Super-Resolution Mapping of a Chemical Reaction Driven by Plasmonic Near-Fields

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Plasmonic nanoparticles have recently emerged as promising photocatalysts for light-driven chemical conversions. The illumination of these particles results in the generation of highly energetic charge carriers, elevated surface temperatures, and enhanced electromagnetic fields around them. Distinguishing between these often-overlapping processes is of paramount importance for the rational design of future plasmonic photocatalysts. However, the study of chemical reactions mediated by plasmonic effects is typically performed at the ensemble level and, therefore, limited by the intrinsic heterogeneity of the catalyst particles. Here, we report an in-situ single particle study of a chemical reaction driven solely by plasmonic near-fields. Using super-resolution fluorescence microscopy, we achieve single turnover temporal resolution and ~30 nm spatial resolution. This sub-particle accuracy permits the construction of a clear correlation between the simulated electric field distribution around individual metal nanoparticles and their super-resolved catalytic activity maps. Our results can easily be extended to systems with more complex electric field distributions, thereby guiding the design of future advanced photoactive materials.
Super-resolution Mapping of a Chemical Reaction Driven by Plasmonic Near-fields

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Abstract

Plasmonic nanoparticles have recently emerged as promising photocatalysts for light-driven chemical conversions. The illumination of these particles results in the generation of highly energetic charge carriers, elevated surface temperatures, and enhanced electromagnetic fields around them. Distinguishing between these often-overlapping processes is of paramount importance for the rational design of future plasmonic photocatalysts. However, the study of chemical reactions mediated by plasmonic effects is typically performed at the ensemble level and, therefore, limited by the intrinsic heterogeneity of the catalyst particles. Here, we report an in-situ single particle study of a chemical reaction driven solely by plasmonic near-fields. Using super-resolution fluorescence microscopy, we achieve single turnover temporal resolution and ∼30 nm spatial resolution. This sub-particle accuracy permits the construction of a clear correlation between the simulated electric field distribution around individual metal nanoparticles and their super-resolved catalytic activity maps. Our results can easily be extended to
systems with more complex electric field distributions, thereby guiding the design of future advanced photoactive materials.

Keywords

plasmonics, photochemistry, near-fields, fluorogenic reactions, super-resolution microscopy, single molecule localization

Introduction

Localized surface plasmon resonances (LSPRs), arising from the coherent oscillation of free electrons upon illumination of metallic nanoparticles,\(^1\) can enhance the rate and change the energy landscape of a chemical reaction.\(^2-5\) For example, LSPRs have been used to enhance the rate of ammonia decomposition on copper-ruthenium nanoparticles\(^6\) and to increase the selectivity of carbon dioxide hydrogenation on rhodium nanocubes.\(^7\) At least three mechanisms have been proposed to explain the observed enhancements: i) the generation of highly energetic non-equilibrium charge carriers that can drive redox reactions, ii) photothermal nanoparticle heating inducing faster chemical turnover according to the Arrhenius equation, and iii) the focusing of light into nanoscale regions of high electromagnetic fields (near-fields) that can accelerate photosensitive reactions.\(^8\) The relative contribution of these mechanisms to the photochemical rate depends on different optical and geometrical parameters.\(^5,9-12\) For example, hot carrier generation and nanoparticle surface temperature increase are the result of non-radiative LSPR decay (absorption), whereas near-fields arise due to radiative decay (scattering). All these mechanisms take place on ultrafast timescales and can contribute simultaneously to the enhancement of a chemical reaction, which makes them very difficult to disentangle experimentally.\(^8,13,14\)

Recent studies have begun elucidating the mechanism underlying a wide range of plasmon-driven processes by carefully characterizing the rate of chemical reactions under different
illumination parameters, while measuring the temperature inside the reactor.\textsuperscript{6,15-18} These experiments are often performed at the ensemble level, resulting in measurements that are averaged over many particles. The catalytic properties of nanoparticles, however, are intrinsically heterogeneous due to particle size distribution,\textsuperscript{19,20} the heterogeneity of active sites,\textsuperscript{21} and the dynamic restructuring of catalytic surfaces.\textsuperscript{22-24}

To address this challenge, in-situ measurements of the catalytic activity of single nanoparticles with single turnover temporal resolution and nanometer spatial resolution are necessary.\textsuperscript{25-28} In this context, super-resolution fluorescence microscopy has emerged as an effective approach due to its ability to interrogate individual catalytic nanoparticles at the single molecule level.\textsuperscript{25} For example, super-resolution microscopy has been used to characterize chemical reactions that are accelerated by the generation of plasmonic hot charge carriers on single nanoparticles.\textsuperscript{29,30} However, the efficiency of hot charge carrier extraction is typically very low due to their extremely short lifetimes.\textsuperscript{31,32} Recently, several studies have proposed an alternative mechanism to explain their plasmon-driven catalysis enhancement, in which the scattered near-fields of plasmonic nanoparticles induce direct optical excitations of adsorbate molecular species.\textsuperscript{33-36} To demonstrate this mechanism, which is not limited by fast electron-electron scattering and could therefore result in high conversion efficiencies, it is important to spatially correlate the photocatalytic activity of individual metal nanoparticles with their plasmonic near-fields.

Here, we utilize super-resolution microscopy to map the activation of a purely field-driven chemical reaction under in-situ conditions. In particular, we irradiate gold nanorods that catalyze the conversion of the nonfluorescent molecule resazurin to its highly fluorescent reduced form resorufin.\textsuperscript{37} The power dependence of the turnover rate and the spatial distribution of the catalytic events unequivocally indicate that the activation mechanism is solely due to the plasmonic near-fields.
Results and discussion

We first synthesize gold (Au) nanorods with a length of $118 \pm 10$ nm and a width of $54 \pm 4$ nm using a previously reported seed-mediated growth technique (Figure S1).\textsuperscript{20} The aspect ratio of these rods results in a longitudinal LSPR at 718 nm, which has been chosen to allow independent excitation of the LSPR with a 730 nm continuous wave (CW) laser, without exciting the reactant (resazurin) or the product (resorufin). We then coat the nanorods with a $\sim 16$ nm mesoporous SiO$_2$ (mSiO$_2$) shell using a previously reported growth method based on the hydrolysis of tetraethyl orthosilicate (TEOS), see Figure 1a.\textsuperscript{38,39} The mesoporous shell with $\sim 2.5$ nm pores\textsuperscript{39} temporarily traps the reaction products and thereby facilitates their detection, which would otherwise be hindered by fast product desorption and fluorescence quenching on Au.\textsuperscript{40} The mSiO$_2$ growth is templated by the hexadecyltrimethylammonium-umbromide (CTAB) ligand of the rods,\textsuperscript{38} which we remove after synthesis to unblock the mesopores. Interestingly, our Au@mSiO$_2$ nanorods show no catalytic activity in the dark, suggesting that the mesopores are not etched all the way to the metallic surface (Figure S2). The extinction spectra and size distributions of the nanorods before and after mSiO$_2$ coating are reported in Figure S1.

