Probing Spatiotemporal Stability of Optical Matter by Polarization Modulation

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Supporting Information

ABSTRACT: Light-driven self-organization of plasmonic nanoparticles via optical binding interactions offers a unique route to assemble mesoscale photonic clusters and chains. However, stability becomes an issue when more nanoparticles are added into the clusters and chains, since the theoretical optical binding strength is inhomogeneous and anisotropic in optical matter systems. Here we study the spatiotemporal stability of optical matter chains self-organized by two to eight ultrauniform gold nanospheres in a linearly polarized optical line trap. Perturbations are introduced into the nanosphere chains by periodically switching the polarization to be either parallel or perpendicular to the orientation of the chains, where the spatial and temporal variation of optical binding strength has been revealed. In addition, we found that the average oscillation amplitude and stability of the particles can be tuned by the frequency of polarization modulation. These results demonstrate a new way to study and improve the stability of optical matter and provide a promising strategy in engineering optical forces at the mesoscale.

KEYWORDS: Gold nanoparticles, optical binding, polarization modulation, spatiotemporal stability

Assembly of plasmonic nanoparticle clusters has attracted increasing research interest due to its potential applications in sensors, lasing, and switching.1−5 These structures usually exhibit remarkably different physical properties far beyond their individual components. For example, the coherent Fano resonances in a plasmonic nanocluster can enhance the optical four-wave mixing6 and second harmonic generation.7 Fano resonances in a plasmonic nanocluster can enhance the stability beyond their individual components. For example, the coherent Fano resonances in a plasmonic nanocluster can enhance the optical four-wave mixing6 and second harmonic generation.7 Among various self-assembly methods,8−12 the optical binding13,14 technique has received special interest due to its versatile manipulation and capability of assembling mesoscale (i.e., interparticle separations of hundreds of nanometers) optical clusters without chemical functionalization of the nanoparticles.15−21 In addition, the optically bound colloidal nanoparticles usually exhibit a few anisotropic characters. For example, optical binding interaction is directional, and the bond length and strength also depend on the light polarization.17,22,23 Anisotropic interactions are the basis of forming complex morphologies,24,25 which are typically forbidden in van der Waals or electrostatic forces based assembly approaches.26,27

Because of strong Brownian motion, optical binding of nanoparticles in solution has only been realized for a few particles.16−19,28,29 Stability is a major issue that limits the assembly of larger-scale optical matter. Stability of optical matter has both extrinsic and intrinsic characters. The extrinsic stability is defined by the optical field profile and light intensity. Optical binding strength is linearly proportional to the light intensity, so larger intensity can make nanoparticle clusters more stable. Demeris and Florin have shown that ultrastrong optical binding of several metallic nanoparticles can be realized in standing wave optical line traps,16 where interference can increase the local intensity by 4 times. We later found that the special profile of a standing wave can give additional stability to nanoparticle chains because the restricted z-axial thermal motion of the nanoparticles can couple to and reduce fluctuations in the lateral plane.29 The intrinsic stability is related to the specific configuration of constituent particles due to the anisotropic and long-range multiple scattering nature of optical binding interactions, yet this intrinsic property is largely unknown. Therefore, probing and improving the stability of optical matter are of great importance in assembling colloidal nanoparticles in large quantity.

Optically bound particle chains are good candidates to study one-dimensional optical matter system.16,17,19,30−34 However, all previous studies were focused on optical binding behaviors in static optical fields, and dynamic optical matter driven by modulated optical binding interactions has not been observed before. In this letter, we have assembled two to eight ultrauniform gold nanoparticles into chains in a linearly polarized optical line trap and investigated their spatiotemporal stability by polarization modulation. The interparticle separations of the nanoparticle chains are forced to oscillate when the linear polarization is modulated periodically with a direction parallel and then perpendicular to the orientation of the chains. We show that the optical binding strength is spatially inhomogeneous along the nanoparticle chains depending on the total number and relative positions of particles, and it is temporally variable depending on the frequency of polarization modulation. In particular, the average oscillation amplitude of the particles can be tuned by increasing the frequency of polarization modulation, where the stability for terminal

