

Power-dependent destabilization forces in trapping nanographene-based nanoparticles

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Abstract

In recent years, plasmonic optical tweezers have been used to trap nanoparticles and study interactions with their environment. An unavoidable challenge is the plasmonic heating due to resonant excitation and the resulting temperature rise in the surrounding environment. In this work, we demonstrate optical trapping of nanographene-based polymeric nanoparticles using metamaterial plasmonic tweezers. We achieved superior trapping performance and trap stiffness values as high as $8.8 \text{ (fN/nm)}/(\text{mW}/\mu\text{m}^2)$ with optical intensities lower than $1 \text{ (mW}/\mu\text{m}^2)$. A range of incident intensities was used to monitor the effect of increasing intensity in the trapping performance. Higher intensities resulted in stronger optical forces, but thermal effects tended to destabilize the trapping. Beyond a critical intensity, where the temperature rise reached 24°C , a

large number of particles were being trapped with lower stiffness values indicating the presence of thermal flows. We, therefore, identified a safe intensity regime to avoid detrimental thermal effects. Our platform is ideal for multiple particle trapping in an array configuration and could be used for stable nanopositioning of quantum emitters with controlled interactions with their environment, potentially useful in the field of quantum technologies.

Keywords: metamaterial plasmonic tweezers, fluorescent nanoparticles, optical trapping, thermal effects, nanographenes

1. Introduction

Quantum emitters (QEs) are nanoscale artificial molecules synthesized with specific properties and a total diameter of less than 100 nm.¹ Some of the main types of solid-state quantum emitters are semiconductor quantum dots (QDs),²⁻⁴ nanodiamonds with nitrogen vacancy (NV) centers,^{5,6} graphene quantum dots (GQDs),^{7,8} fluorescent organic molecules,^{1,9,10} and metal-halide perovskite nanoparticles.¹¹

Advances in chemical synthesis methods have enabled tailoring of QE properties such as size, shape, internal structure, absorption, and emission spectra. Therefore, the ability to control those properties offers highly-tunable photon sources, exhibiting high quantum yield and emitting in a range of wavelengths from UV to IR. QEs have attracted interest from multiple fields such as biology, serving as luminescent probes and biomarkers,^{3,12,13} display industry, as highly-tunable LEDs for next-generation displays,^{14,15} optoelectronics, for light-emitting devices,^{16,17} and, of course, they play a central role in the field of quantum technologies acting as single-photon sources.^{4,18-22}

Due to all the remarkable properties and promising applications of nanoparticle QEs, there was a desire to develop optical trapping techniques to facilitate studies on their optomechanical properties and interactions with the environment.^{23,24} The first demonstration

of single QE trapping was reported by Jauffred et al. in 2008, achieved via conventional optical tweezers using a continuous wave (CW) laser in the infrared with a trapping power as high as 0.5 W to trap a *CdSe/ZnS* QD.²⁵ This power was very high considering today’s standards, and formidable for many applications as it could easily spoil the QD due to the strong laser irradiation and heat transfer.²⁶ A few years later, the same group demonstrated trapping of various semiconductor QDs with lower laser intensity and simultaneous two-photon excitation.²⁷ Aiming to reduce the incident intensity led to trapping of QDs with near-field forces utilizing plasmonic^{28–30} and dielectric structures.^{31,32} Such configurations can significantly reduce the incident intensity required for the trapping, while resulting in stronger trap stiffnesses.^{33,34} Some works have also investigated Kramers hopping in plasmonic nanostructures using trapped QDs, which are ideal due to their high refractive index.^{35,36}

One drawback of QDs is their chemical compositions containing heavy metal elements, typically including cadmium³⁷ or lead.³⁸ Therefore, GQDs have attracted attention as carbon-based and thus environmentally friendly alternative. However, the majority of the GQDs reported in the literature are prepared through solvothermal methods³⁹ and their chemical structures are typically undefined, prohibiting the establishment of precise structure-property relationship and fine-tuning of their optical properties. To this end, molecular nanographenes, namely large polycyclic aromatic hydrocarbons, can be bottom-up synthesized through the methods of synthetic organic chemistry, providing atomically precise GQDs with structure-dependent properties.⁴⁰ Moreover, such molecular nanographenes can be assembled with amphiphilic polymers to prepare fluorescent polymeric nanoparticles.¹³

In this work, we present trapping of nanographene-based polymeric nanoparticles, using a twisted nanographene called double [7]helicene (D7H-NPs).^{13,41} The D7H-NPs had an average diameter of 20 nm, and they were trapped using metamaterial plasmonic tweezers.^{42,43} Previous works have shown that metamaterial plasmonic tweezers are ideal for efficiently trapping sensitive particles that cannot handle high temperatures.^{44,45} Recently, we used the same metamaterial plasmonic tweezers to investigate the optomechanical response of the

trap using gold nanoparticles 20 nm in diameter.⁴³ That work revealed the existence of two types of plasmonic hotspots periodically arranged, resulting in different trap stiffnesses. In this work, we observed similar behavior when trapping the D7H-NPs. However, we progressively introduced errors in classifying the trapping hotspot location with increasing trapping laser intensity. We attributed this observation to the induced heating of the water solution (where the NPs were suspended) with increasing laser intensity. Therefore, we hypothesize that the measured trap stiffnesses at higher intensities were not a result of optical forces alone, but also from the induced thermal forces in the solution.^{46,47}

