Electronic Supplementary Material (ESI) for Chemical Communications

TritonX-100 for three-plasmon gold nanostars with two photothermally active NIR (near IR) and SWIR (short-wavelength IR) channels

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Electronic Supplementary Information

S1. Experimental details

Materials. TritonX-100, Tetrachloroauric acid, Sodium borohydride, Ascorbic acid (AA), Silver Nitrate, Thioctic acid were all purchased from Sigma-Aldrich and used without further purification PEG_{2000}-SH (α-Methoxy- ω - Mercapto poly(ethylene glycol) was purchased from Iris Biotech. Bidistilled water was used in all preparations.

Synthesis. In a typical preparation, the seed solution was prepared in a 20mL vial. 5mL of $HAuCl_4$ $5*10^{-4}$M in water are added to 5mL of an aqueous solution of TritonX-100 0.1M (or 0.2 or 0.3 M). The mixture is gently hand-shaken and a pale yellow colour is obtained. Then, 0.6mL of a previously ice-cooled solution of $NaBH_4$ 0.01M in water are added. The mixture is gently hand-shaken and a reddish-brown colour appears. The seed solution is kept in ice and used in few hours.
The growth solution was prepared in a 20mL vial, 250µL of $AgNO_3$ 0.004M in water, 5mL of $HAuCl_4$ 0.001M in water are added in this order to 5mL of an aqueous solution of TritonX-100 0.2M. Then, a140-400µL volume of an aqueous solution of ascorbic acid 0.0788M are added. The solution, after gentle mixing, becomes colourless. Soon after, 12µL of the seed solution are added. The solution is gently hand-shaken and a grey colour appears and quickly changes to green and becomes more intense. The samples are allowed to equilibrate for 1h at room temperature. The glassware used for seed-growth methods was always pretreated before use. It was washed in aqua regia for 30 min, then washed and filled with bidistilled water and ultrasonicated for 3 minutes before discarding water. The bidistilled water/ultrasound treatment was repeated 3 times.

Coating procedures
A solution of PEG_{2000}-SH $5*10^{-3}$M in water is prepared. 0.1mL of this solution are added to 10mL of the equilibrated GNS grown solutions. This quantity is in 1:10 molar ratio with respect to the total Au in solution (5×10^{-3} mmol). The obtained solution stirred for 1h at RT. Centrifugation (13000 rpm, 11 minutes) allows to collect a pellet of the PEG-coated nano-objects, that is redissolved in 10 mL bidistilled water. Excess PEG_{2000}-SH is discarded with the supernatant.

Quantitative Au determination
We used Inductively Coupled Plasma atomic emission spectroscopy analysis (ICP-OES). 2.0 mL of solution of PEG_{2000}SH-coated GNS were centrifuged and redissolved four times, then treated with 400µL of freshly prepared aqua regia. After the addition of aqua regia immediate oxidation is observed. Each sample was then diluted 1:20 with bidistilled water and analyzed at ICP-OES to determine the Au and Ag content. Data were collected with an ICP-OES OPTIMA 3000 Perkin Elmer instrument

Instrumentation

- UV-Vis spectra were taken on Cary 50 Varian, Cary 6000 and HP8453 instruments, using glass or quartz cuvettes (1 cm).

- Centrifugation was carried out using the ultracentrifuge HermleZ366 with polypropylene 10mL tubes. Before use the test tubes were rinsed then filled with water

and ultrasonicated for 3 minutes. Water was discarded and the washing cycle repeated twice. Ultracentrifugation speed was in the 11000-13000 rpm range.

• Zeta potential was measured with a Zetasizer Nano ZS90 Malvern instrument, equipped with dedicated cuvettes.

• Transmission Electron Microscopy (TEM). Solutions of $PEG_{2000}SH$-coated GNS were diluted from 10 to 100 times with bidistilled water. 10 μL were deposited on nickel grids (300 mesh) covered with a Parlodion membrane and allowed to dry in a dessicator. Images were taken using a JEOL JEM-1200 EX II 140 instrument.

• HighResolution Transimission Electron Microscopy. HRTEM imaging was performed by using a Jeol JEM 2200FS TEM/STEM working at 200 kV. The microscope was equipped with a field emission electron source, a Jeol Si(Li) EDS spectrometer and a CEOS corrector of objective lens spherical aberration. The ultimate point resolution achieved was 0.9 A in HRTEM mode.

• Differential scanning calorimetry measurements were carried out with a DSC Q2000 apparatus interfaced with a TA 5000 data station (TA Instruments, New Castle, DE, USA). The instrument was calibrated using ultrapure (99.999%) indium (melting point = 156.6 °C; ΔH = 28.54 J g^{-1}). The analyses were performed on about 5 mg of sample in open standard aluminium pans under nitrogen flow (45 mL min^{-1}) at a scanning rate of 10 K min^{-1} in the temperature range between – 10 °C and 250 °C. All quantitative data from thermal measurements are the average of three experiments.

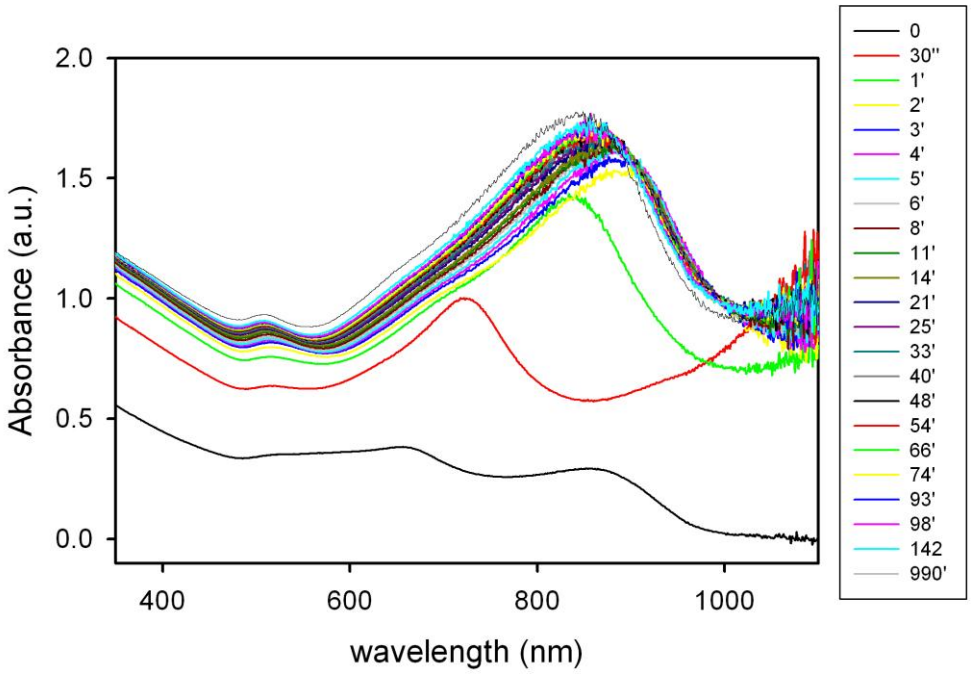
• Thermogravimetric measurements were performed by a TGA Q5000 IR apparatus interfaced with the TA 5000 data station too. Thermogravimetric curves were recorded in a standard alumina holder under a nitrogen flow (3L $h^{-}1$) at a heating rate of 10 K min^{-1} in the temperature range between 25 °C and 600 °C.

