Published in final edited form as:

Nano Lett. 2012 September 12; 12(9): . doi:10.1021/nl301937j.

Enhancing single-nanoparticle surface-chemistry by plasmonic overheating in an optical trap

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Abstract

Surface-chemistry of individual, optically trapped plasmonic nanoparticles is modified and accelerated by plasmonic overheating. Depending on the optical trapping power, gold nanorods can exhibit red-shifts of their plasmon resonance (i.e. increasing aspect ratio) under oxidative conditions. In contrast, in bulk exclusively blue shifts (decreasing aspect ratios) are observed. Supported by calculations, we explain this finding by local temperatures in the trap exceeding the boiling point of the solvent which can not be achieved in bulk.

Keywords

noble metal nanoparticles; plasmon resonance; colloidal chemistry; nano-/microfluidics; gold nanorods; plasmonic heating

Miniaturization is a successful approach to faster, more efficient applications in physics and chemistry. In chemistry, the reduction of reaction volumes is expected to lead to high-throughput, portable analytical and sensing applications, and fundamental insights into single-molecule chemical reactions.¹⁻³ Lab-on-a-chip applications frequently employ micro- or nanofluidic structures.⁴⁻⁷ However, these approaches do not change the outcome of a chemical reaction. Optical trapping on the other hand, being compatible with micro- or nanofluidic systems, is a well-established technique that has been widely applied to single-molecule force and optical spectroscopy, non-invasive manipulation, and chemical reactions monitoring.⁸⁻¹³ More recently, optical trapping has been applied to plasmonic noble metal nanoparticles.¹⁴⁻¹⁶ Due to their localized surface plasmon resonances, noble metal nanoparticles provide strongly enhanced and highly localized electromagnetic fields close to their surface.¹⁷ Their optical and field-enhancing properties allow for manipulating and enhancing fluorescence, Raman scattering, charge and energy transfer, and local temperature.¹⁸⁻²¹ The surface plasmon resonances can be tuned through controlling size, shape and material of the nanoparticles via advanced colloidal chemistry.²² Gold nanorods for instance, display two different plasmon modes: one transversal, in which the electrons oscillate perpendicular to the long axis of the rod, and the other red shifted longitudinal, in which the electrons oscillate along the long axis of the nanorod.²³ The latter mode

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Supporting information. Full experimental details and additional experimental results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

sensitively depends on the nanorod's aspect ratio: the higher the aspect ratio, the more red shifted the longitudinal plasmon resonance.

Here we apply the plasmonic heating effect of a single gold nanoparticle in an optical trap to both accelerate and modify chemical reactions on the surface of the particle. We show that individual optically trapped plasmonic particles modify and accelerate surface-chemistry by plasmonic overheating to yield different and faster results than the corresponding bulk reactions. Individual gold nanorods under oxidative conditions can display a red-shift of their localized surface plasmon resonances corresponding to an increasing aspect ratio, while in bulk exclusively blue-shifts are observed. Simultaneously, the oxidation is accelerated compared to bulk at room temperature. The modification and acceleration of the reaction is predominantly based on plasmonic overheating allowing for particle temperatures exceeding the boiling point of the solvent. The critical role of particle temperature is further illustrated by modified kinetics of single nanosphere growth in the optical trap. Since optical trapping is compatible with emerging nanofluidic systems, this method is applicable to many reactions in the vicinity of particle surfaces, in nanofluidic systems and colloidal chemistry.

Figure 1 illustrates our experiment. A single gold nanoparticle is trapped in three dimensions in aqueous solution with a focused laser beam (1064 nm). The plasmon resonance of the trapped particle is monitored simultaneously via its white light Rayleigh scattering response in a dark-field configuration.²⁴ We report two different experiments: first, a single gold nanorod is optically trapped and monitored in presence of hydrogen peroxide and hydrochloric acid (oxidative conditions, Fig. 1a) and, second, a 40 nm diameter gold nanosphere is trapped and monitored in presence of hydrochloroauric acid and ascorbic acid (growth conditions, Fig. 1b). Both single-nanoparticle experiments are compared to their bulk counterparts. The oxidative conditions in the first case are known to finely tune the plasmon resonance of gold nanorods in the bulk.^{25,26} Gold of the nanorods is etched away from the particle. Due to the stabilizing ligands (CTAB) on the sidewalls of the rod, the etching is faster at the tips. This leads to a reduction of the rods' aspect ratio and a blue shift of the longitudinal plasmon resonance. The growth conditions in the second case represent a well established procedure for isotropically growing gold nanospheres from seed particles in the bulk.²⁷ Full experimental details, as well as a detailed description of our particle temperature simulations employing finite-difference time domain and finite-element calculations, are given in the supporting information. We first describe the results of both experiments and then discuss them in detail.

