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Permanent Fixing or Reversible Trapping and Release of DNA Micropatterns on a Gold Nanostructure Using Continuous-Wave or Femtosecond-Pulsed Near-Infrared Laser Light

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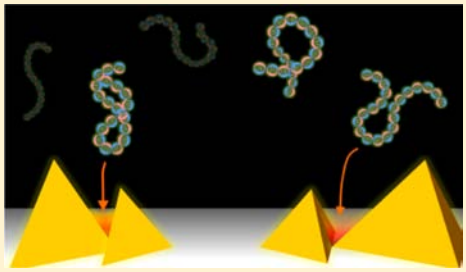
Supporting Information

ABSTRACT: The use of localized surface plasmons (LSPs) for highly sensitive biosensors has already been investigated, and they are currently being applied for the optical manipulation of small nanoparticles. The objective of this work was the optical trapping of λ-DNA on a metallic nanostructure with femtosecond-pulsed (fs) laser irradiation. Continuous-wave laser irradiation, which is generally used for plasmon excitation, not only increased the electromagnetic field intensity but also generated heat around the nanostructure, causing the DNA to become permanently fixed on the plasmonic substrate. Using fs laser irradiation, on the other hand, the reversible trapping and release of the DNA was achieved by switching the fs laser irradiation on and off. This trap-and-release behavior was clearly observed using a fluorescence microscope. This technique can also be used to manipulate other biomolecules such as nucleic acids, proteins, and polysaccharides and will prove to be a useful tool in the fabrication of biosensors.



1. INTRODUCTION

Direct optical manipulation of biomolecules (e.g., nucleic acids, proteins, and polysaccharides) is an important technique in molecular biology and biorelated nanotechnology. However, since optical manipulation and trapping are based on an "optical gradient force" that is proportional to the size of the particle,[1,2] smaller biomolecules are more difficult to trap.[3−5] The gradient force is proportional to the gradient along the intensity of light, and thus, several improved manipulation methods have been proposed to enhance the electromagnetic field (EMF) of the light, including the use of near-field optical devices such as slot waveguides,[6] whispering-gallery mode resonators,[7] and photonic crystals.[8,9] In particular, localized surface plasmon (LSP)-based optical trapping (LSP-OT) has attracted much attention in recent years because it possesses several advantages over other optical trapping methods:[10,11] (i) the EMF enhancement effect of LSP enables the incident light intensity to be significantly reduced for stable LSP-OT; (ii) a nanosized object can be trapped in a nanospace whose volume is much smaller than that of conventional optical tweezers (diffraction limit); (iii) a large and complicated optical setup is not necessary; and (iv) this technique can be potentially combined with microfluidic devices.[12] These advantages also enable LSP-OT to be used in plasmonic applications such as biosensors.[13−15] That is, plasmonic substrates can work as "double-functional" devices where biomolecules trapped by LSP-OT can be subsequently analyzed on the basis of surface-enhanced Raman scattering or fluorescence enhancement.[16−18] To date, many of the studies in the LSP-OT research field have dealt with hard particles (i.e., polymer spheres,[19−24] gold nanoparticles,[25,26] or semiconductor nanocrystals[27]) as trapping targets. The recent implementation of LSP-OT for biomolecules provides us with a valuable tool for the development of biosensors.[28] Since biomolecules are quite small, stable trapping is difficult to achieve.

One possible method to enhance the gradient force would be to use a femtosecond-pulsed (fs) laser for LSP excitation. In 2012, Roxworthy and Toussaint demonstrated that polystyrene or metallic nanospheres were efficiently trapped on a plasmonic structure when fs laser light irradiation was used for LSP excitation.[29] It should be noted that the study of conventional optical tweezers using fs laser light is still an area of active research, since fs laser irradiation frequently results in efficient trapping and discoveries of novel physical phenomena. For instance, Okamoto's group recently demonstrated a nonlinear