We dropcast the Au@mSiO$_2$ nanorods on a coverslip, resulting in an average interparticle spacing of $\sim 6 \mu$m, which allows each rod to be resolved spatially in the microscope. The coverslip is then built into a flowcell and mounted on an inverted fluorescence microscope. We supply a continuous flow of 200 nM resazurin in a 50 mM potassium phosphate buffer with a pH of 7.3 at 50 $\mu$L/min, so that experiments can be performed over several hours. The details of the synthesis and of the optical setup are reported in the Methods section.

At the beginning of each experiment, we first take a transmitted white light image of the sample. We then invert this image, so that the catalyst particles appear as local intensity maxima instead of minima. This inversion allows us to fit all local maxima to a two-dimensional Gaussian and thereby localize all nanoparticles with a $\sim 6$ nm precision (Figure S3).\textsuperscript{41,42} After taking the transmitted light image, we irradiate an area of the sample
Figure 1: In-situ super-resolution catalysis on individual gold nanorods. (a) Transmission electron microscopy (TEM) image of the Au@mSiO$_2$ nanorods after ligand removal. (b) Illustration of the catalytic conversion of resazurin to resorufin. (c) Nanorod extinction (black line) and absorption (green) and emission (yellow) of the reaction product resorufin. (d) Example frame showing the fluorescence of resorufin molecules generated on several catalysts. The image displayed here is cropped from the total field-of-view of 133 × 133 µm$^2$. (e) Zoomed-in area denoted by the white box in (d), showing the emission of one resorufin molecule. (f) Two-dimensional Gaussian fit of panel (e). The resulting molecule position is denoted by the red dot.

of $\sim$100×100 µm$^2$ with a 532 nm CW laser in a total internal reflection (TIRF) configuration (Figure S4). This laser wavelength allows us to simultaneously excite the reaction product resorufin and the transverse plasmon resonance of the nanorods (Figures 1b,c). The reflected signal is filtered with a dichroic mirror and an emission filter such that only the wavelengths $\lambda = 585 \pm 20$ nm are transmitted, before being collected by a sCMOS camera. The nanorod photoluminescence closely follows its longitudinal plasmon resonance ($\lambda = 718$ nm), which is outside the spectral range of the emission filter. Therefore, in our experimental configuration, we do not need to perform background subtraction to remove
the nanorod photoluminescence and we only observe stochastic bursts of fluorescence corresponding to the generation of resorufin molecules.\textsuperscript{37} Similar to the localization procedure for the nanoparticles, we localize these bursts of fluorescence (Figures 1d,e) by fitting them to a two-dimensional Gaussian (Figure 1f), resulting in a localization precision of \( \sim 24 \) nm (Figure S5). Together with the error of \( \sim 6 \) nm in determining the nanoparticle locations, the total localization precision of the experiment is \( \sim 30 \) nm.

Resazurin (Rz) can be converted to resorufin (Rf) via two different mechanisms:\textsuperscript{44} i) a reductive deoxygenation catalyzed by Au, which requires the presence of hydroxylamine (NH\(_2\)OH) as a reducing agent\textsuperscript{25}

\[
2 \text{Rz} + \text{NH}_2\text{OH} + \text{OH}^- \xrightarrow{\text{Au}} 2 \text{Rf} + \text{NO}_2^- + 2 \text{H}_2\text{O} \quad (1)
\]

or ii) a photodriven disproportionation

\[
3 \text{Rz} + \text{H}_2\text{O} \xrightarrow{\hbar\omega} \text{Rf} + 2 \text{Rz}^\bullet + 2 \text{OH}^- \quad (2)
\]

where Rz\(^\bullet\) indicates an oxidized radical of resazurin.

The first mechanism occurs under dark conditions, but can be enhanced by exciting the plasmon resonance of the catalysts.\textsuperscript{29} The second mechanism does not occur under dark conditions and does not strictly require a catalytic surface, but exhibits faster dynamics in the presence of Pd or Au nanoparticles.\textsuperscript{37} These two reaction pathways are characterized by different dependencies of the turnover rate on the laser power. The reductive deoxygenation in equation (1) shows a quadratic power dependence, which has been attributed to the presence of two photoexcited species on the nanoparticle surface.\textsuperscript{29} In the absence of a catalytic surface, the photodriven disproportionation in equation (2) also shows a quadratic dependence, as each reaction involves two photoexcited resazurin molecules.\textsuperscript{37} In the presence of a catalytic surface, however, the turnover rate of the second mechanism increases linearly, suggesting a different reaction pathway involving a single photoexcited resazurin molecule.\textsuperscript{37}
Figure 2: Kinetics of the resazurin to resorufin conversion. (a) Mean turnover rate as a function of time in the absence (black circles) and presence (green triangles) of 10 mM NH$_2$OH. Every point is an average over 1000 frames and 485 particles (black circles) or 331 particles (green triangles). (b) Turnover rate as a function of laser power in the absence (black circles) and presence (green triangles) of 10 mM NH$_2$OH. Each point is the average of ten points in panel (a). Error bars are standard deviations. Solid lines are a fit to $y = ax^b$, where $y$ is the turnover rate, $x$ is the laser power, and $a$ and $b$ are fitting parameters.

