Plasma-Mediated Nanocavitation and Photothermal Effects in Ultrafast Laser Irradiation of Gold Nanorods in Water

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Supporting Information

ABSTRACT: We present a theoretical and experimental study that reveals the physical mechanism underlying the response of an in-resonance gold nanorod (AuNR) in water to a near-infrared ultrafast laser pulse. Results reveal the presence of two different regimes of interaction, depending on the irradiation fluence. For fluences below 3 mJ/cm², AuNRs are in the so-called absorption regime and are shown to strongly absorb energy, leading to a fast temperature increase revealed by the onset of characteristic mechanical vibration of the structure. In situ measurement demonstrates a permanent deformation of the AuNRs occurring for fluences over 100 μJ/cm². In the absorption regime, we show the formation of a nanoscale plasma around the structure, dominated by a photothermal emission from the AuNR, and the generation of a pressure wave. However, no cavitation occurs under the deformation threshold fluence (100 μJ/cm²). For fluences over 3 mJ/cm², in the near-field regime, the energy transfer is dominated by the enhanced near-field around the particle that directly ionizes and heats a nanoplasma in the surrounding water. We theoretically show that bubbles with diameters ≈ 490 nm can be generated in this near-field regime for an incident fluence of 200 mJ/cm². In situ optical characterization of the produced bubbles supports this result and shows that bubbles with diameters ≈ 200–600 nm can be generated for fluences ranging 100–400 mJ/cm². Important shielding of the laser–nanostructure interaction by the surrounding plasma is shown to decrease considerably the near-field enhancement, the energy absorption, and the diameter of the generated bubbles and may explain the smaller bubbles generated around in-resonance 10 × 41 nm² AuNRs when compared to off-resonance 25 × 60 nm² AuNRs and 100 nm AuNPs.

INTRODUCTION

Gold nanoparticles (AuNPs) interacting with laser beams have been extensively used in the past few years in biological media as nanoeffectors,¹−¹⁰ imaging contrast agents,⁵,⁸,¹¹−¹⁴ biosensors,¹⁵ drug delivery vectors,¹⁶,¹⁷ and vapor bubble generators¹⁸−²⁰ for photothermal imaging,²¹−²⁴ photothermolysis,²⁴−²⁷ or gene therapy applications.²⁸−³⁰ The principal characteristic that makes gold NPs so interesting is the possibility to induce a so-called plasmonic resonance in the metal when interacting with an electromagnetic field at a particular wavelength, depending on the size, environment, and structure of the NPs. This phenomenon, first described by the celebrated Mie theory,³¹ consists of the excitation of a collective oscillation of the conducting electrons in the nanostructure, resulting in unusually strong absorption and scattering properties when compared to other nonplasmonic micro and nano absorbers.³² For spherical gold NPs in water, this resonance occurs for an incident irradiation wavelength near 540 nm, with a weak dependence on the particle dimensions. For biological applications, it is usually advantageous to work in the optical window of biological material (600–1100 nm)³³ to avoid issues concerning collateral damage to tissues during treatment or to enhance the effective depth. Since gold NPs resonance lies outside this window, gold nanorods (AuNRs)³²,³⁴−³⁸ and core−shell³²,³⁹−⁴¹ have been proposed as alternative structures having resonance in the near-infrared portion of the electromagnetic spectrum. Optical properties of AuNRs have been extensively studied³²,³⁴ and the apparition of a second plasmon resonance peak in the near-infrared region has been associated with an electron oscillation along the long axis of the NR. The wavelength at which this resonance occurs has in addition been shown to be highly dependent on the length over diameter ratio, making these nanostructures particularly interesting for applications.

Ultrashort pulse laser irradiation of AuNRs, depending on the fluence, are used for in vitro and in vivo imaging,³⁶,³⁷,⁴²−⁴⁴ hyperthermia therapy,⁴⁶ and targeted thermolysis,³⁶,³⁷,⁴⁶ the latter being intimately associated with the formation of vapor bubbles in the cellular environment.²⁵,²⁸,³⁰

In this work, we investigate the response of in-resonance AuNRs in water after being irradiated with near-infrared (NIR) ultrashort pulses as a function of the irradiation fluence. Experimentally supported theoretical results reveal the presence of two distinct regimes of interaction. We show that for...
fluences lower than 3 mJ/cm², the energy absorbed in the AuNRs dominates the energy absorbed in the near-field. The action of the AuNRs on its environment is then limited to thermal effect and to the generation of a nanoscale plasma around the structure due mainly to photothermal emission. We call this regime the absorption regime. In situ spectroscopic measurement allows identification of a damage fluence threshold beyond which the plasmonic properties of the AuNRs are degraded, defining a fluence process window suitable for applications. At higher fluences, results reveal that the near-field enhanced laser irradiation creates and excites a nanoscale plasma directly in the water around the structure. We call this regime the near-field regime. At sufficient fluences, this plasma is shown to trigger a series of events leading to the formation of vapor bubbles in the surrounding medium. Shielding of the laser–plasmon interaction by this plasma will also be shown to alter considerably the AuNRs’ response to the ultrafast laser irradiation.