2. Materials and Methods

2.1 D7H-NPs Synthesis and Properties

The details of the chemical synthesis of D7H molecules and the preparation of similar D7H-NPs were previously published.^{13,41} In this work, D7H-NPs having quasi-core/shell structure, with fluorescent D7H molecules inside the core and hydrophilic moieties of amphiphilic polymers, as the shell, were prepared through a classic nano-precipitation method,¹³ as shown in Figure 1a. 0.25 mg of D7H molecule and 0.5 mg of PSMA (Poly(styrene-*co*-maleic anhydride) purchased from Sigma Aldrich) were dissolved in 5 mL of tetrahydrofuran (THF), the obtained homogeneous solution was added into 15 mL of deionized water under sonication, and was stirred at room temperature with nitrogen bubbling for 48 h to remove THF and produce D7H-NPs. The obtained stock solution was stored in the dark at 4°C.

In Figure 1, we depict the chemical structure of D7H molecule, schematic illustration of the preparation of D7H-NPs, the size distribution, zeta potential, and emission spectrum of the NPs. The size distribution was measured using the dynamic light scattering method (DLS) indicating a diameter of 18.8 ± 0.8 nm. This is a typical size for a quantum emitter, and can be readily trapped and manipulated using plasmonic nanostructures. The DLS measurements were performed using a Malvern Zetasizer Nano ZS 90 (Malvern,

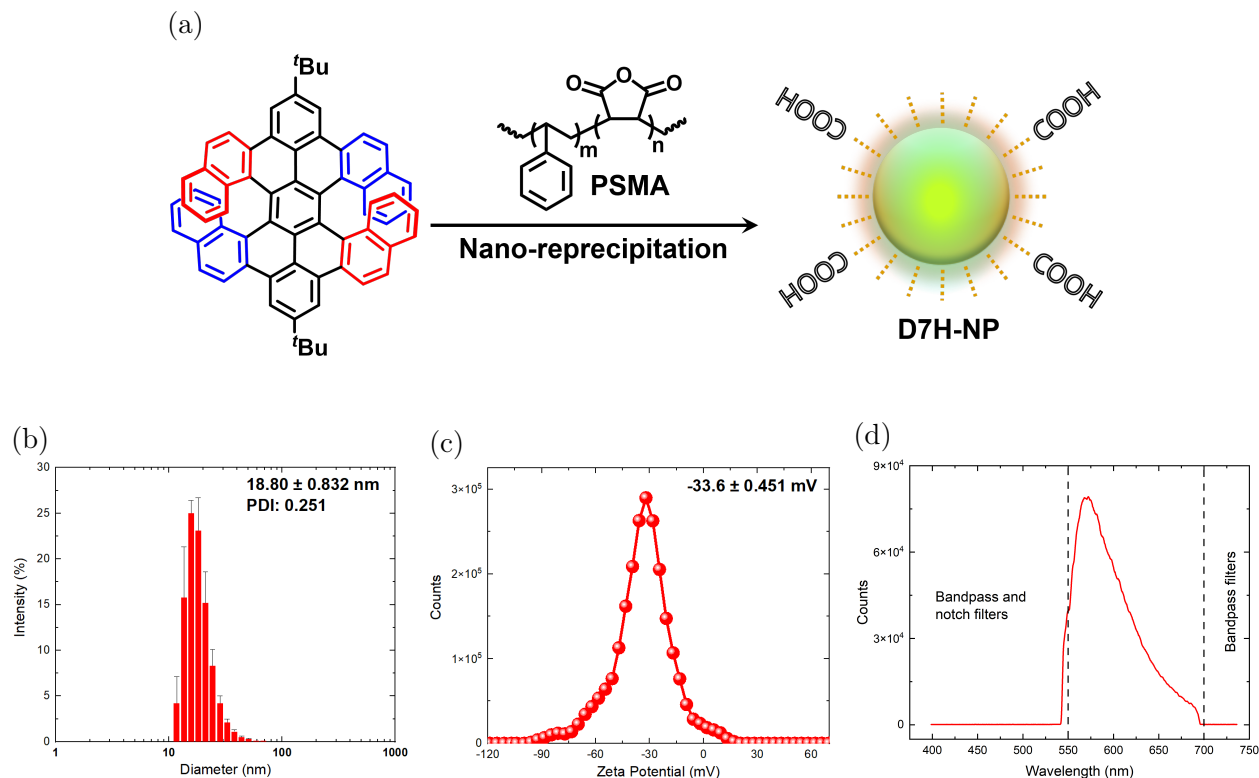


Figure 1: Basic characteristics of the D7H-NPs. (a) Chemical structure and representation of the chemical synthesis of the D7H-NPs, (b) nanoparticle size distribution, (c) zeta potential of the nanoparticles' surface, (d) emission spectrum with a peak at 575 nm.