To discern between these reaction pathways, we measure the turnover rate (number of detected products per catalyst per second) as a function of laser power both in the absence and presence of the reducing agent NH$_2$OH. Figure 2a shows the mean turnover rate as a function of time in the presence and absence of 10 mM NH$_2$OH, under varying laser intensities. To exclude fluorescent impurities, we only consider events detected within 100 nm of a Au@mSiO$_2$ catalyst. The observed trend of the turnover rate on the laser power does not strongly depend on this distance threshold (Figure S6). Every 10,000 frames (corresponding to ~20 minutes) we reduce the laser power in steps of 20 mW from 200 mW to 100 mW and then, to check the reversibility of the laser power dependence, we increase the power back to 200 mW as the final step (right y-axis in Figure 2a). We observe a decrease in
turnover rate with decreasing laser power, which is almost fully reversible (Figure 2a). We also find that this decrease in turnover rate is not due to a decrease in the detectability of the reaction products, as the amount of events that are not localized on a catalyst, such as fluorescent bursts from impurities or reaction products that readsorb on the glass coverslip, does not vary with laser power (Figure S7). As our mSiO$_2$ shells are both thin and porous, we attribute the incomplete recovery of the initial catalytic activity to the partial dissolution of SiO$_2$ in water,\textsuperscript{39,45} which decreases the ability of the shell to temporarily trap the reaction products.

Plotting the turnover rate as a function of laser power and fitting the result to a power law ($y = ax^b$) reveals a quadratic dependence both in the presence and absence of 10 mM NH$_2$OH (Figure 2b). Intermediate NH$_2$OH concentrations also show no influence on the turnover rate (Figure S8). Therefore, we can conclude that our catalysts are inactive for the reductive deoxygenation, as the presence of NH$_2$OH does not alter the reaction kinetics. Furthermore, the catalysts are also inactive for the photodriven disproportionation mediated by a catalytic surface, as we observe a quadratic rather than a linear dependence of the turnover rate on laser power. Interestingly, our power dependence in the absence of NH$_2$OH matches exactly with the behavior observed for the photodriven disproportionation in the absence of a catalytic surface.\textsuperscript{37} This observation suggests that in our system the conversion of resazurin to resorufin is not mediated by electron transfer with Au. Instead, we exploit the capability of Au nanoparticles to focus light into sub-wavelength volumes (near-fields) and thereby accelerate photodriven reactions in the vicinity of the Au surface.

Since in our system no electron transfer takes place between Au and resazurin, we can rule out any contribution from non-equilibrium charge carriers generated through plasmon excitation. We further verify this statement by simultaneously exciting the longitudinal plasmon resonance of the Au@mSiO$_2$ nanorods using a 730 nm CW laser. While at this energy resazurin is not photo-excited (Figure S9), the charge carriers generated by absorption in Au have enough energy to occupy the lowest unoccupied molecular orbital of resazurin.\textsuperscript{37}
Figure 3: FDTD simulations on Au@mSiO$_2$ nanorods. (a) Illustration of the simulation. A p-polarized field $\vec{E}$ with wavevector $\vec{k}$ is injected on an Au@mSiO$_2$ nanorod on a glass coverslip. The source angle $\phi$ is defined as the angle between $\vec{k}$ and $\hat{z}$. The electric field is monitored at the bottom of the nanorod. (b,c) Absorption (b) and scattering (c) cross sections at 532 nm as a function of source angle. The nanorod is p-oriented (black circles), as in panel (a), or s-oriented (green triangles). The critical angle for TIRF is $61^\circ$. (d,e) Electric field intensity $|E|^2$ normalized to the incident field intensity $|E_0|^2$ at 532 nm monitored at the bottom of the Au nanorods for a source angle of $70^\circ$. The nanorod is p-oriented (d), as in panel (a), or s-oriented (e).

However, we observe no change in the kinetics of the reaction when comparing the reaction rate with or without the excitation of the longitudinal resonance of the rods (Figure S9). Furthermore, due to the low power density and large interparticle spacing used in our study, localized and collective photothermal contributions can also safely be ruled out (Figure S10), thereby leaving the plasmonic near-fields as the sole contributor to the resazurin-to-resorufin conversion.

The observation that in our system the conversion of resazurin to resorufin is driven by the plasmonic near-fields suggests that a correlation should exist between the spatial distribution of the electric field around the nanorods and the regions where we observe high catalytic activity. We therefore first simulate the optical response of our nanorods under 532 nm irradiation using a finite-difference time-domain (FDTD) method. We simulate a 118 nm
by 54 nm gold rod with a 16 nm mSiO$_2$ shell on a glass coverslip and we inject a p-polarized field through the glass coverslip (Figure 3a and Methods). The long axis of the rod is pointing along the x axis (Figure 3a), which we will refer to as p-oriented, or along the y-axis, which we will refer to as s-oriented. We monitor the absorption and scattering cross section, $\sigma_{\text{abs}}$ and $\sigma_{\text{sca}}$, and the total electric field intensity inside and outside the rod for various injection angles of the source. For a source angle of 0°, which corresponds to injection normal to the coverslip, the cross sections at 532 nm are higher for the s-oriented rod (Figures 3b,c). This behavior is expected, as 532 nm illumination overlaps with the transverse resonance of Au nanorods (Figure S11), which is preferentially excited when the polarization of the field is perpendicular to the long axis of the rod. However, as the source angle increases, a second transverse resonance with charges oscillating along the z axis is excited. As the rod is always oriented in the x,y-plane, this resonance is excited independent of the rod orientation when the source is off-axis, resulting in the cross sections for p-oriented and s-oriented rods becoming increasingly similar as the source angle increases (Figures 3b,c).

As TIRF illumination corresponds to excitation at very high angles (between 61° and 74° in our experimental geometry), the absorption and scattering cross sections of a nanorod do not depend strongly on the in-plane particle orientation. However, the spatial distribution of the electric field does show distinguishing features. We observe electric field hot spots at the bottom of the nanorod (Figures 3d,e) and relatively weak field enhancement at the nanorod center (Figure S11). For the p-oriented rod the field intensity is $\sim$1.3× higher on the tip away from the incident light than on the tip facing the source (Figure 3d). We do not observe this difference for the s-oriented rod, as this orientation is perpendicular to the propagation direction of the field, which leads to an identical distribution of enhanced fields at the opposing ends of the nanorod (Figure 3e).

The above observations suggest that the turnover rate of a catalyst should not strongly depend on the orientation of the particle, as the scattering cross sections are similar for all orientations. However, the spatial distribution of catalytic events should vary strongly
depending on the particle orientation. In particular, our simulations suggest that for p-oriented rods, we expect to see more light-driven catalytic events on the tip away from the incident light, where the fields are stronger (Figure 3d). For s-oriented rods, however, we expect to see an equal number of events between the front and back tips (Figure 3e).