• Thermograms. We employed a ThermaCAM SC 3000 (FLIR Systems) camera (320x240 microbolometers array) operating in the spectral range of 8-9 μm and a numerical aperture NA = 0.46 x 0.34. The acquisition frequency is 9 Hz with a sensitivity of 0.1°C and an accuracy of ±0.2°C. For direct measurements of the temperature increase of GNS solution under irradiation, 0.6 mg/ml solution of $PEG_{2000}SH$-coated GNS were placed in plastic wells (Nunc, Labtek, D) and irradiated by a collimated 1.2 mm (waist) tunable NIR laser (MaiTai Spectra Physics, CA), working in continuous wave. The thermocamera, placed at a distance of 0.5 m from the sample, measured the heating until a plateau level was reached (typically in a 3-4 minutes) of the GNSs solution. The temperature as a function of time was obtained from a ROI selected on the thermal image.

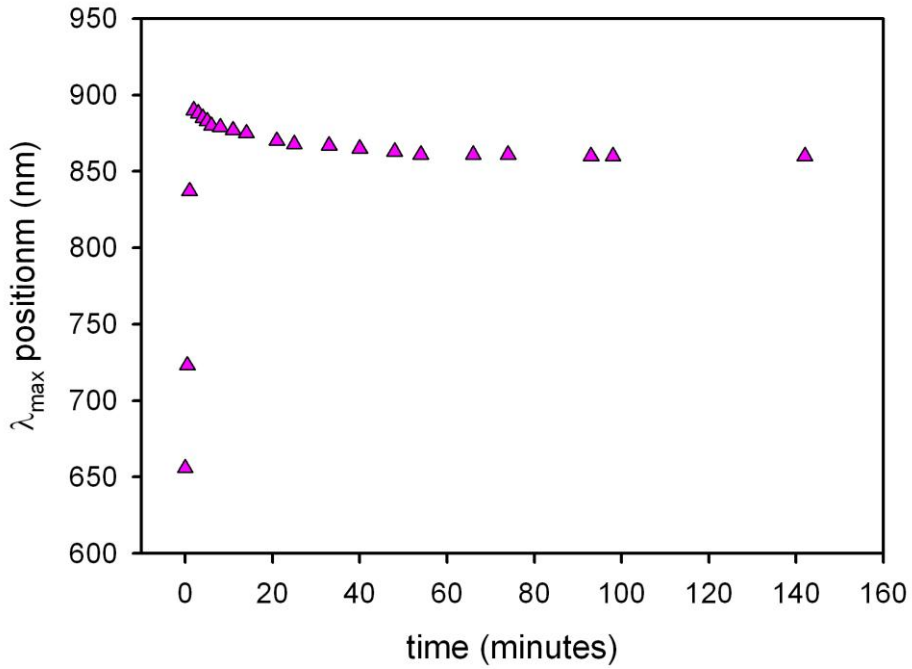
• Two-Photon Luminescence. The two-photon excitation fluorescence imaging was performed on a confocal scanning microscope (BX51 equipped with FV300, Olympus, Japan) modified for direct (non-descanned) detection of the signal and coupled to a femtosecond Ti:sapphire laser (MaiTai, Spectra Physics, CA). The microscope was equipped with a highly efficient water immersion objective (N.A. = 0.95, 20×, water immersion, Olympus, Japan), and the TPL emission was filtered through a short-pass 670 nm filter (Chroma Inc., Brattelboro, VT) and selected by a band-pass filter at 535 nm (Chroma Inc., Brattelboro, VT, HQ535/50).

GNS drop cast on glass cover slides were imaged and on selected Regions of Interests (ROIs) the emission spectrum was acquired by means of a CCD (DV420A-BV, Andor, IRL)-based spectrometer (MS125, Lot-Oriel,UK), connected to the back port of the microscope. The excitation wavelength is variable in the range 730–920 nm with a constant average power on the sample of about 2 mW. Each spectrum is the result of the accumulation of 10–20 acquisitions of 1 s duration.

S2 . Time evolution of growth solution

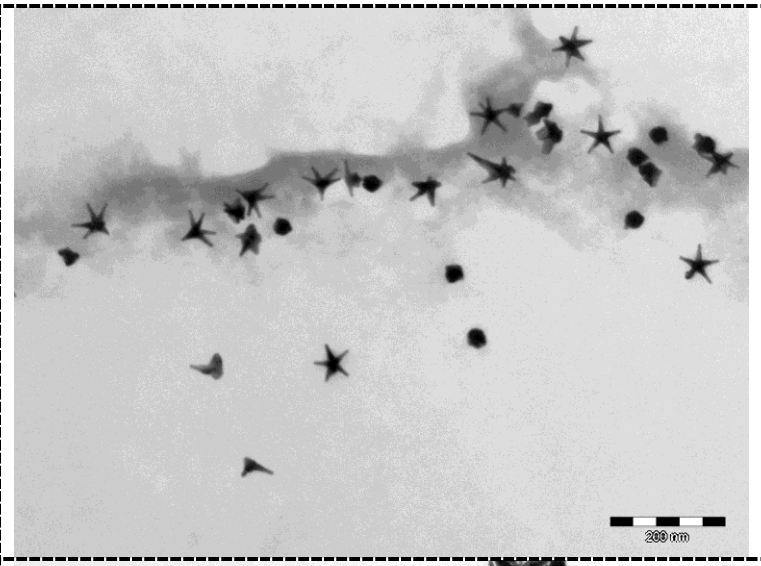
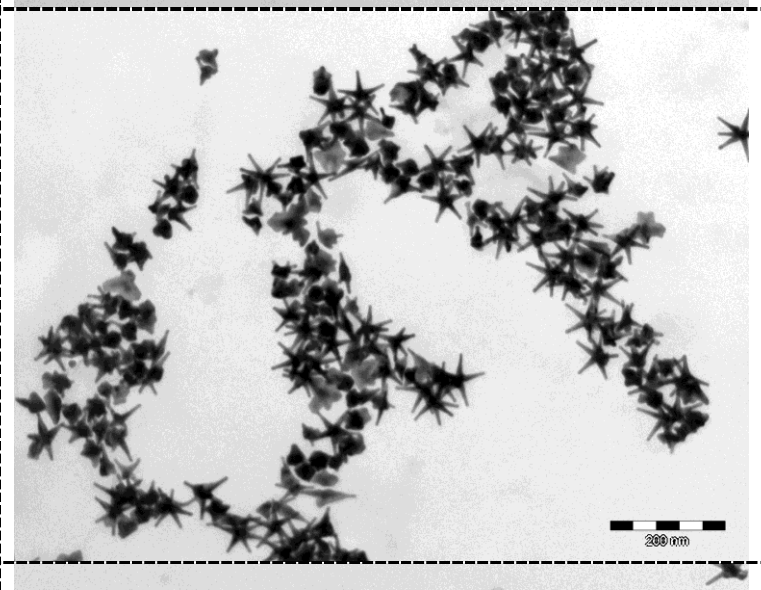
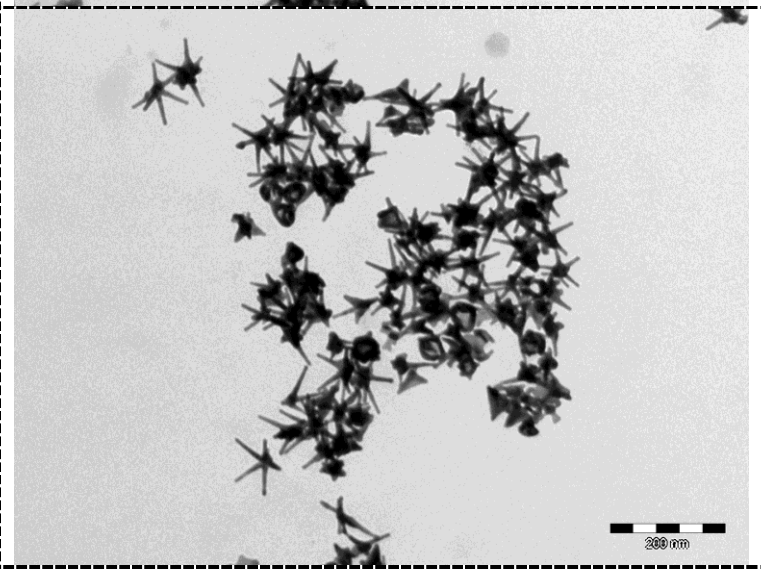


