Plasmonic optical trapping of pyrene-pendant polymer chains by controlling thermophoretic force

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Abstract. Plasmonic optical tweezers (POT) has a high potential for manipulation of nanomaterials due to an enhanced optical force. However, unfavorable thermal effects induced by plasmon excitation have frequently hindered the manipulation. For this issue, we have recently developed a novel non-plasmonic optical tweezers using a nanostructured silicon substrate (B-Si). We called it “Nano-Structured Semi-Conductor-Assisted Optical Tweezers (NASSCA-OT)”. In the present study, we trapped pyrene-pendant polymer chains homogeneously dissolved in water for POT or NASSCA-OT. We used plasmonic gold nanopramidal dimer arrays or B-Si in contact with the aqueous polymer solution. During plasmon excitation with a near-infrared laser light, any sign of optical trapping was never detected in fluorescence microscopy. By contrast, trapping of the polymer chains was obviously observed for NASSCA-OT. Upon laser irradiation, pyrene excimer fluorescence was dramatically increased at the focal spot. These results indicate that NASSCA-OT is a powerful tool for manipulation of molecular materials.

1. Introduction

Nowadays, optical tweezers have undergone explosive developments in accordance with a great progress of lasers. So far, various types of small objects have been trapped under microscopes. In particular, optical tweezers are powerful tools in medical science. Egg cells, blood cells, bacteria, and so on have been manipulated by lab-made or commercially-available optical tweezers [1, 2]. These cells and bacteria have micron-sized dimension.

On the other hand, from a viewpoint of material science, nano-materials such as molecular clusters, DNA, proteins, quantum dots are fantastic targets for optical manipulation, since ordering, phase transition, crystallization, morphological changes, chemical reaction, self-organization etc. would be induced due to intermolecular interactions in micro-assemblies formed by optical trapping. Generally, optical force (radiation pressure) decreases with decreasing particle size. Therefore, it is rather difficult to trap such small nano-materials than micron-sized particles. For such nano-manipulation, a new physical principle enhancing optical forces should be involved into optical tweezers. A powerful candidate for such a novel optical tweezer is “plasmonic optical tweezers (POT)”. However, POT has frequently suffered from thermal effects such as thermophoresis [3]. For addressing this issue, very recently we developed a novel heat-free optical tweezers; Nano-structured Semiconductor-Assisted optical tweezers (NASSCA-OT) [4]. This is based on silicon crystals with nano-structured surfaces (black silicon; B-Si). We demonstrated that NASSCA-OT has a stronger grip (stiffness) than POT.
In the present study, we examined NASSCA trapping of artificial polymer chains homogeneously dissolved in water. The polymer is labelled with pyrene. Trapping behavior was monitored using fluorescence micro-spectroscopy. We demonstrate that NASSCA-OT can optically manipulate these nanometer-sized macromolecules (Figure 1).

2. Experimental methods

2.1. Sample
We synthesized pyrene-labelled poly[N, N-dimethylacrylamide-ram-poly(ethylene glycol) methyl ether methacrylate] [poly(Py-DMA-PEG)] by free radical polymerization as a trapping target. This polymer is homogeneously dissolved in water. Pyrene is a representative fluorescence molecular probe. Fluorescence spectra of pyrene show two important peaks: on the one hand, a monomer fluorescence peak (375 ~ 450 nm), and on the other hand, an excimer emission band at around 490 nm emitted when two pyrene molecules are spatially close to each other. Number average molecular weight of the polymer chains used here was determined to be 1,500,000 by size exclusion chromatography. This polymer was dissolved in 0.1 mol/L NaOH aqueous solution as a sample solution.

2.2. Nanostructured substrates for optical trapping
As a plasmonic substrate, we fabricated gold nanopymidal dimer arrays on a glass substrate by means of angular-resolved nanosphere lithography [5]. The plasmonic substrate has a broad extinction band around 800 nm that is ascribed to a gap-mode plasmonic resonance.

A B-Si substrate was fabricated by plasma-assisted reactive ion etching of a silicon wafer in SF\textsubscript{6}/O\textsubscript{2} [6]. After the etching process nanoneedle structures formed on the silicon wafer. The optical reflection of B-Si is only a few percents over visible and near-IR spectral ranges due to the refractive index gradient around nanoneedles.

2.3. Optical setup
A cw near-infrared (NIR) laser beam (\(\lambda = 808\) nm) for optical trapping was coaxially introduced into an oil-immersion objective lens (\(\times 100, \text{NA} = 1.30\)) on a fluorescence inverted microscope with an ultraviolet (UV) laser beam (\(\lambda = 377\) nm). Fluorescence of pyrene was excited by the UV laser and Hg-lump for fluorescence microspectroscopy and fluorescence observation, respectively. For monitoring the optical trapping behaviour, we selectively obtained fluorescence spectra from the vicinity of the laser irradiation area on the substrate by using confocal optical setup.

![Figure 1. Schematic illustration of NASSCA optical trapping of pyrene-pendant water-soluble polymer chains](image-url)
3. Results and Discussion
First, we examined POT of the polymer. However, any sign of the trapping was never detected when light intensity was $I = 100 \text{ kW/cm}^2$. Presumably, plasmon-enhanced optical force (attractive force) and thermophoretic force (repulsive force) were competing with each other, and an effective trapping force was much decreased, resulting in no trapping.

Next, we investigated NASSCA trapping. Figure 2 shows fluorescence spectrum during NIR laser irradiation (red) together with that without the irradiation (black). By using our optical setup, we successfully obtained an excimer emission peak around 490 nm while a monomer emission peak around 420 nm. Immediately after starting laser irradiation ($I = 100 \text{ kW/cm}^2$), fluorescence gradually increased. As shown in Figure 2, the excimer peak obviously increased at 3 min from starting the laser irradiation. This result indicates that the local polymer concentration increased by NIR laser irradiation onto the B-Si. We estimated the concentration to be 70 w% with an intensity ratio between monomer and excimer emission. It should be noted that such condensation of the polymer was never observed in the absence of black silicon under the same irradiation condition. Namely, we succeeded in NASSCA optical trapping of polymer chains homogeneously dissolved in water. Furthermore, we successfully obtained new fluorescence peak around 520 nm from the trapped polymer chains. Although such fluorescence peak is frequently observed under special cases [7], our results suggest that NASSCA optical tweezers induce the interesting trapping behaviours for soft nanomaterials.

According to our theoretical calculation for spatial distribution of light electric field ($E^2$), $E^2$ should be enhanced with a factor of ca. 5 around nano-needles of a black silicon surface. The origin of the enhancement would be multi-scattering effect in the nano-structure. The present study strongly suggests that NASSCA can potentially manipulate nano-materials without suffering from thermal effects. This will open a new channel toward optical manipulation chemistry.

![Figure 2](image)

**Figure 2.** Fluorescence spectra obtained before NIR laser irradiation (black) and after NIR laser irradiation for 3 minutes (red). These spectra show only excimer emission (around 490 nm) intensity dramatically increases in comparison with monomer fluorescence (375 ~ 450 nm) intensity. Images inset on the right side are fluorescence micrographs. The irradiation time of NIR laser is showed above the images.
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