Rare-earth fluorescence thermometry of laser-induced plasmon heating in silver nanoparticles arrays

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The laser-induced plasmon heating of an ordered array of silver nanoparticles, under continuous illumination with an Ar laser, was probed by rare-earth fluorescence thermometry. The rise in temperature in the samples was monitored by measuring the temperature-sensitive photoluminescent emission of a europium complex (EuTTA) embedded in PMMA thin-films, deposited onto the nanoparticles array. A maximum temperature increase of 19 °C was determined upon resonant illumination with the surface plasmon resonance of the nanoarray at the highest pump Ar laser power (173 mW). The experimental results were supported by finite elements method electrodynamic simulations, which provided also information on the temporal dynamics of the heating process. This method proved to be a facile and accurate approach to probe the actual temperature increase due to photo-induced plasmon heating in plasmonic nanosystems.

Nowadays plasmonic nanostructures find application in many different fields in nanophotonics, as light harvesting and manipulation1–3, fluorescence enhancement4–7, nonlinear optics8–13, biosensing14–20, surface-enhanced Raman scattering (SERS)21–23 and medical therapies24–26. For most of these applications, photo-induced heating is a key issue. On one hand, indeed, the use plasmonic nanostructures as nano-sources of heat and the engineering of the formation of photo-induced thermal hot-spots is at the basis of the emerging field of thermo-plasmonics27, with a variety of applications as optically-assisted drug delivery28,29, photo-thermal cancer therapy24–26,30,31, heat-assisted nanochemistry32–34, and recently the development of plasmonic nano-ovens35 or adaptive lenses36. On the other hand, unwanted photo-heating may represent a severe drawback in many cases, limiting device performances or causing strong sample modifications37,38. For instance when biological molecules are in close proximity to plasmonic nanostructures (e.g., in biosensors or in SERS spectroscopy) local spikes in temperature can cause alteration of their structure and thus their functionality. Moreover, the temperature increase upon external illumination and its spatial distribution in plasmonic nanoarrays were demonstrated to be dependent on the shape, composition and geometrical distribution of the nanostructures, and the conditions of illumination (cw or pulsed)39,40. In this context, the estimation of the actual temperature in plasmonic nanosystems is of paramount importance.

Different approaches have been developed during these years to probe the local temperature at the micro- and nano-scale41, which include scanning thermal microscopy (SThM)42, thermoreflectance microscopy43 and temperature-dependent Raman spectroscopy44. SThM provides the highest spatial resolution, but its major drawbacks are the slow readout rate and the need of contact between the scanning probes and the samples, which may create a thermal bridge and compromise the accuracy in the temperature measurement. The latter two are non-invasive and non-contact techniques, but are unsuitable for metallic surfaces (Raman) or require lengthy calibration procedures (reflectance). Recently two fluorescence-based techniques demonstrated to be very effective to probe the local temperature in the vicinity of metallic nanostructures: (i) fluorescence polarization anisotropy (FPA)45, which exploits the decrease of polarization anisotropy of the emitted fluorescence of specific...
The thickness of the PMMA layer was measured via ellipsometry, while the thickness of the Ag film and the nanoparticles’ height were obtained by AFM measurements.

**Experimental Section**

**Samples preparation.** Ordered arrays of silver nanoparticles were synthesized via nanosphere lithography (NSL). As the first step, a colloidal monolayer of polystyrene (PS) nanospheres was self-assembled on a sodalime-glass (SLG) substrate, according to the method proposed by Giersig et al. The colloidal monolayers were prepared using commercial PS nanospheres with diameter of 330 nm, purchased from Microparticles GmbH (Germany) as a 10% vol. water dispersion. The sodalime-glass substrates were cleaned with acetone in an ultrasonic bath for 2 minutes and then immersed in a “piranha” solution (3:1 mixture of concentrated sulfuric acid and 30% hydrogen peroxide) for half an hour, rinsed with deionized water and dried in a stream of nitrogen. Subsequently, silver was deposited over the monolayer of PS nanospheres by magnetron sputtering in orthogonal geometry. The samples were then immersed in toluene (purchased from Sigma Aldrich) for 2 minutes and sonicated for 1 minute to dissolve the PS nanoparticles and remove them from the substrate. After this step, an ordered array of silver triangular nanoprisms remains on the glass substrates. To finely tune the surface plasmon resonance properties of the nanoarray, and to maximize the absorption of the pump laser used to heat the plasmonic nanostructures in the fluorescence thermometry experiment, the samples were further annealed in air for 30 min at 350 °C. This treatment modifies the shape of the Ag nanostructures, which change from triangular nanoprisms to spheroidal nanoparticles, preserving their ordered arrangement.