**EXPERIMENTAL AND THEORETICAL METHODS**

**Modeling the Ultrafast Laser Interaction with AuNRs.** We developed a complete model that includes the different phenomena that occur following the irradiation by an ultrafast laser of a resonant AuNR in water. Those phenomena are presented in Figure 1. Models previously proposed in the literature 46,47 usually neglect plasma formation in the surrounding medium. However, this plasma, which is generated through a combination of direct photoionization by the enhanced near-field and temperature-assisted photothermal emission from the surface of the nanostructure, turns out to have important effects, especially at high fluences. In particular, the presence of the plasma in the AuNR environment modifies the local permittivity, and consequently has an important impact on the optical properties of the AuNR and the enhanced near-field. The field distribution around the AuNR is calculated from the Helmholtz equation, considering the bulk gold optical properties and the locally modified water permittivity. From the field distribution, the electronic and lattice temperatures are calculated using the bulk gold optical properties and the locally modified water permittivity. From the field distribution, the electronic and lattice temperatures are calculated using a two-temperature hyperbolic model based on the semiclassical Boltzmann transport equation.48 The density and energy time-dependent distributions of the plasma generated in the enhanced near-field are calculated using transport equations. A Navier–Stokes equation system added to a heat transfer equation and supported with an adequate equation of state is used to calculate the thermodynamic state of the water at all times. A combination of the IAPWS95 49 and SESAME 50 equations of state ensures a sufficient validity range.

The phase change of the water is handled using the phase diagram defined by the equation of state. Under the saturation curve, liquid water is in a metastable state until it reaches the kinetic spinodal that represents the limit of mechanical stability where phase explosion occurs.51,52 Beyond that limit, water pressure returns to the saturation pressure and all other parameters return to their phase equilibrium value as water undergoes a phase transformation to a homogeneous liquid–vapor mixture at equilibrium. Surface tension is applied at the interface of the bubble, fixed at a vapor dryness fraction of 10%. This method has the inconvenient drawback of inducing the formation of a smooth water/vapor transition instead of a sharp interface. It has however been proven to adequately capture the pressure and density evolution in water.53 A finite-element scheme is used to solve the system of tightly coupled differential equations. Extensive discussion on the modeling, including equations and details on the parameters used, is presented in section 1 in the Supporting Information as well as in another related publication.18 The mathematical model was solved using a finite-element method, using the Comsol software (www.comsol.com).

**Deformation Threshold Fluence (DTF) Measurement.** The deformation of AuNRs has been induced using a Ti-Sapphire, 6 mJ/pulse, 45 fs, 800 nm laser (Spitfire from Spectra-Physics) with a 1 kHz repetition rate. A 1 × 1 cm² four-face-polished cuvette containing 2 mL of AuNRs with a concentration of 45 μg/mL in a water suspension has been irradiated for 12 h with different fluences. The Gaussian beam spot diameter (measured at 1/e²) was 0.9 cm. The maximum fluence at the center of this Gaussian spot (twice the average fluence) has been considered. Extinction spectra have been recorded every minute perpendicularly to the femtosecond laser beam using a StellarNet EPP2000 spectrometer from SpectraWiz.

**Pump–probe Measurements of AuNRs Vibration.** The 1 kHz, 45 fs, 800 nm laser beam has been separated in two beams (pump and probe) using a beamsplitter for ultrashort pulses. Pump beam maximal fluence was set to 100 μJ/cm² at the center of the 0.9 cm (1/e²) diameter Gaussian beam. Probe beam fluence was 0.2 μJ/cm² with a 0.1 cm diameter. The much lower probe fluence ensures the pump beam dominance on excitation. Both beams were quasi-collinearly aligned (1.3° between beams) and probe beam was centered to the pump beam at the front end of the cuvette containing the AuNRs solution. Both polarizations were horizontal. Probe delay was set using two mirrors installed on an I-M5600PP linear stage from Newport with a 1.25 μm resolution. The setup time resolution was limited to 500 fs due to the angle between the probe and pump beams. Beams were separated geometrically using this angle. Probe beam has been detected using a DET100 photodiode connected to a SR510 lock-in amplifier from Stanford Research Systems.

**Cavitation Bubble Detection.** A He:Ne, continuous wave, 5 mW, 633 nm probe beam has been collinearly aligned with the femtosecond laser. Both beams were focused into the AuNRs sample. The femtosecond pump laser repetition rate is set at 4 Hz for this experiment and a typical acquisition last
Results and Discussion

Optical Properties of AuNRs. In this work, we focus on the interaction between a 45 fs 800 nm ultrafast laser with a 10 nm × 41 nm AuNRs colloidal suspension. Figure 2a shows the calculated absorption, scattering, and extinction cross sections for randomly distributed AuNRs in water as a function of the incident wavelength. Peaks associated with the longitudinal plasmon band (LP) and the transverse plasmon band (TP) are indicated. (b) Cross section of the electric field enhancement distribution in and around a AuNR, showing both field absorption in the particle and near-field enhancement near the tips, when irradiated with 800 nm linearly polarized along the rod’s longitudinal axis. (c) Cross section of the electric field enhancement distribution in and around a AuNR, showing almost no field absorption in the particle and weak near-field enhancement, when irradiated with 800 nm linearly polarized perpendicular to a rod’s longitudinal axis.

