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Flexible thermo-plasmonics: Mechanically actuated control of the photo-induced heat generation

G. PALERMO(1)(2)

(1) *Department of Physics, University of Calabria - Cosenza, Italy*
(2) *CNR-Nanotec - 87036 Cosenza, Italy*

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Summary. — Thermoplasmonics is a new field of Plasmonics in which metallic nanostructures are used to generated heat at the nanoscale. This research area has developed rapidly in the last decade, due to the several applications in nanophotonics, nanomedicine and in many other fields. In this paper, the process of photo-induced heating in this kind of structures is described. A characterization of the heat delivered by a uniform distribution of gold nanoparticles on solid and flexible substrate is reported, along with different methods to control the effects.

1. – Introduction

It is well known that a radiation with a specific wavelength impinging on a metallic nanoparticle can induce the electrons of the conduction band to oscillate coherently with the electric field of the incident light [1]. This leads to a strong absorption, which occurs in the UV-visible region of the spectrum depending on the kind of material, size and shape of the nanostructure. This phenomenon, known as Localized Plasmon Resonance (LPR), represents a way to confine energy in such small nano-objects, which consequently result out of the equilibrium state [2, 3]. The damping of the motion of free charges, due to electron-electron scattering and electron-phonon coupling, yields an increase in the temperature of the nano-object with the resulting heating of the surrounding medium. The way this heating can be controlled and used represents the *hot topic* of Thermoplasmonics [4, 5].

This topic has rapidly developed in the last years, due to countless application areas, such as nanomedicine, photonics, optoelectronics and so on. One of the most important applications in this research field is represented by Plasmonic Photo-Thermal Therapy (PPTT), in which the NPs are driven in cancer cells and burn them selectively, without damaging the healthy tissues surrounding the cancer [6-9]. Another possible application is related to the possibility of photo-releasing drugs or genes bonded to the NP surface [10, 11], or the possibility to locally control the fluid convection or the formation of bubble in a micro-fluid channel [12-14].

Most of the studies carried out so far have aimed at the determination of the heat delivered by a single NP or a limited number of nano-objects, usually arranged in ordered structures, such as arrays or matrices [6,15,16]. In particular, it was shown that, in order to calculate the heat delivered by a single NP, we have to consider the heat power density Q that is related to the absorption cross section σ_{abs} of the NP and to the intensity of the impinging light I by the relation $Q = \sigma_{abs} I$ [4,5].

Then, in a single NP, the temperature increase ΔT with respect to the environment temperature T_0 is directly proportional to Q [17]. The idea behind this work is to move toward systems made of a huge number of NPs, uniformly distributed on a glass substrate and on a flexible polymer to introduce an innovative method to control the photo-induced heat.

2. – Results and discussion

2˙1. *Glass substrate.* – Gold nanoparticles (AuNPs), with a diameter of about 20 nm, were synthesised by exploiting a slightly modified Turkevich method [18]. The substrate is a glass slide, whose surface was properly treated with a Piranha solution (a 3:1 mixture of concentrated sulphuric acid and hydrogen peroxide) for 45 min that yields a negatively charged surface. Next, the substrate was rinsed with copious amounts of water and dried under a stream of compressed air. Substrates were functionalised by dipping in a 5% (v/v) solution of N-[3-(trimethoxysilyl) propyl] ethylenediamine in ethanol for 30 min in order to obtain positively charged surfaces; then, the substrates were rinsed with water, dried, and further put in an oven at 110 °C for a 40 min. The process of NPs deposition was realised by dipping the substrates in a solution of colloidal AuNPs for a specific time that represents a key parameter in the process of deposition of the AuNPs. In fact, by modifying the immersion time in the colloidal solution, it is possible to obtain a different surface density of the NPs (number of AuNPs on μm^2). To estimate the dependence of the photo-heating on the surface density of the NPs we have examined two samples characterised by different values of NPs surface density. We indicate as sample A the sample characterized by a surface density of about 350 NPs μm^{-2}, and indicate as sample B the one characterized by a surface density of 700 NPs μm^{-2}. Realised samples are characterised by the presence of AuNPs on both sides of the substrate; thus, to evaluate the active role of a single NPs layer, a peel off of the NPs from one side is performed in both samples.

