Creating Multifunctional Optofluidic Potential Wells for Nanoparticle Manipulation

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Supporting Information

ABSTRACT: Optical forces have enabled various nanomanipulation in microfluidics such as optical trapping, sorting, and transporting of nanoparticles (NPs), but the manipulation is usually specific with a certain optical field. Tightly focused Gaussian beams can trap NPs but not sort them; moderately focused Gaussian beams allow sorting microparticles in a flow but not NPs; quasi-Bessel beams can sort NPs in a flow but cannot control their positions due to low trapping stiffness. All these methods rely on the axial variation of laser intensity. Here we show that multifunctional and tunable optofluidic potential wells can be created for nanomanipulation by synchronizing optical phase gradient force with fluid drag force. We demonstrate controlled trapping and transporting of 150 nm Ag NPs over 10 μm and sorting of 80 and 100 nm Au NPs using optical line traps with tunable phase gradients in experiments. Our simulations further predict that simultaneous sorting and trapping of sub-50 nm Au NPs can be achieved with a sorting resolution of 1 nm using optimized optical fields. Our method provides great freedom and flexibility for nanomanipulation in optofluidics with potential applications in nanophotonics and biomedicine.

KEYWORDS: Optofluidics, optical trapping and manipulation, optical sorting, nanoparticles

Since the observation of a single-beam optical trap in 1986,1 optical tweezers have gained enormous attention during the past three decades.2−10 Optical forces provide a versatile and noncontact route to control and manipulate small objects, such as optical trapping, sorting, and transporting of micro- and even nanostructures.6,11−15 However, the manipulation is normally specific with a certain optical field. For example, intensity gradient forces, either from a focused laser beam or near-field enhancement of plasmonic antennas and apertures,17−22 can tightly confine multiple colloidal particles but not sort them because they tend to aggregate in optical traps.23 Using differentiated optical forces along the beam propagation direction or in tailored optical lattices, microparticles could be sorted in flowing liquids by using optical chromatography24−27 and optical fractionation.28,29 However, the sorting process becomes difficult as the size of a dielectric NP reduces to 200 nm.30 Optical sorting of 100−200 nm diameter Au NPs has been achieved in experiments based on strong optical extinction forces arising from resonance light excitations.31−33 and multidirectional static sorting of silicon NPs of about 150 nm diameter with a 10 nm difference in size has been proposed based on simulations using noncollinear beams of different wavelengths.34 Very recently, Shi et al. found that potential wells created by synchronized optofluidic dual barriers using a quasi-Bessel beam allow sorting NPs with diameters ranging from 60 to 100 nm with a resolution of 10 nm.15,30 However, these methods do not provide nanometer-scale spatial confinement of the sorted NPs. Controlled optical trapping and sorting of NPs in fluidic environments remains a significant challenge.

The challenge arises from the different regimes of stiffness that optical trapping and sorting normally work with.15 Classic optical traps work with stiffness of 10−6 to 10−4 N/m in order to confine NPs with strong Brownian motion in solution; conventional optical chromatography works with stiffness of 10−8 to 10−6 N/m that can sort microparticles but not NPs.24−27 Shi et al. found that loosely overdamped potential wells with stiffness of 10−10 to 10−8 N/m are suitable for nanoscale optical sorting.15,30 However, the large gap between the stiffness ranges of the two regimes prevents simultaneous optical trapping and sorting at the nanoscale. For example, the 100 nm Au NP in the quasi-Bessel sorting field had a large vibration amplitude over 6 μm due to weak trapping stiffness.30 It seems that nanoscale optical sorting and trapping are incompatible and cannot exist simultaneously. Optical sorting and spatially controlling nano-objects in an accurate way at the nanometer scale is thus a key issue in the field of optical manipulation.35