UK) instrument equipped with a He-Ne laser (633 nm, 4 mW). Measurements were carried out in a polystyrene cuvette at a 173° accumulation angle after equilibrating for 2 min at 25°C. The data were processed by the instrument software (Zetasizer Nano software v3.30) to give the number mean particle size and polydispersity index value by a non-negative least squares method. The zeta potential of D7H-NPs was simultaneously measured by the Malvern Zetasizer Nano ZS 90 instrument, yielding a mean value of -33.6 ± 0.5 mV. We deliberately selected PSMA as the amphiphilic polymer to obtain D7H-NPs with negatively charged surfaces so that the NPs would not stick on the gold surface of the plasmonic nanostructures, since it is also negatively charged. However, electrostatic interactions might still have played some role in the trapping process.⁴⁸ Lastly, the emission spectrum of D7H-NPs was recorded showing a peak at around 575 nm. Emission in the visible range is useful for

quantum technology applications while the NPs could be excited using blue light (490 nm). The experimental details for obtaining the spectrum are described in Section 2.3. It is worth noting that the D7H-NPs are biocompatible, making them ideal for *in-vivo* use in medical applications.¹³

2.2 Metamaterial Fabrication and Characterization

The plasmonic metamaterial array was fabricated on a 50-nm thin film of gold (PHASIS, Geneva, BioNano), using focused ion beam milling (FIB-FEI Helios Nanolab G3UC). The gold was deposited on a borosilicate glass (SiO_2) substrate with a 5 nm titanium adhesion layer. The design was based on the asymmetric split-ring resonator shown in the inset of Figure 3, and the desired geometrical characteristics of the structures were determined using finite element method simulations to achieve a particular resonance wavelength at around 930 nm. An array of 16×16 units was fabricated with a period of 400 nm in both directions. The etched film was then treated with oxygen plasma to remove any deposited gallium residue that resulted during the FIB etching.⁴⁹ Next, we performed microspectrophotometry measurements (CRAIC, 20/30 PV) to obtain the experimental transmission spectrum through the metamaterial array, and, therefore, the experimental plasmonic resonance. In our design, the measured resonance was at 930 nm, therefore we tuned the trapping laser to this wavelength to excite a strong plasmonic field. The metamaterial design and the characterisation methods are the same as those used in our previous work, and the interested reader is directed there for a more detailed description.⁴³

2.3 Optical Trapping Setup

The experimental setup for the trapping experiments is shown in Figure 2a. Linearly polarized light from a Ti:Sapphire laser (Coherent MBR-110) tuned to 930 nm wavelength was used to excite the Fano resonance in the metamaterial array. It was coupled in the setup using a single-mode polarization-maintaining fiber. A polarizing beamsplitter (PBS) ensured

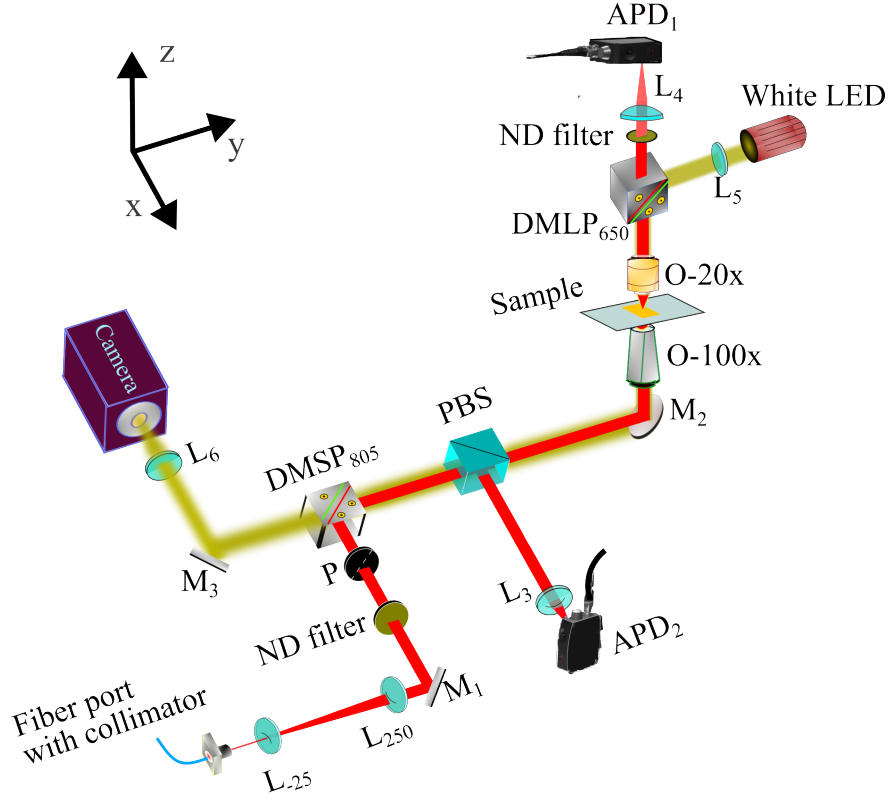
the desired y -axis polarization direction (see inset in Figure 3) while at the same time facilitated the control of incident power by rotating a linear polarizer (P). An objective lens with magnification $100\times$ and NA 1.25 was used to focus the incident light on the metamaterial. Transmitted light through the metamaterial yielded information about trapping events, and was collected by a second objective lens with magnification $20\times$, NA 0.46 and detected on an avalanche photodiode (APD). The APD signal was analyzed using trapping transient analysis and the trap stiffness for each trapping event was calculated.

