Dynamic Coupling of Optically Evolved Assembling and Swarming of Gold Nanoparticles with Photothermal Local Phase Separation of Polymer Solution

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ABSTRACT: Optical trapping of gold nanoparticles (Au NPs) at a glass/solution interface initially generates a periodically aligned structure of a few NPs along the direction perpendicular to a linearly polarized laser. When the number of NPs was increased, this alignment was expanded to the outside of the irradiated focus, forming a single large assembly where the Au NPs dynamically fluctuated like a swarming of bees. The morphology was dumbbell-shape, consisting of two swarms at both sides of the focus, and its size reached about 10 μm . This optically evolved assembling and swarming was studied in poly(*N*-isopropylacrylamide) (PNIPAM) solution, where liquid–liquid phase separation (LLPS) was induced by photothermal heating of the trapped Au NPs forming a microdroplet of highly concentrated PNIPAM. Dynamic coupling of the NPs assembling and swarming with the droplet formation of PNIPAM leads to cooperative optical evolution, through which the assembly was embedded in the single microdroplet.

1. INTRODUCTION

In 1986, Ashkin and co-workers proposed the use of tightly focused laser beams to manipulate individual microscale objects such as polymer spheres.^{1,2} They used the focused laser beams as optical tweezers and applied them to move single living cells, viruses, and bacteria.^{3,4} In solution, various micro-objects are optically trapped at the focal spot and they can be three-dimensionally transferred in a nondestructive way. Since then, the target of optical trapping has been downsized to various nanoscale objects^{5,6} including amino acids,⁷ lipid vesicles,^{8,9} supramolecules,^{10,11} polymer,¹² single-walled carbon nanotubes,¹³ nanostructures,¹⁴ and metal nanoparticles (NPs).¹⁵ In bulk solution, they form a single assembly, which size is initially close to the focal volume of the trapping laser (from sub μm^3 to few μm^3). Once the optical potential is fully occupied, further nanoscale objects cannot usually be captured and are pushed away from the focal spot by the induced scattering force.

The trapping behavior is different when the nanoscale objects are trapped at air/liquid,^{16,17} liquid/liquid,¹⁸ and solid/liquid^{19,20} interfaces. Assembling, orientation, and diffusion properties of molecules, polymers, and NPs at interfaces are different from those in bulk solution due to the surface tension, convection, and microscopic interaction between the two phases. Our group has been demonstrating the important role of the interface in optical trapping by exploring new trapping phenomena which only occur at the interface.^{16,19} Briefly, small nanoscale objects could be trapped, pushed to the interface by

the scattering force of the trapping laser, and stably immobilized there. The accumulation of multiple objects leads to the formation of a single assembly, which is extended from the focus to the outside. This phenomenon is made possible because the trapping laser is scattered, propagated, and interfered through the assembly, forming an attractive potential at the edge of the assembly. Then the assembly grows further by trapping the newly incoming objects at its edge, and the trapping laser further is extended to the new edge. This idea was clearly demonstrated and proven by performing systematic studies on optical trapping of polystyrene (PS) NPs at a solution surface and solution/glass interface. We reported microspectroscopic studies on PS NPs with a diameter of 200 nm and elucidated their optically evolved assembly formation at a solution surface.^{21,22} In the case of PS NPs with a diameter of 500 nm, their optically trapped and periodically arranged assembly is coupled with hornlike arrays of linearly aligned NPs, which extends from the edges of the assembly.¹⁹ The horn formation was only found at the solution/glass interface,

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Figure 1. (a) Chemical structure of PNIPAM and illustration of its conformational structure. (b) Sample chamber sandwiched by two glass substrates. Laser focus point is at the solution/glass interface. (c) Experimental setup for the optical trapping of Au NPs.

and it is reported as a direct indication of the trapping laser propagation.

The aforementioned optical scattering and propagation mechanism giving a single large assembly can be applied not only to PS NPs but also to molecular crystallization by optical trapping. Amino acids¹⁶ such as glycine, L-proline, L-threonine, and L-phenylalanine as well as inorganic molecules of KCl²³ can be crystallized even for unsaturated solutions at the air/solution interface upon 1064 nm laser irradiation. The generated crystal is much larger than the focused beam size, typically reaching a few tens of square micrometers. L-Phenylalanine crystallization is a representative example, on which we have pointed out the contribution of propagation of the trapping laser through the prepared crystal itself.²⁴

Recently, we have been extending these experiments to gold (Au) NPs and we have found a quite new phenomenon characteristic of their inherent surface plasmon resonance.²⁵ Initially, some Au NPs are trapped at the focal spot and they can efficiently scatter the trapping laser light. In the case of the linearly polarized (LP) laser irradiation, dipolar scattering of Au NPs renders light distribution which is perpendicular to the direction of the laser polarization. As a result, few Au NPs shows a linear and periodical arrangement which works like a Yagi-Uda antenna. The scattered light gives an expanded optical potential which can collect more Au NPs at both sides of the assembly outside the focal spot. Therefore, a dumbbell-shaped assembly of (about 5) × (about 10) μm² is prepared along the interface, where Au NPs dynamically fluctuate as bees in a swarm. In the case of circularly polarized (CP) laser irradiation, the trapping laser is expanded to all directions and then the formation of a circle-shaped swarming assembly is observed instead of the dumbbell-shaped one. This new optical trapping phenomenon of assembling and swarming of Au NPs and its laser-polarization dependence have received much attention in the research fields of optical manipulation,

plasmonics, NP dynamics, microfluidics, colloid and interface science, among other fields.

