Optical manipulation of individual strongly absorbing platinum nanoparticles†

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Nanostructures with exceptional absorption in the near infrared (NIR) regime are receiving significant attention due to their ability to promote controlled local heating in biological material upon irradiation. Also, such nano-structures have numerous applications in nano-electronics and for bio-exploration. Therefore, significant effort is being put into controlling and understanding plasmonic nanostructures. However, essentially all focus has been on NIR resonant gold nanoparticles and remarkably little attention has been given to nanoparticles of other materials that may have superior properties. Here, we demonstrate optical control and manipulation of individual strongly absorbing platinum nanoparticles in three dimensions using a single focused continuous wave NIR laser beam. Also, we quantify how the platinum nanoparticles interact with light and compare to similarly sized absorbing gold nanoparticles, both massive gold and gold nanoshells. By finite element modeling, we find the scattering and absorption cross sections and the polarizability of all particles. The trapping experiments allow for direct measurements of the interaction between the nanoparticles and NIR light which compares well to the theoretical predictions. In the NIR, platinum nanoparticles are stronger absorbers than similarly sized massive gold nanoparticles and scatter similarly. Compared to NIR resonant gold nanoshells, platinum nanoparticles absorb less, however, they also scatter significantly less, thus leading to more stable optical trapping. These results pave the way for nano-maneuvering and positioning of platinum nanoparticles and for using these for to enhance spectroscopic signals, for localized heating, and for manipulation of biological systems.

Introduction

In literature, most effort on describing the optical properties and control of metallic nanoparticles has been devoted to gold or silver nanoparticles, despite the huge unexploited potential alternative plasmonic materials may possess. Optical manipulation by a single tightly focused laser beam is mediated by the gradient force which is directly related to the particle’s polarizability. As the polarizability of metallic nanoparticles is higher than that of similarly sized dielectric particles, it is easier to trap individual metallic nanoparticles composed of, e.g., silver or gold than similarly sized dielectric particles.

A plasmonic particle’s absorption and scattering are important both for its optical manipulation and for its plasmonic heating. These parameters are highly wavelength dependent and depend on the particle’s material composition, size and shape. Scattering and absorption by the nanoparticle destabilizes optical trapping and causes local heating and displacement of the trapped metallic particle from the focus. To trap absorbing nanoparticles, it has been suggested to use structured light, for instance doughnut shaped beams, or counter propagating beams, or the photophoretic force to trap strongly absorbing nanoparticles. Optical trapping of large metallic nanoparticles is challenged by the fact that the scattering cross section increases dramatically with particle size, and although optical trapping has been demonstrated of gold nanoparticles as large as 250 nm, it is likely that trapping of these is caused by non-sphericity of the particle and proper stable orientation in the trap. Absorbing gold nanoparticles have also been reported trapped in air, this allowing for aerodynamic constructions.

Here, we quantify the interaction between platinum nanoparticles and light and compare to similarly sized NIR absorbing gold nanoparticles. By finite element modeling (FEM) we calculate the optical properties of platinum nanoparticles (PtNPs) with diameters of 30 nm (Pt30), 50 nm (Pt50) and 70 nm (Pt70), of similarly sized spherical gold nanoparticles (Au50 and Au70), and also of NIR resonant gold nanoshells (AuNShs) with an overall diameter of 150 nm. One reason the particles with sizes between 30 nm and 70 nm are of interest is that this size range is particularly relevant for tumor delivery...
and has potential for cancer treatment.19,20 We compare the performance of solid gold and platinum nanoparticles to NIR resonant AuNS because they, despite their relatively large size, are currently considered the optimal particle for NIR absorption and for nanoparticle based cancer therapies.21–23 To demonstrate the usefulness of strongly absorbing platinum nanoparticles in the life- and nano-sciences we performed 3D stable near infrared (NIR) optical trapping of individual PtNPs. From these trapping experiments, and similar trapping of gold nanoparticles, we quantify the spring constants characterizing the interaction potential between the electromagnetic field and the nanoparticle and relate these results to the theoretical expectations. Overall, we find that PtNPs are excellent absorbers in the NIR compared to similarly sized AuNPs, however, PtNPs still absorb less than the larger NIR resonant AuNS. Also, PtNPs are found to scatter NIR light significantly less than NIR resonant AuNS, and therefore exhibit more stable optical trapping than AuNSs.