Since the dimensions of our catalysts are only a few times larger than our resorufin product localization precision, quantitative comparison between the simulated electric field and the catalysis maps is quite challenging. Additionally, due to partial spectral overlap of the nanorod extinction with the resorufin emission, the latter can couple to the nanorod, resulting in the apparent position of the molecule being 'pulled' toward the nanorod center.\textsuperscript{47,48} However, despite these limitations, our spatial resolution is sufficient to discriminate between the catalytic activity of the two tips of the rods. Therefore, to correlate the observed catalytic activity to the simulated electric field, we look at the in-plane angular distribution of catalytic events.

For each nanorod, we define the positions of the catalytic events relative to the position of the rod, which is known from the transmitted white light image. We then assign an angle $\theta$ to each catalytic event, defined as the angle between the position of the event and the x axis (Figure 4a). This definition of $\theta$ allows us to convert the two-dimensional catalysis map of a single particle (Figure 4b) into an angular distribution (dots in Figure 4c). We then fit this distribution to a function given by the sum of two Gaussian peaks, corresponding to the two tips of the nanorod. The first peak models the catalytic activity of the front tip, i.e. the tip with a negative y coordinate, and is characterised by an amplitude $A_1$ and an in-plane orientation $\theta_0$. The second peak, corresponding to the back tip with a positive y coordinate, has an amplitude $A_2$ and an in-plane orientation $\theta_0 + \pi$ (see also Methods and Figure S12). As both $\theta_0$ and $\theta_0 + \pi$ need to fall within the range between 0 and $2\pi$, we force $\theta_0$ to be $0 < \theta_0 < \pi$. Fitting the angular distribution of single molecule catalytic events allows us to extract the particle orientation $\theta_0$ and the reactivities of the two nanorod tips, $A_1$ and $A_2$ (Figure 4c).
Figure 4: Analyzing catalysis maps as a function of particle orientation. (a) Illustration of the definition of the angle $\theta$ and the particle orientation $\theta_0$. The x component of the wavevector $\mathbf{k}$ is also illustrated. (b,c) Two-dimensional histogram (b) and angular distribution (c) of the products detected on a single Au nanorod. The bin sizes are $30 \times 30 \text{nm}^2$ (b) and $\pi/10$ (c). Panel (b) also contains a white outline depicting the fitted position and orientation of the Au@mSiO$_2$ nanorod catalyst. The orientation $\theta_0$ is extracted from the fit in panel (c). (d) Mean turnover rate as a function of particle orientation (circles) and the simulated electric field enhancement (line), as defined in equation (3). (e) Ratio between the peaks in the angular distribution (circles) and the ratio between the simulated electric field enhancements on the two tips (line), as defined in equation (4). In panels (d) and (e) the points correspond to a bin with a width of $\pi/19$, the x error bars are standard deviations, and the y error bars are standard errors in the mean.

When a particle has $\theta_0$ around 0, the particle is p-oriented. In this orientation $A_1$ corresponds to the reactivity of the tip away from the incident light, where the field is higher than on the tip facing the source (Figure 3d), and therefore we expect $A_1 > A_2$. When a particle has $\theta_0$ around $\pi/2$, the particle is s-oriented. In this orientation the field enhancement on the two tips is the same (Figure 3e), and therefore we expect $A_1 \approx A_2$. Lastly, when a particle has $\theta_0$ around $\pi$, the particle is again p-oriented. However, now $A_1$ corresponds to the reactivity of the tip facing the source and we expect $A_1 < A_2$. The example shown in Figures 4a-c correspond to a particle with $\theta_0 = 175^\circ$ and for which $A_1$ is therefore smaller.
than $A_2$, as shown by the clear peak intensity difference in Figure 4c. Other examples of nanorods with different in-plane orientations can be found in Figure S13.

In Figure 4d, we bin together particles with similar in-plane orientations and plot the measured turnover rates as a function of $\theta_0$. Since the turnover rate scales quadratically with the electric field intensity (Figure 2b), we compare these values to the square of the average simulated electric field intensity outside the nanoparticle. We calculate this value $\eta_{\text{field}}$ by integrating over all mesh cells outside the particle, but within the mSiO$_2$ shell:

$$
\eta_{\text{field}} = \frac{1}{V} \iiint_{r < 16\text{nm}} \frac{|E|^4}{|E_0|^4} dV,
$$

where $V$ is the integrated volume, $r$ is the distance from a mesh cell outside of the nanoparticle to the particle surface, $E$ is the electric field, and $E_0$ is the incident field.

We find that both the turnover rate and the average field enhancement show only a weak dependence on the particle orientation (Figure 4d), as also expected from the similar scattering cross sections of p-oriented and s-oriented nanorods at the experimental illumination angle (Figure 3c). Interestingly, however, we find a clear angular dependence of the peak ratio $\frac{A_1}{A_2}$ on $\theta_0$ (Figure 4e). We compare this value to the ratio between the simulated field enhancement in the half-space occupied by the tip corresponding to $A_1$ and the field enhancement in the half-space occupied by the tip corresponding to $A_2$. We define this value $\frac{\eta_{A_1}}{\eta_{A_2}}$ as

$$
\frac{\eta_{A_1}}{\eta_{A_2}} = \frac{\iiint_{r < 16\text{nm}, \theta_0 - \frac{\pi}{2} < \theta < \theta_0 + \frac{\pi}{2}} \frac{|E|^4}{|E_0|^4} dV}{\iiint_{r < 16\text{nm}, \theta_0 + \frac{\pi}{2} < \theta < \theta_0 + \frac{3\pi}{2}} \frac{|E|^4}{|E_0|^4} dV},
$$

where again we only consider mesh cells outside the particle, but within the mSiO$_2$ shell.

The measured ratio between the photocatalytic activity of the two tips of the nanorods ($\frac{A_1}{A_2}$) matches qualitatively with the simulated ratio between the electric field intensity enhancements on the two tips ($\frac{\eta_{A_1}}{\eta_{A_2}}$), as both show a transition from values $> 1$ for in-plane orientations $\theta_0 < \pi/2$ to values $< 1$ for $\theta_0 > \pi/2$ (Figure 4e). Quantitative agreement be-
between the experiment and the simulation is not expected, as the definitions of $\frac{A_1}{A_2}$ and $\eta A_1 \eta A_2$ are not completely equivalent. Furthermore, mislocalization can limit the ability to experimentally distinguish between the two nanorod tips. The qualitative agreement, however, together with the quadratic power dependence of the turnover rate in the absence of a reducing agent (Figure 2b), unequivocally demonstrate that the plasmonic near-fields are uniquely responsible for the chemical activation under our experimental conditions.