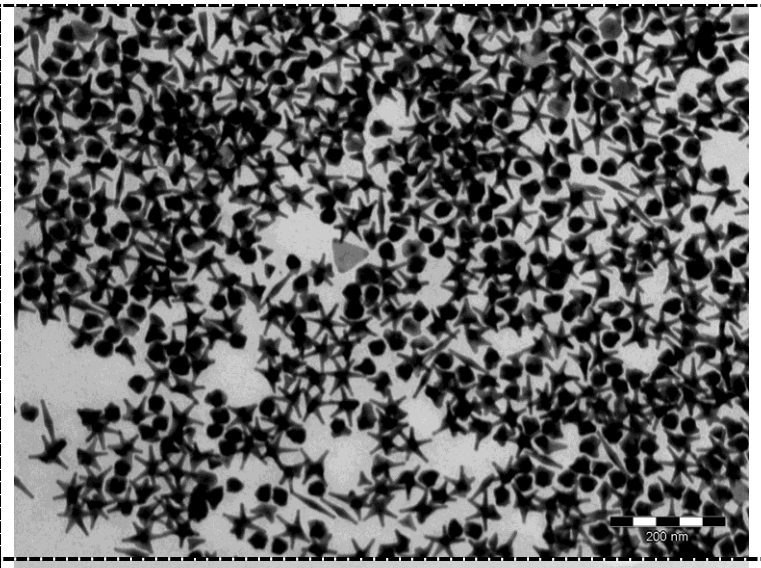
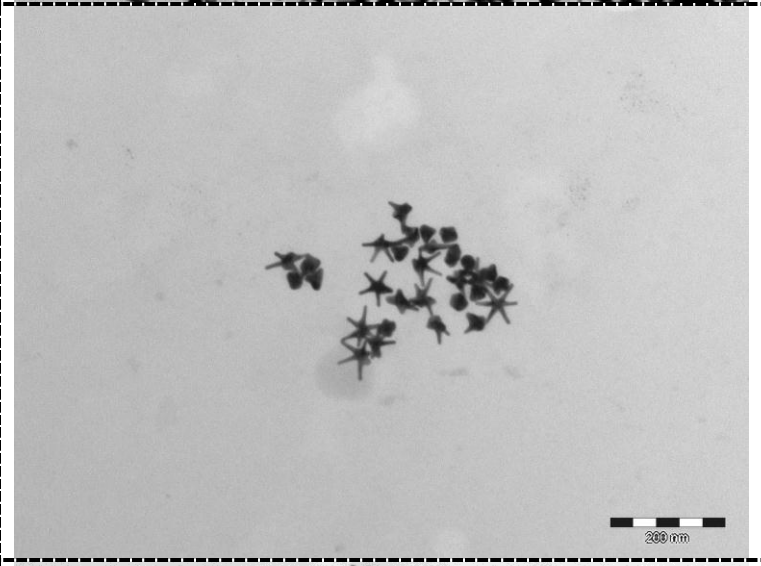
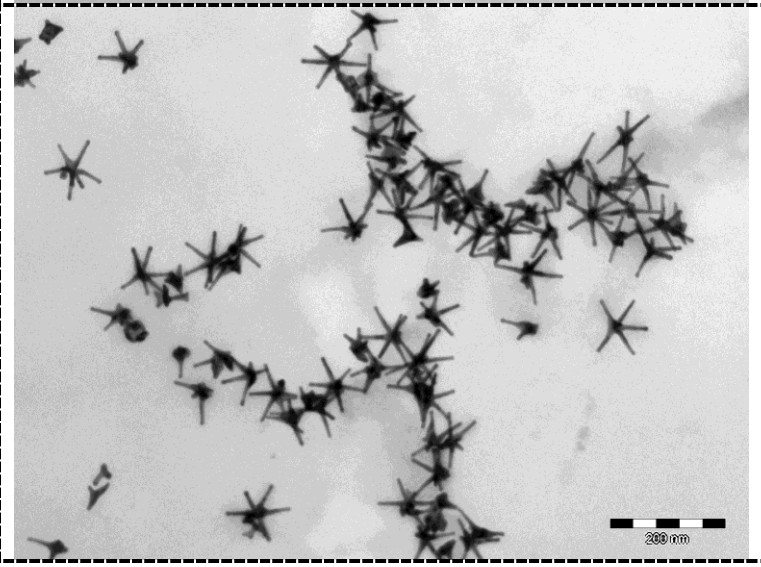
A: UV-Vis-NIR absorption spectra of a growth solution, Triton X-100 0.1M, Ascorbic Acid 1.734×10^{-3}M



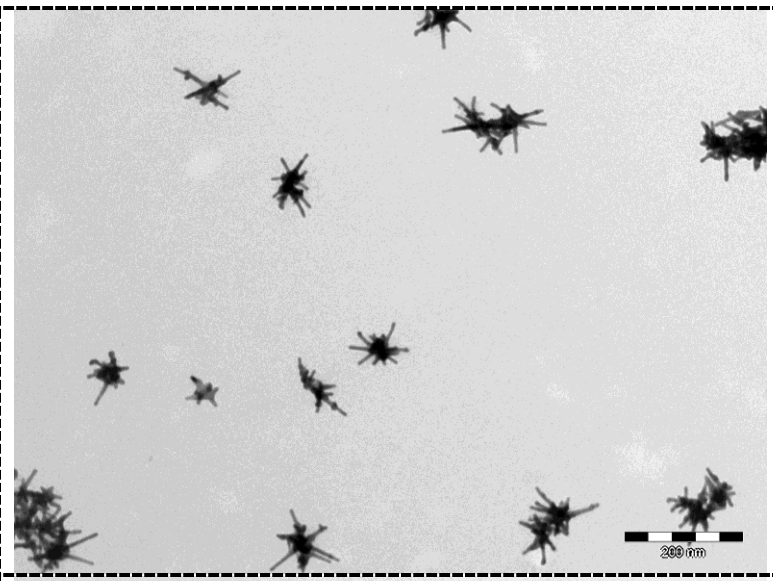
B: position of absorption maximum of the intermediate LSPR as a function of time (data taken from the series of spectra shown above)