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Figure 2. Optical properties of 10 nm × 41 nm AuNRs. (a) Calculated absorption, scattering, and extinction cross sections for randomly distributed AuNRs in water as a function of the incident wavelength. Peaks associated with the longitudinal plasmon band (LP) and the transverse plasmon band (TP) are indicated. (b) Cross section of the electric field enhancement distribution in and around a AuNR, showing both field absorption in the particle and near-field enhancement near the tips, when irradiated with 800 nm linearly polarized along the rod’s longitudinal axis. (c) Cross section of the electric field enhancement distribution in and around a AuNR, showing almost no field absorption in the particle and weak near-field enhancement, when irradiated with 800 nm linearly polarized perpendicular to a rod’s longitudinal axis.

The low pump laser repetition rate avoids accumulation effects and is equivalent to using multiple single-shot experiments. Note that the cw probe irradiation was insufficient to induce significant heating in the sample. The waists of both beam (fs pump and cw probe) were set to (6 ± 1 μm). The probe beam scattered field was filtered out using a spatial filter (15 μm diameter pinhole). Extinction cross section change was thus detected. This detection was made with a Si 1 MHz Agilent oscilloscope.

Existence of Two Regimes of Irradiation. The last section concerned only the linear optical properties of the AuNR that are insufficient to completely describe the physics of the interaction with an ultrafast laser. Indeed, while at low fluences the absorption cross sections calculated from the linear theory are fairly accurate, the energy absorbed directly in the water by nonlinear interaction in the near-field at higher fluences justifies the need for a more complete nonlinear theory.

Using the model presented in the Theoretical Methods and detailed elsewhere,18 we calculated the total energy deposited in the system by a 45 fs 800 nm ultrafast laser pulse linearly polarized along the AuNR’s longitudinal axis as a function of laser fluence. Figure 3 shows separately the energy absorbed in the AuNR (blue line) and in the plasma around the AuNR (green line) for a 10 nm × 41 nm AuNR aligned with the polarization of a 800 nm 45 fs laser pulse. The frontier between the absorption regime and the near-field regime is also indicated on the figure (dashed red line).

The blue line in Figure 3 represents the absorption cross section of the AuNR itself (σ_{abs}^{AuNR}), which in the limit of low fluences is precisely the linear absorption cross section. Note that the apparent discrepancy with the results shown in Figure 3 is precisely the linear absorption cross section.
2a comes from the fact that those results included random contribution from misaligned AuNRs, whereas results presented in Figure 3 only consider aligned AuNRs.

In Figure 3, the green line is the nonlinear absorption cross section arising from the contribution of the plasma electron (σ_{abs}^{plas}) created in the near-field around the AuNR. As the fluence is increased, contribution from σ_{abs}^{plas} becomes more and more important, while σ_{abs}^{AuNR} decreases due to what we will show to be shielding from the plasma. For fluences F > F_{th} = 3 mJ/cm^2, contribution from the plasma exceeds the absorption in the AuNR. This value is in agreement with a recent study from Bisker et al. that calculated a fluence around 2 mJ/cm^2 as the threshold for optical breakdown in the water surrounding a 14 × 56 nm^2 AuNR irradiated with a 45 fs, 808 nm laser pulse. F_{th} represents the limit between two distinct regimes of irradiation. For fluences F < F_{th} = 3 mJ/cm^2, the laser interaction is dominated by the energy absorption within the AuNR itself. This regime is thus called "the absorption regime". For fluences over F_{th}, the laser interaction is dominated by the energy absorbed by the plasma in the near-field. This regime is hence called "the near-field regime". The next sections are devoted to the exploration of the basic mechanisms of the ultrafast laser irradiation of AuNRs in both regimes.

**Absorption Regime. Deformation of the AuNRs.** As mentioned in the last section, the absorption regime is characterized by an energy absorption occurring in a majority in the AuNR itself, the enhanced near-field being too weak to induce important nonlinear energy absorption in water. According to Figure 3, absorption in the near-field overcomes energy absorption in the particle for fluences larger than F_{th} = 3 mJ/cm^2, giving a superior limit to the absorption regime. However, energy absorption in the AuNRs leads to a temperature increase in the lattice that may lead to deformations that can alter their plasmonic properties. We define the deformation threshold fluence (DTF) as the fluence from which the AuNRs’ optical properties, monitored in real-time with a spectrometer (see Figure 4a), are significantly degraded after a 12 h irradiation at 1 kHz. This long irradiation time ensures reaching homogeneity in the sample. As seen from Figure 4b, a blue shift of the extinction peak is visible when the laser fluence reaches ≈ 100 μJ/cm^2. This blue shift arises most probably from the gradual transformation of the resonant AuNRs into small off-resonance spherical NPs, for which the extinction cross section is much smaller than for the AuNRs at 800 nm. The peak blue shift thus allows measurement of DTF around 100 μJ/cm^2. Note that the exact value of the DTF remains quite arbitrary and is a function of the tolerance requirement regarding a specific application. For the vast majority of applications involving low fluence irradiation, it is very desirable that the AuNRs remain intact after the laser irradiation. In what follows, we will thus only consider fluences that lie around or below the DTF (100 μJ/cm^2) and explore in greater depth the laser–nanostructure interaction in what one could call the “subdeformation threshold absorption regime” that is suitable for most applications.