A film of polymethylmethacrylate (PMMA) doped with the europium(III) thenoyltrifluoroacetonate complex (EuTTA, Acros Organics, 95%) was then deposited onto the Ag nanoparticles array (NPA). To obtain this film, a 10% PMMA (MW = 250,000) solution was prepared leaving PMMA in toluene in a oven at 70 °C overnight. In the same way a 50 mM solution of EuTTA in toluene was prepared (since at such a high concentration EuTTA is not stable at room temperature, the solution was used while warm). The PMMA and EuTTA solutions were then mixed together to obtain a concentration of 25 mM of EuTTA and 0.5% wt of PMMA in toluene. The prepared solution was immediately used for coating the silver nanostructures, using a G3P spin coater (Specialty Coating Systems) at 4000 rpm for 60 s. Two reference samples were also produced by depositing the EuTTA-doped PMMA thin-films by spin-coating on the substrates and can be easily removed once the thermal analysis is completed by rinsing the samples in acetone, which will dissolve the film in few minutes without affecting the plasmonic nanostructures making this method extremely effective for the measurement of the actual temperature increase due to photo-induced heating in plasmonic nanosystems.

**Structural and optical characterizations.** Scanning electron microscopy (SEM) measurements of the synthesized samples were performed using a Zeiss Sigma HD FE-SEM, operated at 5 kV and with the signal collected by the InLens secondary electrons detector. Atomic force microscopy (AFM) measurements were done using a NT-MDT Solver-PRO AFM microscope operated in non-contact mode. Optical extinction spectra of the samples were recorded using a JASCO V670 spectrophotometer in the 300–2100 nm range. The spectrophotometer was also equipped with an integrating sphere detector to measure the corresponding scattering spectra. A J. Woolham V-VASE spectroscopic ellipsometer was used to measure the dielectric functions of the EuTTA-doped PMMA layers, the SLG and the Ag film deposited by magnetron sputtering with the same conditions used for the samples.

**FEM simulations.** Optical and thermal simulations were carried out using the Finite Elements Method (FEM). The commercial software COMSOL Multiphysics was used. In the simulations, the honeycomb lattice of the samples in the xy plane was modeled by applying periodic boundary conditions (PBC) to a rhombic unit cell. The unit cell contains two plasmonic nanoparticles, which were modeled as oblated ellipsoids in order to reproduce the experimental shape. Consistently with the experimental values measured by SEM and AFM (described below), we setup a series of FEM models varying the size of the axes, to reproduce the dispersion.

| Sample label | Ag layer | EuTTA-PMMA |
|--------------|----------|------------|
| Eu-SLG       | none     | 20 ± 3 nm  |
| Eu-Ag, film  | continuous film (t = 127 ± 5 nm) | 22 ± 3 nm |
| Eu-Ag, NPA   | nanoparticles array (h = 22 ± 3 nm) | 20 ± 3 nm |

Table 1. Synthesis parameters of the samples investigated in the present work.
were always let under exposure of the \(N\) complex. For this reason, in order to minimize bleaching, the samples were kept in vacuum conditions, at a pres-

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Photoluminescence measurements. A pulsed \(N_2\) laser (emission wavelength \(\lambda_{N_2} = 337\) nm, pulse dura-

Results and Discussion

In Fig. 1a the SEM image in plane view of the synthesized samples is reported; the corresponding 3D AFM image is shown in Fig. 1b. The images show the formation of an ordered array of spheroidal nanoparticles arranged in a honeycomb lattice. From the analysis of these measurements, we determined the geometrical parameters of the nanoparticles: the in-plane radius \(R = 27 \pm 3\) nm and the height \(h = 22 \pm 4\) nm. The optical properties of the synthesized samples are reported in Fig. 1c. The extinction and scattering spectra were measured separately using a spectrophotometer equipped with an integrating sphere detector, while the absorption spectrum (red line in Fig. 1c) was obtained by subtracting the scattering contribution from the extinction spectrum. The graph shows that the absorption peak of the sample matches very well the spectral region in which the most intense lines (488 nm and 514.5 nm) of the Ar laser, used to pump the samples in the fluorescence thermometry experiment, are located. In particular, in the wavelength range 450–550 nm, more than 40% of absorption is obtained in the