Here we report an approach to address this issue by creating optofluidic potential wells using optical phase gradients. Current optofluidic sorting methods15,30,35 rely on the axial variation of laser intensity, where a laser beam propagates...
opposite to the flow direction in order to generate strong optical extinction forces. Phase gradient offers a unique avenue to generate strong lateral optical force in the cross-section of a laser beam, which can be applied to sort and transport metal NPs in static liquid environments, yet the phase gradient alone cannot trap NPs. In this work, we demonstrate that multifunctional and tunable optofluidic potential wells can be created by synchronizing the phase gradient force and fluid drag force, allowing controlled optical trapping, sorting, and transporting of metal NPs with sub-100 nm diameters. The optofluidic potential wells work with stiffness $k \approx 10^{-6}$ N/m, a regime that was considered to work only for microscale sorting. By tuning the phase gradient and laser power of a quasi-one-dimensional optical field (optical line trap) and the velocity of flow, the potential energy distributions of metal NPs can be precisely engineered in the optofluidics. For example, controlled transport of a single 150 nm Ag NP over 10 μm and sorting of 80 and 100 nm Au NPs have been demonstrated with a near-infrared laser ($\lambda = 800$ nm). Additionally, our simulation predicts that simultaneous sorting and trapping of sub-50 nm Au NPs with a sorting resolution of 1 nm can be achieved by optimized optofluidics, for example, using 532 nm light to enhance the optical trapping and sorting forces. Our work bridges the significant gap between nanoscale sorting and optical trapping by using phase gradient forces and provides a unique solution to the “formidable challenge” of nanoscale optical sorting in the conventional regime of optical trapping.

The physical model of the trapping of a single NP between the optical and fluidic barriers is presented in Figure 1a. The optical barrier is dominated by the optical force, and the fluidic barrier is created by the drag force. We propose that in order to create an optofluidic potential well using an optical force and a fluid drag force with opposite directions, the magnitude of the optical force must increase along the flow direction. Note that the drag force is constant in a static flow based on Stokes’ law. There are two ways to obtain this position-dependent optical force: (i) a converging laser beam with increasing axial intensity along the flow direction (Figure 1b-I); for example, the focused Gaussian beam used in traditional optical chromatography and the quasi-Bessel beam used for high-precision sorting satisfy this requirement; (ii) an extended optical field with strong phase gradient in the lateral direction of the laser beam; for example, an optical line trap with tailored phase profile (Figure 1b-II). The phase gradient force acting on a point-like dipole particle is given by

$$F_{\text{phase}} = \frac{\alpha^*}{2} I N \varphi$$

where $\omega$ is the frequency of light, $\alpha^*$ is the imaginary part of the particle’s polarizability, $I$ is the intensity of the field, and $\varphi$ is the phase. The phase profile of an optical line follows a parabolic function of $\varphi(x) = px^2$ along the long-direction ($x$-direction), and the intensity profile follows a Gaussian function of $I(x) = I_0 \exp(-2x^2/\omega^2)$, where $p$ is a phase parameter and $\omega$ is an intensity parameter. These lead to a phase gradient force of $F_{\text{phase}} = \alpha^* \varphi \exp(-2x^2/\omega^2) px$, and the sign of $p$ needs to be positive in order to create the required force in the direction opposite to the fluid flow. Figure 1c shows the calculated optical forces (red line) exerted on a single Ag NP (150 nm in diameter). The forces are centrosymmetric with directions pointing from the center of the line to the tails, and the corresponding energy potential distribution (blue line) indicates the NP is always pushed out of the optical line because no potential well exists with pure optical forces. However, by introducing a Stokes’ drag force, the total force exerted on the NP is no longer centrosymmetric and an equilibrium trapping position (where the total force is zero and restoring force exists around this position) appears. Therefore, we expected the optical-fluidic barriers could confine the NP toward the equilibrium position when the NP is on the left/right of the equilibrium position.

To verify this conjecture, we carried out the trapping experiments in a microfluidic chip (Figure 2a). The width of the channel was 1 mm and its height was 100 μm, allowing dark-field microscopy with a high NA (1.2) objective. As the light propagates along the $z$-direction, the strong scattering force pushes the NP upward, and the NP is trapped near the upper polydimethylsiloxane (PDMS) surface, as shown in Figure 2b. A spatial light modulator (SLM) is used to shape a Gaussian beam ($\lambda = 800$ nm) into an optical line, which is focused into the microchannel by the same objective. As the light propagates along the $z$-direction, the strong scattering force pushes the NP upward, and the NP is trapped near the upper polydimethylsiloxane (PDMS) surface, as shown in Figure 2b. A spatial light modulator (SLM) is used to shape a Gaussian beam ($\lambda = 800$ nm) into an optical line, which is focused into the microchannel by the same objective. As the light propagates along the $z$-direction, the strong scattering force pushes the NP upward, and the NP is trapped near the upper polydimethylsiloxane (PDMS) surface, as shown in Figure 2b.
Figure 2. Trapping of multiple Ag NPs in a flowing environment. (a) A high NA dark-field condenser is used to illuminate the NPs in a microchannel. (b) Schematic of the trapping of a single Ag NP in the optical line near the PDMS surface. The line trap with strong phase gradient creates a lateral force that balances the fluid drag force. The laser propagates along the z-direction. (c) A series of dark-field images that show the trapping process of several Ag NPs in the microchannel. The scale bar is 1 μm.