Figure 1(a) shows the absorbance of the two samples obtained, which can be compared to the absorption cross section of the NPs, since, for small nanoparticles (radius $<\lambda/10$), the scattering cross section σ_{sca} is negligible, and the extinction cross section σ_{ext} can be considered equal to σ_{abs}. Both samples exhibit the plasmonic peak at 505 nm.

To monitor temperature variations, a continuous green laser (532 nm) impinges perpendicularly on the samples and the collective photo-thermal response is acquired by means of a thermographic camera (E40 by FLIR) characterized by a sensitivity of 0.07 °C and a spatial resolution of 2.72 mrad. Control parameters are appropriately set to take into account both environmental and material properties. Measurements are made at light intensity intervals of 0.2 in the range from 0.2 to 1.2 Wcm^{-2}.

By monitoring temperature values of the central pixel of each hot spot, corresponding to the warmest point, it is possible to plot temperature variation $\Delta T = T - T_0$ *vs.* the impinging intensity (T is the maximum temperature acquired for a specific intensity of the pump beam, T_0 is the sample temperature when the pump beam is off). Figure 1(b) shows that a linear increase of ΔT is observed as a function of I in both samples. This

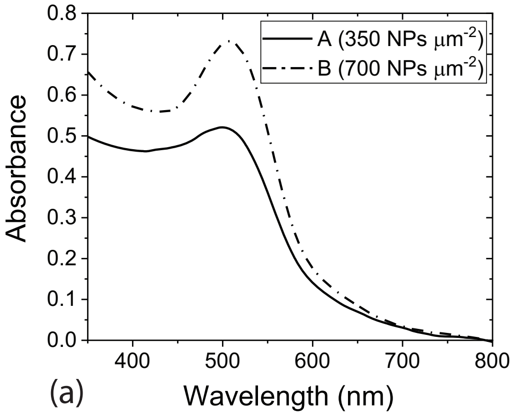

Fig. 1. – Spectral response of AuNPs distribution on glass substrate (a) and temperature response (b) *vs.* intensity for samples A and B.

is due to the linear relation between the heat power density Q and the I intensity pump reported above. The maximum measured ΔT for sample A is $(3.0 \pm 0.5)\,°\mathrm{C}$, while, for sample B, it is $(6.0 \pm 0.5)\,°\mathrm{C}$. These results, that do not depend on the polarization of the pump beam, are in agreement with studies carried out on the collective effect of metallic nano-objects simultaneously excited [16,19,20]. The photo-thermal response of this kind of samples, in fact, strongly depends on the number of NPs, as the resulting temperature variation is related to the contribution of all the nanoparticles that are acted on by the resonant laser light. This means that for a uniform distribution, in which the distance between nanoparticles is such that coupling effects between them can be neglected, the temperature variation ΔT can be controlled by acting on the surface density of the NPs. Depending on the immersion time of the glass slide in the nanoparticle solution it is possible to obtain samples with different values of NPs surface density.

A way to control the temperature variations in samples of this kind is represented by the possibility to change the medium surrounding the AuNPs; σ_{abs}, in fact, strongly

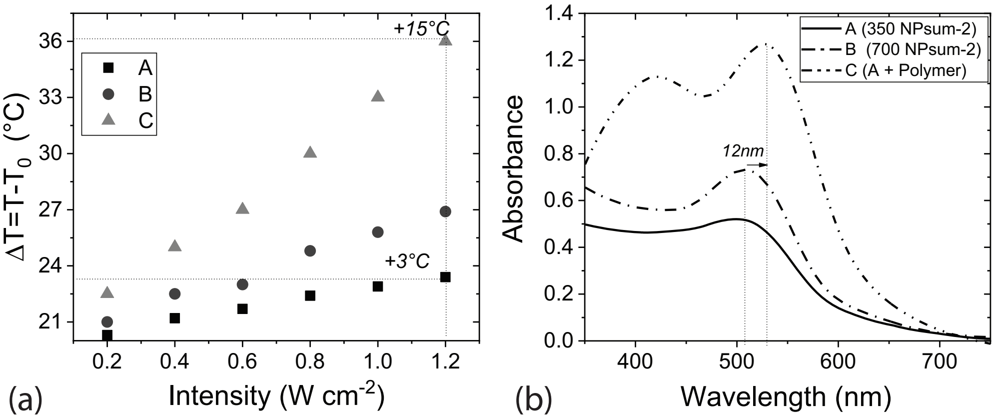

Fig. 2. – Temperature response *vs.* intensity for samples A, B and C (a) and spectral response of the three samples (b).

depends on the polarizability which in turn depends on the dielectric permittivity ε_H of the surrounding medium [1,3,21,22].

