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Optically controlled thermal management on the nanometer length scale

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Abstract

The manipulation of polymers and biological molecules or the control of chemical reactions on a nanometer scale by means of laser pulses shows great promise for applications in modern nanotechnology, biotechnology, molecular medicine or chemistry. A controllable, parallel, highly efficient and very local heat conversion of the incident laser light into metal nanoparticles without ablation or fragmentation provides the means for a tool like a ‘nanoreactor’, a ‘nanowelder’, a ‘nanocrystallizer’ or a ‘nanodesorber’.

In this paper we explain theoretically and show experimentally the interaction of laser radiation with gold nanoparticles on a polymethylmethacrylate (PMMA) layer (one-photon excitation) by means of different laser pulse lengths, wavelengths and pulse repetition rates. To the best of our knowledge this is the first report showing the possibility of highly local (in a 40 nm range) regulated heat insertion into the nanoparticle and its surroundings without ablation of the gold nanoparticles. In an earlier paper we showed that near-infrared femtosecond irradiation can cut labeled DNA sequences in metaphase chromosomes below the diffraction-limited spot size. Now, we use gold as well as silver-enhanced gold nanoparticles on DNA (also within chromosomes) as energy coupling objects for femtosecond laser irradiation with single- and two-photon excitation. We show the results of highly localized destruction effects on DNA that occur only nearby the nanoparticles.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Highly sophisticated scanning probe technologies allow the positioning and manipulation of molecules or groups of molecules with sub-nanometer accuracy. Examples are the manipulation of chromosomes in order to extract genetic material [1] or the restriction of individual DNA molecules [2].

In these cases the serial character limits the throughput seriously and makes it impracticable for greater numbers of samples. Optical techniques, such as laser-beam-based techniques, were used for cutting individual DNA molecules [3] or parts of metaphase chromosomes [4]. They allow a higher throughput but are even more limited in their lateral precision due to the wavelength of the applied light. To increase the precision far below the wavelength a light energy conversion at metallic nanostructures could be a promising approach.

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Table 1. High pulse energy laser systems utilized in the experiments.

Type	Laser system	Company	Pulse length (ns)	Wavelength (nm)	Repetition rate (Hz)
ns	Nd:YAG laser system + amplifier (503-D.NS)	BM Industries	8	532	10
ps	Nd:YLF laser system + regenerative amplifier (ISL2001 M PL)	Intelligent Laser Sys Inc.	0.035	527	1000
fs	Nd:glass- and ytterbium system + regenerative amplifier + SHG crystal (femtoREGEN)	High Q laser	0.000 250	1053 → 527	10 000

The surface plasmons (SP) at the interface between the gold or silver nanoparticles and the dielectric surroundings show pronounced optical absorption resonances due to coupling of the light to the collective electronic excitation [5]. Width and spectral position of the resonance are well described by the Mie theory [6]. The spectral position depends on particle material, size, shape and dielectric environment [7, 8]. The size dependence is introduced by assuming a size-dependent material dielectric function $\varepsilon(\omega, R)$, which can be written as a combination of an interband term, accounting for the response of the d electrons and a Drude term considering the free conduction electrons only [9, 10]. The phenomenological damping constant in the Drude term is related to inhomogeneous line broadening and the lifetimes of all electron scattering processes in the nanoparticle that are mainly due to electron–electron, electron–phonon or electron–defect scattering, and (in the range of tens of nanometers of the nanoparticle diameter) electron–surface scattering. The damping mechanism is often described in terms of a loss of phase coherence of the collective electron oscillation due to scattering of single electrons [5]. Using laser irradiation, this phenomenon can lead to a rise in electron temperature in contrast to the ionic lattice. Electron–electron and electron–phonon collisions will cause the formation of a new thermal equilibrium [11]. This dynamic behavior was studied by pump probe experiments [13]. In [12] the subpicosecond time response of the optical excitation and the relaxation dynamics of the nonequilibrium electrons by the electron–phonon interaction were studied theoretically by the electron–phonon coupling model.

Metallic nanoparticles, which are fabricated by chemical preparation, exhibit surface plasmon effects. In connection with (bio)chemical functionalization, such nanoparticles can be conjugated to various molecules [14, 15] and even a sequence-specific positioning along DNA is possible [16–18]. There are even therapeutic applications of plasmonic heated nanoparticles [19].

In this paper we first investigate the interaction of laser radiation of various laser pulse lengths, intensities and pulse repetition rates with gold nanoparticles immobilized on a PMMA layer in air. Here, the PMMA layer serves as a highly local discrete sensor for the temperature nearby the nanoparticle. After laser irradiation we detected a sinking of the hot nanoparticle and/or the hot or cold ablated nanoparticle fragments by AFM measurements. Also, a change in the

size of nanoparticles on pure glass after laser irradiation can be monitored by AFM. For a specific combination of laser irradiation parameters a parallel temperature increase of the nanoparticle’s surroundings without ablation occurs. Using the electron–phonon coupling model in combination with the heat conduction equation, we simulated the heat conversion in metal nanoparticles during irradiation with ultrafast laser pulses. Various intensities, repetition rates and the complex heat conduction from the nanoparticle into the nonsymmetric, nonuniform 3D PMMA air surroundings were modeled. These results encourage practical applications like ‘nanoreactors’, ‘nanowelding’, ‘nanocrystallization’ and ‘nanodesorption’. Finally, we show experimentally the subwavelength destruction of nanoparticle-labeled DNA in chromosomes as well as in an isolated state by optical single-photon excitation and two-photon excitation with fs laser pulses.

2. Experimental details

2.1. Experimental set-up

For thermal manipulation of technical materials or control of chemical reactions near the gold nanoparticles, a moderate intensity of laser pulses and necessary fluence is required, so that, on the one hand, the desired material manipulation or chemical reaction takes place and, on the other hand, no destruction of nanoparticles, glass slide or other carrier material would occur. First of all, to get optimal conditions for heat conversion, an excitation of the nanoparticle with the resonance wavelength (plasmon or interband) is necessary. In the case of gold nanoparticles with 30 nm diameter we used 530 nm. In addition, the pulse length and pulse repetition rate has to be in a range where nanoparticles absorb effectively a well-determined dose of the incoming light which is then converted into heat.

To reach a certain fluence, either a long irradiation time with small pulse energy per area or a short irradiation time with high pulse energy over the same area [20] is needed. Figure 1 illustrates the relations for laser parameters used in different experiments. For high pulse energy experiments with low repetition rate, different laser equipment was used for heat conversion experiments on pure gold nanoparticles of a PMMA layer (table 1). With the help of amplifiers, a high fluence could be reached by focusing the laser beam by lenses

Table 2. Low pulse energy laser systems.

