DNA on a plasmonic gold substrate using near-infrared cw laser irradiation. (c) Fluorescence micrographs of a DNA assembly on a plasmonic gold substrate using NIR fs laser irradiation. Reprinted with permission from 68. Copyright 2013 American Chemical Society.

Figure 6b shows micrographs of POT of fluorescent-labeled λ -DNA with a cw near-infrared laser. At first glance, the cw laser irradiation has led to the formation of a “micro-ring” pattern on the plasmonic substrate. This result suggests that a repulsive force competing with the radiation force is related to the formation of the microring. We ascribed this repulsive force to thermophoresis due to a photothermal effect, which we also describe below. What is interesting here is that the microring remained even after stopping the plasmon excitation, leading to permanent fixing of the DNA on the plasmonic substrate. We consider that the origin of this fixing can be ascribed to the Coulomb interaction between the DNA and the surface charge on the substrate. On the other hand, we discovered that fs laser excitation results in trap-and-release of the DNA without such fixing. Upon plasmon excitation with the fs laser, a micro-assembly was formed on the plasmonic substrate (Figure 6c).

Stopping the fs laser irradiation led to the release of the trapped DNA molecules. Note that these results were obtained at the same laser intensity (time-averaged) as used in the cw laser light experiment (Figure 7b). Such trap-and-release of the DNA would be due to the strong radiation force generated by the fs laser pulse. Thus, we demonstrated that the POT behavior of DNA could be controlled by switching the plasmon excitation between cw and fs lasers. Permanent fixing of the DNA by a cw laser can potentially be applied to the fabrication of DNA array chips on plasmonic nanostructures. POT of DNA with a fs laser will open new channels for efficient trapping methods of not only nucleic acids but also other biomolecules and smaller molecules.

POT of DNA with a fs laser will open new channels for efficient trapping methods of not only nucleic acids but also other biomolecules and smaller molecules.

We have discussed POT of protein, polymer chains, and DNA. These flexible nanomaterials can be trapped with weaker laser intensities than used for conventional optical tweezers because of the EM enhancement effect of plasmon. However, as shown by the phase separation of trapped thermoresponsive polymer chains (Figure 5b) and the formation of microrings of DNA (Figure 6b), another effect differed from the radiation force seems to work in POT: the photothermal effect. In the next section, we will discuss the photothermal effect, which is worth investigating in order to reveal the overall mechanism of POT.

Photothermal Effect in POT. In order to carry out molecular manipulation with POT, a strong light intensity for plasmon excitation is required because the radiation force decreases considerably with the size of the trapping target ($F_{\text{rad}} \propto a^3$ in eq 1). However, a photothermal effect also takes place upon plasmon excitation owing to lattice relaxation of the metal.^{69,70} Such photothermal effects have recently been discussed in POT studies.^{71–75} We experimentally examined the rise in temperature, ΔT , in close proximity to a plasmonic nanostructure using fluorescence correlation spectroscopy.⁷⁶ We determined ΔT to be 7–9 K for cw and fs near-infrared laser irradiation at 1.0 kW/cm².^{65,68} Such a temperature rise generates a huge temperature gradient on the microscale ($\sim 10^5$ K/m), causing thermophoresis (thermodiffusion or the Ludwig-Soret effect) and thermal convection. Thermophoresis moves particles along a temperature gradient.^{77–80} The direction of transport in thermophoresis depends on the material. Many materials such as polymer nanospheres move from hotter to colder regions.⁸¹ This means that the direction due to thermophoresis is opposite that due to the radiation force. Thus, it acts as a repulsive (exclusive) force. We showed that the strength of the thermal force is comparable to the radiation force in POT.⁸² As a result of a rise in the local temperature, thermal convection is also involved in plasmon excitation. We made real-time observations of the transport of polystyrene nanospheres induced by thermal convection (see the movie in the Supporting Information of the literature⁸²). Upon plasmon excitation, the spheres approached the irradiation area from outside with a velocity of $\sim 5 \mu\text{m s}^{-1}$. The thermal convection

