Plasmonic optical trapping of thermoresponsive gel particles: Trapping behavior change below and above volume phase transition temperature

Yuki Uenobo[1], Shoji Tatsuya[1], Taka-Aki Asoh[2], Yuriko Matsumura[3], Yumi Wakisaka[4], Kei Murakoshi[4], Yasuyuki Tsuboi*[1]

[1]Graduate School of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585, Japan
[2]Graduate School of Engineering, Osaka University, 1-1 Yamadaoka, Suita, Osaka 565-0871, Japan
[3] Faculty of Healthcare, Tokyo Healthcare University, 4-1-17 Gotanda, Shinagawa, Tokyo 141-8648, Japan.
[4]Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-0810, Japan.

E-mail: twoboys@sci.osaka-cu.ac.jp

Optical trapping of soft nanomaterials based on a plasmon-enhanced optical force will potentially develop bio-science and nanoscience. We demonstrated such plasmonic optical trapping (POT) of soft nanomaterials such as an artificial polymer[1] and DNA[2]. The soft nanomaterials showed unique trapping behaviors. For instance, poly(*N*-isopropylacrylamide) (PNIPAM) during POT in water formed a micro-ring at the outside of a plasmon excitation area[1]. In order to clarify the trapping mechanisms, here we singled out nano/micro-particles of thermoresponsive PNIPAM gels. The gel particles swell in water below a volume phase transition temperature (ca. 32 °C) and collapsed with dehydration above the temperature (volume phase transition). On the other hand, plasmonic excitation frequently leads to local temperature elevation. Therefore, for such gel particles, interesting POT behavior may possibly appear on the basis of cooperative coupling of an enhanced optical force and local heating. In the present study, we examined the POT behavior of gel particles below and above the temperature and discussed the trapping mechanisms.

As a trapping target, PNIPAM microgels labeled with rhodamine B were synthesized by emulsion polymerization. Aqueous solutions of the microgel (3.0 wt%) were used for POT. The volume phase transition temperature (*Tc*) was 32 °C. The averaged diameter of swelled microgels was 360 nm below *Tc*, while it collapsed to 140 nm above *Tc*. We used visible laser light (λ= 473 nm) or mercury lamp to excite the fluorescence probes under an optical microscope. As a plasmonic substrate, gold nanopyramidal dimer arrays were fabricated on a glass substrate by means of angular-resolved nanosphere lithography. We focused a cw near-infrared laser beam (λ= 808 nm) at 18 kW/cm^2 to excite gap-mode localized surface plasmon. Two laser beams were introduced into a confocal

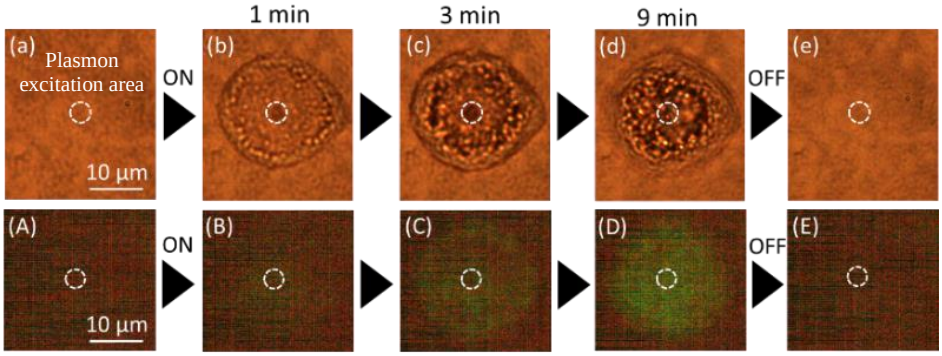

Figure 1. Microscopic images of POT of the microgels below *Tc* (20°C) ((a)-(e); in the bright field observations, (A)-(E); in the fluorescence observations)

fluorescence microscope. The solution temperature was controlled in a range of 13～40 °C using a temperature control stage attached to the microscope.

