# Controllable Micro-ring Patterning of Thermoresponsive Polymer Microgels using Plasmonic Optical Tweezers

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Plasmonic optical tweezers[1] can efficiently trap nanomaterials on a plasmonic nanostructure. In particular, plasmonic optical trapping (POT) of soft nanomaterials potentially hold a great promise for applications in chemistry[2]. We first discovered that trapped soft nanomaterials such as artificial polymers and DNAs formed characteristic micro-patterns on plasmonic nanostructures[3, 4]. The micro-pattern formation would be caused by coupling of an enhanced optical force and photothermal effects. Controlling these forces, we will open up a way to a new trapping technique for soft matters. Here, we investigated POT of thermoresponsive polymer microgels, which are one of representative soft nanomaterials.

We synthesized poly(*N*-isopropylacrylamide) (PNIPAM) microgels[5] labelled with rhodamine B. The microgels exhibit reversible volume phase transitions with response to a change in temperature in water. The averaged diameter of microgels were 360 nm and 140 nm when temperature was below and above a critical temperature (Tc; 32 °C), respectively. For a plasmonic substrate, we fabricated gold nanopyramidal dimer arrays on a glass substrate by means of angular-resolved nanosphere lithography[6]. Gap-mode localized surface plasmon was resonantly excited at 808 nm using a cw near-infrared (NIR) laser beam. We observed the optical trapping behaviors by means of microscopic observation and fluorescence microspectroscopy.

In bright field observation (upper panel in Figure 1), the microgels formed a micro-ring pattern ((B) in Figure 2) at 30 s from the start of plasmon excitation. The micro-ring gradually grew larger toward center of the excitation area, resulting in the formation of a micro-disc pattern ((C), (D)). To get further insight into the POT behavior, we obtained fluorescence images for POT of microgels. At 30 s, the fluorescence images well agreed with the bright field images, indicating that the microgels were stably optically trapped in the plasmon excitation area to form a microgel assembly (micro-disc pattern, (b)). Furthermore, the microgels also formed a micro-ring pattern at the outside of the plasmon excitation area ((b)). With increasing irradiation time, the micro-disc pattern was expanded and consequently merged with the micro-ring ((b) ~ (d)). Turning off plasmon excitation, the micro-object was immediately dissolved and dissipated in solution ((E), (e)). We consider that

POT with such morphological changes is characteristic behavior to soft nanomaterials.

In this way we succeeded in POT of PNIPAM microgel particles. This system showed interesting characteristics. Although the microgels never spontaneously assemble by mutual repulsion due to a surface charge, the microgels assembled even in an outer side of the excitation area. Namely, the microgel assembly (Figure 1, (B) ~ (D), (b) ~ (d)) was larger than the plasmon excitation area.

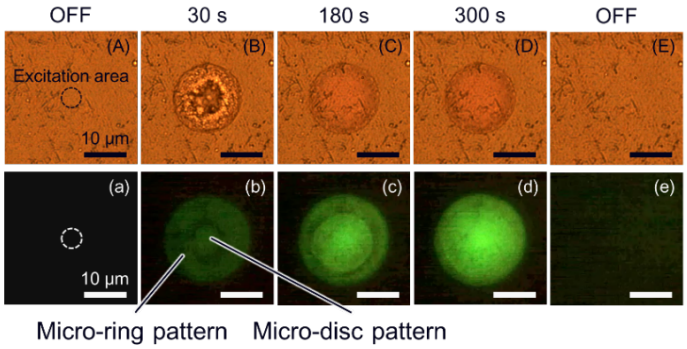


Figure 1. Microscopic observation during POT of PNIPAM microgels ((A)-(E); bright field images, (a)-(e); fluorescence images)

Furthermore, a diameter of the micro-ring pattern could be controlled by adjusting plasmon excitation intensity or the size of excitation area. We succeeded in characteristic multiple micro-ring patterning of microgels by stepwisely increasing the excitation intensity (Figure 2). We discuss the mechanism of such fascinating behaviors in terms of radiation force, thermophoresis, thermal convection, and volume phase transition.

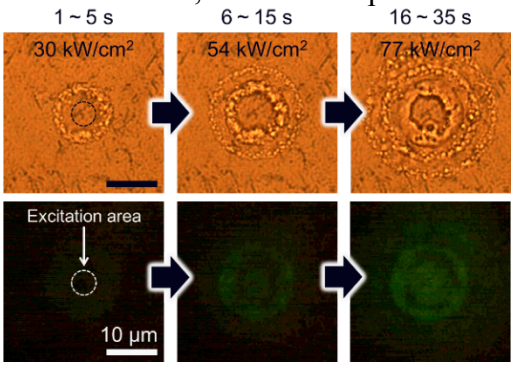


Figure 2. Microscopic observation of multiple micro-ring pattern formation of PNIPAM microgels (above; bright field images, below; fluorescence images)

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