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The ultrauniform spherical gold nanoparticles with a diameter of 101 ± 3 nm were purchased from nanoComposix Inc. The particles are coated by sodium citrate with a zeta potential of −51 mV. A Gaussian beam with wavelength of 800 nm was generated by a Ti:sapphire laser (Spectra-Physics 3900S) and then shaped into an optical line beam using a spatial light modulator. The laser power was fixed at 190 mW. As shown in Figure 1b, the hologram represents the phase modulation caused by a convex cylindrical lens, which is designed to generate an optical line with a diffraction limited width and a broad Gaussian intensity profile along the long axis, where the intensity drops to $1/e^2$ of the maximum intensity at a radius of 3 μm from the trap center on the trapping plane focused by an objective (Olympus UPLSAPO 60XW, NA 1.2). The optical line can tightly confine Au nanoparticles in the transverse direction but allows free movement in the longitudinal direction. The nanoparticles self-organized in the optical line near the upper glass surface of an aqueous sample cell placed on an inverted microscope (Olympus IX71). A full-wave liquid crystal variable retarder (Thorlabs LCC1413-B) was used to switch the light polarization between parallel and perpendicular to the chain orientation. By modulating the voltage of the controller of the liquid crystal retarder, the light polarizations can be changed in a very short time (~60 ms). Because of the limitation of the response speed of the liquid crystals, the maximum modulation frequency in our experiments was set at 5 Hz.

Figure 1c shows the dark-field optical images of optical matter chains with one to eight Au nanoparticles. These chains were obtained by sequentially trapping new nanoparticles from a diluted solution, which occurred in time intervals typically over 10 min, and their images were taken by a camera with frame rates of 300–400 fps (see the Supporting Information, Video 1). The optical matter chains can be stably trapped until the laser is off. Figure 1d presents the trajectories of single to eight particles along the line trap direction with polarization modulation frequency of 0.5 Hz. The modulation cycle time of 2 s is long enough for particles to reach the equilibrium states under two different polarizations. When a single Au nanoparticle is trapped, it exhibits obvious fluctuations near the center of the trap. However, when two or more particles are trapped in the optical field, they show collective motions with smaller fluctuations than a single particle due to optical binding. In addition, there is always a near-one-lambda ($\lambda = 600$ nm for the laser wavelength in water) separation for particles under two different polarizations, but the perpendicular polarization gives smaller interparticle spacings than parallel polarization, leading to oscillation of the nanoparticle chains under periodic modulation of the light polarization direction.

Optical binding of nanoparticles in linearly polarized light can be described by the interactions between coupled radiating dipoles. An oscillating electric dipole, which is induced along the polarization of light, radiates more strongly in the direction perpendicular to the polarization in the far field, where the secondary field generated by interference between scattering and incident fields can be experienced by other induced dipoles (see Figure S1, Supporting Information). As a result, optical binding of nanoparticles is stronger in the perpendicular direction due to the mutual interactions among coupled dipoles, and the optical binding strength increases with the light intensity (Figure S2, Supporting Information).

The average centroid positions of the particles with two different polarizations are extracted from Figure 1d and presented in Figure 2a. Figure 2b shows the average oscillation amplitudes of different particles in the three to eight particle chains. Interestingly, the average oscillation amplitudes of the particles located at the end of the chains almost remained at 125 nm (red line) while their nearest neighbors (orange line) increased from 0 to 120 nm as the particle numbers varied from...
three to eight. These results demonstrate that the optical binding interaction is anisotropic under linear polarization and dependent on the chain length.

To further understand the observed multiparticle arrangements, we calculated the equilibrium optical binding configurations for two to eight Au nanoparticles using an electro-dynamics–molecular dynamics simulation method. The simulation model assumes Au nanospheres (100 nm diameter) illuminated by a linearly polarized plane wave (vacuum wavelength of 800 nm) in water, where the Au nanospheres are movable along a line in a transverse plane of light. Optical forces for the particles are calculated using the Maxwell stress tensor approach, and equilibrium configurations are found when all forces are zero and there are restoring forces to maintain the configurations. As shown in Figure 2c, the predicted interparticle separations are around 600 nm, which is equal to the wavelength of the trapping laser in water. Perpendicular polarization gives particle spacings smaller than that at parallel polarization. Figure 2d further shows that the terminal particles have larger jumps compared to central particles. These calculations generally fit well with our experiment results, except for the oscillation of terminal particles. Although the optical line trap profile is close to a plane wave in one dimension, it still has (weak) intensity and phase gradients that could affect the motion of trapped nanoparticles. The optical binding interaction of terminal particles is weaker than that of central particles, so they are more sensitive to the beam profile, leading to the discrepancy between experimental and computational results in Figure 2b,d.