Figure 2 displays our key result. For single-gold nanorods in the optical trap under oxidative conditions, three distinctly different behaviors can be observed: the longitudinal plasmon resonance of the rod either blue shifts or red shifts over time or does not display a shift at all. All three cases are accompanied by a reduction in scattering intensity. This is in stark contrast to the corresponding bulk reaction in which exclusively blue shifts are observed over a wide range of oxidant concentrations and temperatures (see supporting information). This shows that in the trap, in contrast to bulk, the oxidation can be altered such that the aspect ratio increases and the plasmon resonance red shifts or the aspect ratio stays constant and the resonance does not shift. We also note that the single-particles shift on a time scale of minutes while the bulk reaction takes tens of minutes to complete at room temperature even with ten times higher oxidant concentrations. As we will discuss in detail below, this behavior can be explained by the fact that the local temperatures on the nanorod surface can significantly exceed the boiling point of the solvent. This leads to destabilization of the ligands on the nanorod sidewalls which allows inverting the anisotropy of the etching process.

Fig. 3 displays histograms of the initial scattering peak wavelength of individual nanorods in the trap under oxidative conditions as a function of trapping power and sorted into the three categories described above, i.e. blue shift, red shift, and no shift. Without the trapping laser (single nanorods on a surface without drying) 89% of the nanorods blue shift. At 9.2 MW/cm² ($P_{\min}$) trapping power about 60% of the nanorods red shift, while at powers of 14.7 (P_{med}) and 20.1 MW/cm² ($P_{\max}$), 77% and 72% of the nanorods blue shift, respectively. In addition, with increasing trapping power, the peak of the distributions in Fig. 3 blue shifts. We note that with increasing power we observe increasing numbers of nanorods that melted in the trap on a timescale faster than that would be needed to acquire scattering spectra. These events are not included in the histogram.

Fig. 4 displays the results of the growth experiment. In both bulk and optical trap experiments, a red shift of the plasmon resonance corresponding to the growth of the nanospheres can be observed. However, the time-dependence of the resonance wavelength shift reveals a qualitatively different behavior: in bulk, a saturation-like behavior is observed, while in the trap an acceleration of the shift is observed over time.

We now turn to the detailed discussion of our results and show that the major factor determining the fate of the reactions is the local particle temperature. As described above, the oxidation of the nanorods in bulk is anisotropic since the nanorod sidewalls are better protected by the CTAB ligands than the tips. Therefore, the etching leads to a decreasing aspect ratio and consequently a blue shift of the longitudinal plasmon resonance. The same behavior is observed for individual nanorods on a glass substrate without trapping laser (P_0). Consequently, the observation of a majority of nanorods exhibiting red shifts at low trapping powers indicates that these particles are etched such that the aspect ratio increases. This suggests that in the trap at low trapping power ($P_{\min}$) the ligand shell is destabilized allowing for effective etching of the sidewalls, which increases the aspect ratio. We attribute this destabilization to plasmonic heating of the particle. Indeed, the numerical estimates of the particle temperature displayed in Fig. 3b suggest that the temperature of the red shifting particles at low trapping power is between 90 and 140°C. It has been shown in the literature that CTAB ligands are destabilized in the bulk if the temperature approaches 100°C.²⁸ In this scenario, nanorods exhibiting no shift are likely to exhibit a lower degree of ligand shell destabilization.

Upon further increasing the trapping power (P_{med} , $P_{\max}$), we observe again a majority of blue shifting particles. Since now the particle temperature increases up to 180°C (Fig. 3b), the ligand shell can be expected to be further destabilized. Therefore, an additional mechanism counteracting the etching of the sidewalls must come into play to explain the blue shift. As has been shown in the literature, pronounced melting and reshaping of gold nanorods have been observed for nanorods in the temperature range from 100 to 250°C. These processes are accelerated at higher temperature.²⁹ We therefore attribute the dominance of blue shifts at higher temperature to melting and reshaping of the nanorods, which redistributes material from the tip to the sidewalls and thereby overcompensates the etching of the sidewalls. Indeed, reshaping of our gold nanorods deposited on glass substrates has been observed under the same excitation conditions without oxidants (see supporting information for details). It should be noted, that our particle temperature estimates are consistent with, firstly, previous reports of significant off-resonant nanoparticle heating and, secondly, the fact that we do not observe bubble nucleation.³⁰ Vapor bubbles smaller than 200 nm in diameter would require temperatures in excess of 200°C to nucleate.^{30,31} The increase of particle temperature also explains the acceleration of the reaction as compared to the bulk room temperature case. For any chemical reaction, the activation energy barrier can be overcome more easily at higher temperatures. In the present case, it is particularly intriguing that the particle temperature can exceed the boiling point of

the solvent. Therefore this mechanism is expected to apply to a range of chemical reactions on plasmonic particle surfaces.