Figure 3. Trapping of a single Ag NP with tunable optofluidic potential wells. (a) The calculated position-dependent potential energy of the trapped Ag NP in the optical line as a function of fluid velocity (top panel, where the laser power is fixed at 125 mW) and the laser power (bottom panel, where the fluid velocity is fixed at 230 μm/s). (b) The experimental equilibrium positions (solid squares) of the trapped Ag NP. Contour curves from simulations are also plotted for comparison. These fluid velocities are estimated by fitting the NP trajectories in the trapping plane in the absence of the laser beam.

The scale bar is 1 μm that show the trapping process of several Ag NPs in the microchannel.

The results of these experiments show that the Ag NPs can be trapped in the dual barriers as we expected. The magnitude distribution of the lateral optical force along the line is inhomogeneous, which allows precise positioning of the NPs by tuning the fluid velocity across a wide range. Figure 3a shows the simulated potential energy of a single Ag NP with different fluid velocities (top panel) and different laser powers (bottom panel). The depth of the trapping potential is a function of the fluid velocity and the optical power (Figure S2). Additionally, the simulations reveal that both the fluid drag force and the laser power have significant influence on the potential energy distribution of the NP in the lateral direction of the light: (i) the equilibrium trapping position will shift toward the center of the optical line as the velocity increases, whereas it shifts away from the center with increasing laser power; (ii) with a fixed laser power, the energy barrier vanishes at a high fluid velocity; (iii) with a fixed fluid velocity, the energy barrier vanishes at a low laser power. The measured equilibrium positions of the trapped Ag NP as a function of fluid velocity and laser power are shown in Figure 3b, respectively. As the fluid velocity increases, the NP gradually moves toward the center (zero position) of the optical line and the maximum shift could reach to ~6 μm. On the contrary, as the laser power increases, the NP shifts in the opposite direction as revealed by the power-dependent optical trapping experiments (Movie S1). These results generally fit well with the simulations.

Furthermore, the increase of fluid velocity directly changes the drag force applied on the NP. The NP can be stably trapped in the flowing environment when the optical force $F_{\text{opt}}$ equals the drag force $F_{\text{drag}} = 6\pi\mu R_v$, where $\mu$ is the dynamic viscosity of water, $R$ is the hydrodynamic radius of the NP, and $v$ is the particle’s velocity. Therefore, the measured drag forces at different trapping positions can be used to map the magnitude distribution of the lateral optical force exerted on the NP. The measured forces fit well with the calculated optical forces (Figure S3).

Because the lateral optical force generated by the phase gradient of the optical lines is proportional to $IV\phi$ (eq 1), a series of differentiated trapping potentials can be created by tuning the phase gradient of the optical line with a constant laser power. We designed a series of phase profiles to generate optical line traps with different phase gradients. Figure 4a shows two representative phase distributions of a long ($p = 0.181 \text{ rad}/\mu\text{m}^2$) and a short ($p = 0.826 \text{ rad}/\mu\text{m}^2$) optical line along their long axes (Figures S4–6). A sequential combination of optical line traps with tunable phase gradients can serve as nano-optical conveyor belts that allow dynamic optofluidic transport of single Ag NPs. Figure 4b shows the dark-field images of a trapped 150 nm Ag NP in the microchannel with different phase gradients ($p$) in the range of 0.181 to 0.826 rad/μm². The fluid velocity is kept at ~160 μm/s and the laser power is fixed at 240 mW. The NP continuously moves out of the center (zero position) of the optical lines while being trapped as $p$ decreases and then moves...
toward the initial position as \( p \) changes back to 0.826 rad/\( \mu m^2 \). The corresponding trajectory of the NP is shown in Figure 4c. Note that the time scale for the optically driven motion between the two neighboring equilibrium positions is tens of milliseconds, which leads to the transition steps in the trajectory. Additionally, switching of the phase profiles on the SLM may take a few milliseconds. During these intervals, the fluid drags the NP along the \( x \)-direction in the absence of optical force, which causes the sharp edges in Figure 4c. Figure 4d summarizes the phase-dependent positioning of a Ag NP; the results show a conveyance step of hundreds of nanometers and indicate there is still room for higher transportation of the NP.