Experimental

Nanoparticle characterization

As the optical properties of metallic nanoparticles are strongly dependent on particle size, we performed a size analysis of all particles based on transmission electron microscopy (TEM) images and on dynamic light scattering (DLS) measurements. Representative TEM images are shown in Fig. 1a, c, e and g and as summarized in ESI Table S1† and ESI Fig. S1,† all distributions appear homogeneous and there is a reasonable agreement between the TEM images, the DLS results, and the manufacturer given diameters. Also, by UV-Vis spectroscopy we experimentally determined the extinction cross section of all particles, these are shown in Fig. 1b, d, f and h. These results can be compared to the calculated extinction cross sections for the same particles as shown in Fig. 2, this comparison demonstrates agreement between the measured and calculated values.

Optical trapping

The optical trap was based on a near infrared CW laser (Nd: YVO4, 5 W Spectra Physics Millennia, $\lambda = 1064$ nm) with a Gaussian intensity profile. The trap was implemented in an inverted confocal microscope (Leica DMIRB HC) equipped with a quadrant photodiode (QPD) (S5981, Hamamatsu) in the back focal plane of the condenser to monitor the positions visited by the trapped particle. Care was taken only to utilize the linear range of the detector and the condenser’s aperture was set to optimize the signal to noise ratio.24,25 A CCD camera with a 25 Hz frame rate (Sony XC-EI50) was used to visualize the trapped nanoparticle by transmitted light detection. The laser was focused to a diffraction limit spot by a water immersion objective (HC, PL, APO, 63×/NA = 1.2) or an oil immersion objective (HCX, PL, APO, 100×/NA = 1.4). Water was used as immersion media on the water immersion objective and immersion oil with index of refraction $n = 1.54$ was used on the oil immersion objective to minimize spherical aberration at a trapping depth of $\sim5$ μm away from the coverglass surface.26 The stage could be moved with respect to the trapping laser by a 3D piezoelectric stage (PI 731.20, Physik Instrumente, Germany). Data were acquired using a DAQ card (CB-68LP, National Instruments) and processed using custom-made Labview programs.

Data analysis

The optical tweezers exert a harmonic force, $F = -\kappa x$, with $\kappa$ being the trap stiffness characterizing the optical trap and $x$ being the distance from the equilibrium position. The positions visited by the particle within the optical trap are
recorded by the QPD. The bead performs thermal fluctuations within the harmonic potential exerted by the optical trap, hence, its dynamics is well described by the Langevin equation (here in one dimension):

\[ m\dot{a}(t) = -\gamma v(t) - \kappa x(t) + \mathcal{F}_{\text{thermal}}(t) \]  

where \( m \) is the mass of the particle, \( v(t) \) is the particle’s velocity, \( a(t) \) is the particle’s acceleration and \( \gamma \) is the friction coefficient. \( \mathcal{F}_{\text{thermal}}(t) \) is a stochastic force which is time-dependent and originates from the thermal collisions with the solvent. The Reynolds number characterizing the particle’s motion in water is extremely low, hence, the inertial term, \( ma(t) \), can safely be set equal to zero. By Fourier transforming the Langevin equation one obtains the following power spectrum

\[ P(f) = \frac{K_B T}{\gamma} \frac{1}{f^2 + f_c^2} \]  

where \( \gamma = 6 \eta R \) for a spherical particle with \( \eta \) being the viscosity of water, \( R \) the radius of the particle, and \( f_c \) is the so-called corner frequency, \( f_c = \kappa/2\pi \gamma \).

The experimentally obtained time series were Fourier transformed and the Lorentzian function given in eqn (2) was fitted to the power spectra using the MatLab routines described in ref. 27 which take into account the filtering effect of the photodiode.\(^{28} \) The fits returned \( f_c \) from which \( \kappa \) was found.

**Simulations**

All simulations and calculations of nanoparticle absorption and scattering cross sections were done by finite element modeling (FEM) using relevant packages from COMSOL (Stockholm, Sweden). In order to obtain the electromagnetic fields around the particle, we numerically solved Maxwell’s wave equation:

\[ \nabla \times \mu_r^{-1} (\nabla \times E) - k_0^2 \left( \varepsilon_r - \frac{i\sigma}{\omega\varepsilon_0} \right) E = 0 \]  

where \( \mu_r \) is the relative permeability, the ratio of the permeability of the medium to the permeability of vacuum, which here equals one. \( \omega \) is the angular frequency, \( \varepsilon_r \) is the relative permittivity defined as the permittivity of the particle divided by that of the surrounding media, \( k_0 \) is the vacuum wavenumber, and \( \sigma \) is the electrical conductivity.