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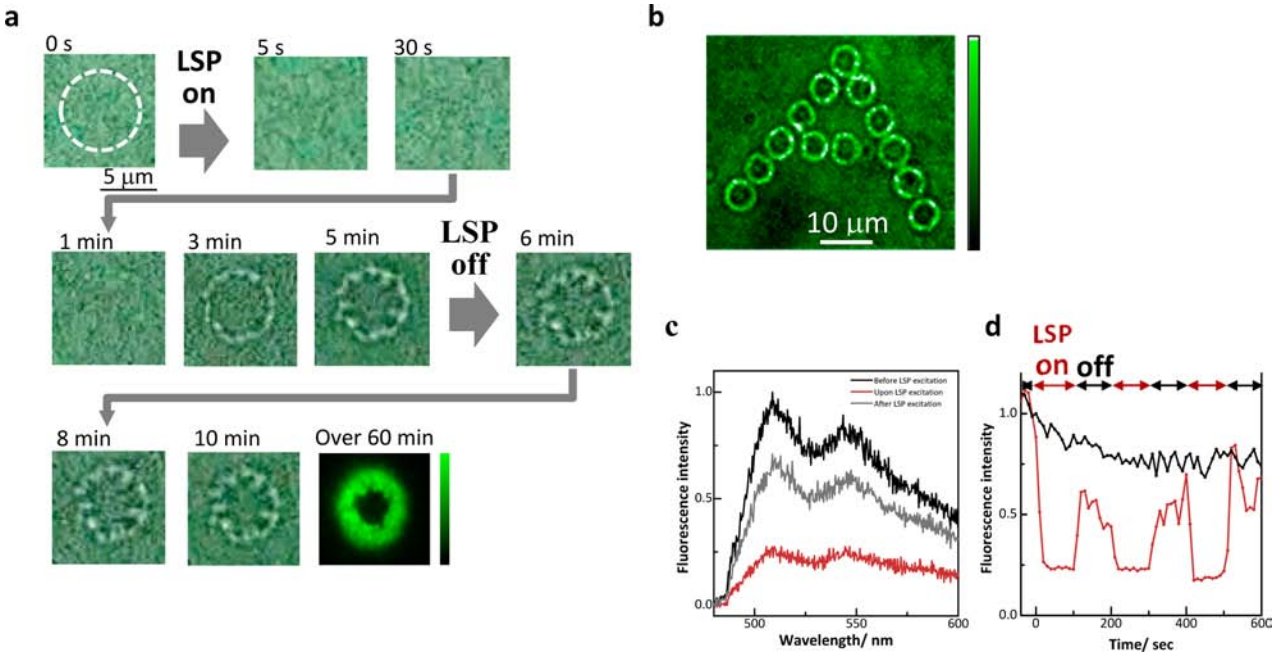

Figure 1. Fixing micropatterns of DNA on a plasmonic AR-NSL gold substrate using cw NIR laser irradiation (7.0 kW/cm^2) for LSP excitation. (a) Bright-field (green background) and fluorescence (dark background) micrographs. The time shown for each image is the cw laser irradiation time, with 0 s being just before the laser was switched on. The cw laser irradiation was turned off at 5 min. The white dashed circle indicates the region covered by the cw laser illumination. (b) Fluorescence micrograph of a letter "A" constructed from 14 microrings of assembled DNA. (c) Fluorescence spectra obtained before (black), upon (red), and after (gray) cw laser irradiation. The spectra were acquired with exposure times of 10 s. (d) Temporal profiles of the fluorescence intensity as the laser was switched on and off repetitively (red, repetition time ≈ 100 s) and without cw laser irradiation (black).

behavior that they called "trap split",[30] and Dholakia's group controlled the two-photon luminescence of trapped nanoparticles.[31] Also, Masuhara's group recently controlled the directions of scattered nanoparticles.[32] Their studies were performed using fs laser beams and could possibly be extended to LSP-OT.

In the present study, we used fs laser light for LSP-OT of λ-DNA and analyzed the LSP-OT behavior, comparing it with that observed when continuous-wave (cw) laser light was used. DNA has been one of the main targets of optical tweezers.[33] We observed clear differences between these two cases (fs laser and cw laser), on the basis of which we propose a novel OT technique for biomolecules.