S3 – TEM images for GNS obtained under various synthetic conditions

	synthetic conditions: TX100 0.05 M [AA] = 1.576×10^{-3}M scale bar = 200 nm
	synthetic conditions: TX100 0.05 M [AA] = 1.97×10^{-3}M scale bar = 200 nm
	synthetic conditions: TX100 0.05 M [AA] = 3.152×10^{-3}M scale bar = 200 nm

	synthetic conditions: TX100 0.15 M [AA] = 8.274×10^{-4} M scale bar = 200 nm
	synthetic conditions: TX100 0.15 M [AA] = 1.024×10^{-3}M scale bar = 200 nm
	synthetic conditions: TX100 0.15 M [AA] = 1.340×10^{-3} M scale bar = 200 nm

S4 – Multibranched object, formed at high [AA] concentration

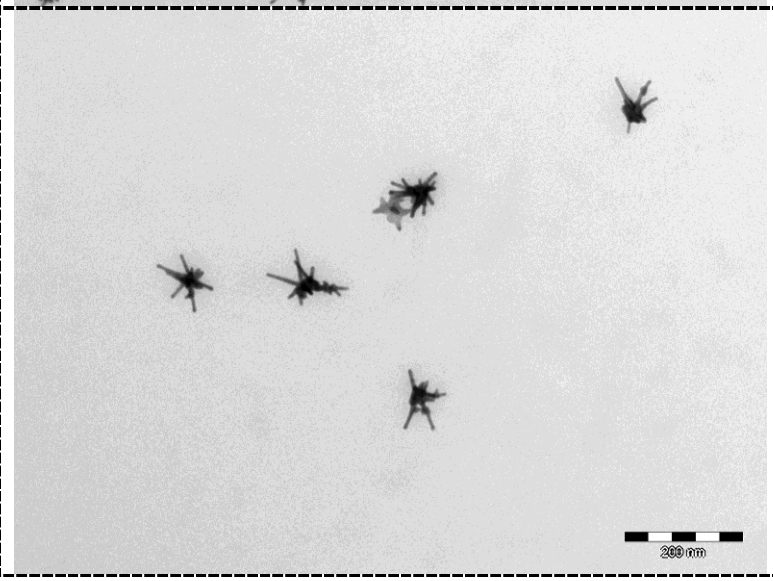


TEM image

synthetic conditions:

[TX100] = 0.10 M
[AA] = 4×10^{-3} M

scale bar = 200 nm

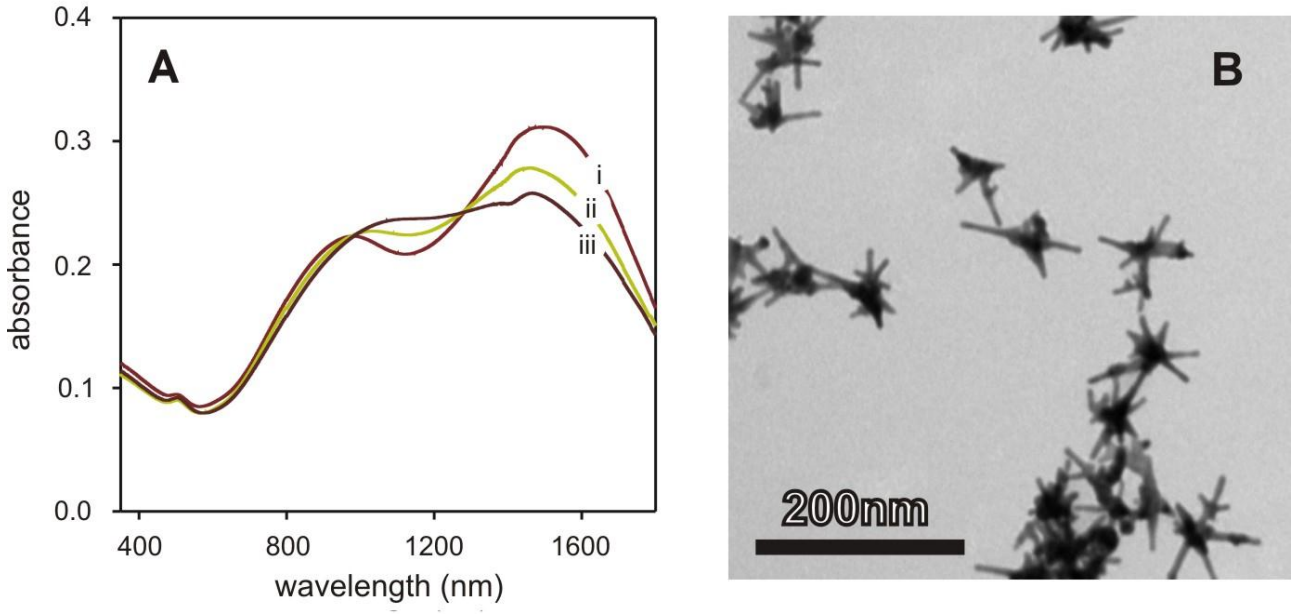


TEM image

synthetic conditions:

[TX100] = 0.15 M
[AA] = 3×10^{-3} M

scale bar = 200 nm



A: absorption spectra in the 350-1600 nm range on growth solutions obtained in 0.050 M TX100 at high [AA]: (i) 4.280×10^{-3}M; (ii) 6.304×10^{-3}M; (iii) 7.880×10^{-3}M. **B**: TEM image of GNS obtained from the solution of spectrum (iii)

S5 – Yields.

Yields have been calculated with this procedure: at the end of the growth process of a typical 10 mL sample, GNS were coated with PEG-SH and then underwent 4 cycles of ultracentrifugation, separation, redissolution in 10.0 mL bidistilled water. At the end of the 4th cycle we can consider that any unreacted Au (i.e. not in form of nanoobjects) is removed. 2.0 mL of the pegilated and purified GNS solution are fully oxidized with 400µL of freshly prepared aqua regia. The sample is then diluted 1:20 with bidistilled water and analyzed at ICP-OES to determine the Au content. This is compared with the quantity of Au added at the beginning of the growth process ($5x10^{-6}$ mol Au)