Immersing a particle into the incident electric field, \( E_{\text{inc}} \), will perturb the field and lead to scattering. Therefore, the total electrical field which is described in eqn (3) is \( E = E_{\text{inc}} + E_{\text{scat}} \). And likewise for the magnetic field, which can be derived from Faraday’s law: \( \mathbf{H} = \mathbf{H}_{\text{inc}} + \mathbf{H}_{\text{scat}} \).

The energy flow can be described by the time-average Poynting vector:

\[ S_{\text{av}} = \frac{1}{2} \text{Re}[\mathbf{E} \times \mathbf{H}^*] \]  

where * denotes complex conjugation. From this we calculate the scattering and absorption cross sections as detailed in the ESI.\(^{\dagger} \)
Results and discussion
Quantification of nanoparticle interaction with electromagnetic field

To quantify how the absorbing nanoparticles interact with light we first used FEM to calculate the electrical field, $\mathbf{E}$ around a Pt70, Pt50, Pt30, and a AuNS particle immersed in water. The normalized magnitude, $|\mathbf{E}|$, is displayed in Fig. 2a–d. For all particles the field is asymmetric. Also, the field is strongest and has the longest range around the AuNS, while both field strength and range decreases with the diameter for PtNPs. For all nanoparticles investigated we calculated the extinction cross section, $\sigma_{\text{ext}}$, which is the sum of the absorption cross section, $\sigma_{\text{abs}}$, and the scattering cross section, $\sigma_{\text{scat}}$: $\sigma_{\text{ext}} = \sigma_{\text{abs}} + \sigma_{\text{scat}}$. The calculations of the optical cross sections are detailed in the ESI† and the results are displayed in Fig. 2e–h for PtNPs and AuNSs. The results for similarly sized massive gold are given in ESI Fig. S2†. For the PtNPs, the optical cross sections peak in the visible, or in the UV for Pt30, however, in the NIR regime there is still a significant absorption which increases with particle size ($\lambda = 1064$ nm is marked by a vertical dotted line in Fig. 2) and numerical values at this wavelength are given in ESI Table S2†. The AuNS has its resonance peak around 800 nm and absorbs significantly more than any of the PtNPs or AuNPs in the NIR regime. Also, it can be noticed that the experimentally measured extinction cross sections, shown in Fig. 1b, d, f and h fit quite well to the calculated ones depicted in Fig. 2.

Optical forces on the nanoparticle

The ability to optically trap nanoparticles depends on their polarizability. A nanoparticle’s complex polarizability, $\alpha = \alpha_r + i\alpha_i$, is related to its optical cross sections in the following manner

$$\sigma_{\text{abs}} = \frac{k^2}{\varepsilon_0} \alpha_i$$

$$\sigma_{\text{scat}} = \frac{k^4}{6\pi\varepsilon_0^2} |\alpha|^2$$

where $k = \frac{2\pi n_m}{\lambda_0}$ with $n_m$ being the refractive index of the surrounding medium and $\lambda_0$ the wavelength in vacuum. Fig. 2i–l shows the polarizability of PtNPs and AuNSs as a function of wavelength, results for AuNSs are shown in ESI Fig. S2†. The numerical values at $\lambda = 1064$ nm are given in ESI Table S2†. The values of $\alpha_i$ are of particular interest because $\alpha_i$ is proportional to the gradient force, responsible for optical trapping, as detailed below.

For the nanoparticles, whose linear dimension is smaller than the wavelength of the trapping laser beam, the optical forces on the particle can be estimated by treating the nanoparticle as a dipole in an electromagnetic field. The two most important contributions to the total external force acting on the particle are the gradient force, $F_{\text{grad}}$, drawing the particle towards the focus, and the scattering force, $F_{\text{scat}}$, which destabilizes the trap. $F_{\text{grad}}$ can be expressed as:

$$F_{\text{grad}} = \frac{1}{4} \alpha_r V \langle |\mathbf{E}|^2 \rangle$$

where $V$ is the electric field. From eqn (7) it can be seen that $\alpha_r$ is directly proportional to $F_{\text{grad}}$ which must be positive in order to pull the particle towards the intensity maximum. From Fig. 2 and ESI Fig. S2† it can be seen that $\alpha_r$ is positive for the PtNPs and the AuNPs, however, $\alpha_i$ is negative for AuNS at wavelengths below 740 nm. This means that PtNPs and AuNPs have a chance of being trappable at all wavelengths investigated, however, it is unlikely that AuNSs can be trapped with wavelengths below ~740 nm.