In order to record the emission spectrum of the D7H-NPs, the setup was modified accordingly. The white light LED shown in Figure 2a was replaced by a laser (Toptica, iChrome, TVIS) with wavelength tuned to 488 nm for excitation of the NPs. This beam was in the opposite direction to the trapping beam. A droplet of the NPs solution was deposited on the metamaterial and allowed to evaporate. Thus, any emitted light was due to the collective excitation of many NPs. To collect the emissions, we added some extra parts in between the PBS and mirror M_2 (see Fig. 2a), as shown in Figure 2b. A dichroic mirror DMLP₈₀₅ was used to guide the emitted light through a series of bandpass and notch filters that were used to block the trapping and excitation lasers, then into a multimode fiber connected to a spectrometer (Andor, Shamrock 500i) to record the spectrum, as shown in Figure 1d.

2.4 Solution Preparation

For the trapping experiments, the D7H-NPs were dispersed in heavy water (D_2O) with a concentration of $0.15\ \mu\text{g/mL}$ based on the total weight of D7H-NPs (D7H and amphiphilic polymer), and surfactant Tween-20 was also added with 0.1% v/v concentration to avoid the aggregation of NPs in the solution. The final solution was shaken well and $8.5\ \mu\text{L}$ were placed directly onto the gold film surface inside a seal spacer with $120\ \mu\text{m}$ thickness, and enclosed on the top with a micro glass cover slip, thus forming a microwell where the NPs were suspended. The sample was then mounted in the setup with the cover slip facing upwards and the glass substrate downwards, with the trapping laser incident from the bottom of the

(a)



(b)

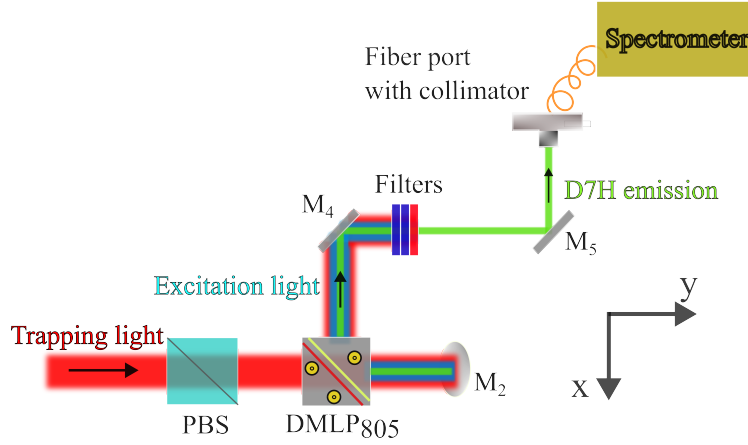


Figure 2: (a) Schematic of the basic configuration of the experimental setup used for the trapping experiments. M: mirror, L: lens, ND filter : neutral density filter, P: polarizer, DMSP and DMLP: shortpass and longpass dichroic mirrors, respectively, PBS: polarizing beamsplitter, O: objective lens, APD: avalanche photodiode. Dimensions not scaled. (b) The parts added in between the PBS and mirror M₂ in order to record the D7H-NPs emission spectrum.

sample (glass substrate side). Detailed description of the experimental processes mentioned in Section 2 can be found in Chapter 3 of the referenced thesis.⁵⁰

3. Results and Discussion

The trapping experiments were performed with increasing incident laser power from 1.5 - 6.5 mW on the sample, corresponding to an intensity range of approximately 0.5 - 2.1 mW/ μm^2 , since the spot size on the sample had a radius of about 1 μm . For each intensity value, the experiment took only a few minutes (less than 10 min) during which the trapping beam was blocked and released in certain time intervals, thus obtaining multiple trapping events. It is worth noting that the first trapping event occurred within just a few seconds after the trapping beam was initially switched on, indicating fast transport and trapping of the NPs which is a unique feature of our design.^{42,43} In total, more than 250 trapping events were recorded and analyzed.