This was demonstrated by depositing a polymer characterized by a refractive index $n_p = 1.61$ on sample A (this new sample is referred to as sample C). In this new sample the temperature variation corresponding to the maximum light intensity is equal to $(15.0 \pm 0.5)\,^{\circ}\mathrm{C}$ (fig. 2(a)). This is a consequence of the variation of σ_{abs} (fig. 2(b)) that results to be ≈140% higher than the value obtained for sample A, characterised by the same NPs surface density but with air as surrounding medium. The observed red-shift of 12 nm of the plasmonic peak for sample C (fig. 2(b)) is due to variation of the dieletric permittivity too: in fact, both amplitude and position of the LPR depend on the value of ε_H [1]; the band centered at 410 nm is characteristic of the polymer deposited.

2˙2. *PDMS substrate.* – Up to now, we have seen that it is possible to control the photo-induced temperature variation of AuNPs by acting on the excitation intensity or on the absorption cross section; in this latter case we can play on the choice of the surrounding medium or on the number of photo-excited nanoparticles at the same time.

A different method to control the heat produced by metallic nanostructures can be obtained by controlling the plasmonic coupling between the nano-objects. In the previously investigated samples, the AuNPs were fixed onto the glass substrate with a fixed inter-distance between them. We consider now a new kind of sample, in which the NPs are attached to a flexible substrate as polydimethylsiloxane (PDMS). In order to vary the interdistance between NPs, a stretching setup, able to finely stretch the sample of a small percentage, was developed. It consists of two clamps, whose distance is mechanically controlled by means of micrometer screw gauge. In order to have a reversible deformation of the sample, we consider a maximum value of stretching percentage of about 20%, which guarantees that the elastic regime of the material is not overturned. The protocol of functionalization of the PDMS substrate is the same used in the case of glass; by using the same immersion times of the flexible substrate in the AuNPs solution we obtain similar values of surface density. The setup used to monitor the temperature variation and the laser source used to produce the photo-thermal effects are the same used for the experiments with the AuNPs on the glass substrates. This time, both spectral and thermal analysis are carried out for two specific polarizations of the impinging

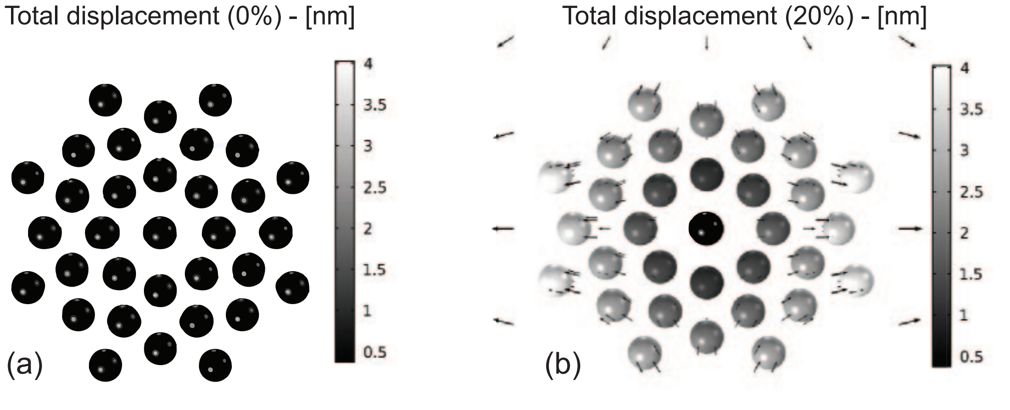

Fig. 3. – Displacement arrangement of the unit cell corresponding to the sample at rest (a) and under stretching of 20% (b).

light, perpendicular and parallel to the stretching direction, respectively. This is because when the sample is stretched, the AuNPs cannot be considered uniformly distributed on the substrate and a new disposition of the nano-objects is obtained for them. Figure 3 shows the NPs distribution on the PDMS substrate at rest (a) and for the maximum percentage of stretching considered (20%) (b) corresponding to an applied strain of 17 KPa. The arrows in fig. 3(b) represent the direction of the applied strain.