2. EXPERIMENTAL SECTION

For samples, we used λ-DNA (48.5 kbp) stained with YOYO-1 (absorption maximum at 490 nm and an emission maximum at 509 nm). For the plasmonic substrate, we fabricated gold nanopyramidal dimer arrays on a glass substrate by means of angular-resolved nanosphere lithography (AR-NSL).[34,35] For LSP excitation, we used a cw near-infrared (NIR) diode laser (λ = 808 nm) or an fs NIR laser (λ = 770 nm, repetition rate = 80 MHz, pulse width = 120 fs fwhm). Both lasers can excite LSPs on the substrate around the absorption maximum. We obtained microscopic images of LSP-OT as bright-field images (background color is green) or fluorescence images (black). A Hg lamp was used for fluorescence microscopy observations. For fluorescence microspectroscopy, the YOYO-1 in the DNA was excited with a cw visible Ar^+ laser (λ = 488 nm, power = 5−10 μW, corresponding to 2.5−5.0 kW/cm^2 at the focus). The cw and fs NIR lasers were loosely focused to a circular spot (diameter $d \approx 5$ μm) on the AR-NSL substrate, while the visible laser was tightly focused approximately at the diffraction limit ($d \approx 0.5$ μm) at the center of the circular spot. Accordingly, we observed fluorescence only from the center of the LSP excitation area. Fluorescence correlation spectroscopy (FCS) was carried out to evaluate the temperature elevation upon LSP excitation. Diffusion of rhodamine 123 in the vicinity of the gold nanostructure upon LSP excitation was monitored with FCS, and the diffusion constants determined were converted into local temperature elevation. All of the experiments were performed under ambient conditions at room temperature (23 ± 1 °C). Details of sample preparation and optical setups were described in previous reports[24,27,36] and the Supporting Information (SI).

3. RESULTS AND DISCUSSION

3.1. Trapping Using cw Laser Irradiation. First, we describe the behavior of DNA trapping when the cw NIR laser (7.0 kW/cm^2) was used for LSP excitation. It should be noted that the laser light intensity used here was clearly insufficient to trap and manipulate DNA directly using conventional optical tweezers.[33] Figure 1a shows a series of optical micrographs of representative DNA trapping behavior. Although we did not observe anything during several tens of seconds of LSP excitation (Figure 1a, 0−1 min), after several minutes of LSP excitation a microring structure was formed and gradually grew in the LSP excitation area (Figure 1a, 1−5 min). The diameter of the microring was consistent with that of the LSP excitation area (focal spot of the cw NIR laser on the substrate surface). After the LSP excitation was switched off, the microring did not disappear but remained stable on the substrate, keeping its shape and size; that is, the microring was physically fixed on the substrate. Fluorescence microscopy clearly detected the bright-green fluorescence of YOYO-1, which retained the ring structure (Figure 1a; background is dark). We also achieved the formation of the microring structure with weaker cw NIR laser irradiation (5 kW/cm^2), although the structure was not observed below 4 kW/cm^2 (see the SI). This fixed structure can safely be ascribed to an assembly of DNA molecules. We were

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able to use such DNA microrings to draw DNA micropatterns on plasmonic substrates, as demonstrated in Figure 1b. We consider that the technique can potentially be used in fabricating DNA array chips.

As shown in Figure 1c, fluorescence microspectroscopy was carried out to detect the emission signal only from the center of the ring pattern. It should be noted that the cw NIR laser did not induce plasmon-enhanced fluorescence of YOYO-1, since the dye is transparent at this wavelength (808 nm) (see the SI). The fluorescence intensity dropped upon LSP excitation, implying that DNA molecules were not trapped at the center of the focal area but instead were excluded from there. After the LSP excitation was switched off, the fluorescence intensity returned approximately to its original intensity. The decrease in fluorescence at the center of the LSP excitation area is not inconsistent with the formation of the ring pattern of the trapped DNA assembly. Figure S1c in the SI shows the dependence of the fluorescence intensity on the cw NIR light intensity, which indicates that DNA was hardly trapped at the center of the focal area at any laser intensity. Figure 1d shows time traces of the relative fluorescence intensity as it was modulated by repetitively switching the LSP excitation on and off (red line) and without LSP excitation as a reference (black line). In the measurement, the fluorescence intensity gradually decreased even without LSP excitation because of photobleaching by the visible laser irradiation. Turning on the cw NIR laser led to a decrease in the fluorescence intensity, which was recovered when the cw NIR laser irradiation was turned off.