Now, in our laboratory, the assembling and swarming phenomenon of Au NPs is systematically studied to obtain comprehensive understanding from different viewpoints such as optical force, light scattering and propagation, optical binding, surface plasmon resonance, photothermal heating, and photothermal convection. Indeed, heating and convection induced by the laser irradiation of Au NPs are extensively studied widely,^{26,27} and these modes should be involved in the present assembling and swarming phenomena. Thus, how the dumbbell-shaped swarming depends on the heating and convection caused by the irradiated Au NPs is one important and necessary issue. Briefly, a first NP is trapped at the focal center, two NPs form a pair of a certain discrete interparticle distance and with its orientation perpendicular to the LP laser, and then three NPs align similarly. The further incoming NPs are pushed out from the focus to the outside, leading to the expanded morphology. It is worth noting that the NPs do not flow out and stay inside the swarms, indicating an interesting confinement behavior.

Here we report a specially designed experiment where a thermoresponsive polymer, PNIPAM, is added. This polymer is soluble in water, when its random coil conformation forms stable hydrogen bonds with water (Figure 1a). If the solution temperature is elevated above its lower critical solution temperature (LCST, 32 °C), the hydrogen bonds with water are broken and its conformation is changed to globular (Figure 1a).^{28,29} PNIPAM globule conformation is hydrophobic, and the different polymer chains associate with each other. Then, liquid–liquid phase separation (LLPS) is induced when its concentration is high. Indeed, if the temperature is locally elevated, which is possible by irradiating Au NPs under a microscope, LLPS can be induced in a small domain to produce a highly concentrated PNIPAM microdroplet. This was already demonstrated by one of the authors (I.A.).^{30,31} In

Figure 2. Light scattering images of Au NPs ($d = 200$ nm) assembling and swarming induced by LP laser irradiation at the solution/glass interface (a) in water, (b) in EG (18.8% w/w), and (c) in PVA (1.75% w/w). Laser power density is 3.4 MW cm^{-2} .

the present experiment, the 1064 nm laser irradiation traps Au NPs and also forms a single PNIPAM droplet. Trapping, local heating, and local LLPS are developed simultaneously, being coupled with each other. The observation and analysis of such dynamically evolving processes give the information on the morphology and size of the swarms and assembly. Optically evolved assembly and swarming of Au NPs and photothermally evolved LLPS cooperatively proceed, for which dynamics is elucidated here as physicochemical processes in the optical manipulation of molecular and NP systems.

2. EXPERIMENTAL SECTION

2.1. Materials and Sample Preparation. All the materials used in this work are commercially available. The average diameters of Au NPs (BBI Solutions) and PS NPs (PolyScience) are 200 and 500 nm, respectively. The Au NPs and PS NPs were diluted to a concentration of 1.4×10^8 particles μL^{-1} in the different aqueous (distilled water) solutions without and with PNIPAM (International Laboratory, $M_n = 300\,000$), ethylene glycol (EG; Sigma-Aldrich Co.) or poly(vinyl alcohol) (PVA; Wako Chemical Co.). The solutions were sonicated for 10 min, and 20 μL of each solution was poured into a 100 μm thick chamber (Electron Microscopy Science) glued between two clean coverslips (Figure 1b). The coverslips were cleaned by immersing them in a 5% detergent solution (Hellmanex III, Hellma) for 12 h.

2.2. Optical Setup for Laser Trapping and Light Scattering Microspectroscopy. All the experiments of this work were performed using an inverted dark-field microscope (Figure 1c); Nikon, ECLIPSE Ti). A 1064 nm continuous wave laser was focused at the upper glass/solution interface through an air-immersion objective lens (60 $\times$; NA 0.95; Nikon; MRD00605). The trapping laser power density was adjusted to 3.4 MW cm^{-2} after the objective lens using a half or quarter wavelength plate combined with a polarizer. Our trapping and swarming behavior was well induced and clearly observed at this power density, while the Au NPs were adhered or not enough Au NPs were collected if the power was higher or lower, respectively. A half and a quarter wavelength plates

were used for generating LP and CP lasers, respectively. A halogen lamp was used as a light source for illuminating the sample through an oil-immersion dark-field condenser lens (NA 1.2–1.4; Olympus). The scattered light from the Au NPs was collected through the objective lens, and the backscattered light of the 1064 nm trapping laser was removed with a 1010 nm short pass filter (Semrock, FF01-1010/SP-25). A CCD camera (jAi CV-S3200, 30 frames per second) was used for imaging, and another CCD camera (Andor, DU401A-BR-DD) coupled with a polychromator (Andor, SR-303i-A) was used for recording the light scattering spectra of Au NPs. For obtaining the scattering light signal around the focal spot, a pinhole (diameter of 300 μm) was inserted into the optical path to achieve a confocal system. The effective confocal diameter was simply estimated to be 5 μm (300 μm pinhole/60 $\times$ magnification). The experimental room temperature was set to 25 ± 1 $^\circ\text{C}$.