Figure 5. Optofluidic sorting of metal NPs. (a) Dark-field images the show the sorting of two Ag NPs (150 and 100 nm in diameter) with a sequential combination of three optical lines with different phase gradients. The laser power is 140 mW and the fluid velocity is 80 \( \mu m/s \). (b) The corresponding trajectories of two Ag NPs. (c) Sorting of multiple 100 and 80 nm Au NPs. The scale bars are 1 \( \mu m \). (d) Calculated optical forces and potential wells of 100 and 80 nm Au NPs using parameters based on the experimental conditions. (e) Calculated potential wells for sorting sub-50 nm NPs with phase gradient parameter \( p = 0.25 \) rad/\( \mu m^2 \), laser wavelength \( \lambda = 532 \) nm, power \( P = 1 \) W, and flow velocity \( v = 455 \) \( \mu m/s \). (f) Calculated potential wells that allow 1 nm sorting resolution with \( p = 0.13 \) rad/\( \mu m^2 \), \( \lambda = 532 \) nm, \( P = 1 \) W, and \( v = 177 \) \( \mu m/s \).
accuracy by further engineering the light phases. The trapping stiffness calculated from the variation of the NP’s position is around $10^{-6}$ N/m, which slightly increases with larger phase gradient (shorter optical lines).

To help elucidate the underlying mechanism of the position shift and the trapping stiffness of a single NP in different optical lines, we calculated the optical forces exerted on the Ag NP along z-direction in Figure 4e (Table S1 for the parameters used in the simulations). The gray dashed line represents the drag force. The results reveal that (i) with appropriate engineering of the phase gradient of the optical lines, the effective trapping length can be adjusted; (ii) the maximum force exerted on the Ag NP in a short trap ($p = 0.831$ rad/μm$^2$) is $\sim3.7$ times larger than that in a long trap ($p = 0.168$ rad/μm$^2$); (iii) the trapping stiffness decreases with the increase of the line length. When the total force (optical and fluidic) on the NP is zero, a larger trapping stiffness would give a much narrower potential well at the equilibrium position, as shown in Figure 4f. Additionally, the simulated equilibrium positions change dramatically with a tunable phase gradient as we expected.

Having demonstrated that these optical line traps can be used to transport a NP, we also investigated their capacity for particle sorting. We calculated the optical force in different line traps as a function of particle size (Figure S7). The forces increase with the particle size, suggesting NPs with different sizes could be separated along the optical line with a fixed fluid flow (drag force), which is similar to conventional optical chromatography. Figure 5a shows the dark-field images of two trapped Ag NPs with diameters of 150 and 100 nm in a sequential combination of optical lines ($p = 0.83, 0.38,$ and 0.25 rad/μm$^2$). The Ag NPs with different sizes have different scattering spectra, so it is easy to distinguish them from the dark-field images (the yellow and green colors present the 150 and 100 nm NPs, respectively). It can be seen from the images that the separation of two NPs is greatly increased as the phase gradient decreases from 0.83 to 0.25 rad/μm$^2$. The corresponding trajectories of two NPs are shown in Figure 5b.

The NPs with diameters much smaller than the wavelength of the light can act as oscillating electric dipoles. When two NPs are trapped in the optical lines, the secondary field generated by interference between scattering and incident fields of one NP can be experienced by the other NP and (Figure S8 compares the optical force exerted on a 100 nm NP with and without the trapping of a 150 nm NP in optical lines), leading to optical binding interactions. Strong repulsive forces will arise when the separation of two NPs is smaller than the nearest optical binding separation, which could provide a minimum interparticle separation of $\sim600$ nm. This is different from other optofluidic sorting methods where NPs are trapped along the light propagation direction, and sorted NPs could aggregate with small separations. The separation of the NPs in the short trap (0.83 rad/μm$^2$) is $\sim700$ nm, which is close to the optical binding separation of two metal NPs in a static liquid environment. Additionally, as the phase gradient changes from 0.83 to 0.38 rad/μm$^2$, the fluctuation of the 100 nm NP becomes much stronger, whereas the fluctuation of the 150 nm NP slightly increases. This phenomenon indicates that the optical binding interaction strongly influences the trapping of the 100 nm NP in the short trap (0.83 rad/μm$^2$), but it can be ignored for the trapping of the 150 nm NP. The fluctuation of the 150 nm NP becomes more obvious in the long line trap (0.25 rad/μm$^2$) due to the broadening of the potential well.