Type	Laser system	Company	Pulse length (fs)	Wavelength (nm)	Repetition rate (MHz)
cw			cw	530	—
ps 1	titanium:sapphire laser (Mira 900HP) + OPO	Coherent APE	3000	530	76
fs 1	titanium:sapphire laser (Mira 900HP) + OPO	Coherent APE	100	530	76
fs 2	titanium:sapphire laser (Mai Tai)	Spectra Physics	100	800	80

Table 3. Single high power laser pulse experiments on 30 nm gold nanoparticles of PMMA (for focus area = 0.1 cm²—ablation pulse energy: 100 fs $\rightarrow$ 280 μ J [25]; and ionization pulse energy: 60 fs: for $R_e = 10^{12}$ s⁻¹ $\rightarrow$ 400 μ J, 1 ps: $R_e = 10^{12}$ s⁻¹ $\rightarrow$ 6, 4 mJ, 10 ns: $R_e = 10^{12}$ s⁻¹ $\rightarrow$ 64 J [5], O: single focused irradiation, S: scanned irradiation with smaller focus).

Wavelength/pulse duration (nm/ns)	Pulse energy (mJ)	Repetition rate (Hz)	Average power (mW)	Focus diameter (μ m)	Fluence (mJ cm ⁻²)	Experimental results in AFM picture
532/8	0.5	10	5	O: 550	200	Figure 3(a)
	1	10	10	O: 550	350	Figure 3(c)
527/0.035	0.76	1000	760	O: 300	160	Figure 3(e)
	1.27	1000	1270	O: 300	240	Figure 3(f)
532/0.0003	0.0016	10000	16	S: 80	36	Figure 3(g)
	0.0024	10000	24	S: 80	54	Figure 3(h)
	0.0040	10000	40	S: 80	90	Figure 3(i)

Table 4. High repetition rate, low power pulse experiments on 30 nm gold nanoparticles of PMMA (for focus area = 0.1 cm²—ablation pulse energy: $\rightarrow$ 280 μ J [25]; and ionization pulse energy: 60 fs: for $R_e = 10^{12}$ s⁻¹ $\rightarrow$ 400 μ J [5]) O: single focused irradiation.

Wavelength/pulse duration (nm)/(ns)	Pulse energy (nJ)	Repetition rate (MHz)	Average power (mW)	Focus diameter (μ m)	Fluence (mJ cm ⁻²)	Experimental results in AFM picture
cw/530		$t = 100 \mu$ s	22	O: 3.5	2.8	Figure 4(a)
530/0.003	0.27	76	22	O: 3.5	2.8	Figure 4(b)
530/0.0001	0.27	76	22	O: 3.5	2.8	Figures 4(c) and (d)

only (table 3). The laser systems for small pulse energy with high repetition rate experiments are shown in tables 2 and 4. Cw, ps1 and fs1 were used for the single-photon excitation experiments on gold nanoparticles on a PMMA layer, too. Here, the same small fluence below the ablation threshold of gold nanoparticles for all single-photon excitation experiments was reached by focusing the laser beam with the same objective inside the microscope (Olympus).

Fs2 is applied for the two-photon excitation experiments done on silver-enhanced gold nanoparticles attached to pure DNA or DNA in chromosomes. Utilizing a laser scanning microscope (LSM 410 from Carl Zeiss Jena) with high numerical aperture objective (oil immersion), ultrafast fs laser pulses with intensities in the range of MW cm⁻²–GW cm⁻² are attained in the tiny focal volume (table 5). Here, two photons at a wavelength of 800 nm excite simultaneously a silver electron within the absorption band at 400 nm. Components in out-of-focus regions do not experience this intense radiation and remain unaffected. In the experiment, gold nanoparticles were used to label DNA as part of the chromosomes. Because gold nanoparticles have a maximum plasmon absorption near 527 nm, it is necessary to perform a silver deposition on the gold nanoparticle labels in order to

Table 5. Two-photon medium power fs laser pulse experiments on gold–silver core–shell nanoparticles sequence-specific labeled on chromosomes DNA or stretched DNA (S—laser scanning mode) (for focus area = 0.1 cm²—ablation pulse energy: $\rightarrow$ 280 μ J [24]; and ionization pulse energy: 60 fs: for $R_e = 10^{12}$ s⁻¹ $\rightarrow$ 400 μ J [5].)

Wavelength/pulse duration (nm fs ⁻¹)	Pulse energy (nJ)	Repetition rate (MHz)	Average power (mW)	Focus diameter (μ m)	Fluence (mJ cm ⁻²)
fs:800/100	0.775	80	62	S: 1	98
fs:800/100	0.27	80	22	S: 1	34
fs:800/100	0.11	80	9	S: 1	14
fs:800/100	0.075	80	6	S: 1	9.5

reach an absorption at about 400 nm (silver, cf figure 2). The thickness of the silver shell can be controlled via time and concentration. The thickness of the silver shell determines the spectroscopic properties such as the resonance wavelength.

Figure 2 presents the extinction spectrum of a typical gold–silver core–shell system in relation to the relative position of the absorption maxima of the pure metals. The absorption peak around 400 nm is very strong for the core–shell system due to increased absorption of silver compared to absorption of gold.

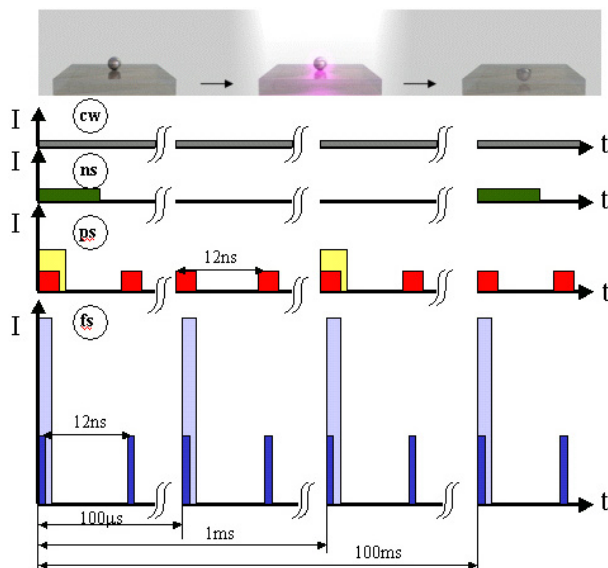


Figure 1. The rectangles illustrate the ratio of pulse intensity, pulse length and repetition rate for the different laser experiments. (cw) continuous wave, (ns) 8 ns laser pulse with 10 Hz pulse repetition rate, (ps) high intensity 35 ps laser pulses with 1 kHz pulse repetition rate and low intensity 3 ps laser pulses with 76 MHz repetition rate, (fs) high intensity 300 fs laser pulses with 10 kHz pulse repetition rate and low intensity 100 fs laser pulses with 76 MHz repetition rate.

In the experiments, 100 fs pulses with a wavelength of 800 nm were used. This compromise gives the possibility of two-photon excitation of the silver-enhanced gold nanoparticles to achieve specific and very local thermal damage around the nanoparticles while endogenous fluorophores are avoided. At this wavelength, water and most organic compounds possess only low absorption and scattering coefficients. However, simultaneous absorption of two or more NIR photons can excite UV or VIS electronic transitions in endogenous or exogenous fluorophores [21]. Endogenous absorbers such as melanin, hemoglobin, chlorophyll, tyrosine, tryptophan, NAD(P)H, flavins, porphyrins, etc. can be destroyed by photothermal, photochemical and photomechanical effects which result in the formation of destructive oxygen radicals, singlet oxygen and indirect DNA damage [22]. The excitation efficiency is indirectly proportional to the pulse length and proportional to the squared power. Therefore, destruction experiments on pure chromosomes have to show, for a given laser pulse length, the upper usable laser intensity for irradiation of chromosomes before they will be destroyed unspecifically.