TX100 = 0.05 M

[AA] (mol/L)	Yield Au(%)
$8.27x10^{-4}$	83
$1.02x10^{-3}$	83
$1.34x10^{-3}$	81

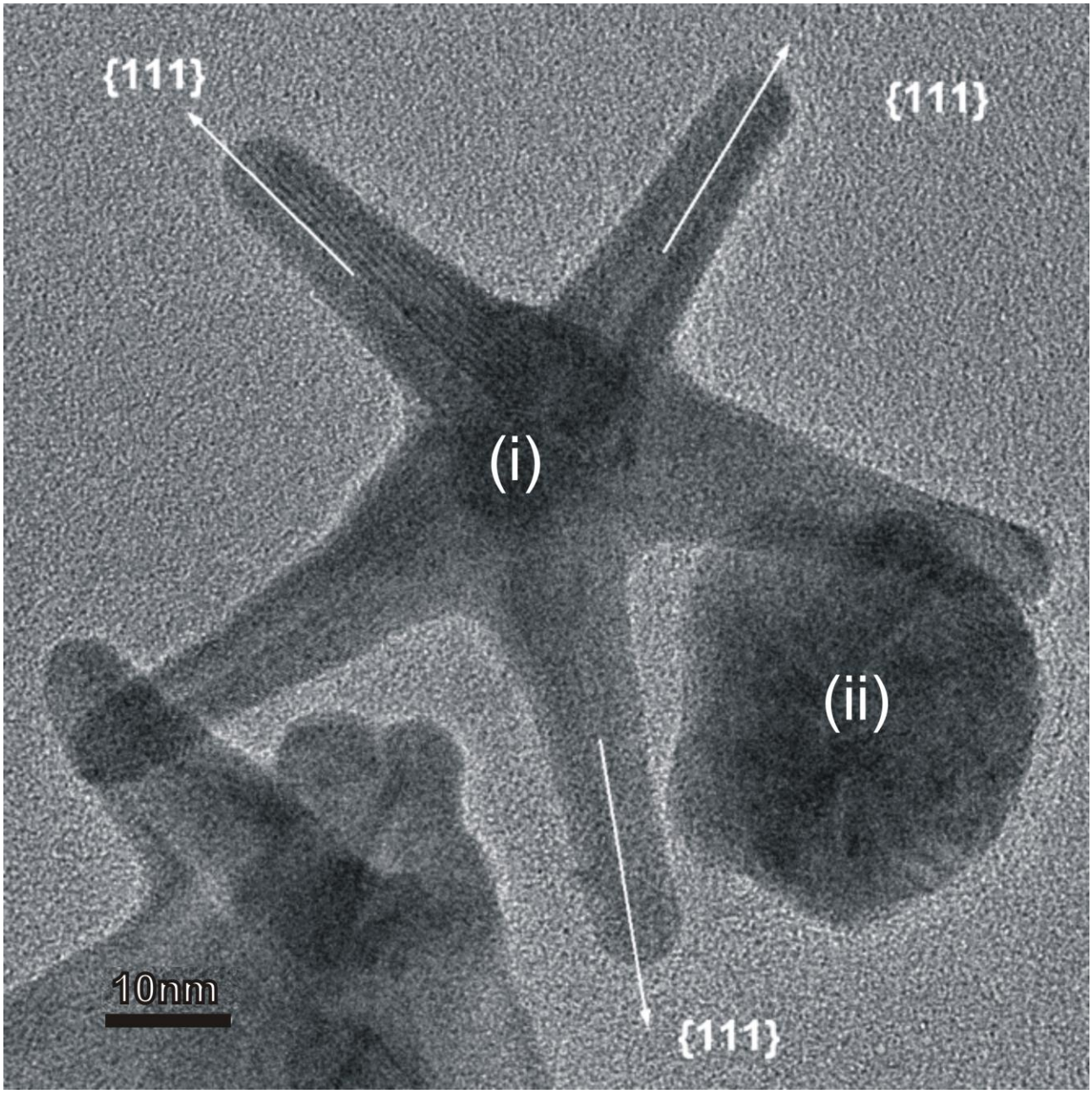
TX100 = 0.10 M

[AA] (mol/L)	Yield Au(%)
$1.10x10^{-3}$	59
$1.34x10^{-3}$	68
$1.97x10^{-3}$	64

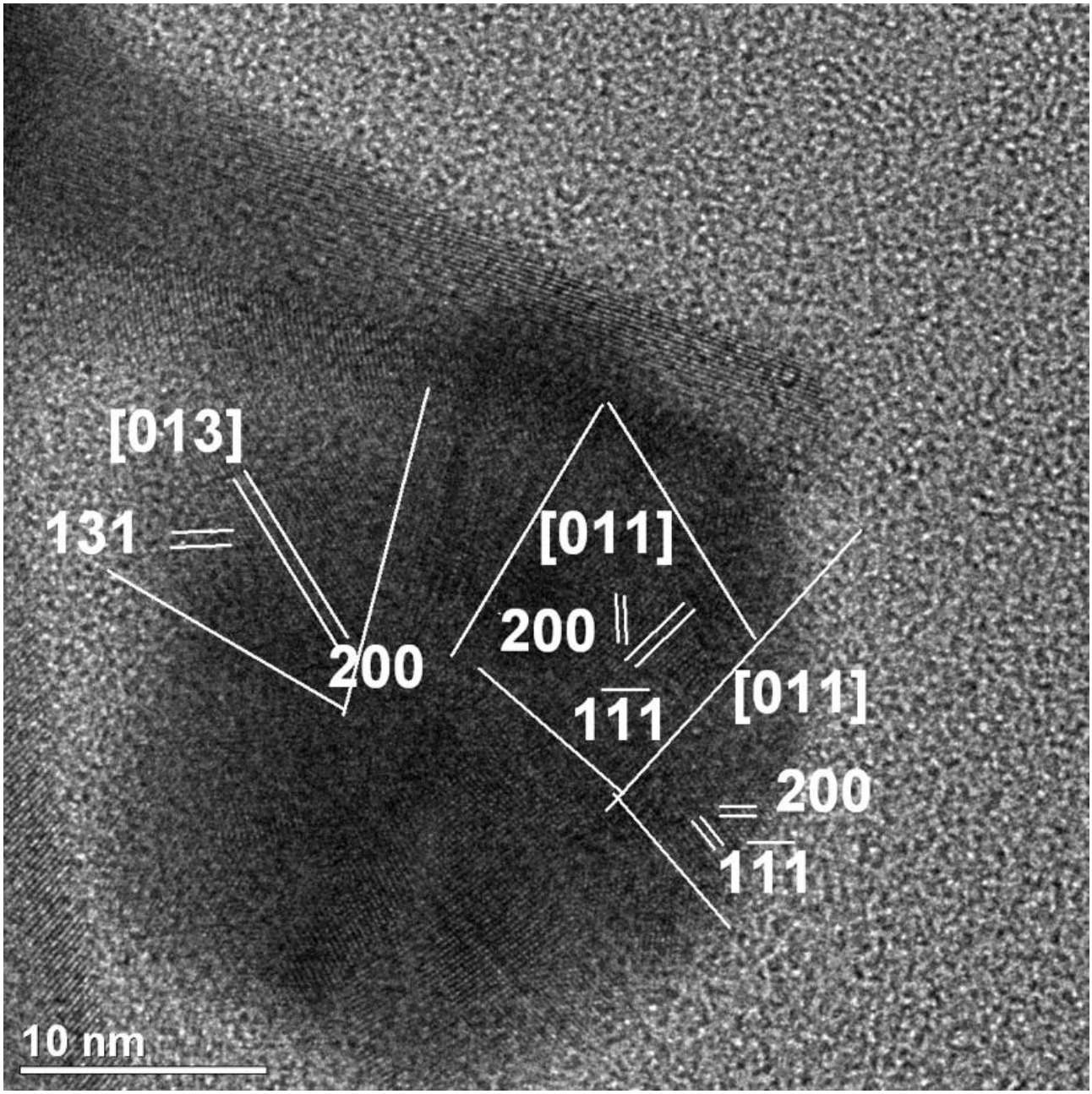
TX100 = 0.15 M

[AA] (mol/L)	Yield Au(%)