**AuNR Heating.** The absorption regime at fluences below the deformation threshold is characterized by a limited impact on both the AuNRs and their surrounding medium, though some effects are still present. In this regime, the laser electromagnetic field is mainly absorbed by the nanostructure, as shown by the clear predominance of the absorption cross section over the scattering cross section at 800 nm (see Figure 2a). Electrons transfer their energy to the lattice in a few ps (τ_{e-ph} ≈ 1 ps),

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**Figure 4.** Deformation threshold fluence (DTF) for 10 nm × 41 nm AuNRs. (a) Optical setup used to measure the DTF. A 45 fs, 1 kHz, 800 nm laser irradiates a AuNR sample for 12 h. The AuNR optical spectrum is monitored in real-time during the irradiation. (b) Blue shift of the position of the extinction peak of the AuNRs sample as a function of the pump laser fluence. Comparison of the shape of the peak before and after irradiation at a fluence of 500 μJ/cm^2 is shown in inset.

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... and continues with the description of the experiments and results related to AuNR heating and deformation.
second pulse is much lower in intensity and is called the probe pulse. This pulse first passes through an adjustable delay line before being directed to the sample, so that it arrives with a certain tunable time delay relative to the pump pulse. The transmission of the probe pulse is then measured, providing information on the state of the AuNR at the specific time corresponding to the time delay. Varying this delay, one can obtain a complete time-dependent characterization of the laser interaction.

Figure 5b shows the oscillation in the transmission of the probe beam as a function of the delay with the pump pulse. The measured period (63 ps) is in good agreement with the 64 ps period predicted by the thin rod theory. The damping of the oscillation results from the combination of viscous stress between the rod and its environment, called homogeneous damping, and an inhomogeneous damping due to the rods’ size distribution within the sample. Based on TEM imaging of the sample and a simple model linking the rod’s size distribution to a specific oscillation period and damping (see Figure 1 in the Supporting Information (SI)), the red curve in Figure 5b presents the simulated variation in the extinction due to the oscillations. The very good agreement indicates that the signal indeed originates from the AuNRs’ structural oscillations.

Figure 6 shows the simulation results for the temperature reached at the center of the AuNR as a function of the incident fluence. Figure 6 also indicates the theoretical melting temperature for 10 nm × 41 nm AuNRs (1254 K), about 10% lower than the bulk melting point because of the reduced dimensionality (SI). Results show that this temperature is reached for a fluence slightly over 120 μJ/cm², in good agreement with the experimental DTF of 100 μJ/cm². A deformation threshold somewhat below the melting threshold, as reported by Link et al., seems indeed reasonable, as high surface energy may lead to important restructuration before complete melting occurs. Link et al. experimentally determined that ~60 fJ was required to melt 11 nm × 41 nm AuNR completely and observed shape transformation after the absorption of ~12 fJ. This is consistent with our result as ~6 fJ per pulse is deposited in the AuNR at 1 kHz at the DTF. Figure 6 also presents the temperature reached in the water at the boundary with the AuNR. This result will be discussed in the section Pressure Wave Generation and Bubble Formation.

**Plasma Formation.** In addition to heat generation in the AuNR, irradiation also triggers the generation of an electronic nanoscale plasma around the structure. This nanoplasma comes from the direct photoionization and collision ionization in the near-field, as well as from a photothermal emission at the metal/water interface. Figure 7a shows simulation results of the plasma generated around the structure 100 fs after a 100 μJ/cm² irradiation. Maximal plasma density occurs in the central region of the AuNR. This is a consequence of the photothermal emission process being dominant over the photoionization process at low fluences. This reflects the huge energy absorption cross section compared to the energy scattering cross section at 800 nm. Maximal plasma density thus occurs near the place where the energy is absorbed the most, heating up electrons in the AuNR and favoring thermal emission into the surrounding water.

Electronic plasma is known to contribute to damaging cells through chemical interactions. Plasma density as low as 1.5 × 10¹⁴ cm⁻³ has been reported to induce cell damage, and density of 2 × 10¹⁶ cm⁻³, to be able to disintegrate cellular organites. AuNRs irradiated in the absorption regime may thus be used as generators of nanoplasma that can be used to locally interact with cellular components in the context of nanosurgery. As shown in Figure 7b, maximal density reached in the vicinity of the AuNR gets over those reference plasma densities for irradiation fluences greater than 1 μJ/cm². Once created, plasma diffuses and can affect a certain volume around the structure. Figure 7c shows the radius of the zone affected by the above-mentioned reference plasma densities as a function of the laser fluence. As seen from this figure, this volume can be finely tuned by changing the laser fluence, leading to the possibility of highly localized processes.

Though the presence of this plasma is desirable for certain applications, it can become rather a problem for others. For
instance, the use of AuNRs as imaging contrast agents or biodetectors requires a minimal impact of the laser irradiation on the surrounding cell environment. However, as seen from Figure 7c, the radius of the affected zone can get quite significant depending on the fluence. For instance, at 100 μJ/cm² a density of 2 × 10^15 cm⁻³ is reached up to 165 nm from the AuNR, and a density of 1.5 × 10^14 cm⁻³, as far as 1.0 μm. The possibility of chemical damage brought by the photothermal emission should thus be taken into consideration and limit the range of suitable fluences when planning to use AuNRs in such applications.