3. RESULTS AND DISCUSSION

3.1. Trapping and Swarming of Au NPs with EG and PVA. Upon focusing the 1064 nm LP laser at the upper glass/water interface, we observed the Au NPs assembly formation in water (Figure 2a). We used a dark-field microscope to image the water/glass interface, and we observed the monitoring light from the halogen lamp scattered by the Au NPs. Consequently, these NPs appeared bright in the images in the dark background. Upon using the LP trapping laser, a few Au NPs were initially arranged perpendicular to the laser polarization. We have already reported that the Au NPs were also aligned parallel to the linear polarization in our previous study,^{2,5} which is again observed in the present work (see, for example, Figure 2a,iv). In Figure 2a, the Au NPs are first aligned perpendicular to the linear polarization, and then they are grown parallel to the linear polarization. Parallel and perpendicular alignments relative to linear polarization are caused by optical binding in a near-field and a far-field region, respectively.³² Optical binding in the near-field can be simply understood by the analogy of electrostatic dipole–dipole interaction like the head-to-tail configuration of J-aggregates.

Figure 3. Light scattering images of Au NPs ($d = 200$ nm) assembling and swarming induced by LP laser irradiation at the solution/glass interface in PNIPAM solution of (a) 0.01% w/w, (b) 0.1% w/w, and (c) 1.0% w/w. (d) Light scattering images of Au NPs swarms or assembly formed by 3 min LP laser irradiation at the solution/glass interface in PNIPAM solution. Concentration: (i) 0% w/w, (ii) 0.01% w/w, (iii) 0.03% w/w, (iv) 0.1% w/w, (v) 0.33% w/w, and (vi) 1.0% w/w. (e) Swarm or assembly size of Au NPs as a function of PNIPAM concentration. Black and red represent the length along the x - and y -directions, respectively. Laser power density is 3.4 MW cm^{-2} .

When the light scattering intensity is high like the case of the Au NPs we used in our study, they are aligned perpendicular to the linear polarization due to the particle–particle interaction through light scattering. This is called optical binding in the far-field region, which is the key driving force leading to the evolution of swarming. Then, more Au NPs gathered around the focus, and finally an expanded dumbbell-shaped assembly was formed outside the focal spot.

In the case of the CP laser, a single assembly was generated and evolved similarly. However, the initial gathering and later swarming gave spherical shapes (see Figure S1). It is notable that both swarming assemblies expand from the focal spot to the outside and their size reaches a few $\sim$ ten μm , although the focused trapping laser beam size was approximately only $1.5 \mu\text{m}$. All the results showed here are equivalent with what we reported previously.²⁵ In this work we have studied how assembling and swarming were modified and Au NPs were confined inside a PNIPAM microdroplet by using LP trapping laser. We did not extend the study with CP laser, because the morphology change is not clearly identified and only a sphere shape is observed for each case (see Figure S1).

We first examined the assembling and swarming by adding EG or PVA as a control reference in terms of viscosity of the additive effect of PNIPAM. The concentration of EG³³ and PVA³⁴ was set to 18.8% w/w and 1.75% w/w, respectively, which has the same viscosity as that of the 1.0% w/w PNIPAM solution.³⁵ This viscosity is 1.4 times higher than that of aqueous solution. As shown in Figure 2, all three different solutions (neat water, 18.8% w/w EG, and 1.75% w/w PVA) showed the formation of swarming assemblies. Furthermore, the characteristic behavior of the Au NPs moving between two swarms was also clearly observed (see Video S1). In the case of the EG solution, the development was even faster compared to aqueous solution and two large swarms were obtained outside the focus as shown in Figure 2b. Compared to the aqueous solution, the dumbbell-shape swarming of Au NPs looked more enhanced. In the case of the PVA solution shown in Figure 2c, the assembly formation took place in the same time scale as in the aqueous solution, and we could confirm that a few Au NPs were periodically arranged at the initial stages. Afterward, when several Au NPs started to join the swarming assembly, its morphology was similar and its size was a little bit smaller compared to the aqueous solution. This means that the

ejection of the NPs from the focus due to the pushing scattering force was hampered and the expansion of the swarming was reduced.