The scattering force, $F_{\text{scat}}$, can be expressed as

$$F_{\text{scat}} = \sigma_{\text{ext}} \left\{ \frac{1}{c} (\mathbf{S} + c \mathbf{v} \times \langle \mathbf{L}_3 \rangle) \right\}$$

where $\langle \mathbf{S} \rangle$ is the time averaged Poynting vector, $c$ is the speed of light, and $\langle \mathbf{L}_3 \rangle = -\frac{\varepsilon_0}{4\pi c^2} \langle \mathbf{E} \times \mathbf{E}^* \rangle$ is the time averaged spin density of the electromagnetic field with $\varepsilon_0$ being the permittivity of the medium and $\omega$ the frequency. As evident from eqn (5)–(8), the only nanoparticle associated parameter affecting the gradient force is the polarizability, while the rest of the parameters originate from the electromagnetic field.

Optical trapping of individual nanoparticles

As the real part of the polarizability of PtNPs is relatively high and the scattering cross section is relatively low in the NIR (numerical values at 1064 nm are given in ESI Table S2†), PtNPs are likely to be trappable by NIR light. Fig. 3b shows power spectra calculated for trapped Pt30 and Pt70 nanoparticles, respectively. The power spectra were well fitted by Lorentzian functions using the routines described in ref. 27 yielding $\kappa_{\text{ss}} = 0.0006$ pN nm$^{-1}$ for Pt30 and $\kappa_{\text{ss}} = 0.0039$ pN nm$^{-1}$ for Pt30 and Pt70, respectively. The positions visited within the trap (inset of Fig. 3b) are Gaussian distributed, thus confirming the harmonic potential exerted by the optical trap. Representative power spectra for Pt50 and AuNSs are shown in ESI Fig. S3†.

All particle types investigated, Pt30, Pt50, Pt70, Au50, Au70 and AuNSs were individually optically trapped using a NIR laser with $\lambda = 1064$ nm and the trapping stiffnesses were found using laser powers in the interval from ~45 mW to ~250 mW at the sample. The particles were either trapped using an oil immersion objective or a water immersion objective. The smallest platinum nanoparticles, Pt30, could only be trapped using the oil immersion objective in conjunction with an immersion media optimized for canceling the spherical aberration. The trap stiffness, $k_x$, as a function of laser power for all PtNPs as well as for the AuNSs using the oil immersion objective are shown in Fig. 4. The lines are linear fits in the directions along ($x$, dashed line) or perpendicular to ($y$, full line) the laser’s polarization. The trap stiffnesses in both principal directions, $k_x$ (hollow circles) and $k_y$ (full circles), increase linearly with laser power for all particles which is a hallmark for normal
optical trapping. The spring constant is expected to be larger
perpendicular to the polarization\textsuperscript{31,32} as experimentally con-
firmed by Fig. 4. The data shown has not been corrected nor
modified in any way, as for instance with the aim of taking
into account a possible effect of heating as done in ref.\textsuperscript{11} and
33. Optical trapping of Pt50, Pt70, AuNS, Au50 and Au70 was
also possible using a water immersion objective, see ESI
Fig. S4,† with nearly identical $\kappa$ for Au and Pt nanoparticles.
However, for AuNSs the spring constants obtained by the water
immersion objective were a factor of $\sim 2$ lower.

To our knowledge, this is the first report of optical trapping
of platinum nanoparticles. The spring constants characterizing
optical trapping of spherical massive gold nanoparticles here
reported compare well to literature.\textsuperscript{3} NIR absorbing AuNSs
were reported trapped in ref. 33 and 34. In ref. 33 the AuNSs
were trapped with wavelengths from 740 nm and 850 nm with
spring constants of $3-8 \text{pN} \mu\text{m}^{-1}$, which compare well to the
values reported here for 1064 nm trapping.