$8.27x10^{-4}$	70
$1.02x10^{-3}$	70
$1.34x10^{-3}$	75

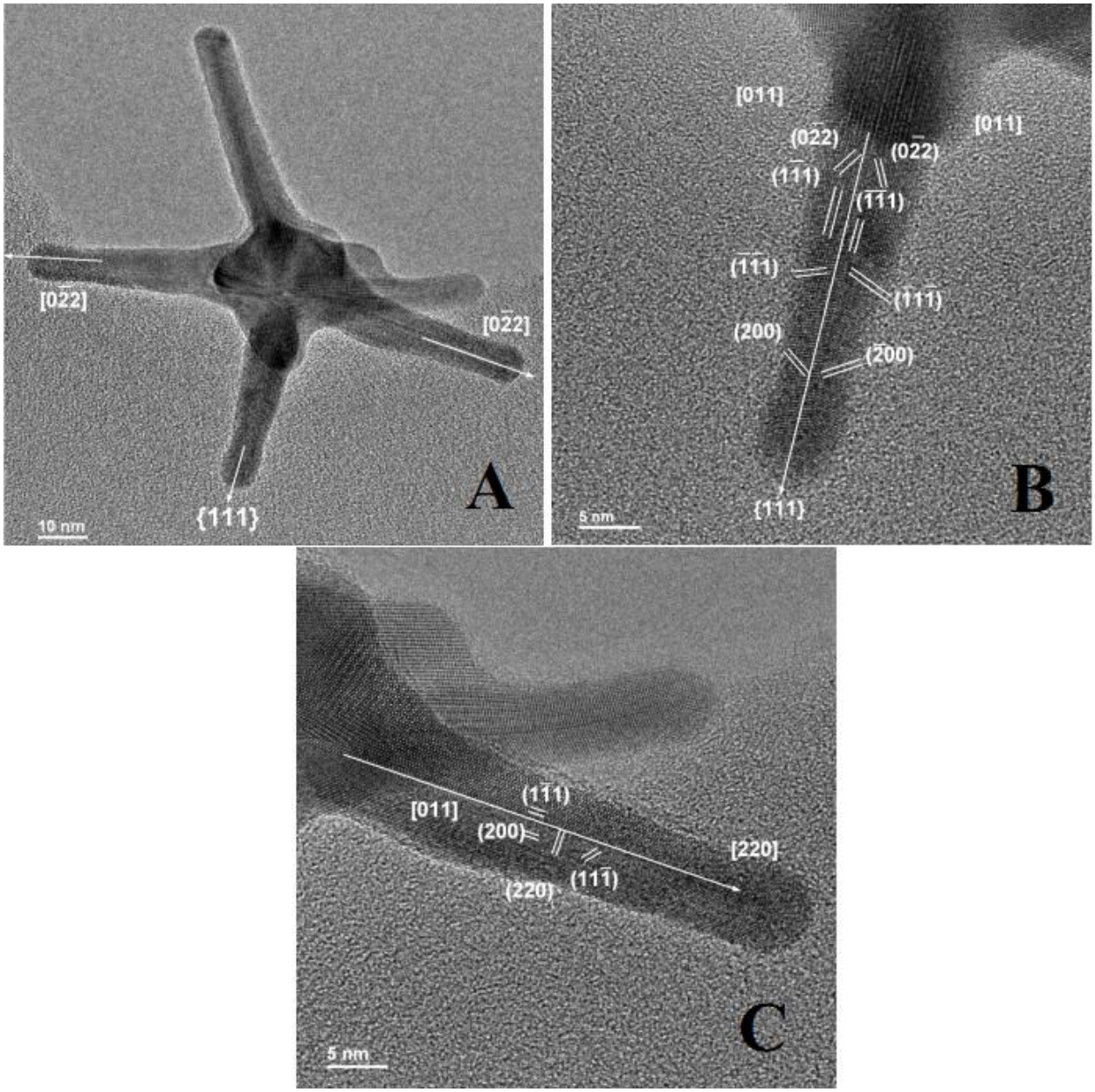
S6 – HR-TEM images



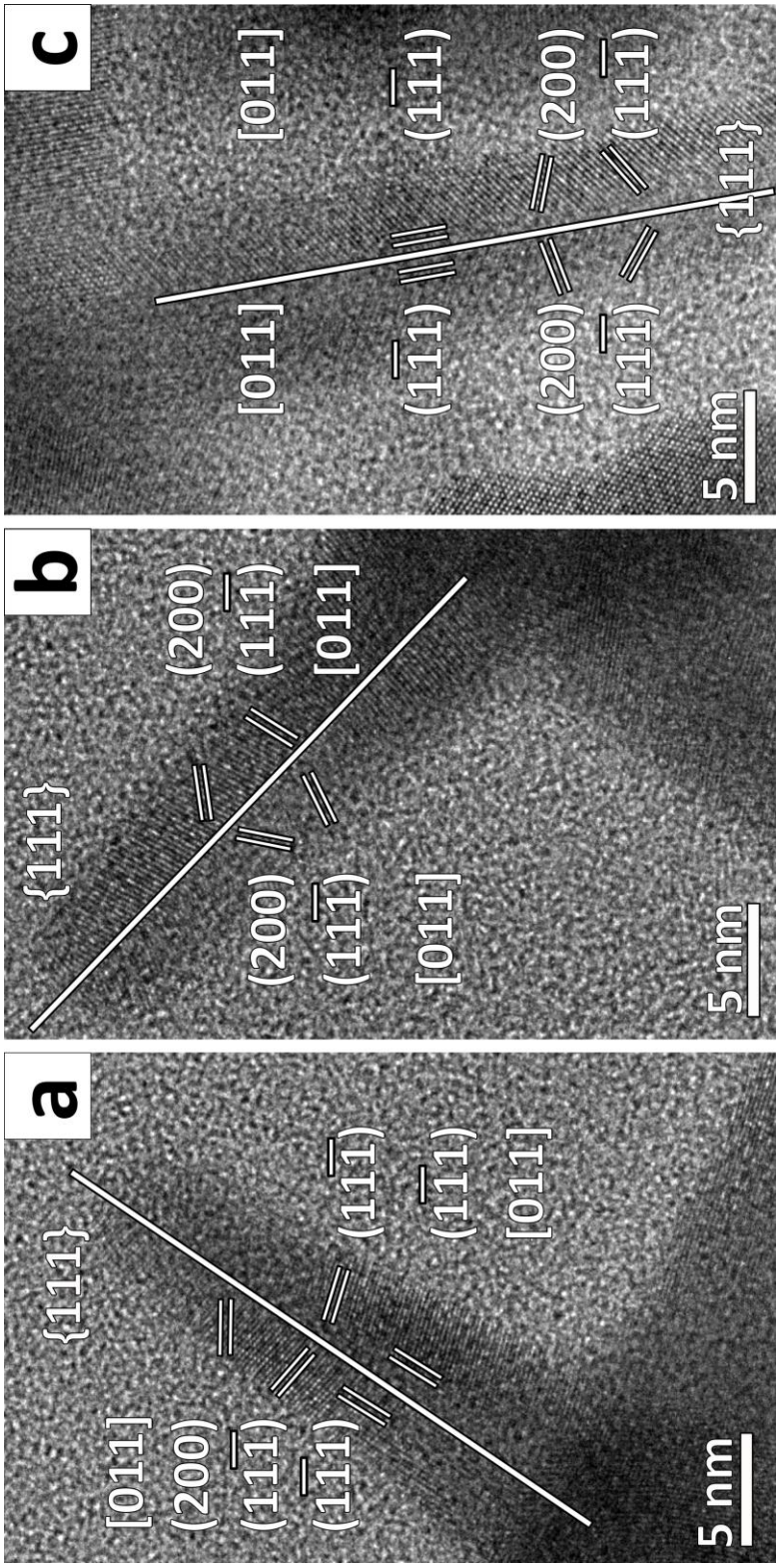
SI6a – object (i): HRTEM on a GNS selected from the solution of spectrum (i) of Figure 1A, main text; object (ii): a polycrystalline spherical nanoparticle