In POT at 20 °C (below *Tc*), a micro-ring of the microgels appeared at the outside of the plasmon excitation area (Fig. 1(b)). Just upon the stop of plasmon excitation, the mosaic micro-ring disappeared immediately (Fig. 1(e)). The fluorescence images well agreed with the bright-field observation (Fig. 1(A)-(F)). This indicates that the micro-ring consists of PNIPAM microgels.

The trapping behaviors were dramatically changed by the control of solution temperature. In POT at 40 °C (above *Tc*), instead of a micro-ring, sub-micro-meter-sized particles appeared and assembled in the excitation area (Fig. 2(b)). The size of assembly was about 4.5 μm, that well agreed with the diameter of the excitation area. During plasmon excitation, a micro-ring was slightly formed at the outside of the excitation area (Fig. 2(c)). Turning off plasmon excitation, the assembly were immediately dissolved in solution, while the micro-ring permanently remained (Fig. 2(e)). The microstructures emitted fluorescence whose intensity gradually increased with plasmon excitation (Fig. 2(A)-(F)).

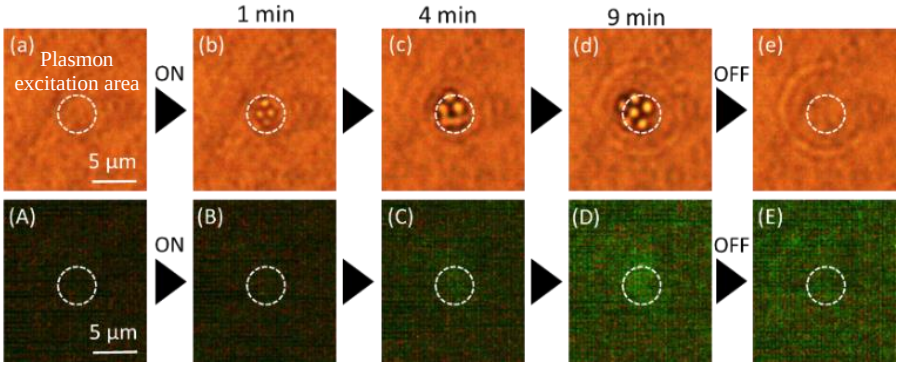

Figure 2. Microscopic images of POT of the microgels above *Tc* (40 °C) ((a)-(e); in the bright field observations, (A)-(E); in the fluorescence observations)

In this way, we showed that the microgels exhibited such interesting trapping behaviors in response to the solution temperature. Such fascinating phenomena would be caused by an enhanced optical force, a photothermal effect, and in particular the volume phase transition of the microgels. We found that plasmon excitation locally increased temperature about 20 K in the excitation area. Below *Tc*, the local temperature elevation in the excitation area induced the volume phase transition of the microgels. The collapsed microgels would form a micro-ring by the enhanced optical force and the photothermal effect. Above *Tc*, all of the microgels in solution were in the collapsed state. Such collapsed microgels hardly aggregates with each other due to mutual electrostatic repulsion by negative surface charges of the microgels. This suggests that an enhanced optical force can overcomes the electric repulsion, resulting in the assembly formation. Thus we demonstrated that the control of solution temperature induced the dramatic change of the microgels trapping behaviors.

Funding:

Acknowledgement: This work was supported by JSPS KAKENHI Grant Numbers JP26288011, JP16K17922, JP16H06506/JP16H06507 in Scientific Research on Innovative Areas "Nano-Material Manipulation and Structural Order Control with Optical Forces".

References:

[1]M. Toshimitsu, T. Shoji, Y. Tsuboi, et al, *J. Phys. Chem. C*, **2012**, *116*, 14610-14618
[2]T. Shoji, Y. Tsuboi, et al, *J. Am. Chem. Soc.*, **2013**, *135*, 6643-6648