All-Optical Patterning of Au Nanoparticles on Surfaces Using Optical Traps

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ABSTRACT The fabrication of nanoscale devices would be greatly enhanced by “nanomanipulators” that can position single and few objects rapidly with nanometer precision and without mechanical damage. Here, we demonstrate the feasibility and precision of an optical laser tweezer, or optical trap, approach to place single gold (Au) nanoparticles on surfaces with high precision (approximately 100 nm standard deviation). The error in the deposition process is rather small but is determined to be larger than the thermal fluctuations of single nanoparticles within the optical trap. Furthermore, areas of tens of square micrometers could be patterned in a matter of minutes. Since the method does not rely on lithography, scanning probes or a specialized surface, it is versatile and compatible with a variety of systems. We discuss active feedback methods to improve positioning accuracy and the potential for multiplexing and automation.

KEYWORDS Optical trapping, optical tweezers, plasmonic, Au, nanoparticle, nanopatterning, directed assembly

The unusual properties associated with surface plasmons, that is, large field enhancements, and long distance coherent transport in single and few nanoparticles are being used to enhance sensitivity in sensors or as a mode of information transfer.1,2 For example, the propagation of single “photons” on 10 μm scales has been demonstrated with single quantum dots coupled to nanowires and with optical or electrical detection.3,4 These excitations can also be coupled into or out of such “plasmonic cavities” with appropriately positioned (metallic) nanoparticles.5 In addition, surface-enhanced Raman spectroscopy (SERS)6 and surface-enhanced fluorescence (SEF)7 allow detection of few and even single molecules that reside in the gaps between closely spaced metal nanoparticles. Such effects can be enhanced or in some cases are only possible when crystalline materials, made by colloidal/chemical synthesis, are used instead of structures made by lithography and vapor deposition.8 Self-assembly is a powerful tool for creating two9–11 and three-dimensional12 arrays of colloidal nanoparticles. However, it is generally limited to regular periodic structures of close-packed geometry. A complementary way to understand the relationship between structure and function in nanoscale structures and devices2 will require the systematic manipulation and placement of single nanoparticles. Optical tweezers could be very useful for such studies and assembly.

The ability to manipulate dielectric particles by optical tweezers (or traps) has evolved greatly since its discovery over two decades ago13 into an invaluable tool for single-molecule biophysics.14 This tool was essential for determining the functional mechanical properties of single biomolecules such as the motor protein kinesin,15 DNA, and DNA polymerase.16 Traditionally, optical trapping in biophysical applications has employed micrometer-sized particles of materials such as polystyrene to execute one-dimensional pulling of significantly smaller molecules. However, the implementation of these techniques in complicated environments, such as within living cells, will benefit from the use of nanometer-sized probes.

The optical trapping of metal nanoparticles in three dimensions was first demonstrated with Au nanoparticles in 1994.17 In recent years, the range of Au nanoparticles that have been successfully trapped and manipulated has grown.18,19 The expanded list includes Au nanorods,20,21 Au bipyramids,22,23 single and multiple Ag nanoparticles,24–26 metal nanowires,26 and semiconductor quantum dots.27 The optical manipulation of Ag nanoparticles was shown to be capable of creating “hot spots” for SERS.28 In addition, it has been shown that the electromagnetic field enhancement associated with surface-bound metal nanostructures is capable of trapping micrometer-size dielectric spheres.29,30

Emerging applications of metal nanoparticles such as biological sensing,31 opto-electronic integration,4 and enhanced photovoltaic conversion32 all benefit from the ability to position the particles at defined locations on a surface. A number of strategies have been developed toward this end, some of which are summarized in a recent review.33 Optical trapping presents a unique solution to address the challenge of multiparticle assembly in that it requires neither lithographic patterning nor mechanical manipulation by scanning probes. Surprisingly, only a few reports have been made on this approach. These involve the optical trapping...
and deposition of larger (>100 nm) dielectric and metallo-dielectric particles from water as well as metal nanoparticles from ethylene glycol.

In this letter, we demonstrate subwavelength positional accuracy for arranging collections of single Au nanoparticles at defined locations on a surface using an optical trap. Single particles are trapped in bulk solution and brought to contact with optically transparent substrates (see Figure 1a,b). Areas tens of square micrometers in size are patterned with single nanoparticles in a matter of minutes. In addition, we quantify the positional accuracy of deposition and compare this with a single nanoparticle’s position fluctuations in the optical trap. The close agreement between the particle’s range of motion in the trap and the positional accuracy in particle placement on the surface suggests that Brownian fluctuations are the main source of positional error. We discuss ways in which this positional error can be reduced and the throughput enhanced.