In Figure 3, a histogram of the normalized trap stiffness values (trap stiffness divided by the incident intensity) is plotted. The values are very high even for low incident intensities when compared with the literature,^{33,34,51} indicating strong and efficient trapping with values as high as 8.8 (fN/nm)/(mW/ μm^2). The histogram seems to consist of two distributions (see dashed lines in Figure 3) owing to the two different types of hotspots excited on the metamaterial array, as explained below.

A detailed investigation of the excited hotspots and their characteristics for trapping experiments can be found in our previous work.⁴³ Briefly, in our metamaterial array, we can excite simultaneously two types of hotspots (referred to as Hotspot 1 & 2), which can be tuned by the wavelength of the excitation laser. Each unit of the metamaterial array possesses two hotspots of type 1 and one of type 2, as shown in the inset of Figure 3. Therefore, we expect that, probabilistically, there will be twice as many trapping events at Hotspot 1 compared with Hotspot 2. The optical force and, as a result, the trap stiffness

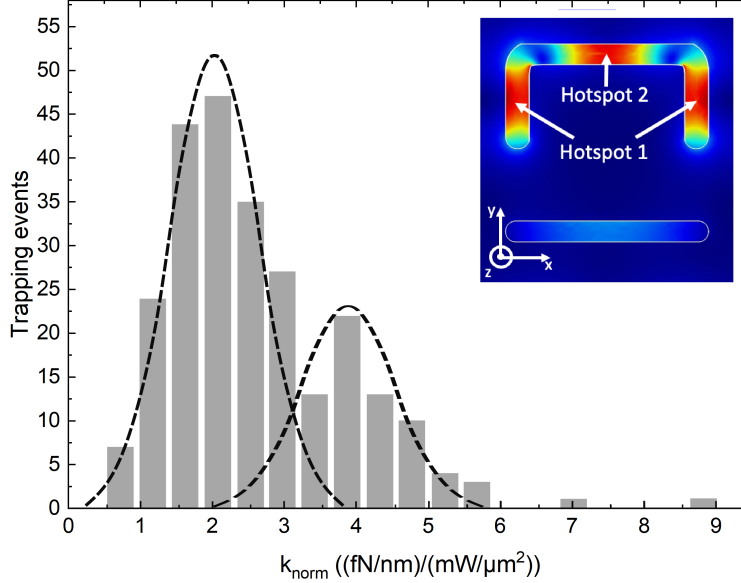


Figure 3: Histogram of the measured normalized trap stiffnesses of the trapped D7H-NPs. The trapping events included were obtained with excitation intensities ranging from 0.59 - 2.1 mW/ μm^2 (1.56 - 6.6 mW). The dashed lines are for visual aid indicating the distribution of trap stiffness values due to the existence of two types of hotspots. Inset shows the simulated electromagnetic field on a unit cell of the metamaterial, depicting the two types of hotspots excited. Inset was reproduced from.⁴³

that a particle experiences in each of the hotspots depend on the cavity - particle coupling. Thus, parameters such as the particle's polarizability and geometrical characteristics of the nanocavity affect the trapping performance accordingly. In our work, the D7H-NPs have a refractive index close to that of a polystyrene particle and therefore, based on simulations, a particle trapped at Hotspot 1 experiences stronger optical forces and a higher trap stiffness compared to a particle trapped in Hotspot 2, see Chapter 4 of the references thesis⁵⁰ for details. Note that for gold nanoparticles of the same size, the behavior of the hotspots is the opposite.⁴³

From Figure 3, we see that many more particles are trapped with low stiffness values, and that, may seem like corresponding to trapping events at Hotspot 2. This finding is unexpected considering the availability of hotspots for trapping, there being twice as many of type 1 than type 2. To investigate this deviation, we plot the number of trapping events for each excitation intensity in Figure 4a. The numbers in blue and red show the events

for Hotspot 1 and 2, respectively, for two intensity regions. We see that, until an intensity of about $1.5 \text{ mW}/\mu\text{m}^2$, there was a ratio of about 2/1 for Hotspot 1/Hotspot 2 trapping events, as expected. For higher intensities, we observed a very large number of trapping events with very low trap stiffnesses. These trapping events, shown in purple in Figure 4a, cannot be classified as occurring in Hotspot 1 or 2 based on their stiffness values alone. Our hypothesis is that the origin of their low measured stiffness values is not due to a weak optical force but rather the effect of an additional destabilization force. Nevertheless, even beyond $1.5 \text{ mW}/\mu\text{m}^2$, there were some trapping events that clearly occurred in Hotspot 1 (see Figure 4a), due to their characteristically high stiffness values.