EG and PVA are known as representative molecules to tune the viscosity in aqueous solution, while they may change the refractive index of the solution leading to different optical force. Fortunately, it is confirmed that refractive index of the resultant solutions is similar for the both additives. Referring the reported indices,^{36,37} we estimate that the refractive index for the solutions of EG (18% w/w) and PVA (1.0% w/w) is 1.351 and 1.361, respectively. Thus, the optical force loaded on the NPs is considered to be similar in both solutions. While EG is a small molecule ($C_2H_6O_2$), PVA is along polymer ($(C_2H_4O)_n$; $n = 500$), which leads to big difference in their microscopic interaction with the Au NPs. As a result, the swarming morphology may be modified. Although the real reason is beyond our current knowledge, the addition of EG or PVA to the solution increases the solution viscosity to the same value of the 1.0% w/w PNIPAM solution and does not change the assembling and swarming capabilities of trapped Au NPs, and their oscillatory behavior to move between the right and left swarms is also retained. The results in Figure 2 show that the EG and PVA cases are a good reference for the following study of the PNIPAM solutions.

3.2. Trapping and Swarming of Au NPs with PNIPAM.

When we added PNIPAM into the solution, the gathering and swarming behavior of Au NPs was modified depending on the PNIPAM concentration and trapping laser polarization (see Video S2). The results for the 0.01% w/w PNIPAM solution are shown in Figure 3a. Initially a small aggregate of Au NPs was observed, later a few Au NPs gave a periodical pattern similar to that without PNIPAM at 1 min, and finally the swarming was attained. After switching off the laser, the NPs disappeared, and no light scattering was detected at 2 min later. This behavior is almost similar to that of the aqueous solution without PNIPAM. In Figure 3(b), the assembling and swarming phenomenon is shown for the case of 0.1% w/w PNIPAM concentration. Initially a periodical structure was formed, and the number of trapped NPs increased with the irradiation time. However, the swarming shape of the assembly was not like a dumbbell anymore. The horizontal and vertical (x - and y -axes in the images, respectively) lengths of the swarming assembly were shortened and enlarged, respectively. Namely, the assembly shrunk along its x -axis and elongated along the y -axis. As the swarming morphology is dumbbell-shaped for the homogeneous aqueous solution, we consider that the elongation of the swarming along the x -axis is suppressed while that along the y -axis is assisted.

It is surprising to see in Figure 3c that the swarming morphology has completely changed from the dumbbell-shaped to circular structures when the concentration of PNIPAM was increased to 1.0% w/w. Although the viscosity of this solution is same as that of the above solutions with PVA and EG, and 1.4 times higher than that of the aqueous solution, a completely different behavior was observed. The trapping of Au NPs was initially slower compared to the other solutions, the first NP was only detected after 44 s, and the incoming following NPs gave a circular shape assembly. The dumbbell-shaped morphology was not observed anymore, which suggests that the initial periodical alignment of the NPs was not attained. We have considered that the dumbbell-shaped swarming evolves from the periodical pattern through dipolar scattering of the trapping laser and is observed when

the gathering NPs are ejected along the direction perpendicular to the laser polarization. Indeed, we cannot find the periodical pattern at any stage; instead, the Au NPs were arranged in a circle as depicted at in Figure 3c, iv–vi for longer irradiation times (1–3 min). Thus, the Au NPs may be aggregated from the very initial stage and scatter the trapping laser light in various directions. It is important to note that the periodical arrangement was never observed, the Au NPs were embedded in a circle-shape, and the assembly size grew for the 1.0% w/w PNIPAM solution.

It is well-known that laser irradiation of the Au NPs results in photothermal heating and therefore elevated local temperature.^{38–40} The present laser trapping of Au NPs may result in temperature elevation above 32 °C, enabling the local domain of highly concentrated PNIPAM to undergo LLPS.^{26,27} Indeed, one of the authors (I.A.) published that 488 nm laser irradiation of a single Au NP on a glass substrate induced local heating and generated a convection flow in a PNIPAM solution.^{30,31} The gathered PNIPAM is accumulated near the Au NPs leading to LLPS, which results in the formation of a single microdroplet where PNIPAM is more concentrated. Thus, one explanation for the present interesting behavior is that the microdroplet of highly concentrated PNIPAM is prepared by photothermal heating of trapped Au NPs. Then, when the microdroplet is formed, the incoming Au NPs are embedded there. To confirm this possibility, we carried out a similar experiment where Au NPs were replaced by PS NPs of 500 nm diameter. We have chosen this particle size, as the individual PS NPs can be visually detected. The PS NPs were collected inside and around the focus at the glass/solution interface, generating a circular assembly as we previously reported.¹⁹ No dipolar scattering was observed, and no large morphology change was obtained for aqueous and 1.0% w/w PNIPAM solutions (Figure S2). Therefore, the spherically aggregated Au NPs observed in the 1.0% w/w PNIPAM solution are characteristic of optically trapped and thermally heated Au NPs.