S6b – Object (ii) in the previous figure, larger dimensions. Polycrystallinity is evidenced



S6c – Panel A gives an example of a GNS presenting both growth along {111} directions given by twinning boundaries of the seed and acting as mirror planes (Panel B, detail of the lowest branch of panel A) and growth along the [220] axes with rotational twinning along the growth axes (panel C, detail of the right branch in panel A)



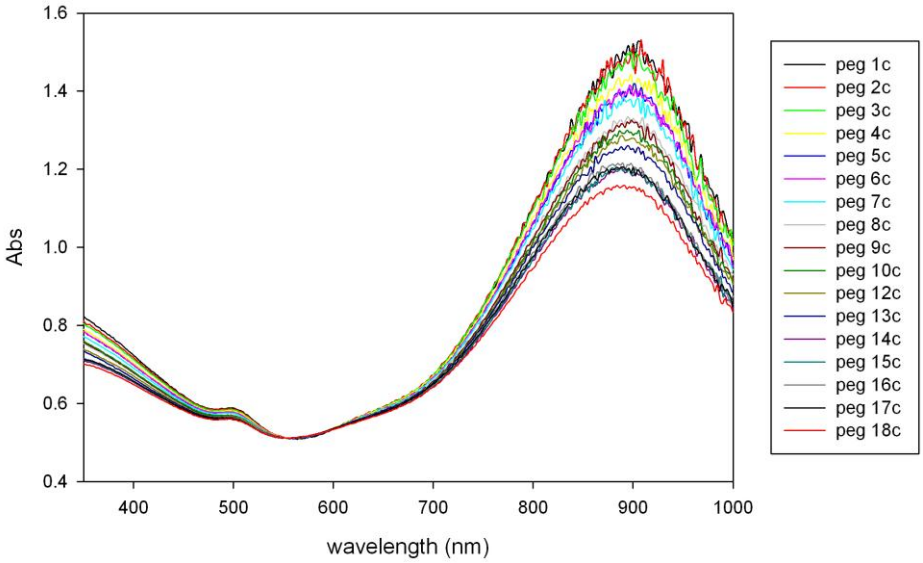
S6D: structural characterization of GNS performed via High Resolution Transmission Electron Microscopy (HRTEM) show a dendritic crystal habit, with branches growing along twinning planes. The measured lattice parameters and crystal directions relationships are consistent with penta twinned Au crystals, sharing their {111} contact planes as preferential directions for the growth of branches. a-c) Close-up High Resolution TEM images of twinned branches from the GNS of Figure 1E. Branches are grown along the {111} contact planes of each twin

S7 – Count of the % of GNS objects

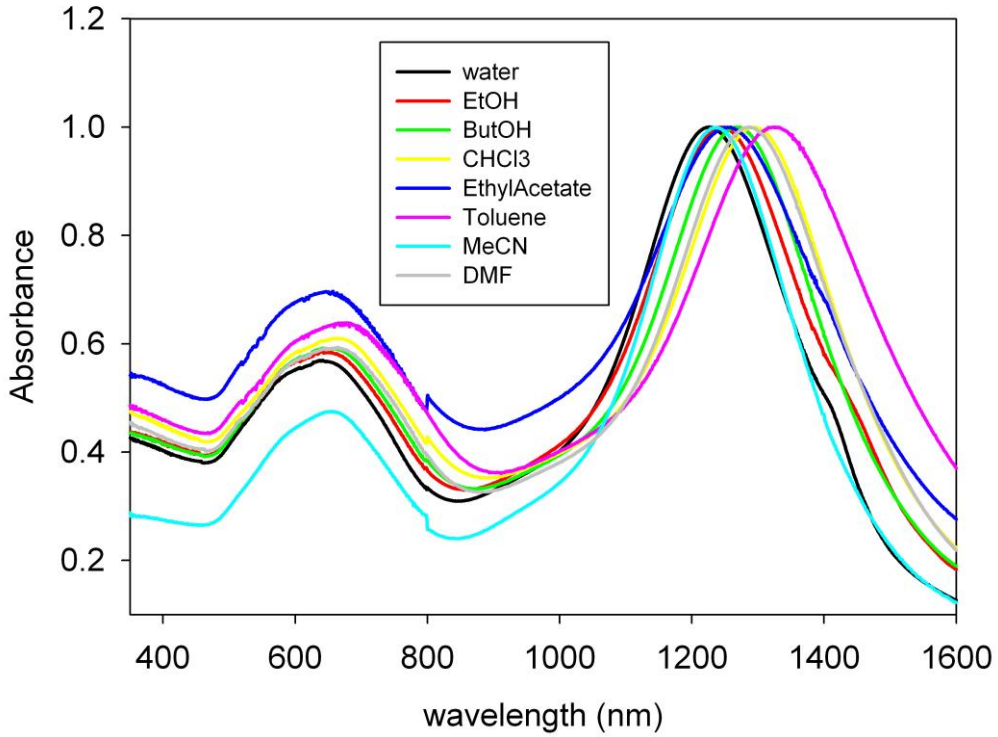
TX100 0.1M		TX100 0.2M		TX100 0.3M	
[AA]	% GNS	[AA]	%GNS	[AA]	% GNS
$1.576x10^{-3}$ M	46	$1.103x10^{-3}$ M	49	$8.274x10^{-4}$ M	56
$1.97x10^{-3}$ M	62	$1.34x10^{-3}$ M	60	$1.024x10^{-3}$ M	69
$3.152x10^{-3}$ M	70	$1.97x10^{-3}$ M	69	$1.34x10^{-3}$ M	75

Counting has been carried out on TEM images obtained from dried solutions prepared in the conditions indicated in the table. The complement to 100% represents poorly developed, spherical objects

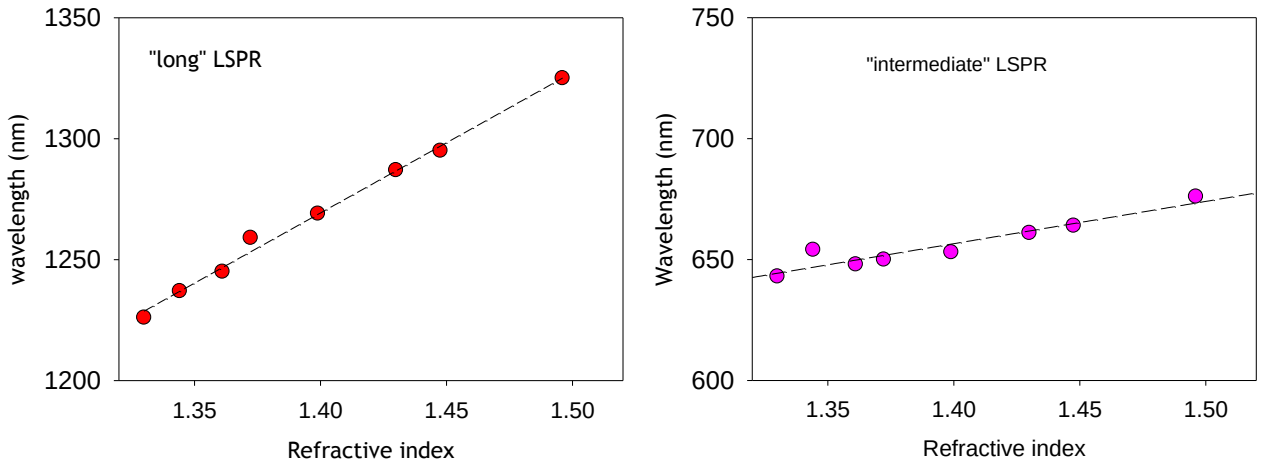
S8 – Pegilated GNS: solution properties



S8A – UV-Vis spectra and ultracentrifugation cycles: a 10 mL GNS sample was pegilated after growth process, then ultracentrifuged (13000rpm, 11'). The clear, almost colorless supernatant was discarded and the pellet redissolved in 10 mL bidistilled water. Spectrum 1c was taken on this solution. Then the same cycle of ultracentrifugation/supernatant discard/redissolution in 10 mL water was repeated 18 times, recording a spectrum after each redissolution process.
The slight decrease after each cycle has to be ascribed to the small leakage of GNS, remaining in the supernatant solution.

