Measurements of extreme orientation-dependent temperature increase around an irradiated gold nanorod

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ABSTRACT

When irradiated at its resonance frequency, a metallic nanoparticle efficiently converts the absorbed energy into heat which is locally dissipated. This effect can be used in photothermal treatments, *e.g.*, of cancer cells. However, to fully exploit the functionality of metallic nanoparticles as nanoscopic heat transducers, it is essential to know how the photothermal efficiency depends on parameters like size and shape. Here we present the measurements of the temperature profile around single irradiated gold nanorods and nanospheres placed on a biologically relevant matrix, a lipid bilayer. ^[1] We developed a novel assay based on molecular partitioning between two coexisting phases, the gel and fluid phase, within the bilayer. ^[2, 3] This assay allows for a direct measurement of local temperature gradients, an assay which does not necessitate any pre-assumptions about this system and is generally applicable to any irradiated nanoparticle system. The nanorods are irradiated with a tightly focused laser beam at a wavelength of 1064 nm where biological matter exhibits a minimum in absorption. By controlling the polarization of the laser light we show that the absorption of light by the nanorod and the corresponding dissipated heat strongly depends on the orientation of the nanorod with respect to the polarization. Finally, by comparing to spherical gold nanoparticles, we demonstrate how a change in shape, from spherical to rod like, leads to a dramatic enhancement of heating when using near infrared light.

Keywords: Gold nanorod, photothermal effect, lipid bilayer, surface plasmon resonance, polarization

1. INTRODUCTION

In recent years, gold nanostructures have attracted growing interest in biophotonics research for their surface plasmon ^[4] properties which feature the collective oscillation of electrons near the surface. In particular, gold nanorods, whose surface plasmon resonances (SPRs) can be tuned to near-infrared region where the near infrared (NIR) biological transparency window locates, show great potential for in vivo biophotonics applications. By efficiently converting electromagnetic radiation into substantial heating, gold nanorods are considered to be promising tools in applications such as photothermal cancer therapy, ^[5, 6] drug delivery, ^[7] tissue soldering ^[8] and *in vivo* photoacoustic imaging, ^[9] where controllable heating is desirable. Meanwhile, owing to the large optical scattering cross sections and dramatic reduction of plasmon damping ^[10] of gold nanorods, they have been shown to be competent candidates as probes in single molecule biophysics (e.g. in two-photon luminescence imaging for cancer cells ^[11]). Thanks to the high degree of polarization anisotropy of gold nanorods, orientation sensing or a polarization dependent interaction with the environment could be realized. For all these applications, it is beneficial to know the exact heating profile around gold nanorods.

Several approaches have been proposed to measure the heating associated with gold nanospheres. Recently, Kyrsting et al. ^[3] have quantified the temperature increase profile of individual gold nanospheres (with diameters from 60 nm to 200 nm) trapped in three dimensions near lipid vesicles with moderate laser power and observed a maximum local temperature increase of 300 K. As for gold nanorods, simulations of the temperature increase around nanorods irradiated by femtosecond laser pulses show that a maximum temperature of 1270 K can be reached for a laser pulse of 4.70 J m⁻² average energy fluence. ^[12] However, direct measurements of heating associated with irradiated single nanorod in a biologically relevant context have not been shown yet.

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Here we present measurements of the heating associated with single gold nanorods under NIR laser illumination on a lipid bilayer based assay. Our method makes no pre-assumptions about the system and only uses the very well characterized phase transitions of lipid bilayers. The results show that the temperature increase around gold nanorods is highly correlated with the orientation of the gold nanorod with respect to the laser polarization. This orientational dependence is not observed for spherical gold nanoparticles. When the long axis of a gold nanorod is parallel to the polarization of the NIR heating laser, the associated surface temperature is significantly higher than that of a gold nanosphere whose volume is two orders of magnitude larger. Our experimental results are supported by theoretical calculations using the discrete dipole approximation (DDA). ^[13] Finally, we report a partial melting of nanorods at extreme temperature when the polarization vector of the NIR heating laser is aligned with the long axis of the nanorod. This effect significantly reduced the absorption cross section of the nanorods in the NIR region and thus shuts down the extreme heating properties, which is important to consider for photo-thermal applications.