Based on above presented results, we here propose for the 1.0% w/w PNIPAM solution that LLPS is induced due to local heating by the irradiation of the trapped NPs in parallel with the gathering of the Au NPs. For the lower concentration of 0.1% w/w of Figure 3b, while some Au NPs were ejected to a long distance, the ejection of others was hampered and/or their ejection directions were curved, which changes the shape of the generated swarming assembly. We consider that, although the LLPS took place, the prepared PNIPAM droplet is not concentrated enough to create a large droplet. Instead, we suppose that the formation of a distribution of multiple liquid-like clusters of PNIPAM gives a less viscous environment compared to the microdroplet. For the higher concentration of 1.0% w/w, a single droplet can be formed at an earlier stage due to local heating by the initially trapped Au NPs. PNIPAM can be quickly and efficiently collected and LLPS should be induced soon around the focal spot, leading to the formation of a single microdroplet. The prepared droplet should be sphere-like shaped due to surface tension, and the gathered and trapped Au NPs would be embedded inside the droplet. This interpretation is in fully agreement with the phenomenon observed in the images of Figure 3c, v and vi.

In order to unravel the PNIPAM concentration effect on the swarming and assembling in more detail, the images obtained after 3 min irradiation for six different PNIPAM concentrations (0–1.0% w/w) are summarized in Figure 3d. Their shape

Figure 4. Light scattering images of Au NPs ($d = 200$ nm) assembly formed by LP laser irradiation in a PNIPAM solution of 1.0% w/w. Laser power density is 3.4 MW cm^{-2} . The assembly rotates counterclockwise at 63–65 s after switching on the laser, which is made clear by coloring the same NPs in sequential images with blue, red, and yellow color.

Figure 5. Sample cell for simulation of the 2D temperature distribution and rough sketch of the obtained convective velocity (a). The 2D temperature distribution in water for (b) a single Au NP ($d = 200$ nm), (c) three Au NPs ($d = 200$ nm), and (d) five Au NPs ($d = 200$ nm). The black line in (c) and (d) represents 305 K in the temperature distribution. (e) Enlarged figure of the simulated 2D convective velocity for 5 Au NPs ($d = 200$ nm) in water.

changed with the increase of PNIPAM concentration, and the length of the assembly along the x - and y -axes obtained from Figure 3d are plotted in Figure 3e. When the PNIPAM concentration was 0.01% w/w, linearly long swarms along the x -direction were observed. Increasing the PNIPAM concentration, the length of the swarms along the x -axis decreased gradually, while an increase was observed for the y -axis. This

trend is clearly shown by plotting the ratio of both lengths as a function of PNIPAM concentration (see Figure S3). For the highest concentrated PNIPAM solution of 1.0% w/w, the ejection of Au NPs perpendicular to the direction of the LP laser is suppressed and the NPs are kept inside the microdroplet.

A more direct confirmation of the droplet formation and rigid arrangement of the NPs inside the droplet was demonstrated in Figure 4. The swarming is in principle dynamic and the Au NPs are fluctuating and exchanging their relative position while keeping its global morphology. This behavior was clearly observed in neat water and solutions with EG and PVA and with 0.01% w/w PNIPAM, although the Au NPs move at different speeds under each condition. However, a completely different behavior was observed for the 1.0% w/w PNIPAM solution. Instead of the dumbbell-shaped morphology, a spherelike assembly was prepared as described above, where the fluctuating movement of the Au NPs was completely stopped. Representative sequential temporal images are shown in Figure 4, indicating that the relative position of the Au NPs was fixed and the NPs embedded inside the microdroplet underwent a rotational movement. This result was accidentally observed for the period of 63–65 s after switching on the laser irradiation. It is concluded that the Au NPs were not adhered on the upper glass substrate but embedded in a rigid medium, that is, in the microdroplet showing the rotation. This observation strongly supports our consideration that a microdroplet with a high concentration of PNIPAM is formed and grows around the focus and there the NPs are embedded. One may consider that the rigid medium is an amorphous solid when the water molecules are expelled from the matrix or a kind of gel that still contains water molecules to some extent. The rigidity of the gel depends on the water concentration. In our case, the Au NPs in the 1.0% w/w PNIPAM solution are embedded in a clearly identified round shape. If precipitation of PNIPAM gives the amorphous solid, the generated aggregate may not be so round and with some inhomogeneities inside. In the images of Figures 3c,d and 4, the aggregate appears transparent and spherical, which supports our idea “microdroplet”.

3.3. Numerical Simulation of Temperature Elevation and Thermal Convection Induced by Trapping of Au NPs. The temperature elevation is critical to understand the present trapping and assembling of Au NPs. The focused beam sequentially traps the Au NPs and forms their swarms, where the NPs are locally heated. Then, the thermal convection starts, collects PNIPAM, and induces its LLPS. All these processes of trapping and heating are dynamically coupled with each other. This temporal evolution is too complex, and its analysis is out of the scope of this work. Thus, we assume photostationary states, which are attained after a while for one, three, and five Au NPs. We calculated temperature distribution around single or linearly aligned Au NPs in the trap by numerical simulation in a way similar to that of our previously reported work,^{30,31} which was carried out with a commercial finite-element mode solver, COMSOL Multiphysics ver. 5.4 (<http://www.comsol.com>). The following heat equation of thermal conduction was applied to estimate the temperature elevation and induced convection flow.