**Pressure Wave Generation and Bubble Formation.** A combination of heat transfer from the plasma relaxation and from the AuNR lattice through a conduction process causes a fast temperature increase in the water medium in ~50 ps. At those fluences, the heat transfer from the conduction process is largely dominant over the plasma-mediated heat transfer. Stress confinement is created, releasing a pressure wave upon its relaxation. Figure 8a shows the pressure around the AuNR 10 ps after a 100 μJ/cm² irradiation. The maximal pressure (~8 MPa) is located near the central part of the AuNR. As shown in Figure 8b, the maximal pressure observed in the water range ~2–14 MPa for irradiation fluences between 10 μJ/cm² and 120 μJ/cm².

The onset of cavitation is often evaluated as the fluence required to heat the surrounding water above the 0.9Tc = 582 K limit, indicated by a red line in Figure 6. From this crude approximation, the theoretical cavitation onset should be slightly over 120 μJ/cm² as temperature at this fluence only reaches ~0.88Tc. The complete hydrodynamic model confirms this prediction and does not show the formation of a vapor bubble around the AuNR at 120 μJ/cm². This result is consistent with the one obtained by Ekici et al., who theoretically determined a somewhat higher 450 μJ/cm² cavitation fluence threshold for 14 × 48 nm NNRs irradiated with a 250 fs, 760 nm pulse. Their model however did not consider any plasma generation. Our results thus demonstrate that, though 10 nm × 41 nm AuNRs are in-resonance with the irradiation and thus highly enhance the near-field, it is not possible to generate cavitation bubbles around them without damaging, deforming, or even destroying them. This represents a major drawback of the use of AuNRs for the generation of vapor bubbles since it prohibits any multipulse operation. In addition, destruction of the AuNRs could lead to the creation of small particles that can be harmful to the cellular environment.

**The near-Field Regime.** For fluences larger than 3 mJ/cm², Figure 3 shows that the laser intensity in the near-field become important enough to trigger a nonlinear absorption directly in the surrounding water that overcomes the absorption in the nanostructure. The energy absorption process is then controlled by the enhanced electric field in the near-field of the nanostructure, hence justifying the name “near-field regime”. Irradiation of AuNRs in that regime is principally motivated by the possibility to create nanoscale vapor bubbles around the structures.

**Plasma Mediated Nanocavitation.** In order to get a better understanding of the physical mechanism leading to bubble formation after an irradiation of the AuNRs in the near-field regime, we simulated the interaction of a 10 nm × 41 nm AuNR aligned with the polarization of a 200 mJ/cm² laser pulse. The simulation has been conducted using the complete model presented in the Theoretical Methods and detailed in section 1 in the SI.

Figure 9 shows the plasma distribution around the nanostructure 100 fs after irradiation, as well as the time evolution of its maximal density. Results show that, unlike in the absorption regime, plasma is principally formed near the tips of the AuNR. Indeed, enhanced near-field is now important enough to allow the formation of a plasma directly in water by photoionization and impact ionization. This result was expected from previous simulations made by Vogel et al., where the laser intensity corresponding to the optical breakdown threshold for the interaction of ultrafast laser with water was calculated. For a 45 fs laser pulse, they found a threshold intensity below 10^13 W/cm², a value more than 1000 lower than the local intensity reached near the tip of the AuNR irradiated with a 200 mJ/cm² laser pulse (~2.6 × 10^16 W/cm², considering the ~77 near-field enhancement). The creation of a plasma around the AuNR at this fluence is in consequence not surprising. Similar results have been found in the case of ultrafast irradiation of off-resonance AuNRs.

Heat transferred from this plasma rapidly increases the water temperature, creating stress confinement that relaxes, emitting a strong pressure wave that originates from the tips of the AuNRs, where the plasma density is the highest (see Figure 10a). This contrasts with the result obtained in the absorption regime where the maximal pressure was rather near the center of the AuNR, due to the localization of the photothermal emission and energy absorption in this range of fluence (see Figure 8a). As shown in Figure 10b, the magnitude of the
The pressure wave is around 180 GPa, almost $10^4$ times higher than those emitted in the absorption regime, below the DTF.

Following the emission of the pressure wave, a vapor bubble is formed around the structure. Figure 10c shows the time evolution of the diameter of this bubble. Simulation shows the formation of a $\sim 490$ nm diameter bubble with a 20 ns growth time and a 45 ns total lifetime. The bubble at its maximal extension is shown in 10 d. The very fast initial growth of the bubble seen in Figure 10c is a consequence of the large pressure under which the bubble is created, due to the ultrafast nature of the laser irradiation. Very fast quasi-isochoric heat transfer from the heated plasma to the water molecules indeed heats the water to a high temperature and pressure state. The very high pressure in the initial stage of the bubble growth leads to a very fast expansion in the first nanoseconds after the bubble nucleation, as shown in Figure 10c.