Conclusion

In summary, we use super-resolution fluorescence microscopy for the in-situ study of a plasmon-driven chemical reaction. By measuring the photocatalytic turnover rate at the single molecule level for various illumination intensities and reducing agent concentrations, we identify the reaction mechanism as a photodriven disproportionation that is not mediated by electron transfer with the metal nanoparticle. Furthermore, by using single molecule localization we show a clear correlation between the simulated electric field distribution and the super-resolution catalysis maps. These results indicate that the fluorogenic process is purely driven by the electromagnetic fields and is therefore independent on the catalytic properties of the plasmonic nanoparticles. Our approach to map scattered near-fields in-situ and with sub-particle spatial resolution can be extended to systems with different chemical compositions and complex field distributions and can thereby guide the design of future advanced materials for photocatalysis, biomolecule sensing, and photonic devices.

Methods

All the chemicals are used as received, without any further purification. Hexadecyltrimethylammonium bromide (CTAB) (98%), NaBH$_4$ (99%), HAuCl$_4$ trihydrate (99.9%), AgNO$_3$ (99.9999%), ascorbic acid (99%), HCl (37% in water), NH$_2$OH (50% in water), tetraethyl orthosilicate (TEOS) (99.999%), K$_2$HPO$_4$ (98%), and KH$_2$PO$_4$ (99%) were purchased from
Sigma Aldrich. Sodium oleate (NaOL) (97%) was purchased from TCI. Ethanol (dried, < 0.01% H₂O) was purchased from Merck. NaOH (98%) was purchased from Alfa Aesar. Resazurin (99%) was purchased from Thermo Fisher. Ultrapure water obtained from a Milli-Q Integral Water Purification System by Merck Millipore was used for all aqueous solutions.

Au nanorod synthesis

We synthesize Au nanorods using a previously reported seed-mediated growth method.⁰⁻²⁰ Au seeds are synthesized by mixing 5 mL 0.5 mM HAuCl₄ and 5 mL 0.2 M CTAB. 600 µL of fresh 0.01 M NaBH₄ is diluted to 1 mL and subsequently added under vigorous stirring. The stirring is stopped after 2 minutes and the seeds are aged at room temperature for at least 30 minutes before use. Ideally, the seeds are used within a few hours to avoid CTAB crystallization.

To synthesize the rods, 3.5 g CTAB and 0.617 g NaOL are dissolved in 125 mL water and kept at 30 °C. 12 mL 4 mM AgNO₃ is added and the solution is kept undisturbed for 15 minutes. After adding 125 mL 1 mM HAuCl₄, the solution is stirred for 90 minutes to reduce the Au³⁺ to Au⁺.²⁰ Then, 750 µL HCl (37% in water) is added to adjust the pH. After 15 minutes of stirring, 625 µL 64 mM ascorbic acid is added. After 30 seconds of vigorous stirring, 200 µL of the above seeds solution is added. The resulting mixture is stirred again for 30 seconds and then left overnight undisturbed at 30 °C.

Mesoporous SiO₂ coating

The nanorods are coated with mesoporous SiO₂ by adapting a previous method.³⁸,³⁹ 40 mL of the above nanorods are centrifuged at 5500 × g for 30 minutes and redispersed in 40 mL 5 mM CTAB. The nanorods are then centrifuged again and redispersed in 5 mL 5 mM CTAB.

To 3 mL of the above nanorods 7 mL water is added to achieve a final CTAB concentration of 1.5 mM. 100 µL 0.1 M NaOH is added to adjust the pH. Then, while continuously stirring at 30 °C, three injections of 30 µL 0.9 M TEOS in ethanol are done separated by 45 minute
time intervals. After the final injection, the solution is kept stirring at 30 °C for ~40 hours.

After synthesis, the solution is diluted with water to a total volume of 40 mL. This solution is then centrifuged three times at 7000 × g for 15 minutes and redispersed in 40 mL ethanol to remove excess SiO₂ and CTAB.

**Ligand removal**

To further remove CTAB and thereby unblock the mesopores, 85 µL HCl (37% in water) is added to 10 mL of the above Au@mSiO₂ nanorod solution in ethanol. This solution is ultrasonicated for 30 minutes in a Branson 5800 ultrasonic bath. After sonication, the solution is diluted to 40 mL with ethanol and centrifuged twice at 7000 × g for 15 minutes and redispersed in 40 mL ethanol. Finally, the solution is centrifuged at 7000 × g for 15 minutes again and redispersed in 10 mL ethanol.

**Optical setup**

The optical setup is based around a Zeiss AxioObserver 7 inverted optical fluorescence microscope. The laser beam from a 532 nm CW laser (CNI MGL-FN-532) is focused into a Thorlabs P3-488PM-FC-2 single mode polarization-maintaining fiber using a Thorlabs PAF2-7A FiberPort. The fiber is connected to a Zeiss TIRF slider, which focuses the laser on the edge of the back focal plane of an oil-immersion objective (Zeiss Alpha Plan-Apochromat 63×/1.46NA). The emission is filtered using a dichroic mirror (Semrock, reflection at λ = 532 nm and λ = 730 nm and transmission from λ = 550 nm to λ = 700 nm) and a band-pass filter that transmits λ = 585 ± 20 nm (Semrock 585/40 BrightLine). The signal is imaged on a Hamamatsu ORCA-Flash 4.0 V3 sCMOS camera with 2048 × 2048 pixels (6.5 µm physical size), which is reduced to 1024 × 1024 pixels using 2 × 2 binning, resulting in an effective pixel size of 129 nm (63× magnification objective and an additional 1.6× magnification in the body of the microscope). The integration time is 100 ms. During the experiment we correct for in-plane drift by tracking fluorescent impurities and for out-of-plane drift using
a focus correction system built into the microscope. Image filtering and Gaussian fitting
are performed in ThunderSTORM. Even events for which the fitted Gaussian has a width \( \sigma < 35 \text{ nm} \) are filtered out, as these are false detections (hot pixels). Events that appear in
consecutive frames are merged. An illustration of the setup can be found in Figure S4.