$$\nabla \cdot (-k \nabla T + \rho C_p T \mathbf{u}) = Q \quad (1)$$

where k , T , ρ , C_p , $\mathbf{u}$, and Q represent the thermal conductivity, the temperature, the density of the solution, the heat capacity of the solution, the flow speed vector, and the heat source, respectively. Q is given in eq 2 as shown below:

$$Q = C_{\text{abs}} I / V \quad (2)$$

where C_{abs} , I , and V are the absorption cross section of the Au NP at 1064 nm, the laser power density, and the volume of the Au NP as the heat source, respectively. The absorption cross section of Au NPs of 200 nm diameter was estimated as $1.64 \times 10^{-15} \text{ m}^2$ at 1064 nm based on Mie theory. The refractive index of the surrounding medium and glass substrate is $n = 1.33$ and 1.52 , respectively. We considered that the addition of 1.0% w/w PNIPAM does not significantly change the thermal/optical properties in comparison to neat water. Temperature-dependent physical properties of the surrounding medium such as thermal conductivity, viscosity, heat capacity, and density were obtained by COMSOL. The 2D configuration of a model cell is shown in Figure 5a where the thickness and width of the solution are $100 \mu\text{m}$ and 1 mm , respectively. The thickness of the glass coverslips was set to $170 \mu\text{m}$. This model is the closest possible to that of our experimental sample cell with relatively low time computing requirements.

The temperature of our experiment room was set to 298 K, while the temperature elevation is always expected during the intense 1064 nm laser irradiation, which is due to the absorption by water. According to the empirical rule reported by Ito et al.,⁴¹ the temperature elevation was estimated to be approximately 2 K. Thus, the temperature distribution in the simulation model was assumed to be uniform and equal to 300 K, and the convective velocity of the fluid was set to zero. The excitation wavelength is 1064 nm and the irradiation laser power density is set to 3.4 MW cm^{-2} based on our experiment. The laser power density I is calculated using following equation:

$$I = \frac{2P}{\pi w^2} \quad (3)$$

where P (laser power) is 30 mW and w (radius of laser spot) is $0.75 \mu\text{m}$. The laser is assumed to homogeneously excite all Au NPs. The thermal conductivities of the Au NP, surrounding medium, and glass substrate are 318, 0.60, and $1.0 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. Interparticle center-to-center distance is assumed to be 250 nm, because the calculation is performed for individual NPs.

Figure 5b shows the temperature distribution for a single trapped Au NP. When one Au NP of 200 nm diameter was irradiated by the 1064 nm laser of 3.4 MW cm^{-2} , the temperature of the NP was calculated to be 306 K. Namely, the temperature of the Au NP itself is slightly above 305 K (32°C) which is the LCST of PNIPAM. The LLPS of PNIPAM can be induced only near the single NP. Figure 5c and d shows the temperature distribution for three and five trapped Au NPs, respectively. The temperature at the center of the trapped Au NPs is 316 and 325 K, respectively, and the diameter of the area, where the temperature is above 305 K, is approximately, 40 and $100 \mu\text{m}$, respectively. PNIPAM can undergo phase transition in these regions, which is much broader than the laser focus (approximately $1.5 \mu\text{m}$ diameter). This consideration corresponds well to our experiment shown in Figure 3c,iii–iv, where the number of trapped Au NPs is 2–6 and their spherelike arrangement is observed instead of the periodical alignment. Further incorporation of NPs from the outside is relatively slow because of the phase transition. Then, upon arrival, they are immediately embedded in the central droplet and accelerate the temperature elevation. Both processes of capturing of the NPs and temperature elevation are coupled with each other and nonlinearly accelerated to form a single droplet.

Figure 6. Light scattering images of Au NP ($d = 200$ nm) swarms or assembly disappearing after blocking LP laser irradiation (a) in water, (b) in EG solution of 18.8% w/w, and in PNIPAM solution of (c) 0.01 % w/w, (d) 0.1% w/w, and (e) 1.0% w/w. (f) Disappearance dynamics estimated from the light scattering intensity of Au NPs as a function of time. Upper and lower graphs represent viscosity and PNIPAM dependences, respectively.

Figure 5e shows the 2D distribution of convective motion for five trapped Au NPs. The red arrows indicate the convective flow, and its size is set to be constant regardless of convective velocity. The convection takes places from the bulk solution to the substrate, and when the convection comes near the interface, its flow turns to go in parallel to the interface, getting away from the trapped Au NPs. The convective velocity in bulk solution and near the substrate was estimated to be 0.6 and $0.1 \mu\text{m s}^{-1}$ at 40 and $5 \mu\text{m}$ below the irradiated Au NPs, respectively. Namely, the convective velocity became slower from the bulk solution near the focal spot, where the Au NPs are optically trapped. Thus, the amount of PNIPAM molecules which are transported to the focal spot was much larger than that of PNIPAM molecules which were moved away from that area. A similar photo-thermal phenomenon was reported for polyethylene glycol and sodium dodecyl sulfate, which were accumulated around a single irradiated Au NP.⁴² These are well supported by the result of thermal diffusion forced Rayleigh scattering of PNIPAM in water.⁴³ Although the diffusion changes around the LCST, the Soret coefficient of PNIPAM is always positive, indicating that PNIPAM is always shifted toward the hot side. Therefore, PNIPAM molecules are preferentially accumulated around the trapped Au NPs, accelerating the LLPS and microdroplet formation, which is well consistent with our experimental observation.