The stability of optically bound particles strongly depends on the interparticle optical binding strength. To develop a better understanding of their correlations, we analyzed the trajectories in Figure 1d and plotted the standard deviations of the fluctuations (σ) of two to five particles with different polarizations in Figure 3a (more data are shown in Figure S3). In our experiments, all particles are confined in the optical line; therefore, the standard deviations of fluctuations around their equilibrium positions could be used to describe their optical stability. We find that the addition of another particle to the chain significantly improves the stability of particles already in the chain. This phenomenon reveals an enhanced optical binding strength for longer particle chains, suggesting deeper potential wells near the optical binding positions.
To help elucidate the underlying mechanism of the spatial stability of chains with different particle numbers, we calculated the optical binding potential energy of two to five nanoparticles with two different polarizations. The light intensity is assumed to be 81 mW/μm², corresponding to the average intensity of the line trap used in our experiments. In Figure 3b, each curve is calculated by taking the integral of the optical binding forces when one particle is moved away from its equilibrium position in the range of −100 to 100 nm, while other particles remaining fixed. The potential energy is presented in the unit of \( k_B T_0 \) where \( k_B \) is the Boltzmann’s constant and \( T_0 = 300 \) K. Zero potential is set at the minimum of each curve. Considering laser heating, the thermal energy for laser illuminated Au particles in one-dimensional chains are estimated to 0.7\( k_B T_0 \) during our experiments (see the Supporting Information). As shown in Figure 3c, the widths of the potential wells at this thermal energy can then be used to evaluate the stability of particles at different polarizations and positions. The simulations display several important aspects: (i) except for the potential well for a particle at the symmetry center of the chain, all other potential wells are asymmetrical due to the long-range optical binding interactions and the asymmetric neighboring environment of the particles; (ii) a particle located at the central area must overcome the largest energy barrier to move from one equilibrium position to others. For particles located far away from the central position, the energy barrier becomes much easier to pass through; (iii) the addition of another particle to the chain increases the optical potential depths and decreases the potential widths of the particles already in the chain, thus improving the optical stability; (iv) the potential wells are much narrower for perpendicular polarization than parallel polarization. These calculations fit well with our experiment data, suggesting a close relationship between the stability of optical matter chains and the number and spatial distribution of constituent particles.

Next, we investigated the temporal stability of three to five Au particles chains by varying the modulation frequency from 0.5 to 5 Hz. Figure 4a–c presents the probability density distributions of separations between two particles for chains with three to five particles under different modulation frequencies (for their trajectories, see Figure S4). The blue, green, orange and red lines present the statistics of all the first, second, third, and fourth equilibrium separations, respectively. For example, in the three-particle chain, the separations between two particles include \( d_{12}, d_{23}, \) and \( d_{13} \), in which \( d_{12} \) and \( d_{13} \) are the nearest neighbors (3-1st), while \( d_{13} \) (3-2nd) is the next nearest neighbor. By analogy, the relation of particle pairs in a chain of five particles involves the nearest (5-1st), the next nearest (5-2nd), the third nearest (5-3rd), and the fourth nearest (5-4th) neighbors.

Note that particles fluctuate further away from the equilibrium positions due to the Brownian motion will result in wider probability density distributions. Besides, in Figure 4a–c, each curve splits into two peaks, which are assigned to two different equilibrium positions caused by the perpendicular
and parallel polarizations. The corresponding positions of the peaks are smaller and the density distribution curves are much narrower with perpendicular polarization. These observations are consistent with Figure 3, showing that optical binding for perpendicular polarization is much stronger. Figure 4d-f shows the optical binding separations for the first, second, third, and fourth nearest neighbors versus modulation frequency. The hollow and solid symbols represent perpendicular and parallel polarizations, respectively.