**Experimental Detection and Characterization of the Vapor Bubbles.** Bubble dynamics have been extensively studied in the past and numerous detection and characterization methods have been developed. Although nanoscale bubbles cannot be readily measured and characterized using direct microscopy technique, it has been shown that it can be detected using an in situ optical detection setup described in Figure 11a. This setup exploits the variation in the extinction cross section of the irradiated sample due to the presence of the vapor bubble around the AuNRs to evaluate their dimensions. A first laser, the ultrafast pump laser (45 fs, 4 Hz, 800 nm, 100 s acquisition time), is focused in a sample (1 cm wide cuvette) containing the AuNR suspension. At such large fluences, rods are expected to be heavily damaged by the ultrafast laser pulse. The slow 4 Hz repetition rate however allows adequate mixing of the AuNR suspension between each pulse, ensuring that only undamaged AuNRs interact with each pump laser pulse. The experiment is thus perfectly equivalent to many, uncorrelated, single-pulse experiments. A second laser, the probe laser (cw, 633 nm, 5 mW), is collinear with the pump laser and its evolution of the diameter of this bubble. Simulation shows the formation of a $\sim 490$ nm diameter bubble with a 20 ns growth time and a 45 ns total lifetime. The bubble at its maximal extension is shown in 10 d. The very fast initial growth of the bubble seen in Figure 10c is a consequence of the large pressure under which the bubble is created, due to the ultrafast nature of the laser irradiation. Very fast quasi-isochoric heat transfer from the heated plasma to the water molecules indeed heats the water to a high temperature and pressure state. The very high pressure in the initial stage of the bubble growth leads to a very fast expansion in the first nanoseconds after the bubble nucleation, as shown in Figure 10c.
transmission through the sample is measured with a photodiode. It is possible to deduce the mean bubble diameter using Mie theory. More details on the technique are available elsewhere.18,65

Figure 11b shows a typical signal obtained at 200 mJ/cm². The increase in intensity near 0 ns is an artifact attributed to nonlinear effects from the high intensity ultrafast pump laser, including self-phase modulation and plasma emission. We can see from this figure a very rapid growth time for the bubble (∼30 ns), followed by a relatively slow recovery (∼300 ns). This slow recovery time is associated with the presence of many bubbles of different sizes, and thus different lifetimes, in the focal volume and to the presence of dephasing oscillating bubbles that contribute to the total signal.18,68 This situation may originate not only from the fluence distribution within the focal volume, but also from the laser interaction with agglomerated AuNRs and gold nanospheres that are inevitably present in the sample. Some scattering may also come from thermal lensing due to the temperature increase in the focal volume.

Figure 11c shows the mean bubble average diameter produced around AuNRs aligned with the polarization as a function of fluence. The method used to obtain this result from the modification of the transmission of the probe laser is described in detail in the SI. In summary, it consists of writing the experimentally measured absorption coefficient as a function of the extinction cross section of individual bubbles, knowing the concentration of the AuNRs and the dimension of the focal volume. It is then possible to deduce the diameter of the bubble from electromagnetic theory that gives the extinction cross section of the bubble as a function of its diameter. Corrections accounting for the contribution of misaligned AuNRs are calculated from the fact that the energy deposited in the water (Ed) is roughly proportional to \( \cos \beta \), where \( \beta \) is the angle between the polarization vector and the AuNR’s longitudinal axis, and from the dependence of the bubble’s diameter (\( d_{\text{bubble}} \)) on the deposited energy (\( E_d \)), estimated as \( d_{\text{bubble}} \approx E_d^{0.45} \) by Siems et al.68 The interested reader is referred to the SI for more information.

For a fluence of 200 mJ/cm², the average bubble produced in the focal volume by AuNRs aligned with the polarization is measured to be \( \sim 430 \pm 50 \) nm. Note that this represents an average bubble diameter. A Gaussian pulse with a given fluence (which is in fact an average fluence) is indeed composed of a spatial distribution of local fluences in the focal volume. This should thus create a distribution of bubble dimensions in the focal volume. We however consider that the average bubble calculated using our method is a good approximation for the size of the bubbles produced by aligned AuNRs irradiated at a local fluence corresponding to the average fluence of the pulse.

Another common method used to evaluate bubble dimensions is the Rayleigh-Plesset equation that relates the lifetime of the bubble to its diameter.

\[
\tau_{\text{bubble}} \approx 0.092d_{\text{bubble}}
\]  

This strict formula may be inaccurate for nanoscale bubbles, but still gives a correct approximation of the maximal bubble diameter in those cases.19,64 The application of this method with ensemble measurement is however complicated by the asymmetric time-shape. Vapor bubbles are usually characterized by growth and collapse times that are fairly symmetric.19,20,64 In the case of an ensemble measurement, this symmetric signal is however superposed with a long-lifetime asymmetric tail that can originate from several phenomena that we already discussed. As this tail is not related to the lifetime of the average bubble, it would not be justified to use the full lifetime of the signal (∼300 ns from Figure 11a) in the Rayleigh-Plesset equation to calculate the average bubble diameter. Assuming that the maximal observed dip in the transmission signal shown in Figure 11b is due in majority to the polarization-aligned average bubbles within the sample, we evaluate the growth time of the average polarization-aligned bubble \( \tau_{\text{growth}} \approx 30 \) ns for a fluence of 200 mJ/cm². According to the known symmetric growth and collapse phase of vapor bubbles, this growth time should approximately correspond to an average bubble lifetime \( \tau_{\text{bubble}} \approx 60 \) ns (see dashed red line in Figure 11b). Using the Rayleigh-Plesset equation, this corresponds to an average diameter ∼650 nm. The error on that value is rather large as the asymmetric tail might influence the position of the minimum in Figure 11b, making the evaluation of the bubble lifetime very approximate. The order of magnitude of the diameter however corresponds with the ∼430 nm diameter found with the optical scattering method.