3.4. Disappearance of Assembling and Swarming Au NPs with PNIPAM. The unique behavior of the single droplet formation is also supported by observing the dispersion process of the Au NPs in their swarming and assembling upon switching the laser off (see Video S3). In this moment, no more attractive force was loaded to the Au NPs and they quickly started to disperse. The dispersion process was analyzed, and the results are summarized in Figure 6f, assuming that the scattering intensity in the images of Figure 6a–e is proportional to the number of NPs. The upper and lower panels show the disappearance behavior of Au NPs for solutions with different chemical additives and for solutions with different PNIPAM concentrations, respectively. The NPs dispersion in solutions with the chemical additives is slower compared to the aqueous solution. In addition, the NPs dispersion in the 1.0% w/w PNIPAM solution is much slower than that in the solutions with EG or PVA, although their viscosity was adjusted to be the same. The NP dispersion in PNIPAM solutions of different concentrations (0.01–0.3% w/w) was slower compared to that in the aqueous solution but much faster than that for 1.0% w/w PNIPAM. It is worth mentioning that the dumbbell-shaped morphology was retained at the first stage of the dispersion as shown in Figure 6. On the other hand, the circle morphology of the 1.0% w/w PNIPAM solution was not identified even at 0.03 s. The initial dispersion losing its shape is characteristic of the microdroplet compared to other swarming systems. The dispersion for

aqueous, EG, PVA, and dilute PNIPAM solutions is different from that for the highly concentrated PNIPAM solution (1.0% w/w), which is consistent with the formation of the single microdroplet formation.

3.5. Light Scattering Spectra of Au NPs with PNIPAM.

The present droplet formation was further confirmed by measuring light scattering spectra of a single Au NP and understanding its local environment. It is known that the Au NP scattering spectrum depends on the refractive index of its surroundings and even on the layer thickness covering the Au NP. Utilizing the spectral measurement system depicted in Figure 1c, we first recorded the backscattering spectra from aqueous and 1.0% w/w PNIPAM solutions, where no Au NP was located in the observation area. Then we measured a single Au NP trapped under the same condition of the laser trapping. To decrease the probability to trap a second Au NP, we reduced the Au NP concentration to 7.0×10^6 particles μL^{-1} . A single NP scattering spectrum was obtained by subtracting the spectrum without any Au NPs from that with a single trapped Au NP, and the results are shown in Figure 7a.

Figure 7. (a) Experimental scattering spectra of a trapped single Au NP. Black and red spectra are obtained in water and PNIPAM solution of 1.0% w/w, respectively. Laser power density is 3.4 MW cm^{-2} . (b) Simulated scattering spectra of a single Au NP ($d = 200 \text{ nm}$). Black and red spectra represent the refractive index environments of 1.33 (water) and 1.52 (PNIPAM⁴⁵), respectively.

Although both spectra are very broad, we can still identify their peak positions. In the case of aqueous solution, it is located around 580 nm, while it is red-shifted to 640 nm for 1.0% w/w PNIPAM solution.

This difference can be ascribed to differences in the refractive index of the surroundings. This fact was elucidated by simulating the light scattering spectra of a single Au NP in two different microenvironments. The light scattering spec-

trum of a single 200 nm diameter Au NP due to surface plasmon resonance is modeled using the online platform "Extinction, Scattering and Absorption Efficiencies of Single and Multilayer Nanoparticles" based on standard Mie theory.⁴⁴ The calculated spectra are provided in Figure 7b. Two environments were simulated by setting the refractive index, $n = 1.33$ for water and 1.52 for PNIPAM (amorphous polymer solid). Previously, Han et al. demonstrated that PNIPAM-shelled Au NPs presented a red-shift in their extinction spectrum when the temperature increased above LCST and in such conditions the refractive index of globule PNIPAM is 1.52.⁴⁵

By comparing the measured and simulated spectra in Figure 7, we found that the peak position of the aqueous solution is common for experiment and simulation, but the measured peak of 1.0% w/w PNIPAM solution is more red-shifted to the simulation peak of 620 nm. This means that the concentration of PNIPAM under laser trapping is higher than that of the original solution of 1.0% w/w, which is consistent with our idea that the Au NPs are embedded inside the microdroplet. Above we proposed that the droplet is prepared through LLPS and the PNIPAM concentration should be high inside the droplet. One of the authors (H.M.) demonstrated that the single Au NP spectrum reflects the surrounding layer up to a thickness close to 300 nm.⁴⁶ Therefore, the present spectral result does not mean that just the Au NP is molecularly covered by PNIPAM or coated by a thin solution layer of PNIPAM but indicates the Au NP is surrounded by a highly concentrated PNIPAM microdomain with a thickness of at least close to 300 nm. Thus, it is concluded that light scattering spectral measurement strongly supports the formation of the PNIPAM microdroplet where Au NPs are embedded.