We consider these results—permanent fixing and the microring pattern—to be caused not only by the LSP-enhanced gradient force but also by photothermal effects accompanying the LSP excitation. In general, resonant laser irradiation of a noble-metal nanostructure gives rise to heat generation as well as EMF enhancement.[37−39] Using FCS, we previously estimated the temperature rise for the present system (cw 808 nm laser light irradiation of 1.0 kW/cm^2) to be $\Delta T \approx 8-9$ K at the surface of the AR-NSL substrate.[36] It should be noted that such a photothermal effect hardly induces thermal denaturation of fixed DNA because the elevated temperature (78−87 °C at 7.0 kW/cm^2) was lower than the DNA melting point (99 °C).[40] However, such heat generation would bring about thermal convection and thermophoresis (thermal diffusion or the Ludwig−Soret effect).[41−43] In the previous report, we found that thermal convection acts in favor of LSP-OT.[24] On the other hand, thermophoresis exerts a repulsive force on the DNA, transporting it from hotter to colder regions.[44−47] Therefore, thermophoresis is the origin of the microring morphology of the assembly. DNA molecules excluded from center of the focal point by thermophoresis were physically fixed on the heated AR-NSL substrate. Yoshikawa and co-workers reported fixing of DNA on a glass substrate using conventional optical tweezers with a cw laser beam.[33] In analogy to this, the origin of the fixing can presumably be ascribed to heat fusion (adhesion).

3.2. Trapping Using fs Laser Irradiation. In contrast, we discovered that when fs NIR laser light was used, DNA molecules could be optically trapped and released on a plasmonic substrate by switching the LSP excitation on and off, respectively. Figure 2a shows representative fluorescence micrographs of DNA trapped using a fs laser. Before LSP excitation, the green fluorescence of the DNA could hardly be seen. Upon LSP excitation by the fs NIR laser irradiation (time-averaged intensity ~7.0 kW/cm^2), we observed homogeneous

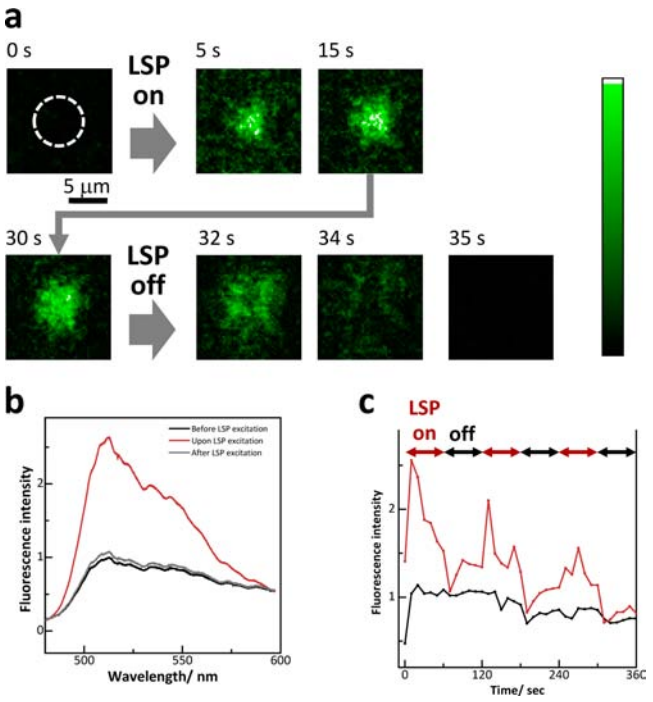

Figure 2. DNA assembly on a plasmonic AR-NSL gold substrate using fs NIR laser irradiation (7.0 kW/cm^2 on average). (a) Fluorescence micrographs. The time shown in each image is the fs laser irradiation time, with 0 s being just before the laser was switched on. The fs laser irradiation was turned off at 30 s. (b) Fluorescence spectra obtained before (black), upon (red), and after (gray) fs laser irradiation. The spectra were acquired with exposure times of 10 s. (c) Temporal profiles of the fluorescence intensity as the laser was switched on and off repetitively (red, repetition time ≈ 60 s) and without fs laser irradiation (black). Each point was acquired with an exposure time of 10 s.

green fluorescence from the irradiation area that can be ascribed to the fluorescence of YOYO-1 intercalated in the DNA. The outline of the fluorescence spot gradually expanded with irradiation time and finally became consistent with that of the fs NIR laser irradiation area (a microdisc assembly). The DNA microdisc assembly was hardly observed under bright-field conditions, suggesting that numerous DNA molecules were not strongly trapped on the substrate. When the fs NIR laser irradiation was turned off (stopping the LSP excitation), the fluorescence disappeared in a few seconds. Thus, the behavior was observed to be a reversible process.