2. METHODS

2.1 Principle of experiments

Gold nanorods were immobilized on a glass surface which was subsequently coated by a gel phase glass supported lipid bilayer. A sketch of the lipid bilayer assay is shown in Figure 1. In Figure 1A, the lipid bilayer consisting of $DC_{15}PC$ molecules was mixed with 2 mol % $DiOC_{18:2}$ or 3% of $DiIC_{18}$ fluorophores. The experiment was conducted on a Leica SP5 confocal microscope into which an optical trap based on a 1064 nm laser beam (Spectra Physics J201–BL-106C) was implemented. Details of the equipment are described in Ref 14. The lasers were focused using a Leica oil immersion objective (PL APO, NA = 1.4, x100). The polarization direction of the laser was rotated in a controlled fashion by rotating a lambda half wave plate placed in front of the laser. As the nanorod was immobilized, the angle between the long axis of the nanorod and the polarization vector of the trapping laser (pink arrow in coordinate system in Figure 1) could be controlled. The fluorophores were excited with a 488 nm Argon laser and their emission was recorded by a photomultiplier tube in the spectral range = 500 nm - 530 nm. We also recorded the reflection image of the nanorod at 594 nm throughout the experiment by using the built-in acousto-optical beam splitter.

A sketch of using this assay to map the temperature gradient around a nanosphere is shown in Figure 1A and B. The chromophore DiIC₁₈ energetically favors the gel phase because of better hydrophobic matching between the saturated hydrocarbon tails of the fluorescent probe and the longer lipid tails in the gel phase. Also, the emission of this fluorophore is highly sensitive to the orientation of the excitation dipole with respect of the laser polarization. In a bilayer the DiIC₁₈ fluorophore excitation dipole is aligned with the plane of the bilayer. In fluid phase bilayers the dipoles will exhibit stronger fluctuations away from the bilayer plane leading to less efficient excitation of the fluorophores. Thus, when the temperature around an irradiated nanoparticle exceeds the phase transition temperature T_m , this assay will yield a dark region whose radius is proportional to the temperature increase around the irradiated nanoparticle.

The experiments were performed at an ambient temperature of 27 °C, hence, before turning on the laser the bilayer was in a well ordered gel state. When a nanorod which was covered by a lipid bilayer was irradiated, it absorbed light and dissipated heat, thus heating up a localized region around the particle. As the temperature exceeded T_m , the bilayer transformed from gel phase to fluid phase. The fluorophores DiOC_{18:2} preferably partitioned into the melted region due to their unsaturated alkyl tails which was visible due to a local increase of fluorescence. ^[1] The bilayer containing DiIC₁₈ fluorophores would result in a local decrease of fluorescence due to the preferred partitioning of fluorophores from the fluid phase into gel phase bilayer. ^[2]



Figure 1. Illustration of the working principle of the lipid bilayer assay. (A) A nanorod is immobilized on a glass surface and is covered by a gel phase lipid bilayer DC₁₅PC containing a low molar fraction of DiOC_{18:2} fluorophores. The fluorophores are excited at 488nm with a Leica SP5 confocal system and the emitted light is collected using a photomultiplier tube. A 1064 nm laser (in red) is tightly focused by a microscope objective, while the orientation of its polarization (pink arrow in coordinate system) is controlled by a half-wave plate. When the temperature around the irradiated nanorod exceeds the phase transition temperature, T_m , the lipid bilayer becomes fluid in the vicinity of the irradiated nanorod, and the melted region is visualized by DiOC_{18:2} fluorophores which preferentially partition into the fluid phase. The mutual dimensions of the nanorod and bilayer are not drawn to scale. (B) The sketch illustrates a similar lipid bilayer assay made of DC₁₅PC lipids as in (A) containing 3 mol % DiIC₁₈ fluorophores. The fluorophores are excited at 549 nm with the same confocal system as in (A) and the emitted light is collected with a photomultiplier tube. When the temperature around the irradiated nanosphere exceeds T_m , the DiIC₁₈ fluorophores partition from the fluid phase lipid bilayer into the gel phase bilayer thus yield a dark fingerprint.