4. SUMMARY AND CONCLUSION

We have studied the optical trapping-induced assembling and swarming behavior of Au NPs in solutions with different PNIPAM concentrations and their respective controls at the glass/solution interface by LP laser irradiation. Initially, a few Au NPs formed a periodical linear arrangement perpendicular to the laser polarization. Afterward, when more NPs joined the arrangement, a single assembly showing a morphology like swarming bees is expanded to the outside of the focal point. Through the present experimental research, we have clarified the assembling and swarming phenomenon in terms of optical trapping, surface plasmon resonance and heating, convection flow, LLPS, and droplet formation, for which advances are summarized as follows.

First, we have directly confirmed the important contribution of photothermal heating of Au NPs to their swarming at the glass/solution interface. The trapping laser scattered from the Au NPs at the focus provides an attractive potential at the surrounding positions, while the intense trapping laser heats up the Au NPs and the surrounding solution. Thus, Au NPs show their vigorous thermal fluctuation while keeping the swarming morphology. Until now, no direct experimental evidence has been given for the heating, but the present result indicates that the temperature is elevated at least above 32°C , which is the lower critical solution temperature for PNIPAM to induce LLPS, yielding a single microdroplet for the 1.0% w/w PNIPAM solution. The temperature simulation supports this finding. The thermal convection flow along the interface is directed from the focus to the outside, which is the same direction of the pushing force due to the light scattering from

the periodically aligned Au NPs like a Yagi-Uda antenna. It is considered that the Au NPs inside the swarms keep the characteristic dynamically fluctuating morphology, which is affected by optical attractive force, thermal convection flow, and Brownian motion under heated conditions.

Second, we have demonstrated that the cooperative evolution of Au NPs assembling and PNIPAM droplet formation is induced by laser trapping at the glass/solution interface. In aqueous solution, Au NPs can move smoothly, so the dipolar scattering of LP laser irradiation determines the growing shape. This situation is not changed by adding EG or PVA, similar to the case of low PNIPAM concentration solutions. For the high PNIPAM concentration solution, however, a few Au NPs are gathered and slowly moving, which leads to local heating. Thus, the convective flow is enhanced, more PNIPAM molecules are accumulated, and eventually the LLPS is induced. Before a periodical alignment is achieved, the movement of the NPs is suppressed, and they are captured inside a small microdroplet prepared by the LLPS. Finally, the embedded NPs scatter the trapping laser to various directions, leading to a circlelike shape. The fact that the Au NPs in the droplet are separated from each other indicates that heating proceeded in parallel with the gathering of NPs. The arrangement of NPs determined the direction of the scattered light and expanded the LLPS to outside. The formed Au NP distribution in the enlarged microdroplet scatters the trapping laser to various directions, which further induces LLPS. These processes are coupled with each other in time and space, for which the cooperative nature is elucidated in the present work.

Third, the assembling and swarming morphology of Au NPs can be modified by tuning the chemical conditions. The swarming at the interface is a new phenomenon, and the morphology is determined by the dipolar scattering of the trapping LP laser due to the initially prepared periodical arrangement of Au NPs. Optical conditions should be critical, and we are examining how swarming is affected by laser power, polarization, objective lens magnification, NA, and other optical parameters. The size and shape of NPs should also be important, and other metals may show different swarming behavior. Here we have successfully showed that the incorporation of chemical additives and their concentration modify the assembling and swarming morphology of Au NPs. Recently, light-controlled swarming and assembling of colloidal particles is receiving much attention,⁴⁷ and their collective nature and control in the designed light field are studied as advanced subjects.^{48,49} The present work will be a base for future works using chemical approaches to investigate the swarming behavior by changing the temperature, tuning the pH, adding salts, proteins, polymers, and functional molecules, and so on.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c02777>.

Scattering images of Au NP assembly; light scattering images of PS NPs assembly; plot showing the ratio of the size of the Au NPs assembly between *x*-direction elongation and *y*-direction elongation as a function of PNIPAM concentration (PDF)

Assembling and swarming dynamics of Au NPs at the surface of aqueous solutions with nothing, 18.8% w/w EG, and 1.75% w/w (5× speed) (AVI)

Assembling and swarming dynamics of Au NPs at the PNIPAM solution surface of 0, 0.01, 0.03, 0.1, 0.3, and 1.0% w/w (5× speed) (AVI)

Disappearing dynamics of swarming of Au NPs at the surface of aqueous solutions with nothing, 18.8% w/w EG, 0.01% w/w PNIPAM, and 1.0% w/w PNIPAM (normal speed) (AVI)

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Author Contributions

I.A. conducted experiments and simulations and wrote the manuscript. C.-H.H. carried out experiments. R.B.-O. conducted simulations and wrote the manuscript. T.K. planned and supervised the project. H.M. wrote the manuscript and organized the discussion. H.M., A.F., and J.H. supervised the project. All authors discussed on the results and commented on the manuscript. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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