**FDTD simulations**

FDTD simulations are performed using Lumerical FDTD. The glass coverslip is simulated
as a semi-infinite lossless dielectric with a refractive index of 1.52. The Au nanorod is
simulated as a spherically-capped cylinder with a dielectric function taken from literature.
The mSiO\(_2\) shell is simulated as a spherically-capped cylinder with a refractive index of
1.4. The surrounding medium has a refractive index of 1.333. A p-polarized total-field
scattered-field source is injected upwards, from inside the coverslip towards the nanorod.
The absorption and scattering cross sections are monitored by placing a transmission box
inside and outside the source, respectively. The electric field is monitored in three dimensions
and x,y slices are plotted in Figures 3 and S11. A fine mesh of 1 nm\(^3\) is used across the
whole volume of the source.

**Fitting the angular distribution**

The angular distribution of catalytic events, see for example Figure 4c, is fitted to

\[
A_0 + A_1 \exp \left[ -\frac{(\theta - \theta_0)^2}{0.9} \right] + A_2 \exp \left[ -\frac{(\theta - \theta_0 - \pi)^2}{0.9} \right] \\
+ A_2 \exp \left[ -\frac{(\theta - \theta_0 - 2\pi)^2}{0.9} \right] + A_2 \exp \left[ -\frac{(\theta - \theta_0 + \pi)^2}{0.9} \right],
\]

where \( A_0 \) is a vertical offset, \( A_1 \) and \( A_2 \) are the peak amplitudes, \( \theta \) is the angle as defined in
Figure 4a, and \( \theta_0 \) (0 < \( \theta_0 < \pi \)) is the orientation of the particle. The peak with amplitude
\( A_2 \) appears several times to ensure continuity from \( \theta = 0 \) to \( \theta = 2\pi \) for all values of \( \theta_0 \). We
pick 0.9 as the peak width, as this results in a width similar to that of a \( \cos^2 \) function, see
Figure S12. We can exclude systematic errors in detecting the catalyst positions, as this
would result in an uneven distribution of $\theta_0$ values, which is not what we observe, see Figure S12.

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**Author contributions**

All authors conceived the project; R.F.H. and M.P. performed the experiments; R.F.H. analyzed the data and performed the FDTD simulations; A.B. supervised the project; all authors contributed to writing the paper.

**Competing interests**

The authors declare no competing financial interest.

**Supporting Information**

The following files are included.

- Supporting information: spectra and size distributions of the Au nanorods before and after mSiO$_2$ coating; the Au@mSiO$_2$ nanorods show no catalytic activity in the dark; localization of the catalysts in the microscope; illustration of the optical setup; localization precision of the resorfin molecules; the observed power dependencies do not
strongly depend on the distance threshold; the observed power dependencies are not
due to a change in product detectability; NH$_2$OH does not influence the reaction ki-
etics; independently exciting the LSPR of the Au@mSiO$_2$ nanorods does not alter the
reaction kinetics; photothermal contributions are negligible; FDTD spectra at normal
incidence and electric fields monitored at the nanorod center; fitting function and $\theta_0$
histogram; single particle catalysis maps and angular distributions.

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Supporting Information for:

Super-resolution Mapping of a Chemical Reaction Driven by Plasmonic Near-fields

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References
1 Spectra and size distributions of the Au nanorods before and after mSiO₂ coating

The Au nanorods are synthesized¹ and coated with mesoporous SiO₂ (mSiO₂)²,³ using previously reported methods. After mSiO₂ synthesis, we observe a slight red shift of the resonance (Figure S1a), due to the increase in refractive index around the nanorods. After ligand removal, we observe a slight resonance broadening (Figure S1a), which we attribute to a slight loss in sample uniformity due to HCl etching. Size distributions are measured from transmission electron microscopy (TEM) images before mSiO₂ coating (Figure S1b) and after ligand removal (Figure S1c) using ImageJ. Representative TEM images can be found in Figures S1d,e.
Figure S1: (a) Normalized UV-Vis spectra of the rods before (black) and after (blue) mSiO\(_2\) coating, and after ligand removal (green). The longitudinal resonances are at 708 nm (black), 717 nm (blue), and 718 nm (green). The transverse resonances are at 531 nm (black), 530 nm (blue), and 529 nm (green). (b) Size distribution of 80 nanorods before mSiO\(_2\) coating. (c) Size distribution of 89 nanorods after ligand removal. The reported values for the length and width result from Gaussian fits of the distributions, see the lines in panels (b) and (c). The reported errors are the standard deviations of the fitted Gaussians. (d,e) Representative TEM images of the nanorods before mSiO\(_2\) coating (d) and after ligand removal (e).
2 The Au@mSiO$_2$ nanorods show no catalytic activity in the dark

We characterize the catalytic activity of the Au@mSiO$_2$ nanorods in the dark using UV-Vis spectroscopy. The white light source of the spectrometer (Perkin Elmer Lambda 1050) is not expected to induce any catalytic activity due to its low power density. We prepare a cuvette with 1 mL 50 mM pH 7.3 potassium phosphate buffer with 10 µM resazurin and 20 mM NH$_2$OH. We then add 100 µL of the Au@mSiO$_2$ nanorods after ligand removal at an optical density of $\sim$0.35 and consecutively measure absorption spectra for 2 hours. The absorption of resazurin is characterized by a peak at 602 nm (Figure S2a) and the absorption of resorufin by a peak at 572 nm (Figure 1c of the main text). As can be seen in Figure S2b, the Au@mSiO$_2$ nanorods show no catalytic activity in the dark.