In summary of this experimental section, the optical probing technique presented demonstrates the plasmonic-enhanced generation of vapor bubbles around AuNRs for fluences over ∼75 mJ/cm². This optical technique allows evaluation of the dimensions of the bubble. However, large errors are introduced by the use of an ensemble measurement. At 200 mJ/cm², the diameter of the average polarization-aligned vapor bubbles is ∼380–480 nm. This result agrees with the theoretical results (∼490 nm diameter bubble, a 20 ns growth time, and a 45 ns total lifetime) that was obtained in the last section, hence supporting the plasma-mediated mechanism put forward in this work.

Plasma Shielding of the Plasmon Resonance. The domination of the plasma in the cavitation mechanism is quite surprising considering the linear optical properties of the AuNRs presented earlier (see Figure 2a) showing a net domination of the energy absorbed in the AuNR. However, this calculation only considered linear optical properties of the AuNR-water system, and is therefore no longer valid for high laser intensity. Hence, despite the fact that the linear absorption cross section of the AuNR is over 10 times higher than the scattering cross section at the irradiation wavelength (see Figure 2a), because of the nonlinear absorption in water and the high near-field enhancement, interaction of the AuNR with its environment is controlled by the near-field that generates and heats a plasma directly in the water. Simulation results show that the energy absorbed in this plasma is indeed around 5.7 times superior than the one absorbed directly in the AuNR at 200 mJ/cm² (see Figure 3). This situation is very similar to the one presented in a recent study from Boulaïs et al.18 that demonstrates the domination of the nanoplasma formed around an AuNP on the cavitation mechanism following an off-resonance 800 nm ultrafast irradiation. However, unlike the off-resonance interaction, the irradiation in the present case heavily damages the AuNRs. The use of AuNRs as generators of vapor bubbles is thus limited to single-pulse applications for which the possible degradation of the AuNRs does not constitute an important issue.

The similarity with the off-resonance case can be easily understood by noting that, because of the excitation of a plasma around the nanostructure, the local permittivity is altered during the laser irradiation. The AuNR thus progressively loses its resonant characteristics during the time of the laser pulse...
and a majority of the energy absorption is moved from the AuNR itself to the plasma in the surrounding water. Figure 12a shows that transition during a 200 mJ/cm² laser–nanostructure interaction. Results show that at the beginning of the interaction, when no important plasma density is present, the absorption cross section of the AuNR (σ_{\text{AuNR}}) is equivalent to the linear absorption cross section (σ_{\text{abs}}), and that the absorption cross section of the surrounding plasma (σ_{\text{plasma}}) is null. With time, the enhanced near-field interacts non-linearly with the water and creates a plasma around the AuNR. This plasma absorbs energy from the electromagnetic field and modifies the local permittivity, so that σ_{\text{abs}} drops well below σ_{\text{plasma}} and that σ_{\text{plasma}} becomes dominant. The modification of the local permittivity indeed alters the resonance condition so that a 800 nm irradiation is no longer resonant with a 10 nm × 41 nm AuNR, explaining the important decrease of σ_{\text{abs}} seen in Figure 12a. We call this phenomenon “plasma shielding of the plasmon resonance”. This alteration in the resonance condition also affects the near-field environment. As seen from Figure 12b, the modified permittivity degrades notably the electric field enhancement factor, the maximum of which goes from 77 (see Figure 4b) to around 2.6. This reduction explains the strong decrease of σ_{\text{plasma}} observed in Figure 12a between 150 and 200 fs.

The importance of plasma and plasma shielding on the cavitation process is further revealed from the comparison of bubbles generated around in-resonance and off-resonance AuNRs. Figure 13 shows the experimental signal due to the bubbles generated around 25 × 60 nm² AuNRs (LP plasmon band near 620 nm) following an off-resonance 150 mJ/cm², 800 nm, 45 fs laser pulse. Using exactly the same methodology as before (see last section), the amplitude of this signal is shown to correspond to ∼650 nm diameter bubbles. Those bubbles are thus even larger than those produced around in-resonance AuNRs (∼430 nm, Figure 11c). This observation is further confirmed by the off-resonance bubbles lifetime (∼60 ns) that also corresponds to a bubble diameter ∼650 nm. This lifetime is very similar to that of bubbles produced around in-resonance AuNRs. However, as discussed previously, deducing bubble diameters from lifetime yields large uncertainties due to the ensemble measurement. The similar observed lifetimes are therefore not in contradistinction with the slightly larger bubbles obtained from the amplitude of the signal.

This result is very surprising and cannot be explained by the linear absorption properties of the AuNRs. The absorption cross section of the polarization-aligned 25 × 60 nm² off-resonance AuNRs (∼288 nm²) is indeed much smaller than that of the 10 × 41 nm² in-resonance AuNRs (∼6500 nm²). Accordingly, one would expect a much smaller bubble to be produced in the off-resonance case, in strong opposition with the experimental results. The introduction of the plasma-mediated cavitation mechanism resolves this paradox. Using the model presented earlier, simulations shows an energy deposition of ∼9.9 pJ in the plasma around the off-resonance AuNRs. This is much larger than the 1.4 pJ energy deposited around the in-resonance AuNRs, due to shielding from the plasma. In consequence, the proposed plasma mediated mechanism explains why larger bubbles are observed. A similar idea can explain the size of the bubbles (∼800 nm in diameter) generated around off-resonance AuNPs that have been reported in a previous study.18 Similar modeling has in this case shown a 12 pJ nonlinear energy deposition around the AuNP, consistent with the large bubbles that are experimentally observed. This result brings yet another experimental support to the plasma-mediated mechanism put forward in this work.