2.2. Analysis methods

For the characterization of samples before and after exposure, images in overview optical dark-field contrast were made with an Axiotech microscope (Carl Zeiss Jena, Germany). Scanning force microscopy (SFM) images (topography) with a Dimension 3100/Nanoscope III (Digital Instruments, Santa Barbara, CA) using tapping mode in air were performed for detailed analysis. The images were only flattened by the software.

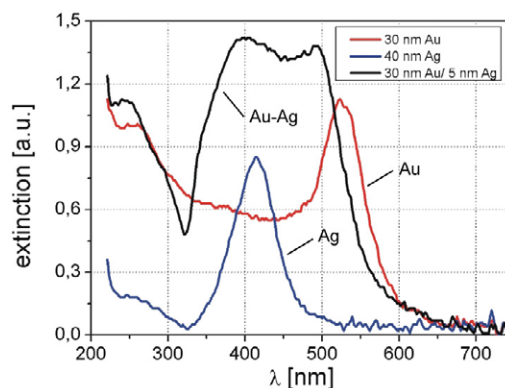


Figure 2. Extinction spectra of nanoparticle solutions of 30 nm gold particles, 40 nm silver particles and core-shell systems of 30 nm gold core with 5 nm silver shell.

2.3. Preparation of samples

For the first experiment, glass substrates were purchased from Paul Marienfeld GmbH. Cleaning was performed using acetone, ethanol and distilled water followed by a chemical activation in a 1:1:1 solution of HCl:H₂O₂:H₂O. Cleaned and activated glass substrates were coated with PMMA by spin coating a solution of 2% PMMA in ethyl acetate (500 rpm for 10 s, 3000 rpm for 60 s). The layer was 50–70 nm thick. Gold nanoparticles were immobilized on the PMMA layer by incubation of the samples in a nanoparticle solution overnight at room temperature followed by rinsing in distilled water and air-stream drying.

Prior to unspecific nanoparticle labeling of human metaphase chromosomes, the surface was blocked by incubation with 1% PEG (polyethyleneglycol) for 15 min at room temperature. The solution of positively charged gold nanoparticles (Genogold, BBI, UK) was incubated with the samples as delivered for 15 s at room temperature. The charged gold nanoparticles were bound to the DNA backbone by electrostatic interaction. After the particle labeling, the gold particles were enlarged with a silver enhancement kit (SEKL 15, BBI UK) for 3 min. The resulting particle diameter was approx. 70 nm as measured by AFM. Genogold was also used for unspecific labeling of stretched DNA bundles.

In the next experiment, samples coupled by specific molecular interactions were used as described before [32]. The same procedure was applied for specific labeling of stretched DNA in the last experiment.

3. Theoretical simulation methods

We examined the relaxation dynamics of the electron temperature by the electron-phonon coupling model [12]. The time evolution of the electron temperature T_e and the effective lattice temperature T_l is described by the coupled differential equations

$$\begin{aligned} c_e(T_e) \frac{\partial T_e}{\partial t} &= \kappa \Delta T_e - G(T_e - T_l) + P(t) \\ c_l \frac{\partial T_l}{\partial t} &= G(T_e - T_l). \end{aligned} \quad (1)$$

Here $c_e(T_e)$ is the temperature-dependent electronic heat capacity, c_l is the lattice heat capacity, κ is the thermal conductivity, G is the electron–phonon coupling constant and $P(t)$ is the excitation energy density per unit time and unit volume in a particle. The first term on the right-hand side, representing thermal conductivity losses from a particle to the matrix, can be neglected for a few picoseconds after laser irradiation. The value of G is $3 \times 10^4 \text{ J ps}^{-1} \text{ m}^{-3} \text{ K}^{-1}$ [11]. We used the parameters of $c_e(T_e)$ and c_l with $c_e = c_0 T_e$, $c_0 = 66 \text{ J m}^{-3} \text{ K}^{-2}$ [8] and $c_l = 3 \times 10^6 \text{ J m}^{-3} \text{ K}^{-1}$ [11]. As transient absorption a value of 27% was taken [23].

The conductive heat transfer from the gold nanosphere to the PMMA matrix starts after equilibration of the electron gas with the lattice. The model for heat transfer by conduction is described by the heat equation

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = q \quad (2)$$

with the following material properties: ρ is the density, C_p is the heat capacity, k is the thermal conductivity and q is the heat source. The two subdomains are a gold particle modeled as a truncated sphere with radius 15 nm without a cup of 5 nm height and the PMMA matrix as a cuboid $200 \text{ nm} \times 200 \text{ nm} \times 100 \text{ nm}$. The gold properties are the density $\rho_{\text{Au}} = 19300 \text{ kg m}^{-3}$, the heat capacity $C_{p\text{Au}} = 129 \text{ J kg}^{-1} \text{ K}^{-1}$ and the thermal conductivity $k_{\text{Au}} = 317 \text{ W m}^{-1} \text{ K}^{-1}$, while the PMMA properties are $\rho_{\text{PMMA}} = 1190 \text{ kg m}^{-3}$, $C_{p\text{PMMA}} = 1420 \text{ J kg}^{-1} \text{ K}^{-1}$ and $k_{\text{PMMA}} = 0.19 \text{ W m}^{-1} \text{ K}^{-1}$. The initial temperature in the gold particle is 344 K (the lattice temperature after the fs pulse) and the initial temperature of the PMMA matrix is 300 K. At the boundary between the two subdomains the continuity interior boundary condition is valid:

$$-\mathbf{n}_{\text{Au}} \cdot (-k_{\text{Au}} \nabla T_{\text{Au}}) - \mathbf{n}_{\text{PMMA}} \cdot (-k_{\text{PMMA}} \nabla T_{\text{PMMA}}) = 0. \quad (3)$$

As a boundary condition of the PMMA cuboid we set on all surfaces (without the top surface) the prescribed temperature of 300 K, the heat bath of the surroundings. The top boundaries are described by external natural cooling conditions [24]

$$-\mathbf{n} \cdot (-k \nabla T) = h(T_{\text{inf}} - T) \quad (4)$$

with the horizontal surface upside

$$h = 0.54 F_{\text{lam}} \left(\frac{\Delta T}{L} \right)^{0.25} \quad (5)$$

with

$$F_{\text{lam}} = k \left(\frac{Ra}{L^3 \Delta T} \right)^{0.25} \quad (6)$$

with the Rayleigh number Ra and the characteristic length L .

4. Experiments on PMMA substrates

4.1. Results

The AFM images in figures 3(a) and (b) show gold nanoparticles lying on a pure glass slide after laser irradiation

with 532 nm wavelength and 8 ns pulses (in water). At fluences of 200 and 280 mJ cm^{-2} simultaneous melting and ablation occur. Figure 3(c) shows gold nanoparticles on a PMMA layer after laser irradiation with the same pulse length but a higher fluence of 350 mJ cm^{-2} . The central dark region depicts the hot sunken main gold nanoparticle and the smaller dark regions around the central dark region point to gold nanoparticle fragments which were sunken into the PMMA layer.