In this paper, we will mainly focus on the results acquired with the lipid assay with $DiOC_{18:2}$ as fluorescent marker since this assay gives a bright fingerprint. In the bilayer assay using $DiIC_{18}$, a dark fingerprint could in principle also be caused by a non-desirable bleaching of the $DiIC_{18}$ by the heating laser. Moreover, the fluorescence excitation maximum for membrane-bound $DiIC_{18}$ is around 549 nm, hence, it could potentially be excited by two photon absorption of the 1064 nm laser and consequently suffers from bleaching. To avoid such artifacts, we have focused on the fluorescent marker $DiOC_{18:2}$, whose excitation maximum is at 488 nm. This minimizes two-photon absorption of the NIR laser and undesired photobleaching. Intrinsically, a bright fingerprint cannot be caused by bleaching.

2.2 Lipid bilayer preparation

The lipid bilayer was made from 1,2-dipentadecanoyl-sn-glycero-3-phosphocholine (DC₁₅PC, Avanti Polar Lipids). A Lipid bilayer consisting solely of DC₁₅PC lipids has a well-defined phase transition temperature $T_m \sim 33^{\circ}$ C above which the molecular ordering changes from a tightly packed and ordered gel phase into a more disordered fluid phase. It is energetically favorable for 3,3'-dilinoleyloxacarbocyanine perchlorate (DiOC_{18:2}) fluorophores to partition into the fluid phase of a lipid bilayer due to their unsaturated alkyl tails. Therefore, to image the fluid melted region, we incorporated 2 mol % DiOC18:2 fluorophores into DC15PC bilayer. The lipids and fluorophores were first dissolved in chloroform and then evaporated onto a glass vial under nitrogen flow to create a thin film. Subsequently, the film was dried in vacuum for 2 hours. The lipid film was afterward hydrated with PBS (pH = 7.4, 150 mM NaCl) buffer at 37 °C, pH=7.4. To form small unilamellar vesicles, we extruded the hydrated lipid mass through filters with 50 nm pores at T = 37 °C. Finally, 200 μ L of these extruded vesicles with 5 μ L CaCl₂ (100 mM) solution were flushed into a perfusion chamber and allowed to fuse to the glass for 2 hours at 37 °C forming a lipid bilayer on a glass surface which had been thoroughly cleaned and plasma etched (Harrick Plasma). It is important that this incubation temperature is above the gel-to-fluid phase transition temperature at $T_m = 33$ °C. Excess lipid vesicles were thoroughly washed out by vigorous pipetting using de-ionized water 15 times. The final experiments were also conducted in pure water containing no salt. Upon cooling to a temperature below the phase transition temperature the bilayer forms a gel the area of which is approximately 20 % smaller than that of the fluid phase, thus potentially leading to cracks and holes. However, by incorporating the positive charged fluorophore $DiOC_{18:2}$ and using oxidized hydrophilic glass surfaces, the stability of gel phase bilayer was largely improved and no visible cracks formed, a similar strategy as used in Ref 15. To prepare the lipid bilayer incorporated with chromophores $DiIC_{18}$, the detailed description can be found in Ref 2.

2.3 Preparation of the sample chamber

The stock solution of nanorods (*Nanopartz*TM) was diluted 200 times in deionized water and sonicated for 5 minutes in order to prevent aggregation. The rod solution was then flushed into an open chamber and allowed to adhere to the glass surface (thickness 0.17 mm) for 5 minutes. Subsequently, the liposome solution (as described above) was added, thus creating a bilayer covering the nanorods. The gold nanospheres with diameter d = 200 nm were diluted 100 times in deionized water and also sonicated for 5 minutes. The solution containing gold nanospheres was added after the formation of the bilayer.