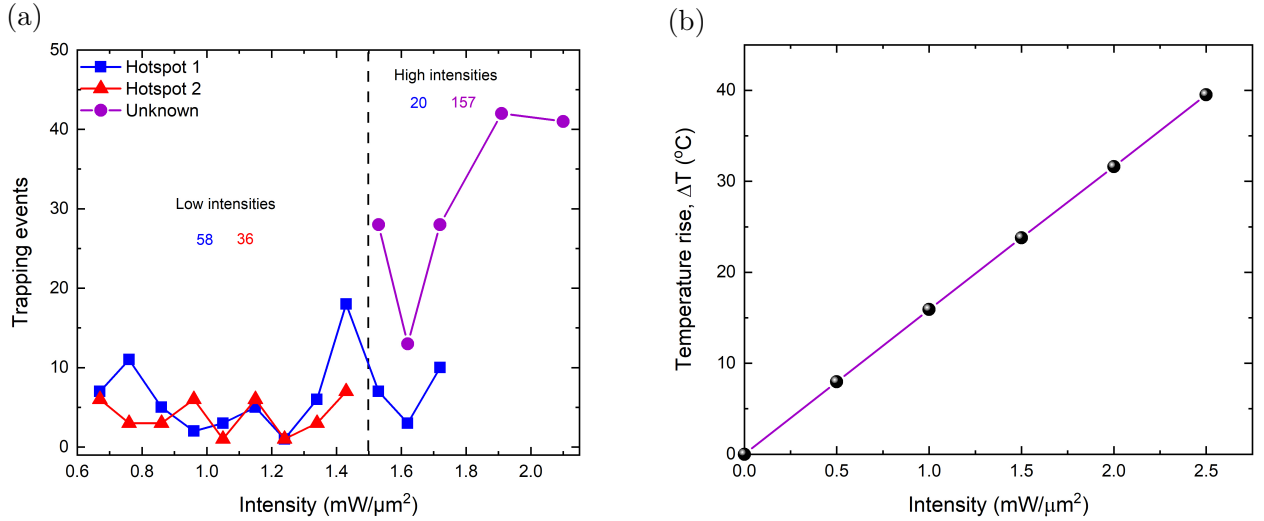


Figure 4: (a) Trapping events occurred for each excitation intensity, classified as taking place at Hotspot 1 (blue line), Hotspot 2 (red line), or undetermined (purple line). The numbers in blue, red, and purple correspond to the number of trapping events, respectively. (b) Simulated temperature rise at the center of illumination on the gold film as a function of the incident laser intensity. There is a temperature rise of 15.9°C for every $1 \text{ mW}/\mu\text{m}^2$ intensity increase.

To determine other effects that could reduce the trap stiffness, we considered plasmonic heating and the subsequent temperature rise of the surrounding environment (water) as we increased the laser intensity. In Figure 4b, we simulated the temperature rise at the center of illumination on the metamaterial structure, with parameters matching the experimental

conditions. A linear relationship is observed as expected from theory,⁵² showing a rise of about 15.9°C per 1 mW/ μm^2 intensity increase. At 1.5 mW/ μm^2 there is a temperature rise of about 24°C, which is sufficient to generate strong temperature gradients and convection currents that hinder efficient trapping.^{47,52} The temperature for which thermal effects start contributing (positively or negatively) to the trapping process depends on many parameters such as the gold film deposition (thickness, adhesion layer, substrate),⁵² the height of the microwell where the particles are suspended,^{32,53} the Soret coefficient of the nanoparticles and their interaction with surfactants,^{46,47} the plasmonic design,^{54,55} and so on. Hence, controlling the trapping landscape as the incident intensity increases is very complicated and, therefore, it is highly desirable to trap with low intensities.

Considering our experimental conditions, an incident laser intensity lower than 1.5 mW/ μm^2 should be used. The temperature change at this intensity (24°C) is typical in similar experiments.^{47,56} Above this temperature, the temperature gradients created strong convection flows in the solution that facilitated fast transport of thermophilic particles toward the hottest areas,^{34,46,57,58} leading to fast trapping of a large number of particles (see Fig. 4a); the convection flows transported particles close to the hotspots from a distance further than the optical forces range. However, due to their momentum and kinetic energy on approaching the hotspots, the particles were harder to trap, leading to lower stiffness values. This affected particles trapped in both hotspots and, therefore, we cannot determine the trapping location (Hotspot 1 or 2) by the measured stiffness value alone for these (purple) trapping events.

The effect of temperature rise may also come into play at even lower intensities. In Figure 5, we plot the trap stiffness histograms for trapping events with laser intensities up to 1 mW/ μm^2 (Fig. 5a) and up to 1.5 mW/ μm^2 (Fig. 5b). Interestingly, we see that for intensities lower than 1 mW/ μm^2 , the distributions of events over the two hotspots are distinguishable, with more trapping events at Hotspot 1, as expected. However, even before the incident intensity exceeds 1.5 mW/ μm^2 , we see that it is harder to distinguish

between the two distributions (Fig. 5b) implying that heating effects were already present. In addition, looking at the average stiffness values ($k_{1,norm}$ and $k_{2,norm}$), we note that, as we include higher intensities, the average value decreases for both hotspots owing to thermal effects. Therefore, using an intensity of less than $1 \text{ mW}/\mu\text{m}^2$ should be a safe regime to trap nanoparticles efficiently.