Using laser radiation with the same wavelength but shorter pulse length of 35 ps the necessary fluence for gold nanoparticle to sink into the PMMA layer was smaller. Here, already at 160 mJ cm^{-2} smaller dark regions (figure 3(e)) can be seen. At higher fluences of 240 mJ cm^{-2} hot sunken fragments around the central sunken main particle were observed (figure 3(f)).

In the case of 300 fs laser pulses with (not so high) fluences of 36 mJ cm^{-2} and 54 mJ cm^{-2} , respectively, only the main particle sinks into the PMMA layer (figures 3(g) and (h)), but ablation of the gold nanoparticles occurs (not shown here). Increasing the fluence to 90 mJ cm^{-2} results in very bright regions around the dark central region (figure 3(i)). Here, only the main particle sinks into the PMMA layer while the fragments remain on top of the PMMA layer. All these described experiments produce heat around the nanoparticle but destroy the particle during laser irradiation.

To prevent fragmentation and ablation during laser irradiation and heat production we used 100 fs laser pulses with fluences below the ablation threshold of 2.8 mJ cm^{-2} but with high pulse repetition rates of 76 MHz (figure 4(c)). Here, one can see only very small dark regions, caused by sinking gold nanoparticles.

Figure 4(d) shows the same experiment with gold particles on a pure glass slide. No fragmentation and no ablation is observed by AFM imaging before and after laser irradiation (section analysis not shown).

Assuming that the same dose of cw laser energy would heat the nanoparticle in the same way, we irradiated the gold nanoparticle on PMMA with a cw laser (530 nm wavelength) with the same fluence (2.8 mJ cm^{-2}) and the same time as the fs irradiation. Here, we could not observe any sinking of the nanoparticle into the PMMA or any particle ablation (see figure 4(a)). To answer the question regarding the possible use of less expensive laser sources, figure 4(b) shows a result of nanoparticle irradiation with ps pulses of the same fluence and the same repetition rate as fs pulse irradiation, with the results shown in figure 4(c). These results suggest that using ps pulses with high repetition rate is not sufficient for reaching a high temperature resulting in a sinking into the PMMA layer.

4.2. Discussion

At ns pulses the pulse intensity is small, but the long pulse duration heats the nanoparticles. After 30 ps the particle reaches melting temperature. Because of ineffective additional absorption of photons when the lattice is already hot and probably in a molten state, the fast thermal expansion unfortunately stimulates acoustic phonons, followed

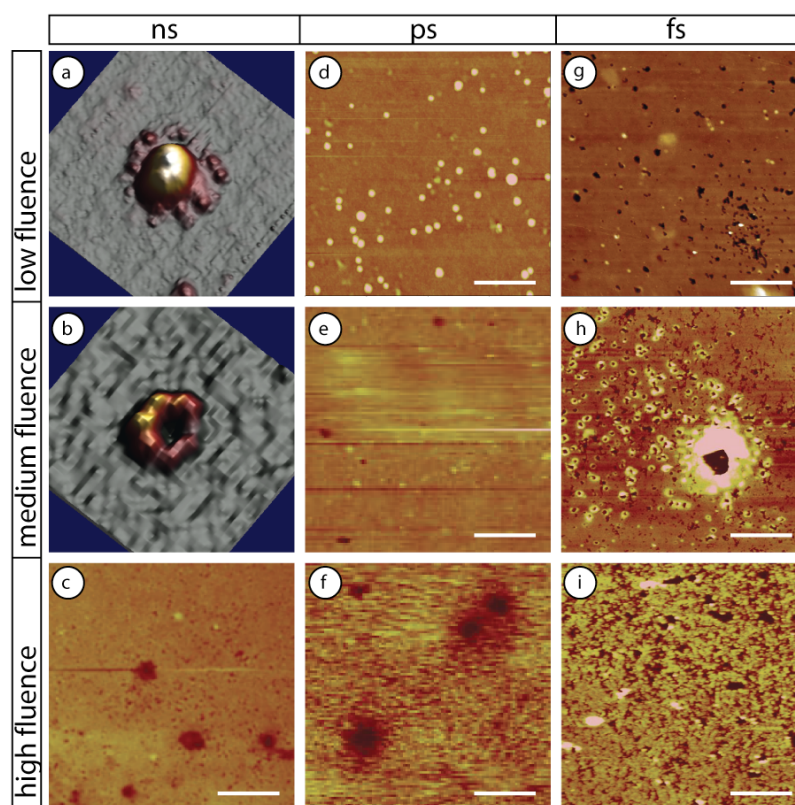


Figure 3. AFM images of ns, ps and fs laser pulse experiments on 30 nm gold nanoparticles on a 50 nm PMMA layer. (a), (b) Perspective views $0, 25 \mu\text{m} \times 0, 25 \mu\text{m}$. (c)–(i) Top views with scale bars of $1 \mu\text{m}$. Because PMMA has a high viscosity at temperatures above the glass transition (T_g bulk = 100°C [26]), our T_g seems to be in the range of 75°C (for a discussion see section 4.3). The thin PMMA layer serves as a thermosensitive reporter to the temperature experienced. Hot nanoparticles will sink into the PMMA and this effect can be detected by AFM scans (holes appear as dark regions). Nanoparticles, which do not sink into the PMMA, appear as bright structures. The laser parameter for the left column are: 8 ns, 10 Hz and fluences of 200 mJ cm^{-2} (a), 280 mJ cm^{-2} (b) and 350 mJ cm^{-2} (c), respectively; for the center column: 35 ps, 1 kHz and for fluences = 90 mJ cm^{-2} (d), 160 mJ cm^{-2} (e) and 240 mJ cm^{-2} (f), respectively; and for the right column: 300 fs, 10 kHz and fluences of 36 mJ cm^{-2} (g), 54 mJ cm^{-2} (h) and 90 mJ cm^{-2} (i), respectively.

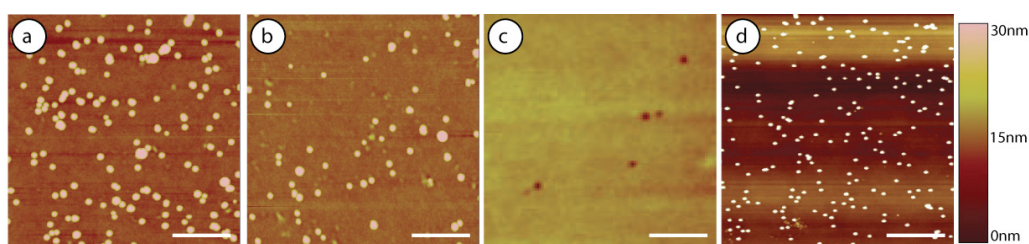


Figure 4. AFM images of different laser pulse experiments on 30 nm gold nanoparticles on a 50 nm PMMA layer (scale bar = $1 \mu\text{m}$). Here the laser parameters were wavelength = 530 nm, laser pulse repetition rate = 76 MHz (for (b), (c) and (d)) and (a) continuous wave (cw), 2.8 mJ cm^{-2} , (b) 3 ps, fluence = 2.8 mJ cm^{-2} , (c) 100 fs, fluence = 2.8 mJ cm^{-2} (parameter used for simulation in figures 5, 6 and 7), (d) the same as in (c) but for gold nanoparticles on pure glass without a PMMA layer.

by fragmentation of the nanoparticles. This means that hot pieces of particles will split off and results in fragmentation of the nanoparticle (dark areas in figure 3(c)). With increasing nanosecond laser pulse intensity, the transition from melting to fragmentation is rather gradual. As a result both processes can occur simultaneously.