When comparing the NIR optical trapping performances of
the different nanoparticles, it is informative to consider the
optical characteristics of the particles at 1064 nm (given in ESI
Table S2). Within the error bars, $\kappa_{\text{Pt70}}$ is identical to $\kappa_{\text{Pt50}}$
except for the fact that $\alpha_{r,\text{Pt70}}$ is 4 times larger than $\alpha_{r,\text{Pt50}}$. The
reason $\kappa_{\text{Pt70}} \approx \kappa_{\text{Pt50}}$ is probably that $\sigma_{\text{scat,Pt70}} \sim 10 \times \sigma_{\text{scat,Pt50}}$
hence, the scattering force will be much larger on Pt70 than
on Pt50, thus possibly displacing Pt70 into a local intensity
minimum. Likewise, the fact that $\kappa_{\text{AuNS}} \sim 2 \times \kappa_{\text{Pt70}}$ despite that $\alpha_{\text{AuNS}} \sim 20 \times \alpha_{\text{Pt70}}$, can be explained by noting that the scattering cross section of a AuNS is approximately 400 times larger than of a Pt70 nanoparticle.

Knowing the particle’s absorption cross section and the intensity distribution at the site of the trapped nanoparticle one can theoretically estimate the trapped particle’s temperature using Mie theory. Using an NA = 1.4 oil immersion objective, it is reasonable to assume a beam waist of 700 nm (for $\lambda = 1064$ nm). Furthermore, we assume a laser power of 100 mW at the focal plane and use thermal conductivities of 71.6 W (Km)$^{-1}$ for platinum, 317 W (Km)$^{-1}$ for gold, and 0.6 W (Km)$^{-1}$ for water. Using these values and the absorption cross sections given in ESI Table S2, the temperature increase for a trapped Pt70 particle would be 698 K, for a Au70 particle 79 K, and for a AuNS 1994 K, where all particles are assumed to be located in the focus of the laser beam. However, the fact that the scattering cross sections for these particles are rather high, in particular for the AuNS, renders it highly likely that the particles do not reside in the focus of the optical trap. Rather, the particles are probably stably trapped in lower intensity lobes as reported for gold nanoparticles. Therefore, the actual temperatures of the trapped particles are expected to be lower than the theoretical estimate given above. The value of $\kappa$ will depend on the intensity gradients at the exact localization of the particle; if the particle is stably trapped in a local intensity maximum, $\kappa$ is expected to be lower than if trapped at the focus (albeit, $\kappa$ is still measured to be linear with laser power). The Brownian motion of such hot trapped nanoparticles, from which $\kappa$ is obtained, is complicated as the particles move within a temperature gradient falling off at distances comparable to the particle’s diameter. Furthermore, the viscosity is strongly temperature dependent, thus affecting the thermal fluctuations within the optical trap in a non-trivial manner.

### Conclusion

In summary, by finite element modeling we found the optical cross sections and polarizability of massive platinum nanoparticles (PtNPs) with diameters between 30 nm and 70 nm, of massive gold nanoparticles (AuNPs) of similar sizes and of slightly larger gold nanoshells (AuNSs) which are known to have a strong absorption in the NIR. We find that the PtNPs absorb NIR light ten fold better than similarly sized AuNPs, hence, PtNPs have a huge potential as light to heat converters and may easily heat hundreds of degrees Celsius. The PtNPs, however, still absorb less than the larger AuNSs. The PtNPs scatter similarly to AuNPs and significantly less than AuNSs. These properties, together with the fact that the real part of the polarizability for PtNPs is relatively large, makes possible optical manipulation of individual PtNPs by a tightly focused laser. We experimentally demonstrated stable and efficient 3D optical trapping of individual PtNPs with diameters between 30 nm and 70 nm by a NIR laser beam and quantified the interaction between all nanoparticles investigated and the electromagnetic field. PtNPs trap nearly as strongly as AuNSs despite their polarization being –20 times lower and this is probably due to the fact that the scattering force is significantly higher on a AuNS than on a PtNP. Our study stresses the importance of looking beyond the canonical gold and silver in the search for nano-materials with optimal properties for optical manipulation and plasmonic heating. PtNPs and also possibly TiN nanomaterials are promising and much overlooked candidates for bio-related applications, as for instance for selected cell fusion or for photothermal cancer treatment.

### Conflicts of interest

There are no conflicts to declare.

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