It is now worth nothing that, in the case of the stretched disposition (fig. 3(b)), we obtain the formation of AuNPs *chains* due to the elastic nature of the substrate. Indeed, when an elastic material as PDMS is stretched in a given direction, a corresponding compression in the direction perpendicular to the stretching one is obtained; this leads to an approach of the AuNPs in the direction perpendicular to the stretching direction.

Figure 4 shows the absorbance of the AuNPs on PDMS substrate for visible light polarized parallel (fig. 4(a)) and perpendicular (fig. 4(b)) to the stretching direction, respectively, with the sample at rest, stretched at 10% and 20%. As we can see, in the case of light polarization parallel to the stretching, a decrease and a red-shift of about 4 nm are detected while, in the case of light polarization perpendicular to the stretching,

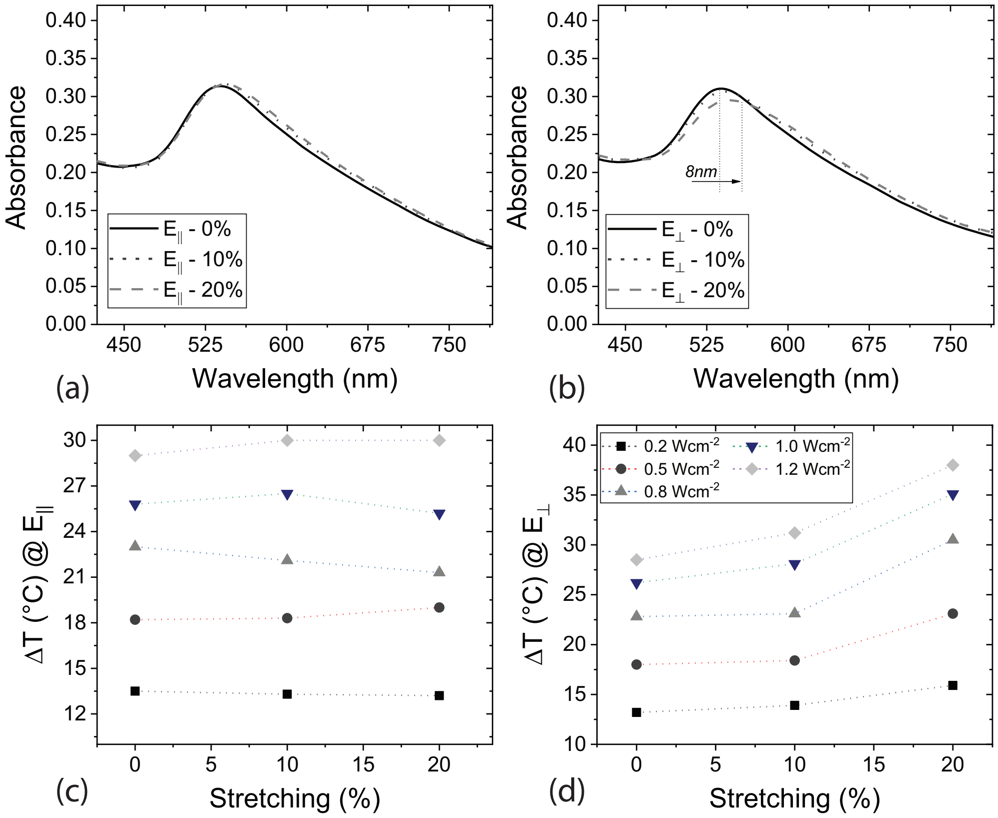

Fig. 4. – Spectral response of the sample acquired while increasing the applied strain from the rest condition (0%) to 20% stretching for a white light probe polarized parallel ($E_{\parallel}$) (a) and perpendicular ($E_{\perp}$) (b) to the stretching direction. Temperature variations of the sample as a function of the stretching percentage induced by irradiating with a CW green laser (532 nm) polarized parallel (c) and perpendicular (d) to the stretching direction.

a the red-shift of about 8 nm and a more pronounced decrease are observed. These results are in agreement with the studies carried out by Caputo *et al.* [23-26], whose aim was to obtain an active control of the plasmonic properties of metallic NPs.

