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Monolayers of gold nanostars with two Near-IR LSPR capable of additive photothermal response

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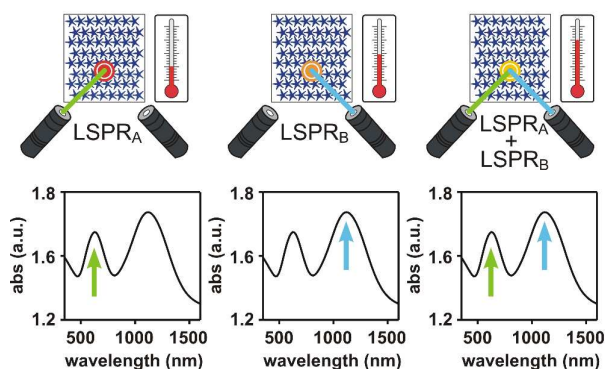
Monolayers of photothermally responsive gold nanostars on PEI-coated surfaces display two Localized Surface Plasmon Resonances (LSPR) in the near-IR region that can be laser-irradiated either separately, obtaining two different T jumps, or simultaneously, obtaining a T jump equal to the sum of what obtained with separate irradiations.

Gold nanostars (GNS) are gold nanoparticles with a central core and three or more branches protruding from it, displaying a set of remarkable chemical and physical properties.[1] GNS typically have two localized surface plasmon resonances (LSPRs), one falling at 500-550 nm (due to the transveral oscillation of the valence electrons in their branches) and one falling between 600 and 1200 nm due to the longitudinal oscillation of the electrons along the branches.[2,3] As for all noble metal nanoparticles, the radiation strongly absorbed by LSPRs is converted into heat via the fast (2-5 picoseconds) electron-phonon coupling with the metal lattice followed by phonon-phonon processes on the 100-400 picosenconds timescale.[4] The LSPRs of GNS may fall in the biologically transparent near-IR window (NIR, 750-1100nm) and GNS use for antitumoral[5,6] and antibiofilm[7] non invasive photothermal laser treatments has been envisaged. However, for through-tissues photothermal medical applications,[8] low intensity sources are to be used.

Scheme 1 Pictorial representation of the rationale behind this paper. The absorption spectra in the lowest row are the actual absorption spectra of the slides used in this work (Figure 1D, red, not normalized)

As an example, ANSI, the American National Standard for Safe Use of Lasers, has stated that for long skin exposure (0.1-500 min) the maximum allowed irradiance is 0.22 W/cm^2 at 700 nm, 0.32 W/cm^2 at 800nm and 1.00W/cm^2 in the 1050-1400nm range.[9] In this communication we present nanostructured surfaces that have more than one intense LSPR in the NIR range. These can be irradiated in two different wavelength ranges using one, the other or both NIR LSPRs as pictorially described in Scheme 1. Such surfaces may be of great interest, as they would allow to reach high local temperatures by the addititve action of two converging laser beams, each one kept at low irradiance. For this we used GNS with a fairly regular shape (five-branched, see Figure 1A) recently described by us[10] that feature three LSPR bands. The LSPR at the shortest wavelength (550 nm) is very weak and it is due to the transversal oscillation of the valence electrons of the branches (and to some undeveloped spherical objects). The intermediate and longest wavelength LSPRs give instead intense absorptions whose position can be tuned by reaction conditions between 600 and 900 nm (LSPR$_A$) and 1050 and 1600nm (LSPR$_B$). We have now made monolayers of such GNS on glass slides, pre-modified with a layer of polyethyleneimine (PEI) silane, on which GNS adhere with a kinetically controllable process.