2.4 Temperature quantification

The method for temperature quantification was published in our previous publication ^[1] and is here reviewed.

To quantify the temperature increase, T, at a distance r from the center of a particle, one can model the nanoparticles as spherical heat radiators with an effective radius, R_{eff} , placed in an infinite medium with thermal conductivity κ ,^[16]

$$\Delta T(r) = \frac{IC_{abs}}{4\pi r\kappa} \qquad r \gg R_{\rm eff} \qquad (1)$$

Here, *I* is the laser intensity incident on the particle and C_{abs} is the absorption cross section of the particle at the irradiating laser wavelength. Although equation 1 was originally derived for a spherical particle of radius R_{eff} , it has been proven to be valid for arbitrarily shaped particles at distances $r >> R_{eff}$ if R_{eff} is chosen as the radius of a sphere with the same volume as the rod-like particle.

For a constant laser intensity, *I*, equation 1 can be rewritten as:

$$\Delta T(r) = \frac{C}{r} \tag{2}$$

where $C = IC_{abs}/4\pi\kappa$ is a constant including all physical parameters that are difficult to determine experimentally. Using equation 2 together with knowledge of the phase transition temperature T_m and of the radius of the melted region r_m provides *C*. Hence, we can quantify the temperature profile at a given laser intensity at any distance $r >> R_{eff}$.^[17]

However, as one moves closer to the surface of a nanorod, the non-spherical shape becomes important for its temperature profile. The temperature increase at the surface of the metallic nanoparticle can still be calculated by introducing a morphology-dependent parameter $.^{[17]}$ For spherical particles, equals to one. The value of a nanorod is a function of its aspect ratio. For a 20 nm x 100 nm nanorod, = 1.2. ^[17] The temperature at the surface can be calculated simply by dividing equations 1 or 2 by and substituting *r* with R_{eff} .

One needs to keep in mind that the model assumes an infinite medium around the irradiated nanoparticles, whereas in reality, the nanoparticles are placed in between a water-glass interface. Detailed discussion of the impact on the temperature interpretation with a presence of an interface can be found in Ref 1.

2.5 Laser intensity

To make a reasonable estimate of the laser intensity at the focal region we measured the total laser power transmitted through the objective, P, with a power meter. The spot size of the focused laser beam in the bilayer plane was measured by using the laser to bleach an area on an Alexa fluorophore labeled bovine serum albumin (BSA) layer. The laser had a Gaussian intensity profile, the radius of the laser spot size at half maximum, R, was measured to be 0.85 µm. The average intensity of the laser illumination, I, was thus approximated as $I=P/\pi R^2$.

3. RESULTS AND DISCUSSION

3.1 The melting fingerprints

To obtain the temperature profile around a nanoparticle with Equation (2), we first have to quantify the size of the melted region on the lipid bilayer. As shown in the left panels of Figure 2, typical melting fingerprints consist of a circular micron-sized bright (with fluorophore $\text{DiOC}_{18:2}$) or dark (with fluorophore DiOC_{18}) region centered around the metallic nanoparticle. The bright fingerprints are surrounded by a ring shaped darker region from which the fluorophores $\text{DiOC}_{18:2}$ have been depleted after partitioning into the central fluid region (most clearly visible in the left panel of (A)). Line profiles through the center of these typical melting finger prints are shown in the right panels of Figure 2. To accurately determine the radius of the melted region, we have performed a rotational average and smoothening of the circularly symmetric melted fingerprint to obtain a radial intensity profile. We defined the radius of the melted region, r_m , as the distance from the center of the melted region to the point where the intensity curve is equal to the background plus the noise level and inserted it into Equation (2) to compute the temperature profile around a nanoparticle.