In order to measure the heating of the samples, we also performed a pump-and-probe experiment using the multi-line cw Ar laser with a frequency of 2 Hz. A cw multi-line Ar laser was employed as the pump source for heating the samples. The three most intense lines of the Ar laser (concentrating about 70% of the total emitted power) are at 514.5 nm and 488 nm; no line selection was done for this experiment in order to maximize the incident power, close to the maximum of its excitation peak. The laser was operated in burst mode, with 128 pulses per burst at a

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In order to measure the heating of the samples, we also performed a pump-and-probe experiment using the multi-line cw Ar laser
as the pump source to excite the LSPR of the plasmonic nanoparticles arrays, thus inducing the heating of the nanoparticles. The N$_2$ pulsed laser was used as the probe, to excite the Eu$^{3+}$ luminescent emission of the EuTTA-doped PMMA layers. EuTTA, similarly to other $\beta$-diketonate complexes, exhibits a narrow emission band that can be excited upon UV excitation via a Dexter intra-molecular energy-transfer from the lowest triplet excited state of the ligands to the quasi-resonant energy state of the rare-earth ions (antenna effect). This step is crucial in determining the quantum yield and thus the temperature dependence of the Eu$^{3+}$ luminescence intensity. A sketch of the measurement configuration is reported in Fig. 2a. Particular care was taken to align the pump (Ar) and probe (N$_2$) laser beams on the same spot on the sample (the diameter of the illuminated spot was 1 mm), to make sure that the measured Eu$^{3+}$ PL signal was coming from the heated zone. During the measurements, the samples were placed in a cryostat with quartz windows, at a pressure lower than 0.5 mbar, and an external heater was used to maintain the sample holder at the constant temperature of 24 °C. In Fig. 2b we reported the temporally integrated Eu$^{3+}$ photoluminescence (PL) intensity (at $\lambda_{\text{Eu}^{3+}} = 613$ nm) of the three samples—Eu-Ag$_{\text{NPA}}$, Eu-Ag$_{\text{film}}$ and the reference sample Eu-SLG—measured switching on and off the pump Ar laser. To excite the Eu$^{3+}$ luminescence, the N$_2$ laser (probe) was operated in the burst mode, with 128 pulses per burst; the Eu$^{3+}$ PL signal was normalized to the energy of the N$_2$ laser which was simultaneously measured with an external photodiode. In the “laser on” configuration, the measurements were taken for three different values of the Ar laser power, corresponding to full power (173 mW), 2/3 of the maximum (116 mW) and 1/3 of the maximum (58 mW). Considering that the diameter of the illuminated spot on the sample is 1 mm, these values corresponds to power density values of 22.0 W/cm$^2$, 14.7 W/cm$^2$ and 7.3 W/cm$^2$, respectively. 5 measurements of the Eu$^{3+}$ PL signal were recorded for each configuration. To let the samples thermalize, the pump laser was shined on them for 5 minutes before performing the “laser on” measurements. Then the Ar laser was shut down and the samples were let cool down for 20 minutes before taking the “laser off” measurements. The results in Fig. 2b show that if the EuTTA-doped PMMA layer is deposited over the Ag nanoparticles array (sample Eu-Ag$_{\text{NPA}}$), the Eu$^{3+}$ PL signal exhibits a drastic decrease in intensity when the sample is illuminated by the pump laser. The effect is completely reversible and proportional to the pump power. A similar behavior is observed also with the sample Eu-Ag$_{\text{film}}$, in which the EuTTA-doped PMMA layer was deposited over a homogeneous silver film, but the PL intensity drop is much smaller compared to the nanostructured sample, and can be detected only using the pump laser at full power; no effect is visible at lower pump powers. Finally, regarding the reference sample Eu-SLG, no reduction of the Eu$^{3+}$ PL intensity is observed when the pump laser is shined on the sample, even for the highest pump power. Such a different behavior among the samples is consistent with the different absorption properties of the three samples in the spectral region of the pump Ar laser. Indeed, in the spectral range 450–550 nm, we estimated an average absorption higher than 40% for the Eu-Ag$_{\text{NPA}}$ sample, while it was about 7% for the Eu-Ag$_{\text{film}}$ sample and less than 3% for the reference sample Eu-SLG. Moreover, the results reported in Fig. 2b clearly show that the Eu$^{3+}$ luminescent emission intensity is correlated with the Ar power and thus can be used to determine the samples’ temperature. A comment has to be made at this point. The PL emission lifetime too was demonstrated to be temperature-dependent and thus could be used to determine the samples’ temperature as well.
Nonetheless, even if its measurement can be less affected by stray light or residual bleaching, the PL lifetime sensitivity to temperature changes resulted to be slightly lower than for the PL intensity. To highlight this, the following figures-of-merit can be introduced:

\[ S_I = \frac{\Delta I}{I_{\text{off}}} \quad \text{and} \quad S_\tau = \frac{\Delta \tau}{\tau_{\text{off}}} \]

where \( \Delta I = I_{\text{on}} - I_{\text{off}} \) and \( \Delta \tau = \tau_{\text{on}} - \tau_{\text{off}} \) are, respectively, the differences in intensity and lifetime of the Eu\(^{3+}\) PL emission when the pump Ar laser is turned on and off. \( S_I \) and \( S_\tau \) represent the sensitivity to temperature changes induced by the laser-heating that can be obtained in the two ways, and in the present case we get: \( S_I = -7 \times 10^{-3} \degree C^{-1} \) and \( S_\tau = -5 \times 10^{-3} \degree C^{-1} \). Moreover, it is important to note that the accurate estimation of the lifetime could get complicated if the luminescence temporal decay differs from a single exponential decay, as it is for the samples investigated in the present work. As an example, we reported as inset in Fig. 3(b) the temporal decay of the Eu\(^{3+}\) PL intensity of the Eu-Ag\(_{\text{NPA}}\) sample detected with the Ar pump laser off (black curve) and on (173 mW, blue curve); the light-red lines are the best stretched-exponential fits. The diameter of the illuminated spot was 1 mm.

Figure 2. (a) Schematics of the experimental configuration: the cw Ar laser was used to heat the plasmonic nanoparticles by absorption at their LSPR, while the N\(_2\) pulsed laser was used as the probe, to excite the Eu\(^{3+}\) luminescence; during the measurements, the samples were placed in a cryostat, under a vacuum (\( P < 0.5 \) mbar), and the sample holder was kept at a constant temperature of 24 \(\degree\)C. The diameter of the illuminated spot was 1 mm. (b) Eu\(^{3+}\) luminescence intensity upon illumination with the pump Ar laser at different powers, for the three samples investigated. A reversible, power-dependent drop of the Eu\(^{3+}\) luminescent intensity occurs when the EuTTA-doped PMMA layer is deposited on top of the silver nanoparticles array (sample Eu-Ag\(_{\text{NPA}}\)); a much smaller effect (detectable at the highest pump power only) appears for EuTTA on the homogeneous silver film (sample Eu-Ag\(_{\text{film}}\)), while no effect was observed from the reference sample in which EuTTA-doped PMMA was deposited on a soda-lime glass (sample Eu-SLG).

Figure 3. (a) Calibration curve of Eu\(^{3+}\) PL emission intensity versus temperature. (b) Temperature as function of the power of the pump Ar laser of sample Eu-Ag\(_{\text{NPA}}\). Inset: PL temporal decay of the sample with the pump Ar laser off (black curve) and on (173 mW, blue curve); the light-red lines are the best stretched-exponential fits. The diameter of the illuminated spot was 1 mm.

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For all these reasons, in the present work we preferred to use the same way, we determined a maximum temperature of 27 °C, up to 43 ± 2 °C when illuminated by the Ar laser at full power (173 mW). In the same way, we determined a maximum temperature of 27 ± 2 °C for the Eu-Ag_film sample, while no increase in temperature was measured for the Eu-SLG reference sample.