Fluorescence microspectroscopy at the center of the fs NIR laser irradiation area provided further supporting evidence for such trap-and-release behavior (Figure 2b). The YOYO-1 fluorescence was clearly observed in the spectra, and the fluorescence intensity increased upon LSP excitation and then decreased to its original intensity when the LSP excitation was stopped. This indicates that the DNA molecules were reversibly trapped and released in the area illuminated by the fs NIR laser. It should be noted that the fs NIR laser irradiation did not induce fluorescence of DNA via two-photon absorption in the present case. Two-photon fluorescence was clearly ruled out because the fluorescence was not observed unless the region was simultaneously illuminated with visible light (from the 488 nm laser light or Hg lamp) and fs laser light. Details are given in the SI.

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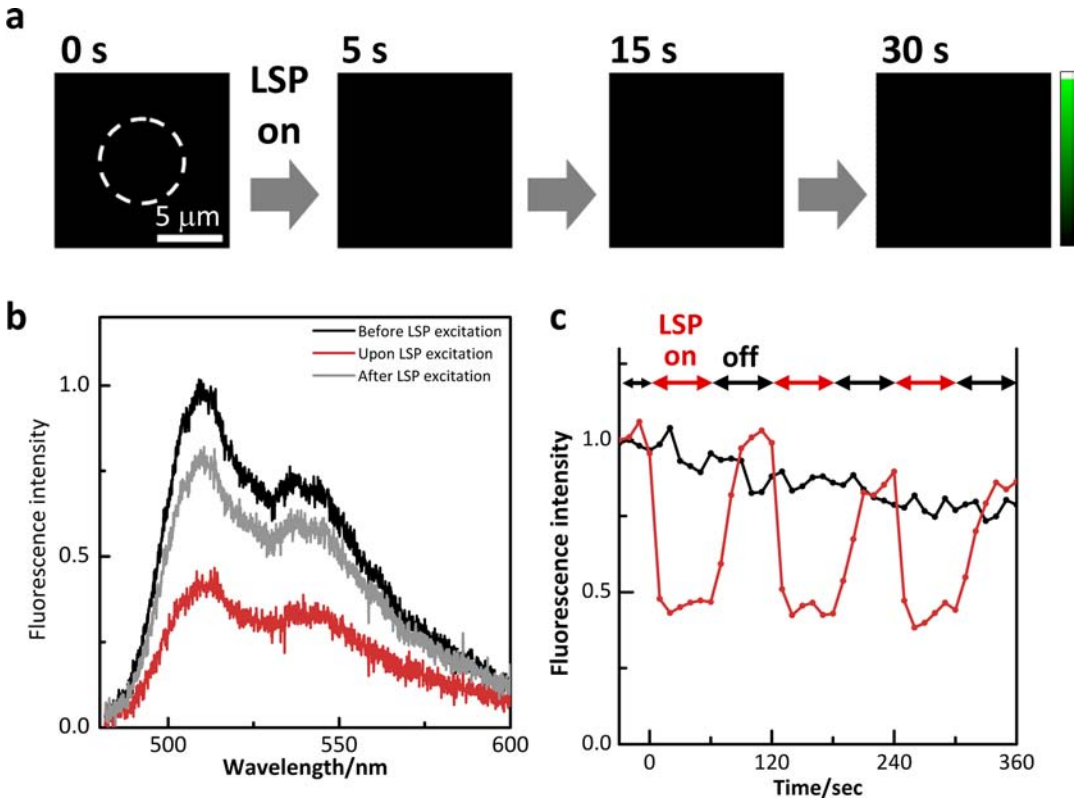

Figure 3. DNA assembly on a thin gold film with no nanostructure using fs NIR laser irradiation (7.0 kW/cm^2 on average). (a) Fluorescence micrographs. The time shown in each image is the fs laser irradiation time, with 0 s being just before the laser was switched on. The fs laser irradiation was turned off at 30 s. (b) Fluorescence spectra obtained before (black), upon (red), and after (gray) fs laser irradiation. The spectra were acquired with exposure times of 10 s. (c) Temporal profiles of the fluorescence intensity as the laser was switched on and off repetitively (red, repetition time ≈60 s) and without fs laser irradiation (black). Each point was acquired with an exposure time of 10 s.