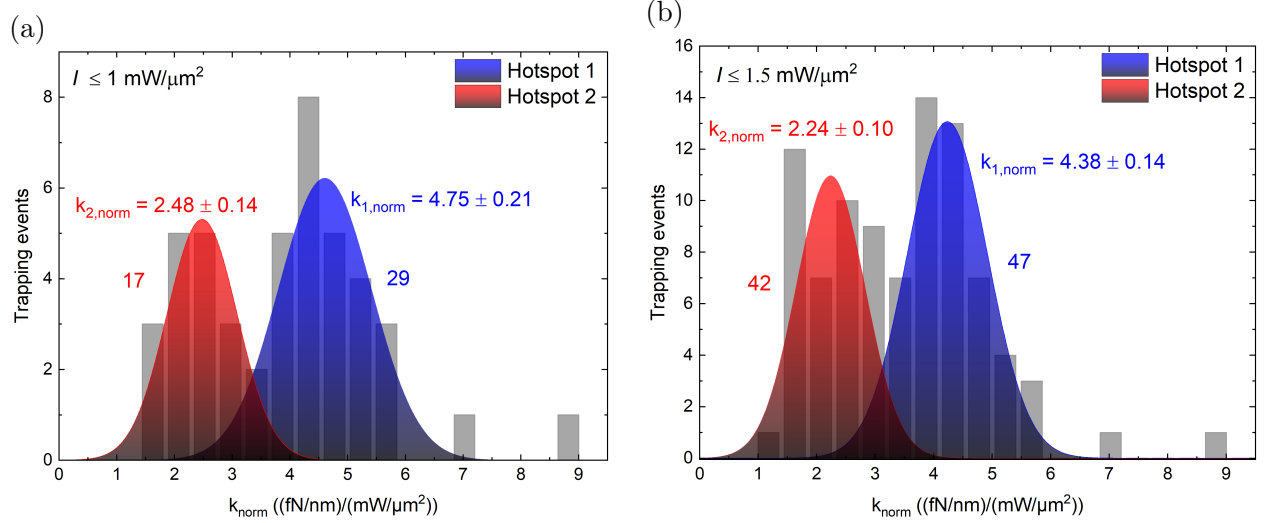


Figure 5: Histograms of the measured normalized trap stiffnesses when we include trapping events with excitation intensities (I) of up to (a) $1 \text{ mW}/\mu\text{m}^2$ and (b) $1.5 \text{ mW}/\mu\text{m}^2$ with Gaussian fits on the hotspot distributions. The values $k_{1,norm}$ and $k_{2,norm}$ refer to the average stiffness value for particles trapped in Hotspot 1 (blue curve) and Hotspot 2 (red curve), respectively. The numbers in blue and red refer to the number of trapping events.

Based on the theory of optical forces, the trap stiffness increases linearly with the intensity.⁵⁹ Thus, the normalized trap stiffness (trap stiffness divided by the intensity) should be constant as a function of intensity if only optical forces are present. In our case, as shown in Figure 6, the normalized trap stiffness linearly decreases with increasing intensity by about $1.5 (\text{fN/nm})/(\text{mW}/\mu\text{m}^2)$ per $1 \text{ mW}/\mu\text{m}^2$ for both hotspots. Evidently, the temperature increase and the resulting thermal flows counteract the strong optical forces, with both phenomena linearly correlated to the incident intensity, therefore resulting in inefficient trapping. It worth noting once again that given the experimental conditions in this work, working with as low an intensity as possible leads to the most efficient trapping. That may

also be due to self-induced back-action (SIBA)-assisted trapping since we excited the plasmonic field with a near-resonant wavelength.^{43,60} Finally, an interesting observation is that for those trapping events at high laser intensities, leading to low stiffness values (see purple points in Fig. 6), the normalized trap stiffness remained constant with increasing intensity. This could be due to thermal effects and optical forces reaching an equilibrium beyond a critical temperature. Investigating the trapping process in this high intensities regime is an interesting topic for future study.