Heat transfer from laser-irradiated gold nanoparticles in colloidal solutions is a complex process. Observed ΔT values are proportional to laser irradiance, sample absorbance, heat capacity of the sample and Au concentration.[11] The solution's temperature reaches a maximum value in several minutes, due to slow heat diffusion in the solvent and to self-filtering effects exerted by concentrated nanoparticles, decreasing the solution volume effectively irradiated by the laser beam.[10,11] We bypass most of these disadvantages by using a monolayer of GNS that are solvent-free and directly exposed to the laser beam. Moreover we measure T with a thermocamera (see ESI S1), an instrument that reads temperature on the surface of objects. In addition, being the target bidimensional, two laser beams can be easily focalized on the same spot. At the best of our knowledge, simultaneous laser-irradiation of two different LSPRs of the same nanoparticle has never been reported. LSPR$_A$ and LSPR$_B$ are separated by a 450-600 nm gap, depending on synthetic conditions. Our constraint is to have GNS with both LSPRs matching our available laser sources. Accordingly we choose the conditions[10] necessary to obtain LSPR$_A$ at ~ 680 nm and LSPR$_B$ at ~1320 nm in their colloidal solution (ESI S2.2.1 for details). Figure 1D shows the solution absorption spectrum (black dashed line) and Figure 1A shows a TEM image of these GNS. PEI-silane grafting on glass is already described[12] (ESI S2.3 for preparation details), based on the well established silane monolayers chemistry. GNS adhesion on glass slides takes place by deeping the PEI-silane

pre-coated slides in a GNS colloidal solution (Au = 60 μg/mL) for 7-18 hours. By adhering on PEI-coated glass, $LSPR_A$ and $LSPR_B$ shift to the blue reaching ~ 630nm and ~ 1100 nm (see Figure 1D, solid colored spectra) almost exactly
5 matching the wavelengths of 633 nm and 1064 nm of two of the laser sources at our disposal.
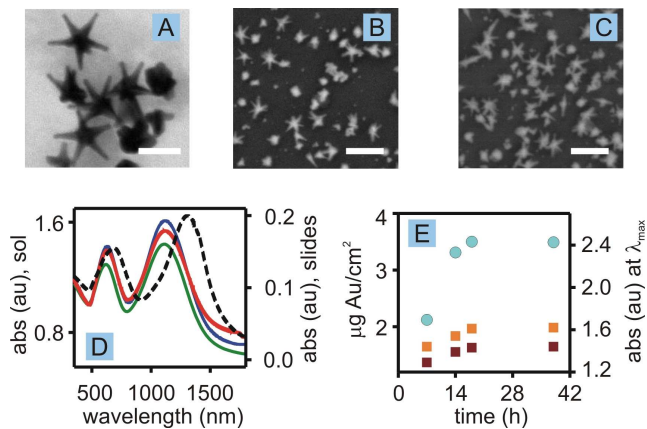

Fig.1 A: TEM image of the used GNS from their colloidal solution (scale bar 50 nm). **B**: SEM BSE image of the GNS monolayer on a PEI-coated
10 glass slide, 7 hours immersion time (scale bar 200 nm). **C**: same as B, after 14 hours immersion time. **D**: absorption spectrum of GNS colloidal solution (black dashed, right vertical axis) and of the GNS monolyar obtained from it with 7 (green), 14 (red) and 18 (blue) hours immersion time (left vertical axis). The spectrum for 38 hours immersion time is
15 almost identical to that at 18 hours and not shown. **E**: surface concentration of gold on the glass slides used for the photothermal experiments vs immersion time (cyan circles); absorbance (normalized at 486 nm) vs immersion time of the same glass slides on the LSPR maxima (625 nm brown squares, 1115nm orange squares)