Increasing the pulse intensity (using high energy 35 ps pulses) separates the melting and the obvious fragmentation regimes. As can be seen (figure 3(e)) no fragmentation, but ablation (not shown here) is recognized by AFM scanning of

the radiated area. Only the main particles sink into the PMMA. Figure 3(f) shows sunken fragmented pieces of nanoparticles surrounding the sunken main particle.

In the case of a high power fs laser pulse, the absorption of the photons by the electrons (100 fs), the electron–phonon relaxation (heating of the lattice < 10 ps), the melting (30–35 ps) and the phonon–phonon relaxation (cooling of the lattice > 100 ps) are well separated in time. During fs pulses, there is no time for plasma development. Heat diffusion into the material is negligible. As a consequence of the limited

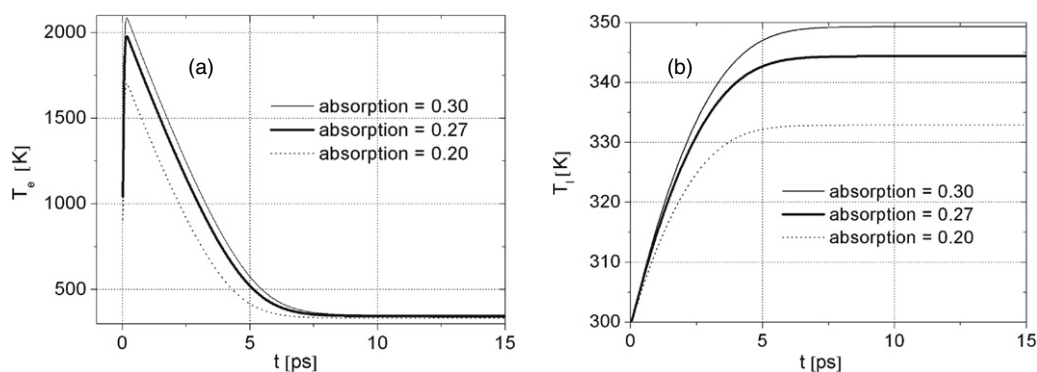


Figure 5. (a) Time dependence of the electron temperature T_e for different transient absorptions. (b) Lattice temperature T_l of 30 nm gold spheres, also for different absorptions.

heat diffusion during pulses, the heat loss into the bulk is minimized. This leads to a reduced ablation threshold. As can be seen in figures 3(g)–(i), high intensity femtosecond pulses (a 300 fs laser pulse is 26 600 times more intensive than a 8 ns pulse) heat the electrons in the nanoparticle very fast and very effectively (no hot lattice during the electron heating), so that atoms are ionized. The cold ions can absorb more photons and the hole ions (carriers) in the nanoparticle split off into some pieces. The AFM images of the radiated area show no sunken hot fragments comparable to the many small dark areas around the sunken main particle (see figures 3(c) and (f)). In contrast, higher areas around the sunken dark main particles can be identified. This points to cold nanoparticle pieces deposited around the main particle. Smaller fluences (36 mJ cm^{-2}) above the fs pulse ablation threshold of 2.8 mJ cm^{-2} (which is 10–100 times smaller than for 8 ns pulses) show that only the main nanoparticles sink into the PMMA (figure 3(g)). Here, melting of the gold nanoparticle is claimed at fluences of 54 mJ cm^{-2} .

To avoid ablation, small power fs laser pulses (in the range slightly below the ablation threshold, 2.8 mJ cm^{-2}) with a very high repetition rate (76 MHz) were used (see table 4). An irradiation of gold nanoparticles on pure glass slides shows no ablation (see figure 4(d) and section analysis (not shown here)). Controlled heating of the nanoparticle (see the theoretical simulation) with adjustment of the pulse repetition rate (figure 4(c)) proves that fs laser pulses with a small fluence of 2.8 mJ cm^{-2} can lead to a sinking of nanoparticle into the PMMA layer, too. Additionally, the very local increase of temperature of the surroundings near the nanoparticle, caused by the minimal heat capacity of the small nanoparticle, is very important. To test the effectiveness of the heat conversion at fs laser pulse intraband excitations (400 nm wavelength single-photon excitation and 800 nm wavelength two-photon excitation at fluences of 2.8 mJ cm^{-2}) future work is in progress.

The experiments show that fs irradiation provides a more effective heat conversion mechanism than cw lasers. The explanation is that, at higher electron temperatures after fs excitation, the occupation of higher electronic states leads to an increased scattering rate ([27, 28], Fermi liquid theory [29] equation (12)) and thus to an increased damping of the plasmon oscillation. In the theoretical section we simulated

this complex behavior of the nanoparticle—taking into account the environment and the interaction with low power fs laser pulses with high repetition rate.

4.3. Simulation of heat conversion

The electron–phonon coupling model simulation shows a high electron temperature near 2000 K with relaxation times of 5 ps (see figure 5(a), absorption 0.27) for 30 nm gold nanoparticles fs laser radiation and dielectric surrounding parameters. At the same timescale the temperature of the nanoparticle lattice increases from a room temperature of 300–344.5 K (see figure 5(b), absorption 0.27). 10 ps after the first femtosecond laser pulse, the particle lattice temperature is below the glass transition temperature. The glass transition temperature of bulk PMMA is 373 K. Thin PMMA films (<50 nm) layered on certain glass substrates [30] or plasticizer effects, caused by solvent included in the PMMA matrix, can reduce the glass transition temperature dramatically. Therefore, here the nanoparticle can sink into the PMMA after the first femtosecond laser pulse. Another explanation is the desorption of molecules nearby the nanoparticle surface [31]. Further work is in progress in order to elucidate the mechanism.

To simulate the heat transport into the nonuniform PMMA and surrounding air environment we numerically solved the heat conduction equation by finite element methods (FEM). The most prominent result in figure 6(a) is that the temperature increase of the PMMA is very local (only 40 nm). This is caused by the low heat capacity of the nanoparticle (see figure 6(b)). Secondly, at the end of the period between two femtosecond laser pulses (12 ns) there is only a very small temperature increase of 0.25 K in PMMA at $z = -40 \text{ nm}$ below the nanoparticle surface (see figure 6(c)). Also the temperature difference at this point ($z = -40 \text{ nm}$) between the temperature maximum at 4.5 ns and the temperature after 12 ns is only 0.7 K. This encourages us to increase the temperature by additional femtosecond pulses, each of them after 12 ns.