Au nanoparticles were synthesized in a manner similar to published protocols with the exception that AgNO₃ was not used in the growth solution. Briefly, Au “seed” particles were synthesized by adding 0.3 mL of freshly prepared 10 mM NaBH₄ solution to 20 mL solution containing 0.125 M HAuCl₄ and 0.25 mM sodium citrate under heavy stirring. This seed solution, which consisted of citrate-stabilized Au nanoparticles with a diameter of ~3 nm, was aged for at least 2 h at room temperature prior to use. Next, a 0.1 M cetyltrimethylammonium bromide (CTAB) solution was prepared and heated to ~30 °C to dissolve the CTAB. To this solution was added, in order, 0.5 mL of 10 mM HAuCl₄, 0.2 mL of 1 M HCl, 0.08 mL of L-ascorbic acid, and finally a varying amount (~30–80 µL) of the seed solution under gentle stirring. After 2 h, a red color emerged, and the solution was removed from heat.

This procedure produces predominantly spheroidal Au nanoparticles of ~40 nm diameter with CTAB as a passivating layer. Excess CTAB was removed by centrifugation and resuspension in a manner similar to what has been previously described. Briefly, the excess CTAB in solution after synthesis was allowed to precipitate either at room temperature overnight or at 4 °C for a few hours. The remaining solution was then decanted and centrifuged at 9500 rpm for 10 min. The precipitate was resuspended in 18 Ω resistivity water, and the resulting solution was diluted 10-fold in water for all experiments described. Assuming that each purification step reduces the CTAB concentration by a factor of 10, the CTAB concentration would then be 10⁻⁴ M. Similarly, the resulting pH is ~5. On the basis of a calculation of the molar absorption coefficient for similarly sized par-

![FIGURE 1. Schematic of single nanoparticle trapping (a) and deposition (b). (c) Dark-field image of typical pattern used for the determination of the precision of deposition (scale bar 2 µm). (d) “U of C” pattern created from 37 single nanoparticles (image acquired using 60× objective for collection, scale bar 4 µm). (Smoothing is applied to the DF images for presentation.)](image)
ticles, the typical colloid concentration is estimated to be $1.6 \times 10^{-11} \text{ M}^{38}$.

Standard no. 1.5 glass coverslips (Fisher Scientific) were functionalized with polydiallyldimethylammonium chloride (PDDAC, Aldrich, very low MW) according to the procedure described in Burgin et al.$^{37}$ The positively charged polymer provides a repulsive interaction with the positively charged nanoparticles, slowing spontaneous deposition on the surface and allowing surface patterning without spontaneously deposited particles being observed over 100s of $\mu$m$^2$ in the typically $\sim 60$ min experiment time. That is, the particlesurface interaction is made to be repulsive at longer range due to electrostatic interactions and a relatively low ionic strength with a potential barrier that is $> k_B T$ in magnitude.$^{39}$ Chambers of 120 $\mu$m thickness were fabricated using commercially available spacers (Grace Bio-Laboratories SA-S-1 L). Unless specified otherwise, particles were deposited on the bottom surfaces of these chambers (closest to the microscope objective). Deposition on the upper surface could also be achieved with notably lower precision of deposition and less selectivity toward single nanoparticles. This will be discussed below.

The optical trap was implemented using a home-built wavelength-tunable Ti:Sapphire laser operating at a wavelength of 817 nm. A Faraday isolator (Optics for Research) was used to prevent back-reflections from entering the laser cavity that cause laser instability and noise. The beam was spatially filtered using a diamond pinhole (Lenox Laser, 50 $\mu$m diameter) and then expanded to slightly overfill the microscope objective’s back aperture. This beam was then guided into an Olympus IX71 inverted microscope. A reflective neutral density filter (Edmund Optical) was used to reflect $\sim 50\%$ of the beam (intensity) into a 60x water immersion objective lens (Olympus UPLSAPO) used for all particle trapping experiments described here. The sample was mounted on a closed-loop piezoelectric stage (Physik Instrumente P-561) that provided sample positioning accuracy of a few nanometers.

Unless specified otherwise, dark-field (DF) images of deposited particles were obtained using an oil-immersion dark-field condenser (Olympus) with a numerical aperture (NA) range of 1.2–1.4, a 40x objective (Olympus UPLSAPO, NA 0.9) and a 150 W halogen white light source (Cuda Products). The DF images were acquired using a Watec 902B camera, and particle positions were determined both by the use of the “center of mass” analysis function in ImageJ (NIH) as well as by centroid analysis with commercial software (Diatrack). The particle position fluctuations in the trap were established by imaging light from the trapping laser scattered from the trapped nanoparticle using a Sony XCD-V60 camera operating at 180 frames per second. The particle position at each frame in the video was determined by centroid analysis using commercially available particle tracking software (Diatrack). Despite the object’s dimensions being significantly smaller than the diffraction limit, we were able to localize the centroid of the object with high precision using these methods.$^{40–42}$

By manually changing the fine focus on the microscope, a particle trapped some distance away from the coverslip surface (usually $>10 \mu$m) could be brought in contact with and made to adhere to the surface (Figure 1a,b). The piezoelectric stage was used to move the sample to a given position in the lateral (XY) plane. In this way the “U of C” pattern shown in Figure 1d was created in $\sim 1$ h.