Figure 2. Typical bright and dark melting fingerprints of nanoparticles measured on lipid bilayer assays. The left panels of (A) and (B) show the confocal images of fluorophores $\text{DiOC}_{18:2}$ partitioning into fluid regions around an irradiated gold nanosphere (diameter = 200 nm) (A) and a gold nanorod (20 nm x 100 nm) (B) under identical illumination conditions (1.8 x 10^{10} W/m^2). Whereas the left panel of (C) is the confocal image of fluorophores DiOC_{18} partitioning from fluid regions into gel phase regions around an irradiated gold nanosphere (diameter = 200 nm) under 3.2 x 10^{10} W/m^2 laser illumination. The right panels show the corresponding intensity line profiles of the yellow dashed lines in (A), (B) and (C).

Since a bright fingerprint minimizes the effects of photobleaching as discussed in section 2.1, we will mainly focus on results obtained by using the assay which yields a bright melted region. This is particularly useful when looking and small particles over extended periods of time during which bleaching can occur in the local area surrounding the particle. We have also optically trapped individual gold nanosphere above the lipid bilayer and the heat associated with a gold nanosphere in an optical trap can be readout on the lipid bilayer by quantifying the radius of the melted region. When moving the chamber around with a piezoelectric stage while keeping the trap steady, one can see that the lipid bilayer responded simultaneously to the dissipated heat by showing bright tracks along the trace of the movement as shown in Video 1. The high sensitivity to temperature elevation and the real time response of the lipid bilayer show great promise in the biophysics applications where real time monitoring of the change of temperature is required.



Video 1. Real time temperature sensing of the lipid bilayer (incorporated with $DiOC_{18:2}$ fluorophores) assay. A gold nanosphere was trapped in 2D by optical tweezers operating at 1064 nm. When moving the chamber around with a piezoelectric stage, the lipid bilayer responded simultaneously to the heat by showing bright tracks along the movement and recovered rapidly when the nanoparticle was moved away. Include this text at the end of the caption: http://dx.doi.org/3203391; 4; 53408

3.2 Orientation dependent anisotropic heating of gold nanorods

Contrary to the absorption spectrum of nanospheres which shows only one peak, the plasmon resonance of gold nanorods splits into two modes: A longitudinal mode parallel to its long axis and a transverse mode orthogonal to its long axis. In our experiments, the nanorods were chosen such that their relatively broad longitudinal resonance included the wavelength of the heating laser. The orientation of the polarization vector of the NIR laser could be controlled relative to the nanorods which were firmly adhered to the glass surface. Figure 3A shows a series of confocal images from an experiment where a nanorod was irradiated with varying orientations of the polarization vector of the NIR laser. Figure 3C (blue triangles, dashed blue line) shows the temperature increase 50 nm from the center of the nanorod as a function of polarization vector and a maximum when the rod is parallel to the polarization vector. Thus, we demonstrated a strong orientation dependence of the heating around an irradiated nanorod with temperature increases ranging up from a few degrees up to 120 °C depending on the dimensions of the particular rod and laser intensity used in the experiments. These results are, to our knowledge, the first direct measurements of the exact temperature profile around an irradiated nanorod and of how the temperature profile depends on the orientation of the nanoparticle.

For comparison, the same experiment was carried out on gold nanospheres, the confocal images are shown in Figure 3B and the temperature increase plotted in Figure 3C (green squares and dashed green line). As expected, the temperature increase around a spherical nanoparticle showed no dependence on its orientation with respect to the polarization vector.

The temperature increase is directly proportional to the absorption cross section of the nanoparticle (Equation 1). The absorption cross section of a metallic nanosphere at a certain wavelength can be correctly calculated using Mie theory. ^[18, 19] However, Mie theory cannot be directly applied for the calculation of the absorption cross section of a rod-shaped particle. Instead, we calculated the absorption cross section of a gold nanorod by using the discrete dipole approximation (DDA). ^[13] We used the DDA implementation reported in Refs 20 and 21 to simulate the absorption cross section of gold nanorods (20 nm x 100 nm) for different orientations of the gold nanorod with respect to the polarization of the laser. The absorption cross section of the orientations of the orientation gax (4.04 x $10^{-3} \,\mu\text{m}^2$) was slightly larger than the absorption cross section of the off-resonance nanosphere (3.69 x $10^{-3} \,\mu\text{m}^2$) which has a 100 times larger volume. The angular dependence of the nanorod absorption cross section is shown in Figure 3C (red circles). The plot confirms the expected cosine square dependence between the absorption cross section of the rods and the orientation of the laser polarization (full red line). ^[22]