20 To give a hint about the possibilities of this approach, it must be stressed that GNS with different aspect ratio of the branches and different LSPR position can also been grafted on the PEI-coated slides. As an example we synthetized and used GNS with $LSPR_A$ at 835 and $LSPR_B$ at 1530nm (ESI S2.2.2)
25 observing analogous LSPR shifts on the slides (ESI S3, TEM and SEM images are also included), with the grafting process kinetically controllable as for the GNS with shorter wavelength LSPRs (see below). Amines binding on Au nanoparticles is generically attributed to coordinative or even
30 covalent[13] interactions. As we used colloidal solutions of GNS at neutral or slighlty acidic pH, we believe that in our case also electrostatic interactions are to be considered, taking place between the partially protonated PEI and the weakly negative GNS surface (Z = -9 mV). The blue shift of LSPRs
35 from solution to monolayers formed on slides is due to the change in the GNS local refractive index (*n*), following the medium change from water (*n* = 1.333) to air (*n* = 1.0003). The linear LSPR shift with *n* is a known phenomenon.[14] We investigated it in our case by grafting GNS on the internal
40 wall of a glass cuvette pre-coated with PEI and by recording absorption spectra after filling the cuvette with solvents of different *n* (ESI S4). We found a λ shift of 120nm/RIU (refractive index unit) for $LSPR_A$ (the used solvents strongly absorb over 1100 nm, preventing reliable measurements on
45 $LSPR_B$).
The intensity of the LSPRs absorption of glass slides is a

function of the duration of the PEI-coated surfaces immersion in the GNS solution. We also analyzed the quantity of gold actually grafted on glass vs time of immersion by GNS
50 oxidation with aqua regia and ICP-OES analysis (inductively coupled plasma optical emission spectroscopy). A linear increase is found for both LSPR absorption and Au surface concentration, turning into a plateau at 18h, Figure 1D and 1E, with densities of 2.12, 3.31 and 3.50 μg Au/cm^2 for the
55 examined slides prepared with 7, 14 and 18 h immersion time (see the analogous behaviour of the slides prepared with GNS with higher aspect ratio in ESI, S5). SEM-BSE (back scattered electrons) images taken at representative immersion times of 7h and 14h are shown in Figure1B-C, respectively. The
60 pictures agree with the observation that the surface density is proportional to the immersion time (larger images in the ESI, S6).
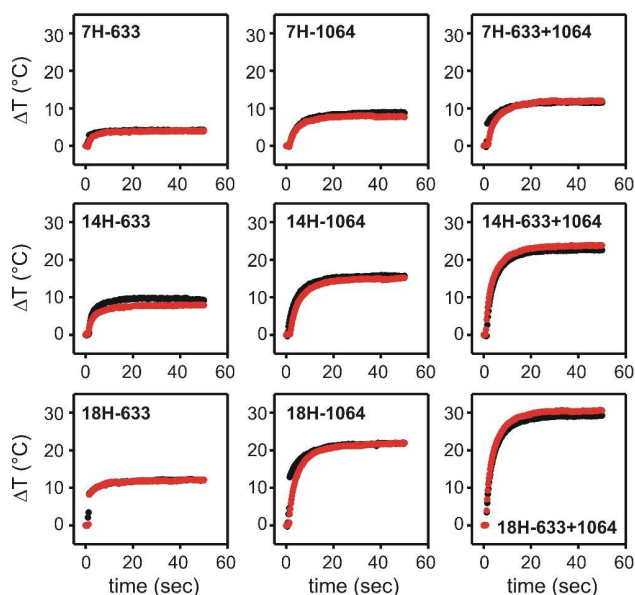
Fig.2 Thermograms (ΔT vs time) for the examined couples of slides.
65 Legends inside each graph indicate the coating time (7, 14 or 18 hours) and the applied laser source(s). Point of the same color (black or red) indicate, in each row, the data collected on the same slide. Time is expressed in seconds and ΔT in °C in all cases (some legends have been omitted for sake of graphical clarity)