The placement of each particle could be monitored via dark-field scattering of incoherent light. It was found that the colloidal particle solution must be slightly unstable with respect to precipitation for this deposition to occur; this condition is easily achieved via the aforementioned purification and dilution steps. The final centrifugation step (rather than simply allowing for CTAB precipitation) was essential to achieve particle adhesion on the surface. Without this step, particles could be optically trapped in solution but not deposited onto the surface. On the basis of this observation, we believe that the CTAB concentration is brought below the critical micelle concentration (CMC), which is approximately $1 \text{ mM}$,$^{43}$ during the course of the experiment. Below the CMC, the layer of CTAB coating the particle surface becomes unstable. This fact has several ramifications; first, the charge on the particle (and thus any repulsive electrostatic force) is reduced. Second, the disruption of the ligand shell exposes the alkyl tail of CTAB to solution thus promoting adhesion with the underlying glass substrate (by hydrophobic or van der Waals interactions). The first effect corresponds to the reduction of the electrostatic repulsion component of the Derjaguin, Landau, Verwey, and Overbeek (DLVO) potential, while the second effect promotes the van der Waals attraction component of the potential.$^{39}$ In experiments performed without the PDDAC coating on the glass surface, the particles rapidly precipitate onto the surface, both thereby creating randomly arranged particles in the area designated for pattern formation and removing particles from solution leaving few to be trapped.

In addition, particles could be placed on the upper surface of the coverslip sandwich. However, this process was less selective toward single nanoparticles. Unlike trapping on the bottom coverslip (closer to the objective), which requires the gradient force to pull the particles down, the scattering force is also capable of pushing particles onto the upper coverslip surface. Thus, aggregates in solution (or any strongly scattering object) will be pushed onto the top coverslip.

We measured dark-field spectra of particles deposited on a glass surface (bottom of the chamber) to verify that single Au nanoparticles are deposited (Figure 2a). These spectra show the characteristic Au particle plasmon resonance peaked at $\sim 560$ nm.$^{38}$ Some intensity variation is observed in the scattering signal from the deposited particles that is attributed to the polydispersity in Au nanoparticle sizes present in the sample. The variation in scattering intensity
can be quite significant since the scattering cross section varies as \( r^6 \) (where \( r \) is the particle radius).

In addition, similar scattering spectra can be measured for particles trapped in solution (Figure 2b). The difference between the spectrum shown in Figure 2b and the spectrum of the particle trapped and deposited on the glass surface (Figure 2a) is likely due to the aforementioned polydispersity in the sample (i.e., the spectra in Figure 2a,b are not for the same particle). Changes in the size of Au nanoparticles can shift the scattering peak by up to 90 nm. Measurement of the scattering from trapped particles in solution suggests the possibility of “filtering” a desired plasmon resonance from a spectrally heterogeneous mixture (i.e., a typical Ag nanoparticle colloid preparation) with concomitant selective deposition.

Finally, the dark-field scattering of the trapped and deposited particles can even be observed by eye through the microscope eyepiece (using the 40× objective for collection). A green color, characteristic of the particle plasmon near 550 nm, is observed. Although multiple particles could fit within the ~500 nm diffraction limited spot, aggregates consisting of two or more closely spaced Au nanoparticles would exhibit a significantly red-shifted color and extinction maximum. Although some aggregates are observed when depositing on the upper coverslip surface, this is not observed for the Au nanoparticles trapped and deposited particles on the bottom surface, demonstrating the greater selectivity provided by the gradient force. We have not attempted SEM or AFM characterization since the sample cells used preclude such imaging.

Scattering spectra of a single, isolated particle immobilized on the glass surface were collected before and after laser irradiation for 1 min with a similar power to that used during the experiment. No change in the scattering spectrum is observed. Thus, we conclude that the optical trapping beam does not damage the particle. This is reasonable in that the wavelength of the trapping laser (~800 nm) is far below the wavelength of the particle plasmon resonance (~550 nm) and the absorbance is exceedingly small.

A nanomanipulation tool requires sufficiently precise positioning to be useful. The precision of nanoparticle deposition was determined in the following manner. Particles were trapped using the 60× objective and deposited in patterns defined by the piezoelectric positioning stage (see Figure 1b for a typical pattern). A mark made with a razor blade on the coverslip allowed the sample to be removed and the same area imaged with the 40× objective. Statistical measures of the precision of deposition could then be obtained as a function of power by comparing the distance between the DF scattering spots observed on the camera to the distance the stage moved (2.00 µm in most cases). In this way, the precision of deposition was determined from the standard deviation of the measured positioning errors as shown in Figure 3. In this figure, each filled circle corresponds to a single interparticle distance. Power is an upper estimate of the total power delivered to the sample based on manufacturer’s specification of the objective lens’ transmission.