Figure 3. Strong dependence of gold nanorod heating on its orientation with respect to the laser polarization vector. (A) Confocal images of the melted region around a gold nanorod (20 nm x 100 nm) as function of the relative rotation angle of the polarization vector with respect to the axis of the rod. (B) Same as (A) but for a d = 200 nm gold sphere. (C) Left axis: Radii of the melted regions in (A) and (B) for the nanorod (blue triangles) and the sphere (green squares), respectively. Right axis: DDA Simulations of the absorption cross section (red circles) as a function of the angle between the polarization vector and the long axis of the nanorod.

3.3 Gold nanorod heating rate and surface melting

It has been shown in literature that the temperature around gold nanospheres increases linearly with laser intensity. To explore the laser intensity and temperature increase dependency for the on-resonance gold nanorods (20 nm x 100 nm), we measured the radius of the melted region for 53 gold nanorods while keeping the laser polarization vector parallel to the long axis of the nanorods. Figure 4A shows the transmission electron micrograph of the gold nanorods used in the experiments. Image analysis yielded a size distribution of (Length=97.2 \pm 25.5) nm x (width=20.6 \pm 2.0) nm (mean \pm standard deviation). The relatively large spread in size and shape of the nanorods as shown in Figure 4A gives rise to different locations of the longitudinal resonance peak for the individual rods. Thus, heterogeneous heating behavior of the nanorods was expected. Figure 4B shows the radius of the melted region for 15 randomly chosen gold nanorods from the same batch (out of 53 measured in total). The measured radius is proportional to the surface temperature of the individually irradiated nanorods according to Equation (1). The size of the melted region increased with laser intensity within a certain intensity interval for all the rods. However, the temperature increase around some of the rods, for example rod number 1, 4, 13 and 15, has mysteriously dropped to 0 despite an increase in laser intensity.



Figure 4. Temperature increase as function of laser intensity for a random selection of irradiated nanorods oriented along the laser polarization vector. (A) Transmission electron micrograph of the gold nanorods used in the experiments, image analysis yielded a size distribution of (length=97.2 \pm 25.5) nm x (width=20.6 \pm 2.0) nm (mean \pm standard deviation). (B)The graph shows the radius of the melted region for 15 randomly chosen gold nanorods from the same batch (out of 53 measured in total). The measured radius is proportional to the surface temperature of the individually irradiated nanorods. The heterogeneity in heating characteristics reflects the different sizes, shapes, and aspect ratios of the individual rods originating from the same batch.