70 The photothermal behaviour of three couples of slides prepared with 7, 14 and 18 h immersion times in GNS solutions have been studied using our laser sources at 633 nm (30 mW power, beam waist 0.5 mm, 15.3 W/cm^2 irradiance), and 1064 nm (50 mW power, beam waist 1.2 mm, 4.4 W/cm^2
75 irradiance). The difference in irradiance between the 633nm and 1064nm sources is unfortunately unavoidable, due to the instrumentation available in our laboratories (ESI, S1.2). However, it does not affect at any extent the significance of the experiments. Thermograms where recorded first
80 irradiating at 633 nm, then at 1064nm and finally, with the two lasers beams converging on the same spot, irradiating simultaneously at 633 nm and 1064 nm. Figure 2 illustrates the results of the full set of experiments. The thermograms for each slide (black and red points for slide 1 and 2,
85 respectively) are expressed as ΔT (T_t-T_0) vs time. A steady

state is attained very rapidly, the maximum temperature being reached after ~ 10 seconds. More in detail, all thermograms can be fit to a double exponential growth with growth times $\tau_1 = 1.6 \pm 0.4$ s and $\tau_2 = 7.8 \pm 1.0$ s (ESI, S7). These are independent of the surface density of the slides (i.e. immersion times) and of the irradiation wavelength. The growth times are shorter than those measured on gold nanostars suspensions ($\tau_1 = 4.8 \pm 0.4$ s and $\tau_2 = 100 \pm 22$ s)[15] and are probably due to the thermal diffusion on the slide surface through the gold layer from the irradiated spot (faster) and from this to the environment through air (slower). As a further example of the difference with what we found in the aqueous colloidal solutions of analogous GNS,[10] T plateau was reached after 4 minutes. Moreover, using the same 1064nm laser source and identical irradiance as here, we observed a plateau ΔT of only 7 °C on solutions containing these GNS at a concentration as high as ~ 600 µg Au/mL.[10] Irradiation of $LSPR_B$ yields a larger ΔT than irradiation of $LSPR_A$, even though the 1064nm laser source has a lower irradiance than the 633nm one, in agreement with the larger absorbance and extinction coefficient of $LSPR_B$, see Figure1D. Moreover, Figure 2 shows that ΔT values are additive: irradiating simultaneously at 633nm and 1064nm gives ΔT values at the plateau that, for each slide, are the sum of the ΔTs obtained irradiating the single LSPRs. This corresponds to the behaviour pictorially described by Scheme 1. It is often stated in the literature that irradiation at a plasmon resonance results in the collective excitation of all the valence electrons of a nanoparticle.[4,15] Apparently, what happens here is the excitation of all valence electrons in two simultaneous different modes (corresponding to $LSPR_A$ and $LSPR_B$) and their simultaneous electron-phonon relaxation, a process that may appear impossible. However, using the low-power continuous laser sources of our experiments, we excite just a fraction of the valence electrons, as it is made obvious by the observation that ΔT values depend linearly on the laser power impinging on the sample surface, in the power interval allowed by our instruments (0-30 mW and 0-50 mW for the 633 and 1064 source, respectively). Moreover, as we have hypothesized in the original paper on the preparation of these GNS,[10] the two transversal collective resonant electron oscillations ($LSPR_A$ and $LSPR_B$) are due to the presence, in each nanostar, of single branches and of co-linear couples of branches. In the latter case the LSPR absorption takes place at a largely red-shifted wavelength, in agreement with what happens when gold nanoparticles aggregate forming elongated objects.[16,17] We may thus also hypothesize that the conduction electrons involved in each LSPR belong to separate gold domains, that behave independently both as regards electron excitation and electron-phonon (i.e. thermal) relaxation.

Thanks to the tunability of both LSPRs positions through the seed-growth synthetic process[10], the obtained monolayers represent the prototype of GNS-based surfaces capable of reaching three different levels of temperature by irradiation of two LSPRs in the NIR biotransparent range (700-1100 nm). In perspective, in the case of a prothesis or an implant affected by biofilm formation, with a nanostructured surface as that presented here a progressively increased local bactericidal[10] T

increase could be obtained by through-tissues irradiation of $LSPR_A$ or $LSPR_B$ or both, keeping irradiance in each case under the allowed safety values.

Notes and references

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