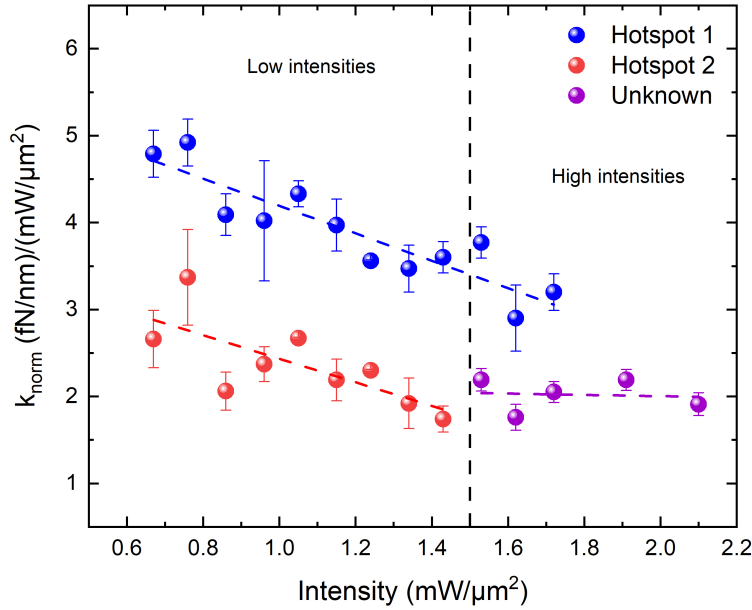


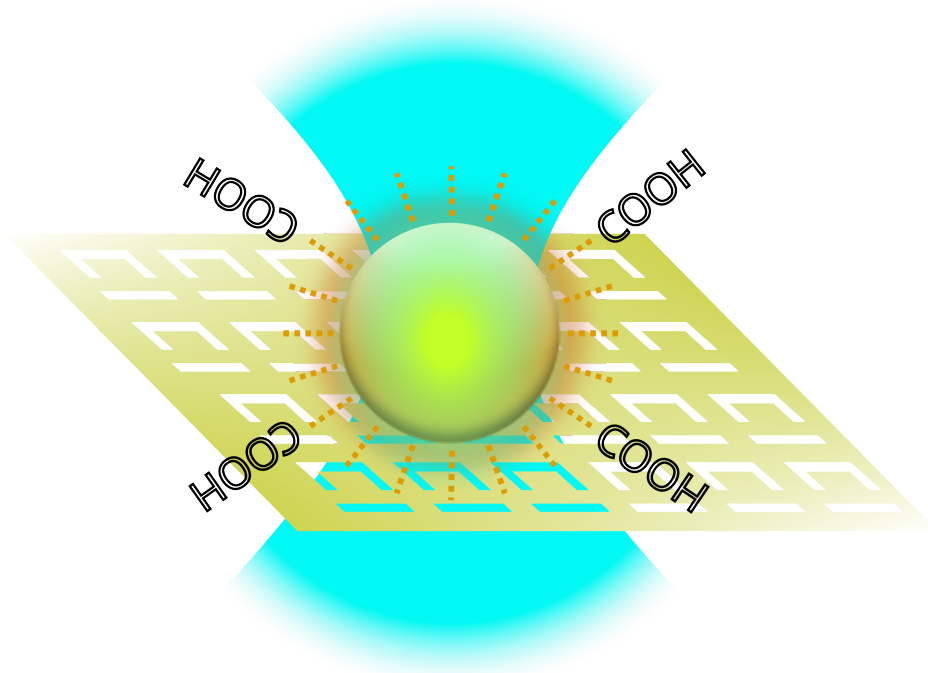
Figure 6: Normalized trap stiffnesses as a function of the excitation laser intensity for the two hotspots (blue and red), and for the trapping events which cannot be classified in one or other of the hotspots due to the low values (purple).

4. Conclusions

We demonstrated trapping of custom-synthesized nanographene-based D7H-NPs using a metamaterial plasmonic tweezers. Multiple trapping events were achieved with a range of incident laser intensities. The stiffness values measured were very high ranging between 0.47 - 8.8 (fN/nm)/(mW/μm²) and, based on statistical analysis, the hotspot location (Hotspot 1 or 2) where a particle was trapped could be determined. However, we noticed a discrepancy


in the expected particle trapping distribution, which was caused by the temperature rise and induced thermal flows in the solution as the incident laser intensity increased. The method used to classify the trapping hotspot locations only considered optical forces and, thus, is insufficient beyond an incident intensity of about $1.5 \text{ mW}/\mu\text{m}^2$ where thermal effects come into play. At this intensity, the temperature rise was about 24°C , based on simulations. Beyond this temperature we observed fast transport of particles towards the hotspots, and the resulting trap stiffness values were low due to destabilization of the trapping mechanism. Further analysis showed that, even for intensities lower than $1.5 \text{ mW}/\mu\text{m}^2$, thermal effects appeared, and trapping with intensities lower than about $1 \text{ mW}/\mu\text{m}^2$ is desirable if one wants to completely avoid thermal effects. Investigating the trapping performance beyond the critical intensity (or temperature) is an interesting topic since our data imply that beyond that an equilibrium is reached between the optical and thermal forces. Being able to control the trapping process in this high intensity/temperature regime may be useful for nanopositioning of quantum emitters in an ordered array for potential use as scalable single-photon sources and studying collective radiative interactions.

TOC Graphic



Trapping of a D7H-NP on a plasmonic metamaterial array using near-field forces.

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