We quantified the sources of positional error, including both the lateral localization of the particle in the trap as well...
The observed standard deviation $\sigma_{\text{obs}}$ of the particle’s freedom of motion was determined as a function of power. Extrapolation of these data to infinite power (i.e., the intercept for $1/\text{power}$) allows quantifying and removing systematic noise sources not related to the particle’s motion, namely shot noise and finite pixellation noise. Assuming a Gaussian profile for both the particle fluctuation within the optical trap and the detector noise, $\sigma_{\text{noise}}$, allows obtaining the corrected standard deviation, $\sigma_{\text{corr}}$, as

$$\sigma_{\text{corr}} = \sqrt{\sigma_{\text{obs}}^2 - \sigma_{\text{noise}}^2}$$

The corrected standard deviations so obtained (Figure 4b) can then be related to the optical trap force constant via the equipartition theorem

$$\frac{1}{2} \kappa \sigma_{\text{corr}} = \frac{1}{2} \kappa g T$$

where $\kappa$ is the force constant and $k_B$ is Boltzmann’s constant. The force constants obtained in this way are plotted in Figure 4c for both X and Y axes in units of fN/nm. After scaling for power, the force constants determined in this work (~0.04 pN nm$^{-1}$ W$^{-1}$) are very similar to those obtained by Hansen et al. for similarly sized Au nanoparticles.

The standard deviation of the particle’s position fluctuations within the trap, ~30 nm, is less than the value of ~100 nm obtained for the standard deviation of particle deposition precision. The difference between these two values is to be expected for several reasons. First, it is likely that some amount of mechanical settling or drift is present in the sample over the course of the measurement or is caused by the repeated translation of the objective (up and down) relative to the coverslip chamber by distances in excess of 20 µm. A control measurement of the latter source of drift gives an estimate of this mechanically induced drift to be about 20 nm.

Second, based on the slowed rate of spontaneous deposition of nanoparticles on the surface it can be concluded that the repulsive barrier of the DLVO potential between the particle and the surface is at least several $k_B T$ in height. As the trapped particle is pulled down toward the glass–water interface and against this potential, it will preferentially shift along the Z-axis to a position farther from the objective. This will lead to a stronger gradient force in Z but a weaker force in the lateral (XY) plane, thus leading to increased position fluctuations in the lateral plane near the surface. Thus, the standard deviation of particle position fluctuations in solution are expected to be less than the standard deviation of position errors for particles deposited on a surface. Furthermore, at small separations, hydrodynamic interactions between the nanoparticle and surface can add additional (repulsive) forces and, of course, the
precise nature of the optical focus will change as the beam is drawn into the substrate.

In this letter, we have demonstrated that single Au nanoparticles can be withdrawn from liquid solution and positioned on standard glass coverslips with subwavelength precision (~100 nm) using an optical trap. The accuracy of our method is comparable to that recently reported in a trapped particle based photolithography method yet the optical trapping/depositing is significantly less complex to conduct than either lithography or scanning-probe-based methods. Like the latter, the technique presented here is essentially serial. However, since registry between a mechanically controlled tip and the sample surface is not required, nanopositioning based on optical traps have the potential to operate significantly faster and in environments difficult for scanning probes to access (e.g., inside living cells).

One way to improve the precision of positioning is to reduce the trapped particles’ Brownian fluctuations (and the presumed increase in fluctuations that occur when approaching the surface; see previous discussion). This could be accomplished by the introduction of an error-sensing feedback loop that uses either fast beam deflection optics or time-varying electric fields integrated to “correct” the particle position. A feedback loop coupling a nanoparticle’s fluctuations to a time-varying electric field was demonstrated by Cohen et al. in an “anti-Brownian electrophoretic trap.” These methods could significantly reduce fluctuations in the XY plane during particle deposition.

Furthermore, the automation of the various steps in the deposition method described herein could significantly increase the patterning speed. The introduction of photochemistry to affix the nanoparticle to the surface, as has already been demonstrated, would be useful for this purpose. In addition, the use of holographic optical trap (HOT) arrays or other types of structured optical fields could speed up the process further by multiplexed trapping and depositing.

In particular, holographic optical trap arrays could allow for the creation of user-definable periodic and a-periodic patterns covering thousands of square micrometers. Assuming a 5 W laser source divided into 50 optical traps (covering 50 μm²) and assuming that this area can be patterned in 1 ms (more than enough time to move the stage and flash a UV light source), then the corresponding patterning speed is 3 mm²/min.

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REFERENCES AND NOTES