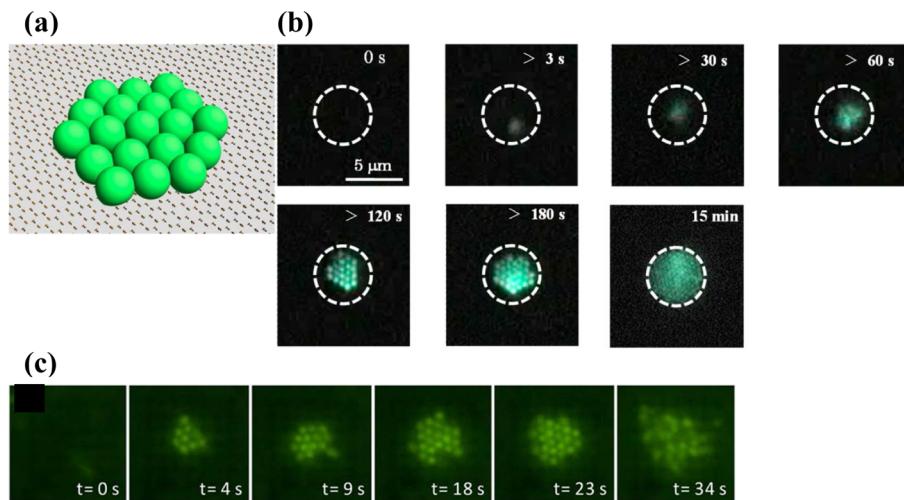


Figure 7. (a) Schematic illustration of a 2D closely packed assembly of 500 nm diameter polystyrene nanospheres trapped on a plasmonic nanostructure. (b) Fluorescent micrographs of a closely packed assembly of nanospheres on gold nanopymidal dimer arrays. The circles shown by the white dotted lines correspond to the plasmon excitation area. Reprinted with permission from 82. Copyright 2012 American Chemical Society. (c) Fluorescent micrographs of 500 nm diameter polystyrene nanospheres on four gold nanodisk arrays. Reprinted with permission from 85. Copyright 2013 American Chemical Society.

assisted the supply of polystyrene nanospheres toward the irradiation area. Without such thermal convection, it takes a longer time to trap a particle at the gap (we have to wait until the particle comes across the gap by natural diffusion). In order to conduct POT, we must control not only the radiation force but also the thermophoresis and thermal convection. Effects of thermophoresis and thermal convection on POT system should be further discussed together with plasmon-enhanced radiation force. In 2014, Roxworthy et al. theoretically predicted fluid convection induced by local heating due to photothermal effect and also experimentally observed such a fluid convection ($>1 \mu\text{m s}^{-1}$) on plasmonic arrays fabricated on an indium–tin oxide (ITO) substrate.⁷⁵ They pointed out that the fluid convection in the POT system was rarely due to Rayleigh–Bérnard convection, which was mistakenly referred in POT studies. Although the POT system coupled with photothermal effect still remains unclear, it would have fascinating physical phenomena.

To suppress the photothermal effects, two approaches have been proposed; (1) fabricating a plasmonic nanostructure on a heat sink^{23,83} and (2) decreasing the number of plasmonic nanostructures in the illumination area.⁷¹ K. Wang et al. fabricated plasmonic gold nanopillars on a copper heat sink for POT of polystyrene nanospheres.²³ Theoretical simulations indicate that the rise in temperature with the nanopillars on the heat sink in water (50 K at 10 MW/cm²) is a 100 times less than that with gold nanopillars on a glass substrate (49 K at 0.1 MW/cm²) because the thermal conductivity of copper is higher than that of water. By controlling the photothermal effects as well as the radiation force, we discovered the formation of a 2D-closely packed assembly of polystyrene nanospheres (Figure 7a)⁸² and a microring pattern of DNA on plasmonic substrates (Figure 6b).⁶⁸ Figure 7a shows fluorescence micrographs of the 2D-closely packed assembly of fluorescent polystyrene nanospheres ($d = 500 \text{ nm}$) trapped inside the plasmon excitation area. What is important here is that self-organization of the nanospheres proceeds automatically with POT. This trapping behavior of 500 nm polystyrene nanospheres was also observed for other plasmonic substrate.^{84,85}

Following our work, Chen et al. also demonstrated such 2D-closely packed assembly on array of four gold nanodisks (Figure 7b).⁸⁵ This effect possibly plays a key role in creating 2D colloidal crystals on plasmonic nanostructures. As mentioned above, the photothermal effects should be taken into account in explaining the mechanism for POT. We expect that new trapping behavior will be discovered on the basis of the radiation force combined with the photothermal effects.

As mentioned above, the photothermal effects should be taken into account in explaining the mechanism for POT.

Future Outlook of POT. For the conclusion to this Perspective, we describe briefly the future direction of POT. In the vicinity of active plasmonic sites, nanoparticles can be efficiently trapped using weaker laser intensities in comparison with conventional optical tweezers. The motion of the trapped nanoparticles can be precisely controlled on the nanoscale depending on the size of active plasmonic site. In this Perspective, we highlighted the recent developments and the advantages of POT; (i) POT on chiral plasmonic structures, (ii) POT with a fs pulsed laser, and (iii) resonant POT. We expect that the manipulation of extremely small molecules will soon be established. In pioneering work toward such molecular manipulation, POT of proteins, polymer chains, and DNA was discussed. These demonstrations provide future prospects for the application of POT combined with conventional plasmonic applications. For instance, because plasmonic nanostructures are used as highly sensitive chemical and biological sensors, POT of analyte molecules will make a significant contribution to high-throughput, highly sensitive plasmonic sensors. In another application, plasmonic photochemical reactions will proceed efficiently using POT of photosensitized molecules or photocatalysts. However, understanding the mechanism of POT is complicated because of the photothermal effects that accompany the plasmon excitation. Experimental and theoret-

cal studies on thermal convection and thermophoresis at the micro- and nanoscales are beginning to overcome this significant challenge, suggesting that control of these effects will enable us to bring about self-organization of 2D colloidal crystals and microassembly of polymer chains and DNA. These investigations will provide us with more insight into the fundamental mechanism of POT and give us inspiration for further POT applications. We anticipate the future applications of POT to be the crystallization of proteins, the sorting of chiral molecules, the transport of single molecules, and so forth. We believe that plasmonic optical tweezers will become an indispensable tool for manipulating nanoparticles and molecules in the same way that conventional optical tweezers have been proven to be a valuable micromanipulation tool.

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