It is worth noting that, first, the particles have much higher probability in occupying the equilibrium position under perpendicular polarization. Second, the probability density for particles with two different polarizations can be greatly influenced by the modulation frequency. As the frequency increases, the probability density for particles with perpendicular polarization increases while with parallel polarization it decreases. In addition, the separation of the two peaks decreases and finally merges together at 5 Hz. These observations demonstrate two important results: (i) the interparticle separation can be changed by laser polarization modulation frequency; (ii) at a high modulation frequency, the nanoparticles can overcome the weak potential well caused by the parallel polarization and prefer to occupy the equilibrium configurations corresponding to the perpendicular polarization. These findings, in turn, provide a new method to dynamically control the interparticle separations of optical matter by polarization modulation.

Figure 5 shows the modulation frequency dependent oscillation amplitude and position-specific stability of the five-particle chain. Because of the strong optical binding strength for the central particle (particle index 3), the amplitude almost remains at 0. For other particles (particle index 1, 2, 4, 5), the oscillation amplitude decreases as the frequency increases, and it decreases by 53% for the terminal particles. More importantly, the standard deviations of fluctuations with two different polarizations both decrease as modulation frequency increases, even though stronger perturbations are expected at higher frequency. With parallel polarization, the stability of the terminal pairs under 5 Hz modulation frequency is improved as much as 48% compared with 0.5 Hz modulation frequency.

To understand the enhanced stability and redistribution of probability density, we checked the time scale for the optically driven motion between the two equilibrium positions when switching the polarization direction, and that for Brownian diffusion at the equilibrium positions (see the Supporting Information). Both time scales are typically on the order of magnitude of 0.1 ms, which is much shorter than our modulation periods. However, the driven forces between the equilibrium positions have different amplitudes in different directions (Figure S5, Supporting Information), resulting in an anisotropy of the applied potentials. Anisotropic potentials applied by oscillating forces can bias the Brownian motion of a particle and lead to spatial redistribution of probability density, which is a possible reason for the shift of probability density of optical binding toward the equilibrium configuration at perpendicular polarization. In addition, periodically forcing a Brownian particle could lead to biased Brownian motion along the force direction. Recently, we found that the stability of a nanoparticle chain confined by an optical line trap on a glass surface is strongly affected by fluctuations of nanoparticles along the beam propagation direction (i.e., z-axis); if the z-axial thermal motion is restricted, the stability of optical binding can be largely improved. Therefore, if the Brownian motion of Au nanoparticles is biased along the optical line trap with reduced z-axial fluctuation, we would expect to see the improved stability under periodic forces associated with polarization modulation.

In summary, we have used a combined experimental and computational approach to demonstrate intriguing aspects in the stability of one-dimensional nanoparticle chain with strong optical binding interactions. The optical binding strengths of gold nanoparticles with parallel and perpendicular polarizations are different, resulting in versatile oscillation dynamics of the nanoparticles with polarization modulation. The nanoparticles have much higher probability in occupying a more stable potential well caused by the perpendicularly polarized light, due to biased Brownian motion. The spatiotemporal stability of the optically bound nanoparticles can be improved when the polarization modulation speed is fast and the optical binding is strong enough to suppress the thermal motion. We have shown that the optical polarization modulation is a new approach to probe and control the optical binding interaction in an optical matter system. These novel findings provide a promising strategy in manipulating optical forces and improving the spatiotemporal stability of optical matter at the mesoscale, which can potentially lead to the assembly of larger-scale optical matter with designed functionalities.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b05128.

Montage of eight independent clips showing single to eight gold nanoparticles trapped by an optical line with 0.5 Hz polarization modulation (AVI) montage of seven independent clips showing optical binding of five Au nanoparticles confined by an optical line with different polarization modulation frequencies (AVI)
Polarization-dependent optical binding interactions, power-dependent optical binding of a chain with three gold nanospheres, standard deviations of two to eight particles under different optical polarizations, thermal energy for laser illuminated Au nanoparticles, and timescales of optically driven motion and Brownian motion.

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Notes
The authors declare no competing financial interest.

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REFERENCES
(9) Mann, S. Nat. Mater. 2009, 8, 781–792.