To explore the sorting resolution of our system, we tested NPs with smaller size differences. Figure 5c shows the dark-field images of multiple 100 and 80 nm Au NPs trapped in an optical line ($p = 0.25$ rad/μm$^2$, Movie S2). The laser power is 400 mW and the fluid velocity is $\sim175$ μm/s. The results show that the Au NPs could form linear dimer and trimer structures due to optical binding in the flowing environment and could separate into two clusters with an average separation of $\sim5$ μm. Figure 5d shows the calculated optical forces and potential wells of 100 and 80 nm Au NPs. The dashed lines give the drag forces on the NPs with fluid velocity of 175 μm/s. Note that the drag force is linearly proportional to particle size, so the forces are different for the two NPs. The calculated equilibrium positions for the 100 and 80 nm NPs are $x = -9.1$ and $-5.7$ μm, which agree with the experiment results.

So far no optical or optofluidic experiments have ever achieved precise sorting of sub-50 nm NPs and the demonstrated best sorting resolution is 10 nm for Au NPs between 60 and 100 nm diameter (note that the paper in ref 15 used radii of 30–50 nm to describe the particle sizes). Our phase-gradient-based potential wells are promising to overcome both limitations. The minimal particle size (80 nm) used in our experiments is limited by the weak optical forces that can be exerted on smaller NPs using the $\lambda = 800$ nm light, which is far away from the surface plasmon resonances of Au NPs. Our calculations show that if using 532 nm light, a wavelength widely used for sorting Au NPs, the phase gradient forces would allow simultaneous sorting and trapping of sub-50 nm NPs as shown in Figure 5e (also see Figure S9 for the optical force and sorting resolution as a function of the particle size and fluid velocity), and the sorting resolution can even reach 1 nm by tuning the phase gradient (Figure 5f). It is worth noting that the laser-induced thermal effects may affect the optical sorting especially under resonant excitation (see Notes on photothermal effects in the Supporting Information).

The best sorting resolution can only be achieved by optimizing heat dissipation, for example, using substrates with high thermal conductivity or integrating a heat sink into the microfluidic channel. The optical sorting and trapping may be further improved by using a standing wave optical line trap created over a reflecting surface that offers tighter confinement along the z-direction.

In this work, we mainly focus on demonstrating the feasibility of nanomanipulation by tuning the optical phase in optofluidics at the single NP level. In the experiments, the width (short-axis) of the optical line trap ($\sim500$ nm) is much narrower than that of the microfluidic channel. As a result, just a fraction of particles could be attracted to the sorting plane, which affects the throughput of particle sorting. The sorting efficiency may be improved by applying a series of parallel optical line traps in the microfluidic channel or using the flow focusing method. In addition, the NPs are trapped in a line and the maximum number of particles is determined by the length of the optical line. The number can be increased by increasing the line length, although higher laser power is needed in order to maintain the stiffness of the trap. Alternatively, the sorted NPs could be continuously stored into different chambers by designing suitable optofluidic chips (Figure S10).

Compared to the intensity-gradient-based sorting used in previous reports, phase gradient forces offer greater...
Moreover, current optofluidic combination of optical lines to create directive and force and around a few micrometers. Optofluidic super resolution of 1 nm can be achieved with this method further predict that optical sorting of sub-50 nm NPs with a trapping potentials, we have successfully demonstrated optical trapping, sorting, and transporting of metal NPs with diameters of 80–150 nm in microfluidic channels. Our simulations further predict that optical sorting of sub-50 nm NPs with a super resolution of 1 nm can be achieved with this method using optimized laser wavelength, phase gradient, and fluid velocity. The separation distances of NPs in our experiment are around a few micrometers. Optofluidic manipulation of biological objects may require even longer separation distances,6 which can be achieved by tuning the phase gradient to increase the length of an optical line trap while keeping the laser intensity. Creating potential wells with phase gradient fills the gap between nanoscale optical sorting and optical trapping and adds another dimension to optofluidics that will significantly impact nanomanipulation in microfluidics. Compared to intensity-gradient force, the phase gradient force provides more freedom and flexibility for nanomanipulation, which will broaden the horizon of optofluidics for new applications in biology and “lab-on-a-chip” devices.6,14,47

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b03844.

Methods, additional figures, and notes on laser-induced thermal effects (PDF)

Optofluidic trapping of a single Ag NP with different laser powers (AVI)

Optofluidic sorting of 100 and 80 nm Au NPs (AVI)

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**Author Contributions**

Z.Y. conceived the project. F.N. fabricated the microfluidic chip, carried out the experiments, and analyzed the data. F.N. and Z.Y. performed the FDTD simulations. F.N. and Z.Y. wrote the manuscript.

**Notes**

The authors declare no competing financial interest.

**REFERENCES**