**CONCLUSION**

In summary, we demonstrated that the interaction of an ultrafast laser impulsion with an in-resonance AuNRs is highly dependent on the fluence of the incident radiation. Calculations revealed the presence of two distinct regimes of irradiation that depend on the laser fluence. For F < 3 mJ/cm², the AuNRs are in the absorption regime and the laser energy is mainly absorbed in the AuNR itself. Results show that below the deformation threshold fluence (fluence <100 μJ/cm²) the AuNR’s structural integrity is not compromised and the field enhancement due to the plasmonic interaction leads to low heating of the AuNR, small amplitude pressure wave emission, and low-density plasma generation in the surrounding medium. This plasma is mainly produced by a photothermal emission from the AuNR’s surface due to field absorbed directly in the AuNR. It moreover brings the possibility to use AuNRs as nanoplasma generators that can induce highly localized chemical damage to cell components in the context of nanosurgery. We however showed that no bubbles were generated around the AuNRs for irradiations with fluences below the deformation threshold.

For F > 3 mJ/cm², the AuNRs are in the near-field regime and the laser energy is absorbed directly in the water surrounding the AuNR through a photoionization process that occurs due to the enhanced near-field. Using a complete modeling of the nanocavitation mechanisms, we theoretically demonstrated the formation of ∼490 nm diameter vapor bubbles around the AuNRs following a 200 mJ/cm² single

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**Figure 12.** Plasma shielding of the plasmon resonance. (a) Variation of the absorption cross section of the AuNR (blue line) and of the surrounding plasma (green line) relative to the linear absorption cross section as a function of time. (b) Cross-section of the electric field enhancement factor at the time corresponding to the pulse maximum.

**Figure 13.** Experimental variation in the transmission signal of the probe beam following a 150 mJ/cm², 45 fs irradiation of off-resonance 25 × 60 nm² AuNRs. A zoom near the minimum (∼30 ns) is shown in the inset. This signal corresponds to bubbles with diameters ∼650 nm produced around polarization-aligned AuNRs.
pulse irradiation. In situ optical characterization of the produced bubbles is consistent with this result, supporting the plasma-mediated cavitation mechanism put forward in this work. Bubbles with diameters ~200–600 nm are measured for fluences ranging 100–400 mJ/cm². However, irradiation at those fluences has been shown to destroy the AuNRs, raising potential toxicity concerns and compromising the efficacy of multipulse processes or scanning procedures.

The plasma responsible for the cavitation is non-linearly created directly in the water by the enhanced near-field around the AuNR and not by the absorbed field, in opposition to what is the case in the absorption regime. We showed that this plasma shields the laser-plasmon interaction, alters the resonance condition, and transforms the role of the AuNR in term of energy transfer. Simulation results demonstrated the strong influence of that plasma on the field distribution around the plasmonic nanostructure. It has been shown to induce a strong decrease in both the field enhancement around the AuNR and the energy absorbed in the AuNR, explaining the smaller bubbles produced around in-resonance AuNRs when compared to off-resonance AuNRs and off-resonance AuNPs, which was unexpected from their linear optical properties. This result offers another experimental evidence for the plasma-mediated cavitation mechanism discussed in this paper.

ASSOCIATED CONTENT

Supporting Information
Details on the model for the AuNR oscillations and melting temperature. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
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REFERENCES

(28) Baumgart, J.; Humbert, L.; Boulais, É.; Lachaine, R.; Lebrun, J. J.; Meunier, M. Off-resonance plasmonic enhanced femtosecond laser
Immunotargeted Nanoshells for Integrated Cancer Imaging and Cancer Photothermal Therapy Using Transferrin-Conjugated Gold


mediated near-infrared thermal therapy of tumors under magnetic
optoporation and transfection of cancer cells.

The Journal of Physical Chemistry C

femtosecond laser pulses.

Ben-Yakar, A. Thermal analysis of gold nanorods heated with

metallosungen.

biomedicine.

continues in the development of smaller, more penetrable probes for
nanorods: electrochemical synthesis and optical properties.

1997

Nat. Nanotechnol.

gold nanorod.

membrane integrity.

imaging and photothermal therapy in the near-infrared region by using

(41) Lal, S.; Clare, S. E.; Halas, N. J. Nanoshell-enabled photothermal

(45) Li, J. L.; Day, D.; Gu, M. Ultra-Low Energy Threshold for


(65) Lachaine, R.; Boulais, E.; Neumann, J.; Brinkmann, R. Self-limited growth of laser-

(64) Vogel, A.; Linz, N.; Freidank, S.; Paltauf, G. Femtosecond-laser


Nat. Nanotechnol.


(66) Weninger, K. R.; Barber, B. P.; Putterman, S. J. Pulsed Mie


(58) Pelton, M.; Sader, J. E.; Burgin, J.; Liu, M.; Guyot-Sionnest, P.; Gosztola, D. Damping of acoustic vibrations in gold nanoparticles.

Nat. Nanotechnol.


(54) Link, S.; Wang, Z. L.; Eversole, D. S.; Lee, M.; Yang, D.; Paltauf, G.; Meunier, M. Effect of