Furthermore, since scattering intensity is roughly proportional to the square of the particle volume, the data displayed in Fig. 2 allow for estimating the etching rates. Using the average scattering intensity of 26 nanorods and the average nanorod volume as determined from TEM images as standard, we estimate the etching rates for the nanorods shown in Fig. 2 to be 200-500 atoms per second and nanorod with an initially larger rate of ~1500 atoms per second and nanorod for the case of the blue shifting nanorod.

Further evidence for the critical role of the particle temperature is obtained from the growth experiment. In bulk, the saturation-like behavior of the resonance shift over time can be attributed to the depletion of Au(III) ions in the solution, which slows down the growth. In contrast, in the optical trap, the seed particle in the trap is heated and thus grows faster than the non-trapped seed particles. Since the heating becomes more efficient with increasing diameter of the particle (Fig. 4d), this acceleration becomes more and more significant. At an appropriate seed particle concentration, the trapped particle grows at virtually constant Au(III) concentration, while Au(III) is depleted in bulk reactions. Therefore it is possible to grow bigger particles faster in a trap.

In conclusion, we demonstrated that chemical reactions on the surface of single plasmonic nanoparticles can be plasmonically-enhanced and modified in an optical trap. In particular, single gold nanorods in the trap can be etched such that their aspect ratio either increases or decreases while in bulk it exclusively decreases. The major factor determining the outcome and kinetics of the reactions is the particle temperature, which can exceed the solvent boiling point due to plasmonic heating. Therefore, this mechanism is expected to apply to a number of reactions on plasmonic particle surfaces. Furthermore, optical trapping is compatible with emerging lab-on-a-chip applications employing micro- or nano-fluidic systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Financial support from the European Research Council (ERC) through the Advanced Investigator Grant HYMEM, from the Deutsche Forschungsgemeinschaft (DFG) through the Nanosystems Initiative Munich (NIM), and from the Humboldt Foundation (W.N.) is gratefully acknowledged.

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Figure 1.

Cartoon illustration of the single-nanoparticle reaction in an optical trap. (a) A single Au nanorod is trapped under oxidative conditions. Au(0) on the particle surface is oxidized to Au(III) by H₂O₂ in an acidic aqueous solution and released into solution. (b) A single Au nanosphere is trapped under growth conditions. Au(III) from solution is reduced to Au(0) by ascorbic acid in an acidic aqueous solution and deposited on the nanoparticle surface.

Figure 2.

Comparison of the oxidation of Au nanorods in the optical trap and in bulk solutions. (a) Typical time evolution of single-nanorod scattering spectra exhibiting a blue-shift (left), no shift (middle), and red-shift (right) of the resonance wavelength during oxidation in the trap, respectively. Trapping power density is 20.1 MW/cm^2 . Time intervals between spectra are 21.1 sec, 19.2, and 27.3 sec for blue-, no-, and red-shift, respectively. H_2O_2 concentration was 49 mM, solution temperature $\sim 30^\circ\text{C}$. The dip in the spectra around 532 nm is due to the 1064 nm notch filter used to block the trapping laser wavelength. Integration times were 2, 0.4, and 1 sec for blue-, no-, and red-shift, respectively. (b) Time evolution of the extinction spectra of Au nanorods during oxidation in bulk solutions at 25°C . Time interval between the spectra is 2 min. H_2O_2 concentration in the bulk solution is 490 mM.

Figure 3.

(a) Histograms of initial plasmon resonance wavelength of gold nanorods under oxidative conditions grouped according to blue shift (blue bars), red shift (red), or no shift within 7-5 nm (grey) of the resonance upon oxidation. Panels represent different trapping powers: P_0 (no trapping, rods on a glass substrate) 25x blue shift, 1x red, 2x no shift; $P_{min} = 9.2 \text{ MW/cm}^2$, 8x blue shift, 23x red shift, 7x no shift; $P_{med} = 14.7 \text{ MW/cm}^2$, 17x blue shift, 3x red shift, 2x no shift; $P_{max} = 20.1 \text{ MW/cm}^2$, 29x blue shift, 6x red shift, 5x no shift. (b) Calculated nanorod temperature in the optical trap as a function of resonance wavelength under different power densities. The temperature was obtained from Comsol simulation on the basis of FDTD calculations on absorption cross sections. For full details see supporting information.

Figure 4.

Comparison of the growth of Au nanospheres in bulk solutions and of single nanospheres in the optical trap. (a) Time evolution of the extinction spectra of Au nanospheres during growth in bulk solutions at 95°C. Time interval between spectra is 16.1 sec. (b) Typical time evolution of single-particle scattering spectra of a Au nanosphere during growth in the trap at 27°C. Time interval between spectra is 4.8 sec. Trapping power density was 20.1 MW/cm². The dip in the spectra around 532 nm is due to the 1064 nm notch filter used to block the trapping laser wavelength. Integration times were 0.4 s. (c) Comparison of the time-dependent resonance wavelength shift between nanospheres in bulk solutions (a) and the optical trap (b). (d) Simulated particle temperature in the optical trap as a function of particle diameter.