![Figure S2](image_url)  
Figure S2: (a) 172 consecutive absorption spectra of 100 µL Au@mSiO$_2$ nanorods added to 1 mL 50 mM pH 7.3 potassium phosphate buffer with 10 µM resazurin and 20 mM NH$_2$OH. (b) Extinction peaks of resazurin at 602 nm (black) and resorufin at 572 nm (blue) as a function of time.
3 Localization of the catalysts in the microscope

The catalysts are localized using a transmitted white light image (Figure S3a). This image is inverted (Figure S3b), so that the catalysts appear as local maxima instead of local minima. Each local maximum is then fitted to a two-dimensional Gaussian using ThunderSTORM, see also Figures 1e,f of the main text. The localization precision $\sigma_{\text{loc}}$ is calculated using

$$
\sigma_{\text{loc}}^2 = \frac{\sigma_{\text{PSF}}^2 + a^2/12}{N} + \frac{8\pi\sigma_{\text{PSF}}^4 b^2}{a^2 N^2},
$$

where $\sigma_{\text{PSF}}$ is the standard deviation of the fitted Gaussian, $a$ is the effective pixel size (129 nm), $N$ is the number of detected photons, and $b$ is the standard deviation in the residuals between the experimental emission profile and the fit. This calculation results in an average estimated localization precision of $\sim 6$ nm (Figure S3c).

Figure S3: (a,b) Transmitted white light image of the catalysts before (a) and after (b) color inversion. The image displayed here is cropped from the total field-of-view of $133 \times 133 \mu m^2$. (c) Histogram (485 particles) of the estimated localization precision of the catalyst positions, calculated using ThunderSTORM.\textsuperscript{4}
4 Illustration of the optical setup

Figure S4: Illustration of the optical setup.
5 Localization precision of the resorufin molecules

Figure S5: Histogram ($\sim6\times10^6$ events) of the estimated localization precision of the molecule positions, calculated using ThunderSTORM.$^4$
6  The observed power dependencies do not strongly depend on the distance threshold

In our analysis of the dependence of the turnover rate on the laser power (Figure 2 of the main text) we only consider events detected within 100 nm of the catalysts. The observed dependencies do not significantly change for thresholds ranging from 50 nm to 500 nm, as indicated by the relatively constant value of the fitted power law exponent $b$ (Figure S6).

Figure S6: Turnover rate as a function of laser power in the absence of NH$_2$OH for different values of the distance threshold $R$. Solid lines are a fit to $y = ax^b$, where $y$ is the turnover rate, $x$ is the laser power, and $a$ and $b$ are fitting parameters.
7 The observed power dependencies are not due to a change in product detectability

As the 532 nm laser also excites the reactions products, changing its power density could result in a change in the product detectability. When fitting the experimental data we fit all local maxima in all frames, i.e. we do not preselect regions of interest at the catalyst locations. By using this procedure we detect reaction products at the catalyst positions, but we also detect fluorescent impurities or reaction products that readsorb on the coverslip (Figure S7, top). Since we know the catalyst positions from the transmitted light image (Figure S3), we can filter out these impurities by only considering events detected within 100 nm of a catalyst (Figure S7, middle). Conversely, we can filter out detections on the catalysts and only consider fluorescent impurities (Figure S7, bottom). We find that the number of detected impurities per frame does not change within the range of laser powers that we use and that, therefore, the product detectability remains unaltered.
Figure S7: (top) Total number of detections per frame in the experiment without NH$_2$OH reported in Figure 2 of the main text. (middle) Number of detections within 100 nm of a catalyst. (bottom) Difference between the total number of detections and the detections within 100 nm of a catalyst.
8 NH$_2$OH does not influence the reaction kinetics

In this experiment we flow in 200 nM resazurin together with a certain concentration of NH$_2$OH in a 50 mM pH 7.3 potassium phosphate buffer over a sample of Au@mSiO$_2$ nanorods. We acquire 10,000 frames (~20 minutes) for every concentration. When switching between reactants, we allow the system to settle for at least 15 minutes before acquiring the next 10,000 frames.

As can be seen in Figure S8, the turnover rate does not vary with NH$_2$OH concentration.

![Figure S8](image.png)

Figure S8: Mean turnover rate (averaged over 369 particles) as a function of NH$_2$OH concentration. Error bars are standard deviations.
9 Independently exciting the LSPR of the Au@mSiO$_2$ nanorods does not alter the reaction kinetics

In this experiment we flow in 200 nM resazurin together with a certain concentration of NH$_2$OH in a 50 mM pH 7.3 potassium phosphate buffer over a sample of Au@mSiO$_2$ nanorods. We acquire 20,000 frames (≈40 minutes) for every concentration. During the first 10,000 frames we only use a 532 nm CW laser to excite the resorufin molecules and the transverse LSPR of the nanorods. During the second 10,000 frames, we also use a 730 nm CW laser to excite the longitudinal LSPR of the Au@mSiO$_2$ nanorods. The 730 nm CW laser only excites the LSPR and does not excite the resazurin molecules (Figure S9a). When switching between reactants, we allow the system to settle for at least 15 minutes before acquiring the next 20,000 frames.

According to previous density functional theory calculations, the energy gap between the Fermi level of Au and the lowest unoccupied molecular orbital of resazurin is smaller than 1 eV, so a non-equilibrium electron excited in Au under 730 nm (1.7 eV) irradiation should have enough energy to occupy this energy level and reduce resazurin. However, for any NH$_2$OH concentration, the 730 nm CW laser does not change the kinetics of the reaction (Figure S9b). Therefore, this experiment is further evidence that in our system no electron transfer takes place between Au and resazurin.
Figure S9: (a) Resazurin absorption (black) and Au@mSiO$_2$ nanorod extinction (blue). The 730 nm laser (black vertical line) only excites the nanorods and not the resazurin. (b) Mean turnover rate (averaged over 369 particles) for different NH$_2$OH concentration with the 730 nm laser turned off (black circles) or on (green triangles). The power density for the 730 nm laser is 2.0 \times 10^6 \text{ W m}^{-2}. Error bars are standard deviations.
10 Photothermal contributions are negligible

The temperature increase $\Delta T_{\text{local}}$ on a single nanorod can be calculated using

$$\Delta T_{\text{local}} = \frac{\sigma_{\text{abs}} I}{4\pi\beta \bar{\kappa} R_{\text{eq}}},$$

(2)

where $\sigma_{\text{abs}}$ is the absorption cross section of a single nanorod ($2 \cdot 10^{-14} \text{ m}^2$), $I$ is the illumination intensity ($1.3 \cdot 10^7 \text{ W m}^{-2}$), $\beta$ is the thermal capacitance coefficient of a nanorod, $\bar{\kappa}$ is the average thermal conductivity of the surrounding medium, and $R_{\text{eq}}$ is the radius of a sphere with a volume equal to the volume of the nanorod (38 nm). The thermal capacitance coefficient $\beta$ is defined as

$$\beta = 1 + 0.96587 \ln \left( \frac{l}{w} \right),$$

(3)

where $l$ and $w$ are the length and width of the nanorod. With $l = 118$ nm and $w = 54$ nm, this equation gives $\beta = 1.59$. The average thermal conductivity of the surrounding medium $\bar{\kappa}$ can, in first approximation, be defined as

$$\bar{\kappa} = \frac{\kappa + \kappa_s}{2},$$

(4)

where $\kappa$ is the thermal conductivity of the medium (0.6 W m$^{-1}$ K$^{-1}$ for water) and $\kappa_s$ is the thermal conductivity of the substrate (1.38 W m$^{-1}$ K$^{-1}$ for glass). These parameters result in a local temperature increase $\Delta T_{\text{local}} \approx 35$ mK.