Since the absorbance of the gold nanorods at 1064 nm is highly dependent on the aspect ratio, the dramatical decrease in heating is expected to be related to an abrupt shape change. The structural stability of nanoparticles is different from their bulk counterparts. The structural stability of nanorods exposed to high temperatures has been measured by irradiating rods with pulsed lasers ^[23] or simply by incubating nanorods at various temperatures. ^[24] A gradual conversion of gold nanorods into spheres was found already at 200°C - 300°C, which is well below the bulk melting temperature of gold. This transformation from rod shape into a more spherical shape inevitably blue shifts the longitudinal plasmon resonance frequency thus resulting in less absorption and heating at NIR.^[25] The occurrence of temperature induced shape changes of irradiated nanorods was supported by 3 representative confocal and reflection images of the nanoparticles before and after the heating cycle as shown in Figure 5A. Reflection images of Rod 1 (framed in blue in Figure 5A and plotted in blue squares in Figure 5B) at the beginning and the end of the heating cycle are shown in the bottom panels. The confocal images reveal that the temperature of the rod is higher in the first image than in the last image despite the increase of laser intensity. The reflection images of Rod 1 were acquired using a 594 nm laser. The reflection image directly reflects the scattering of light from the particle and therefore a change in the reflection image must be caused by either a change in shape or size of the nanorod. For Rod 1 the reflection image at the end of the heating cycle is significantly darker than that at the beginning of the cycle. This is because the plasmon peak of the transformed rod became blue-shifted thus resulting in stronger scattering of the 594 nm imaging laser. The fact that the reflection images of the thin nanorods appear darker than their background whereas larger spheres appear bright with respect to the background is consistent with observations of silver and gold nanoparticles in Ref. 26 and Ref. 27. Simultaneously, the moving away of the plasmon peak from the 1064 nm laser explains the loss of dissipated heat. Rod 2 (framed in green in Figure 5A and plotted in green circles in Figure 5B) probably experienced a minor surface melting thus blue-shifting the resonance peak slightly away from 1064 nm. We attribute the differences among the individual rods to the relatively large spread in size and shape as shown in the TEM graph in Figure 4A which give rise to different locations of the longitudinal resonance peak. No significant changes were observed in the reflection images of the nanosphere (framed in red in Figure 5A and plotted as red triangles in Figure 5B), for which an increase of radius of the melted region was linearly proportional to the incident laser intensity.

Upon repeating the heating cycle we noticed that generally, the heating curves for nanorods are not reversible (see in inset of Figure 5B). Typically, the second temperature versus laser intensity curves (ii and iv) fall underneath the first cycle (i and iii) and the second curve is typically linear. This supports the hypothesis that during the first cycle the rod was irreversibly transformed into a more spherical shape. In contrast, the temperature versus laser intensity curves for irradiated nanospheres were completely reversible when the cycle was repeated.



Figure 5. Heat induced shape changes of irradiated nanoparticles. (A) Fluorescent confocal images (upper panels) and confocal reflection images (lower panels) acquired simultaneously of two individual gold nanorods. The left part of the images corresponds to a low intensity and in the right part the intensity is increased. (B) Heating curves versus for two representative individual rods (green circles and blue squares, respectively corresponding to the first and second image in (A)) and one d = 200 nm sphere (red triangles) corresponding to the last image in (A). The Inset shows the radius of the melted region as a function of laser intensity for two consecutive heating cycles of two individual rods.

By fitting the initial linear part of the trace shown in Figure 5B and using the area of the focal region of the laser beam $(2.27 \ \mu m^2)$, we deduced the heating rate of rods and spheres. For the 200 nm sphere we measured a heating rate of 1439 K/W, which is close to the 1650 K/W reported from the same type of particle in Ref 2. The temperature versus laser intensity traces of the individual nanorods (oriented along the polarization vector of the laser) differed significantly more than the traces for the nanospheres. Also, the fact that the heating rate of a rod is not exactly linear but levels off with laser intensity (probably because of shape remodeling) complicates a determination of the rod heating rate. If we, however, perform a linear fitting to the first three points for rod 1 (blue squares in Figure 5B) then we obtain an extreme heating rate of 4405 K/W. As the increase in temperature versus laser intensity most likely is not linear and has to pass through (0, 0) this number is an underestimation of the true initial heating rate.

4. CONCLUSION

Using the molecular partitioning in a well characterized phase transitions of lipid bilayers, we measured the heating associated with irradiation of gold nanorods. The results show that the temperature increase around gold nanorods is not only dependent on the power of lase radiation, it is also highly correlated with the orientation of the gold nanorod with respect to the laser polarization. A well designed gold nanorod for applications in NIR spectra range can absorb and dissipate heat as efficiently as a gold nanosphere with 100 x larger volume. Thus, gold nanorods are excellent candidates in photothermal applications where space is limited. However, when the surface temperature increase on the surface of gold nanorods exceeds 200 °C, a partial melting of the rod into a more spherical shape occurs. This dramatical reduction of photothermal efficiency is well worth considering in photothermal applications.

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