Another interesting fact is a high temperature gradient near the particle surface (see figure 6(d)). On the particle's surface we simulated a maximal temperature difference between the two laser pulses of 42 K. After 1 ns, this temperature difference at the particle surface is only 27.5 K

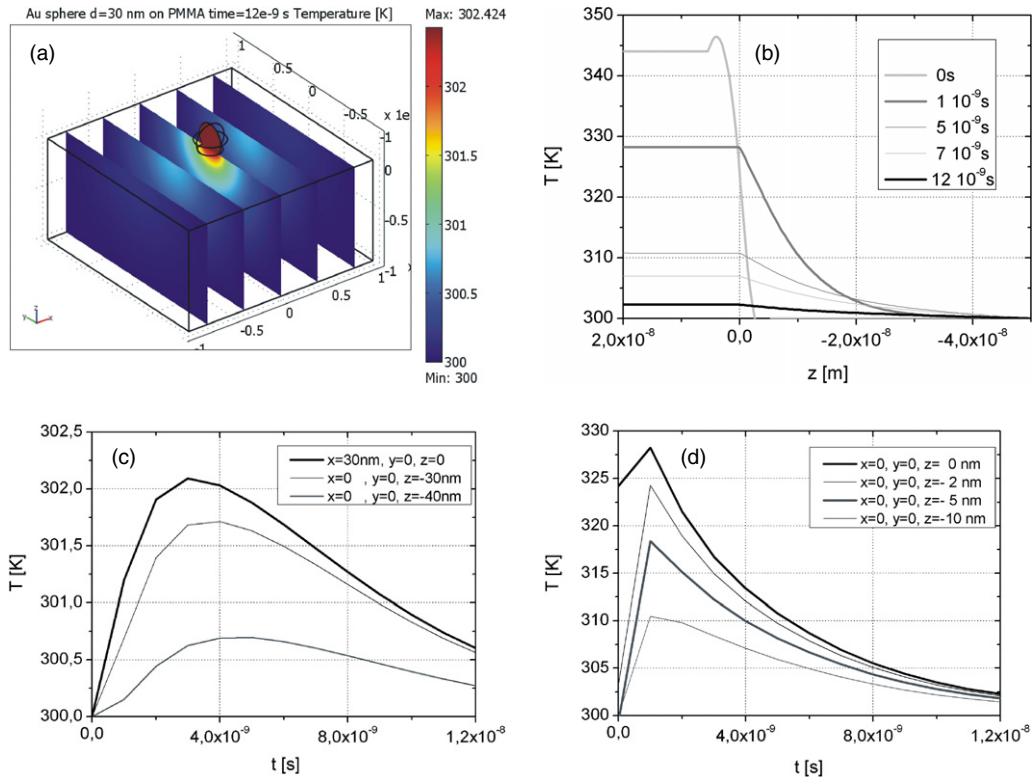


Figure 6. (a) 3D FEM simulation of the temperature distribution of a 30 nm gold sphere on PMMA 12 ns after the femtosecond laser pulse. (b) temperature for different times after the laser pulse at different vertical positions under the nanoparticle. The particle surface is here at the position of 0 m. (c) Temperature development at different positions vertically below ($z = -30$ nm, $z = -40$ nm) and next to the nanosphere. (d) The same as in (c) for small distances from the nanosphere surface ($z = 0$ nm, -2 nm, -5 nm, -10 nm).

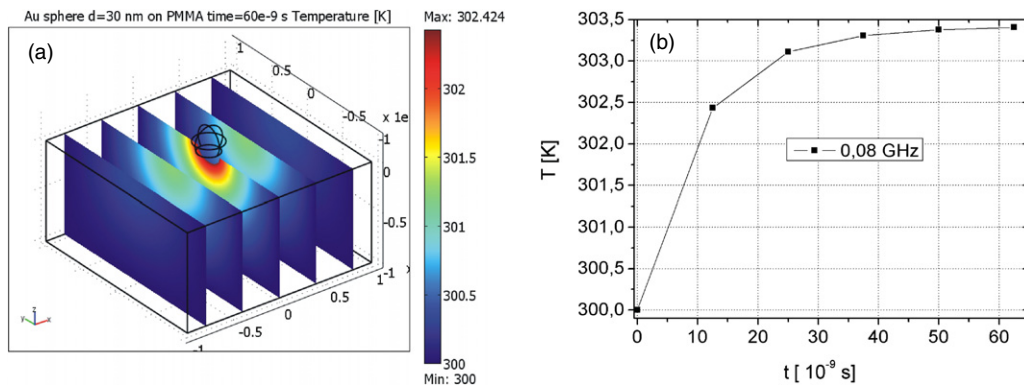


Figure 7. (a) 3D FEM simulation of the temperature distribution of a 30 nm gold sphere on PMMA after five femtosecond laser pulses with 80 MHz pulse repetition rate. (b) Temperature of the nanosphere after different numbers of femtosecond laser pulses with 80 MHz pulse repetition rate.

and in a distance of $z = -10$ nm a temperature difference of only 7.5 K is observed. This allows for a temperature control between two femtosecond laser pulses by using space- and time-controlled femtosecond laser pulses in interaction with a number of different shaped nanoparticles. To overcome the temperature difference restriction (for gold nanoparticles, higher laser intensity would ablate the particles) the material and shape parameters of the particles, the number of particles and the environment could be varied.

Further simulations show the results after a number of ultrashort pulses in a time distance of 12 ns. Every pulse

increases the temperature of the particle. Figure 7(a) shows the temperature in the PMMA surrounding after five pulses. After only five pulses a balance between cooling of the air and PMMA surroundings (convection and heat conduction) and the periodic heating of the nanoparticle is reached. We find that the maximal temperature change, which we can use, is only 3.5 K (see figure 7(b)). An increase of the femtosecond laser pulse repetition rate (time between two pulses is only 1 ns) should lead to a further increase of the temperature change. The simulation in figure 8(b) shows a nanoparticle temperature of 420 K after 12 ns. In principle, any temperature

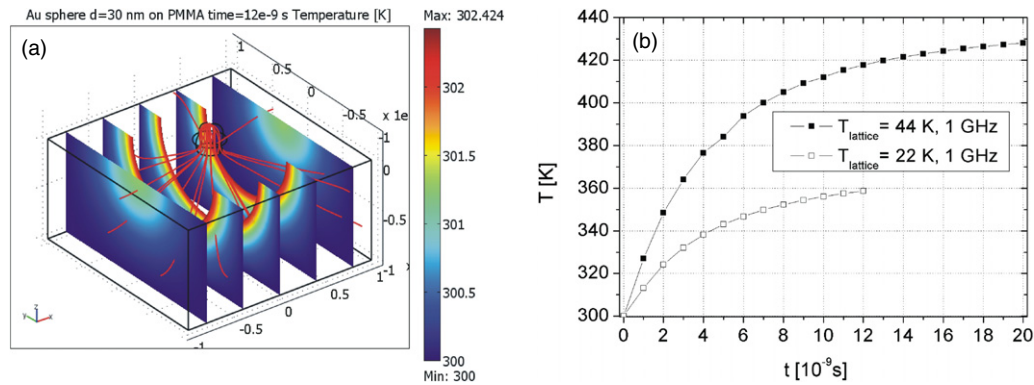


Figure 8. (a) 3D FEM simulation of the temperature distribution of a 30 nm gold sphere on PMMA after 12 fs laser pulses with an assumed 1 GHz pulse repetition rate; the red line shows the heat flux. (b) Temperature of the nanosphere 1 ns after different numbers of femtosecond laser pulses with an assumed 1 GHz pulse repetition rate (two different laser pulse intensities and therefore two different lattice temperatures (44 K, 22 K)).