However, the simultaneous illumination of many nanoparticles can lead to macroscopic collective heating effects, which can be orders of magnitude larger than the local temperature increase. If we approximate our drop casted catalysts as a periodically spaced infinite array illuminated by a Gaussian beam, the collective temperature increase $\Delta T$ due to photon absorption can be calculated using

$$\Delta T = \frac{\sigma_{\text{abs}} P}{\bar{\kappa}} \sqrt{\frac{\ln 2}{4\pi}} \frac{1}{HA} \left( 1 - 4\sqrt{\ln[2]A} \right),$$

(5)
where $P$ is the power of the illumination (100 mW), $H$ is the full width at half maximum of the Gaussian beam (100 µm), and $A$ is the unit cell area of the lattice.

In our samples the interparticle spacing is typically $> 2$ µm, and on average $\sim 6$ µm. For example, in Figure S3, an area of $\sim 100$ µm$^2$ contains 17 particles, with an average interparticle spacing of $\sqrt{100/17} = 2.4$ µm. As we are approximating our dropcasted catalysts as a periodically spaced infinite array, this interparticle spacing yields a unit cell area $A > 4$ µm$^2$. The estimated temperature increase, $\Delta T$, for these interparticle spacings is $\sim 1 - 2$ K, see Figure S10.

According to the Arrhenius equation, the rate constant $k(T)$ of a chemical reaction increases exponentially with temperature:

$$k \propto \exp\left[-\frac{E_a}{k_B T}\right],$$  
(6)

where $E_a$ is the reaction activation energy and $k_B$ is the Boltzmann constant. Assuming an initial temperature of 300 K and an activation energy of 38.2 kJ mol$^{-1}$, a 2 K increase would then give a rate enhancement

$$\frac{k(302)}{k(300)} = 1.1.$$  
(7)

In our experiments we are varying the laser power and the interparticle spacing can locally be higher than 2 µm, so a rate enhancement of 1.1 is an upper limit. Therefore, photothermal effects cannot explain the large variations (up to 5-fold) in turnover rate observed in Figure 2 of the main text.
Figure S10: Temperature increase $\Delta T$ as a function of the unit cell area $A$. 
11 FDTD spectra at normal incidence and electric fields monitored at the nanorod center

Figure S11a shows the absorption and scattering spectra obtained in FDTD simulations with the source impinging at normal incidence. By summing these spectra, we obtain a simulated extinction cross section that matches well with the experimentally measured nanorod extinction (Figure S11b). Figures S11c,d show the electric field enhancement at the nanorod center for a source angle of 70°. These enhancements are lower than those observed at the bottom of the nanorod (Figure 3 of the main text).

Figure S11: (a) Absorption and scattering cross sections when the nanorod is p-oriented (black and dark grey, respectively) or s-oriented (dark green and light green, respectively). The source angle $\phi$ is $0^\circ$. (b) Comparison between the experimental bulk extinction spectrum (green) and the simulated extinction spectrum (black). (c,d) Electric field intensity $|E|^2$ normalized to the incident field intensity $|E_0|^2$ at 532 nm, monitored at the center of the nanorod. The nanorod is p-oriented (c) or s-oriented (d). The source angle $\phi$ is $70^\circ$. 
12 Fitting function and $\theta_0$ histogram

We fit the angular distribution of catalytic events to

\[
A_0 + A_1 \exp\left[-\frac{(\theta - \theta_0)^2}{0.9}\right] + A_2 \exp\left[-\frac{(\theta - \theta_0 - \pi)^2}{0.9}\right] \\
+ A_2 \exp\left[-\frac{(\theta - \theta_0 - 2\pi)^2}{0.9}\right] + A_2 \exp\left[-\frac{(\theta - \theta_0 + \pi)^2}{0.9}\right],
\]

where $A_0$ is a vertical offset, $A_1$ and $A_2$ are the peak amplitudes, $\theta$ is the angle as defined in Figure 4a of the main text, and $\theta_0$ ($0 < \theta_0 < \pi$) is the orientation of the particle. The peak with amplitude $A_2$ appears several times to ensure continuity at $\theta = 0$ and $\theta = 2\pi$ for all values of $\theta_0$. We pick 0.9 as the peak width, as this results in a width similar to that of a $\cos^2$ function, see Figure S12a. We can exclude systematic errors in detecting the catalyst positions, as this would result in an uneven distribution of $\theta_0$ values, which is not what we observe, see Figure S12b.

![Figure S12: (a) $\cos^2 \theta$ (black) compared to the fitting function for the angular distributions (blue). The parameters for the fitting function are $A_0 = 0$, $A_1 = 1$, $A_2 = 1$, $\theta_0 = 0$. (b) Histogram of the obtained values for $\theta_0$. The bin size is set to $\pi/19$.](image)
13 Single particle catalysis maps and angular distributions

In Figures 4a-c of the main text we showed how we extract the particle orientation from the two-dimensional super-resolution catalysis map. Further examples are shown below in Figure S13.

Figure S13: Further examples of single particle catalysis maps (a,c,e,g,i,k,m) and the corresponding angular distributions (b,d,f,h,j,l,n). Panels (a,c,e,g,i,k,m) contain a white outline depicting an Au@mSiO$_2$ nanorod. The orientation $\theta_0$ is extracted from the fits in panels (b,d,f,h,j,l,n). Bin sizes are 30 $\times$ 30 nm$^2$ (a,c,e,g,i,k,m) and $\pi$/10 (b,d,f,h,j,l,n).
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