In Figure 2c, a time trace of the relative fluorescence intensity modulated by repetitively switching the LSP excitation on and off (red line) is shown, together with the profile when the LSP excitation was turned off (black line). The fluorescence intensity responds to switching of the LSP excitation on and off, indicating trapping and release of DNA in the illuminated area. Such trapping behavior was not observed in the absence of gold nanostructures on the substrate. As a reference, we investigated the behavior of DNA when fs laser irradiation (with the same irradiation parameters as in Figure 2) was used in combination with a thin gold film without such nanostructures (prepared by a simple vacuum deposition). In this case, we did not detect any sign of an increase in fluorescence intensity (Figure 3). Instead, this system exhibited the opposite behavior: the YOYO-1 fluorescence decreased and recovered to its original intensity when the fs laser excitation was turned on and off, respectively, suggesting a photoinduced repulsive force such as the Soret force. These results clearly indicate that such a trap-and-release process was triggerd by fs laser excitation of LSPs on the gold nanostructure.

3.3. Trapping Mechanism. The above observations suggest that the fundamental mechanisms associated with cw and fs NIR laser excitation of LSPs are different from each other. To reveal the origin of the trap-and-release behavior, we used FCS to estimate the temperature elevation induced by the fs laser irradiation and found that $\Delta T \approx 7-8$ K at 1 kW cm^{-2} irradiation (averaged intensity) at the surface of AR-NSL substrate. This value is similar to the ΔT obtained using cw NIR laser irradiation at a given laser intensity. Representative data and details are described in the SI. Therefore, it is not adequate to ascribe the different trapping behaviors in the cw and fs NIR laser experiments to a difference in ΔT. Such considerations were further supported by the results that DNA was never trapped at the center of the LSP excitation area even when the cw laser power was reduced to decrease the photothermal effect (Figure S1 in the SI). Consequently, we consider the origin of the trapping and release of DNA to be attributable to an intense gradient force during fs pulse irradiation. Indeed, since the peak energy of a fs laser in a single pulse is much higher than that of a cw laser (by a factor of ~10^5), conventional optical tweezers using a pulsed laser can supply a sufficient gradient force that is relatively higher than that using a cw laser.[30−32,48,49] Such an intense gradient force by each fs laser excitation pulse would overcome the repulsive thermal force (thermophoresis), resulting in a microdisc assembly of DNA (Figure 2). The 12 ns intervals between femtosecond pulses during fs excitation would prevent DNA from being fixed on the substrate. The trap-and-release process proceeded in several tens of seconds (within 1 min) during fs laser excitation (Figure 2), while the permanent fixation needed a longer cw laser excitation over a few minutes (Figure 1). This also leads to a tentative conclusion that the former (trap-and-release) behavior is triggered by the intense gradient force generated by the fs laser whereas the latter one (permanent fixation) needs accumulation of heat in addition to the gradient force. It should be noted that both of the forces (trapping force and Soret force) were evaluated to be on the order of femtonewtons for LSP-OT of an artificial polymer system.[36]

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Although challenging tasks such as theoretical calculations of gradient forces and molecular dynamics simulations (a simple calculation for DNA diffusion is shown in the SI) still remain in order to discover the overall mechanism of fs-LSP-OT, we have demonstrated that the fs laser is a powerful tool for LSP excitation in LSP-OT of DNA. The present demonstration of switchable trapping behavior using a cw or fs laser provides important information for the development of a novel method for molecular trapping.

4. CONCLUSIONS

We have demonstrated switchable LSP-based optical trapping (either permanent fixing or reversible trapping and release) of DNA on a plasmonic substrate using NIR laser irradiation. While the former was achieved with a cw laser, the latter was performed only with a femtosecond-pulsed laser. LSP excitation using the cw laser led to a permanently fixed DNA assembly with a well-defined microring structure on the plasmonic substrate. Photothermal effects induced by LSP excitation may play a crucial role in fixation of DNA on a plasmonic substrate. On the basis of this, micropatterns of DNA with desired shapes were formed on the plasmonic substrate. On the other hand, with the fs laser, reversible trapping and release of DNA was successfully achieved by switching the fs laser irradiation on and off, respectively. LSP-OT using a fs laser will open a new channel for efficient trapping method of not only nucleic acids but also other biomolecules (proteins and polysaccharides) and smaller molecules. This demonstration of permanent fixing and the reversible trapping and release of DNA offers potential applications in the fields of chemical and biosensors.

■ ASSOCIATED CONTENT

Supporting Information

Optical setup, sample preparation, excitation intensity dependence, nonlinear optical effects on fluorescence behaviors, FCS measurements, and diffusion distance of DNA during the interval between two adjacent fs laser pulses. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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