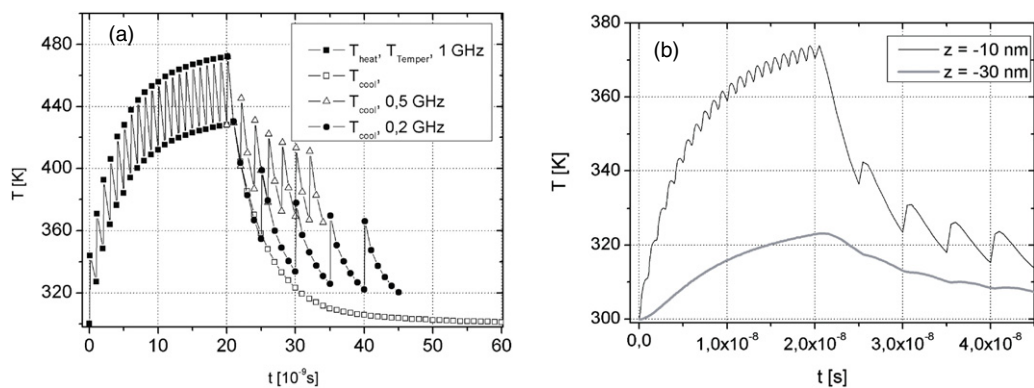


Figure 9. (a) Simulation of nanoparticle heating by an assumed laser repetition rate of 1 GHz for 10 ns (0–10 ns), followed by a temper zone (10–20 ns) and at last a cooling zone with several cooling rates, realized by laser pulses with lower assumed pulse repetition rates (0.2 GHz, 0.5 GHz) and cooling without laser pulses. (b) The same as in (a) but for the temperature in PMMA 10 nm below the nanoparticle ($z = -10$ nm) and 30 nm below the nanoparticle ($z = -30$ nm).

increase, any constant temperature or any temperature decrease (in a temperature range between 20 and 150 °C) should be possible by controlling the pulse repetition rate and the laser pulse intensity below a maximal fluence of 2.8 mJ cm^{-2} (figure 9(a)). In PMMA in a distance of 10 and 30 nm below the nanoparticle the temperature can be controlled, too. Here, the temperature increases after the pulse are not so significant and the maximum achievable temperature is lower (figure 9(b)).

5. Experiments on chromosomes and DNA

Fs laser irradiation with a wavelength of 800 nm (two-photon excitation) does not destroy the pure PMMA layer but causes an excitation of the plasmon band of silver-enhanced gold nanoparticles that transfers the energy to phonon excitation of the silver lattice and afterwards to the surrounding PMMA. This transport of heat is locally limited on the nanometer scale. This approach should be applied to sequence-specific labeled DNA by use of nanoparticles. Earlier work showed that fs laser irradiation is able to destroy chromosomes unspecifically with a 100 nm precision [4]. It could be demonstrated that the

power needed to destroy nanoparticle-decorated chromosomes is lower than the power for cutting pure chromosomes by a laser with comparable energy [32].

These results offer the possibility to radiate and to damage DNA (that was sequence-specific labeled by silver-enhanced gold nanoparticles) without destruction of pure DNA. For the proof of this conclusion we used human chromosomes labeled at the centromere region. The power used for irradiation was 18 mW (28 mJ cm^{-2} fluence). This low power and the optimized laser parameters do not destroy pure chromosomes.

Metaphase chromosomes sequence-specific labeled with silver-enhanced gold nanoparticles are shown in optical dark-field contrast (figure 10(a)). An advantage of this contrast mode is the optical visibility of metallic nanoparticles (even for subwavelength structures). Several particles are marked by arrows. In order to investigate the changes induced by laser irradiation on the nanometer scale AFM imaging was applied. The arrows in figure 10(b) indicate nanoparticles on metaphase chromosomes before laser irradiation. A section analysis of the AFM image shows that the particles have a height of about 50 nm above the chromosome surface (particles on the same sample positioned directly on the glass substrate beside the

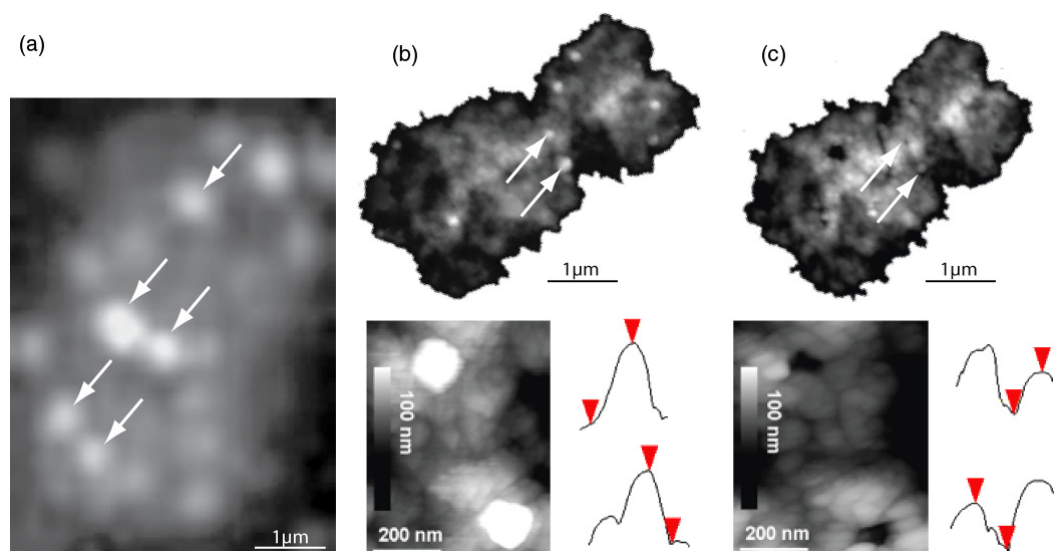


Figure 10. Metaphase chromosomes sequence-specific labeled with silver-enhanced gold nanoparticles shown in optical dark-field contrast microscopy (a). AFM images of nanoparticles coupled to the chromosome surface before (b) and after (c) laser irradiation. Pictures below (b), (c) are enlargements of marked particles on chromosomes and section analyses.