Thermal analysis is performed by considering the same stretching percentages as in the spectral analysis. For the three cases (sample at rest, 10% and 20% of stretching) the intensity I of the cw laser light (532 nm) is varied in the range 0.2–1.2 $\mathrm{Wcm^{-2}}$. An increase in the impinging light intensity, in accordance with the case of the AuNPs on the glass substrate, leads to an increase in the temperature variations. Once the intensity of light is fixed, samples are stretched and the corresponding variation of temperature is acquired. In the case of light polarized parallel to the stretching direction ($E_{\|}$), the variation of temperature ΔT results to be almost indipendent of the stretching percentage (fig. 4(c)) while, in the case of of the light polarized perpendicular to the stretching direction ($E_{\perp}$), the variation of temperature ΔT increases as the percentage of stretching increases. ΔT_{MAX}, defined as the difference between the highest temperature measured when irradiating with the highest intensity and the enviroment temperature remains almost constant when increasing the stretching in the case of $E_{\|}$, while it varies by about $(15.0 \pm 0.5)\,^{\circ}\mathrm{C}$ in the case of $E_{\perp}$. In the latter case the ΔT_{MAX} is not in accordance with the detected decrease of σ_{abs}.

2˙3. *Numerical approach.* – In order to explain the observed photo-thermal behavior, a numerical simulation is carried out by means of the Finite Element Method Simulator (Comsol Multiphysics 5.4), by considering a distribution of AuNPs that can well represent a unit cell of the sample. To estimate the total displacement (fig. 3) and the distribution of the electric field (fig. 5) the Solid Mechanics and Electromagnetic Wave-Frequency Domain Module were used [27-29]. To arrange the NPs in accordance with the real distribution we have taken into account that their distribution on the PDMS substrate is driven by the electrostatic force, in a configuration that maximizes the distance between them. These inter-particle distances are compared with the distance estimated by the Scanning Electron Microscopy analysis of the samples.

The electric field distribution shows an increase in its value which, in the case of stretched geometry, for $E_{\perp}$ light (fig. 5(b)), is three times higher than the value obtained in the sample at rest (fig. 5(a)). This behavior, that is quite different from the other cases, shows the formation of NPs chains due to the compression of the sample in the direction perpendicular to the stretching direction. The close proximity of the AuNPs yields the appearance of hot spots responsible for increasing the temperature. The procedure is totally reversible and repeatable. The relation between the temperature variation and the enhancement of the near field is an open study which we are working on [30].

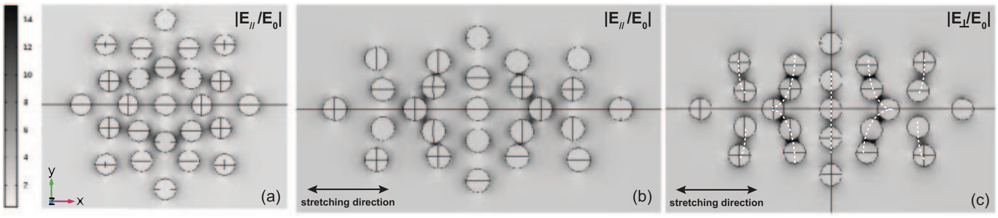

Fig. 5. – Finite element method simulations reporting the plasmonic field distribution around the AuNP arrangement in rest condition (a) and under 20% stretching, for an exciting beam with $E_{\|}$ and $E_{\perp}$, respectively.

3. – Conclusions

In this paper we report on the possibility to exploit an innovative method to control the generation of heat by using metallic nanoparticles (AuNPs) immobilized on a glass substrate. We have shown that a finely control of the temperature variation can be obtained by acting on the intensity of a resonant laser light, on the number of NPs that are photo-excited at the same time and on a change of the material surrounding them. We define this approach as "static approach", in which no modification of the inter-particle distance occurs. If the AuNPs are attached on a flexible material as PDMS, a new scenario opens to control the photo-induced heating. In this case, indeed, the application of a mechanical strain leads to a modification of the inter-particle distance responsible for a re-arrangement of the NPs distribution which, in its turn, yields the behavior of the system which depends on the polarization of the impinging resonant light. This study represents a preliminary analysis of a new opto-mechanical control of thermoplasmonic properties of metallic nanoparticles.

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