As mentioned above, the rise in temperature experienced by the Ag NPA can be related to the strong absorption of the Ar laser beam at the LSPR of the silver nanoparticles array (Fig. 1c). This is confirmed by the results of the thermal analysis performed by electrodynamic simulations. In Fig. 4a we reported the comparison between the measured and FEM simulated temperature of the silver nanoparticle array for the different pump laser powers. An optimal agreement between the simulations and the experimental data is obtained. Moreover, the results are consistent with the model proposed by Baffou and co-workers for photo-induced heating of plasmonic nanoparticle arrays upon continuous illumination. According to Baffou’s model in the case of cw illumination two different temperature regimes can be reached: a temperature confinement regime in which hot-spots of temperature are formed in proximity of the plasmonic nanostructures and a temperature delocalization regime where a uniform temperature is obtained throughout the whole nanoarray. In order to discriminate between these two regimes a dimensionless parameter—the 2D confinement parameter ζ—was introduced by the authors, defined as ζ = \( \frac{R}{2p} \), where \( p \) is the interparticle distance, \( L \) is the size of the illuminated area and \( R \) is the nanoparticles’ radius: for \( ζ < 1 \) the delocalization regime is reached, while values of \( ζ > 1 \) correspond to the regime of temperature confinement. In the present case we get \( ζ \approx 10^{-3} \), which indicates that the full delocalization of the temperature can be reached in the investigated nanoarray. This finding is further supported by the results of our FEM simulations. In Fig. 4b we reported the simulated temperature map of the Ag nanoparticle array, estimated in stationary conditions at the maximum pump power (173 mW). By looking at the color bar on the right, it emerges that at equilibrium the very same temperature is reached throughout the whole NPA and between the silver nanoparticles and the surrounding EuTTA-doped PMMA film. In particular, this result further confirms that EuTTA-doped PMMA thin films represent an accurate thermometric probe to estimate the actual temperature of plasmonic nanostructures. Furthermore, the simulations provided information on the time scales of the thermalization process. In Fig. 4c we plotted the evolution of the simulated temperature, as a function of time, for the three values of the pump laser power: at all the three powers the temperature grows exponentially, with the same time constant \( τ_\text{th} = 0.44 ± 0.01 \text{ ms} \), and thus the sample’s surface reaches the stationary temperature in about 2 ms. During the experiment, the samples were always let thermalize under Ar pump laser for about 5 min before taking the PL measurements, that is for a time interval \( Δt >> τ_\text{th} \). In this way the stationary regime was definitely reached, which further guarantees the accuracy of the temperature estimate obtained by the measurement of the Eu³⁺ luminescence intensity.
As a final remark, we would like to underline that the results of the present method are not restricted to the particular case-study presented. Our samples were designed to have (i) low absorption at the Eu excitation intensity of the N_{2} laser (to avoid unwanted spurious temperature rises), (ii) high absorption at the Ar heating laser. Indeed, if the heating laser matches the samples’ plasmonic resonance, whose absorption cross-section is the highest, the expected temperature variation is the largest. Accordingly, if the working wavelength of the heating laser is out of the main plasmonic resonances, the expected temperature rise will simply scale linearly with the reduced cross-section.

Conclusion
Rare-earth fluorescence thermometry has been employed to measure the laser-induced plasmon heating of an ordered array of silver nanoparticles synthesized by nanoparticle lithography, upon illumination with a cw Ar laser. EuTTA-doped PMMA thin-films deposited by spin-coating on the samples have been used as the thermometric probe, by monitoring the temperature-dependent Eu^{3+} photoluminescence emission in the visible range. Proper thermal treatments of the silver NPA have been performed in order to match the surface plasmon resonance of the nanoarray with the main lines of the pump Ar laser to maximize the photo-induced heating of the samples. In this condition, a maximum temperature increase of ΔT = 19°C has been determined in the silver nanoarray, upon illumination at the maximum power of the pump Ar laser (173 mW). The experimental findings have been supported by the results of FEM electrodynamic simulations, which provided also information on the temporal dynamics of the heating process: an exponentially-saturated rise in temperature was evidenced at all the three pump powers employed, with a time constant τ = 0.44 ± 0.01 ms. In conclusion, rare-earth fluorescence thermometry with EuTTA-doped PMMA thin-films proved to be a facile and accurate method to probe the actual temperature increase due to photo-induced plasmon heating in plasmonic nanosystems. Moreover, the moderate rise in temperature evidenced – even at the highest pump laser power – is interesting particularly considering the use of plasmonic nanoparticles arrays as intensity-interrogated sensors for bio-molecules, which could be denatured by an excessive temperature increase. Typically lamp sources with a much lower power are used for the measurements with plasmonic biosensors, but the present results indicate that also higher power cw laser can be safely employed.

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**Author Contributions**

G.M. conceived the experiments. G.P. prepared the samples. T.C., G.P., G.P. B.K. conducted the experiments and analysed the data. N.M. performed simulations. G.P. G.P. and T.C. wrote the manuscript. All authors reviewed the manuscript.

**Additional Information**

**Competing Interests:** The authors declare no competing interests.

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