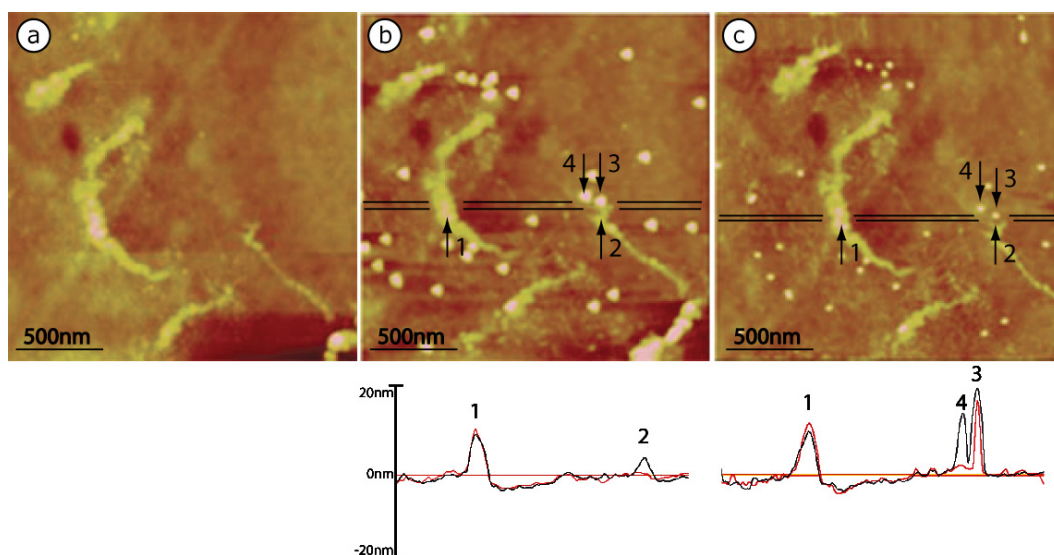


Figure 11. (a) AFM images of stretched DNA bundles without gold nanoparticles. (b) The same stretched DNA bundles as in (a) decorated by gold nanoparticles prior to irradiation. (c) After single-photon femtosecond laser excitation with a wavelength of 530 nm. (Bottom left) Black curve shows the section analysis before laser irradiation, red curve shows the section analysis after laser irradiation (arrow 1—height of pure DNA is the same before and after irradiation, arrow 2—height of DNA nearby a nanoparticle changes after laser irradiation, suggesting DNA destruction). (Bottom right) Section analysis for a position between particles 3 and 4 (arrow 3—height of the nanoparticle prior to and after the irradiation is roughly the same, i.e. no ablation of the gold nanoparticle, arrow 4—the AFM measurement in slide b) was done with a poor tip (broader particles as in (c)); therefore this section analysis shows for the edge of particle number 4 a difference in height, which is an artifact).

chromosomes show a statistical height of 60 nm—not shown here). The picture in figure 10(b) shows an AFM enlargement of two particles. The corrugated chromosome surface is clearly visible in the background.

The same chromosome was imaged after laser treatment (figure 10(c)). Now the particles have disappeared and cavities (visible as dark regions) are detected at the former particle positions (indicated by arrows). A section analysis of the AFM image shows a depth of about 25 nm for the cavities. We cannot

exactly measure the diameter of the original cavities, because measurements of lateral dimensions are problematic with AFM due to tip-sample convolution. The range should be about 70–100 nm—only insignificantly larger than the diameter of the nanoparticle itself. Observation of control particles located on the glass substrate exhibiting a size reduction of a maximal 20% suggest that the particles on the chromosomes are also still preserved to some extent but are enclosed in the chromosome matrix after the laser treatment.

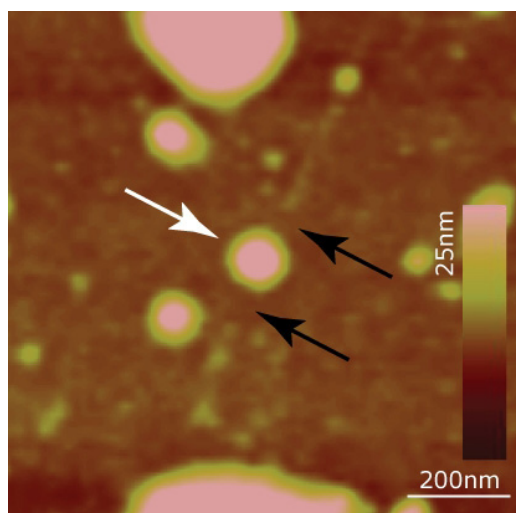


Figure 12. After single-photon excitation of gold nanoparticles (wavelength 530 nm) DNA is missing along 50–100 nm (black arrows) directly adjacent to the particle (white arrow).

However, the height of particles above the chromosome surface was smaller. We conclude that only the DNA/protein matrix is destroyed by heat transferred from the particle. Thereby, the particle sinks into the biological matrix causing a small cavity (see figure 10(c)). The result confirms that the laser induces damage to the system. However, the fluences (28 mJ cm^{-2}) are above the ablation threshold (2.8 mJ cm^{-2}). The results also show structural changes of nanoparticles located outside the chromosomes. This observation leads to the assumption of a partial ablation of the nanoparticles in combination with a significant sinking of the remaining particle structure into the chromosome material.

In the next experiment, stretched DNA bundles (figure 11(a)) were decorated by gold nanoparticles and imaged by AFM prior to (figure 11(b)) and after (figure 11(c)) fs laser irradiation with a wavelength of 530 nm. Here, single-photon excitation of the gold nanoparticles arranged along linear DNA molecules destroys the DNA near the nanoparticles. Destruction of pure DNA far away from the nanoparticles was not observed. Using single-photon excitation the fluence in the range of the ablation threshold of the gold nanoparticles (2.45 mJ cm^{-2}) can reduce the ablation to a minimum but maximize a highly local DNA destruction nearby the nanoparticles simultaneously (see figure 11 bottom).

In the last experiment, gold nanoparticles attached to stretched DNA were identified and imaged prior to laser irradiation (not shown here). After laser treatment with single-photon excitation of the nanoparticles with a wavelength of 530 nm, the regions were relocated and imaged again. The image in figure 12 demonstrates the high spatial resolution of AFM that allows the identification of individual DNA structures as well as nanoparticles. After laser irradiation, the DNA is missing at regions directly adjacent to the particle (approximately 50–100 nm in each direction, see figure 12). This proves the effect of the laser-induced nanoparticle-mediated energy conversion.

6. Summary

A contactless, highly parallel and controllable heat conversion process based on 30 nm gold nanoparticles and femtosecond laser irradiation is demonstrated. Using single-photon excitation at 800 nm, 100 fs and intensities of 2.8 mJ cm^{-2} (almost) no ablation of the nanoparticles could be observed. The conversion of light energy to heat results in a small temperature increase per pulse, only in a highly localized subwavelength dielectric environment. By adjusting the pulse repetition rate of the femtosecond laser, a certain heat rate, temper cycle and cooling rate is possible. A very fast control of temperature between two pulses appears possible. Further experiments will explore the potential of the described principle in other fields that require nanolocal heat control such as ‘nanoreactors’, ‘nanowelders’, ‘nanocrystallizers’ or ‘nanodesorbers’ in nanochemistry, nanotechnology and medicine.

Using femtosecond laser irradiation (below the ablation threshold) with single-photon excitation on gold nanoparticles attached to DNA, the destruction of DNA adjacent to gold nanoparticles is theoretically discussed and experimentally demonstrated. However, in biological systems the green excitation wavelength could be absorbed by various other biological molecules which could be damaged, too.

Otherwise, using femtosecond laser irradiation and two-photon excitation on silver-enhanced gold nanoparticles in biological systems only heat conversion and destruction of biological systems (chromosomes) in combination with ablation and destruction of the sequence-specific bound metallic nanoparticle is possible.

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