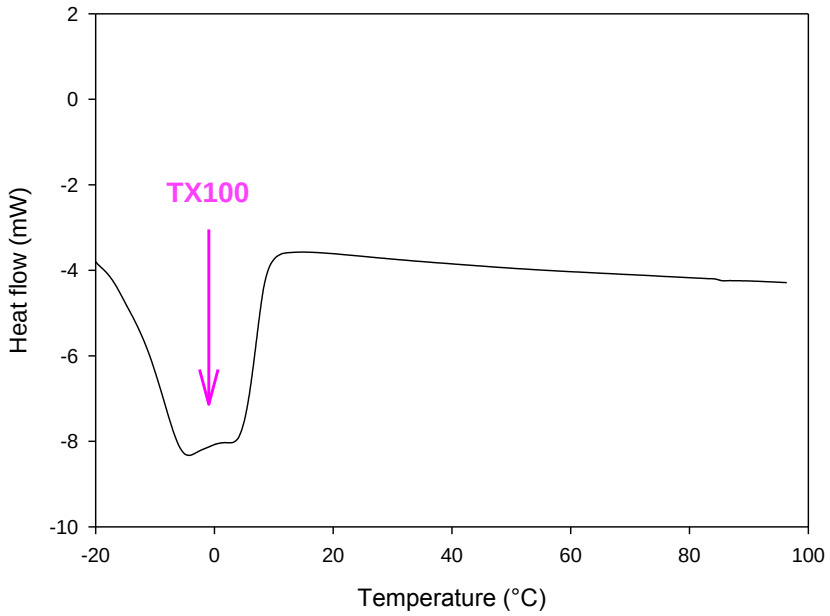


S8B - Spectra in solvents ranging from water to toluen. The preparation of the solutions used for these spectra was as follows: a solution of PEG_{2000}-SH $5*10^{-3}$M in water was prepared. 0.4mL of this solution were added to 40mL of GNS after growth (conditions: [TX100]=0.1M; [AA]=$1.28*10^{-3}$M). The mixture was stirred for 1h at room temperature. Then, the sample was ultracentrifugated (13000rpm, 11') and the pellet re-dissolved in 40mL of bidistilled water. This sample was divided into 8 portions (5mL each). Each portion was ultracentrifugated (13000rpm, 11'), ther supernatant discarded and the pellets dried under vacuum. 5mL of the chosen solvent (water, ethanol, n-buthanol, chloroform, ethyl acetate, toluene, acetonitrile, DMF) were added to each solid portion. After sonication, redissolution of the particles was achieved, yielding blue, clear solutions. UV-Vis-nIR spectra of the different portions were registred, using 1mm cuvette and the pure solvents as blank.

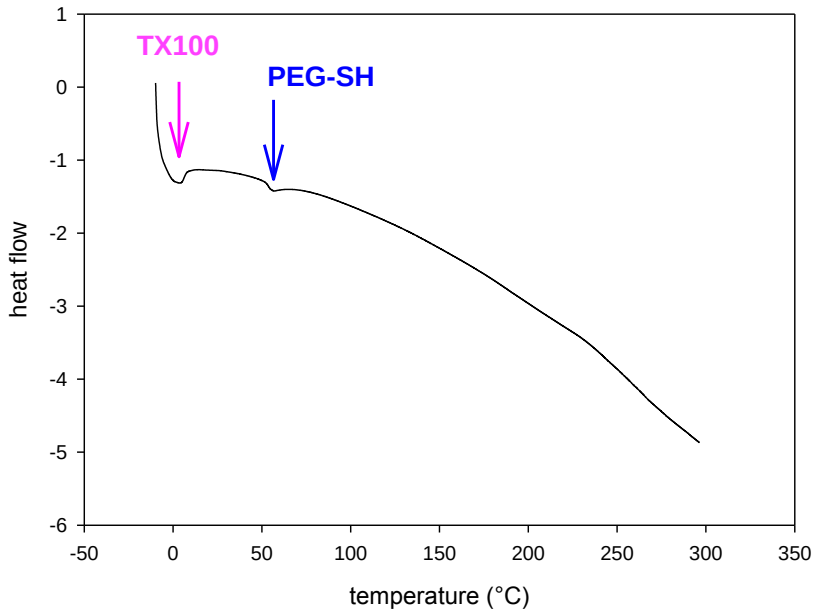


S8C: plot of the position of the LSPR maximum vs η (refractive index of the solvent) showing the expected linear trend for both the long (left) and intermediate (right) LSPR. Both plots have a 150nm-large wavelength scale, to allow direct comparison of the different wavelength/η dependance.

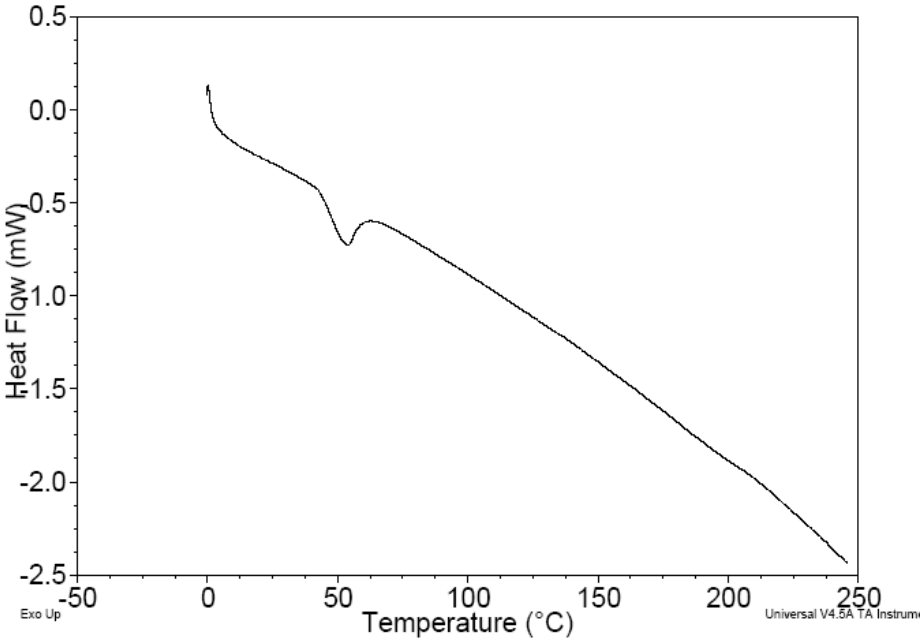
S9 – DSC (differential scan calorimetry) and TGA (thermogravimetric analysis)



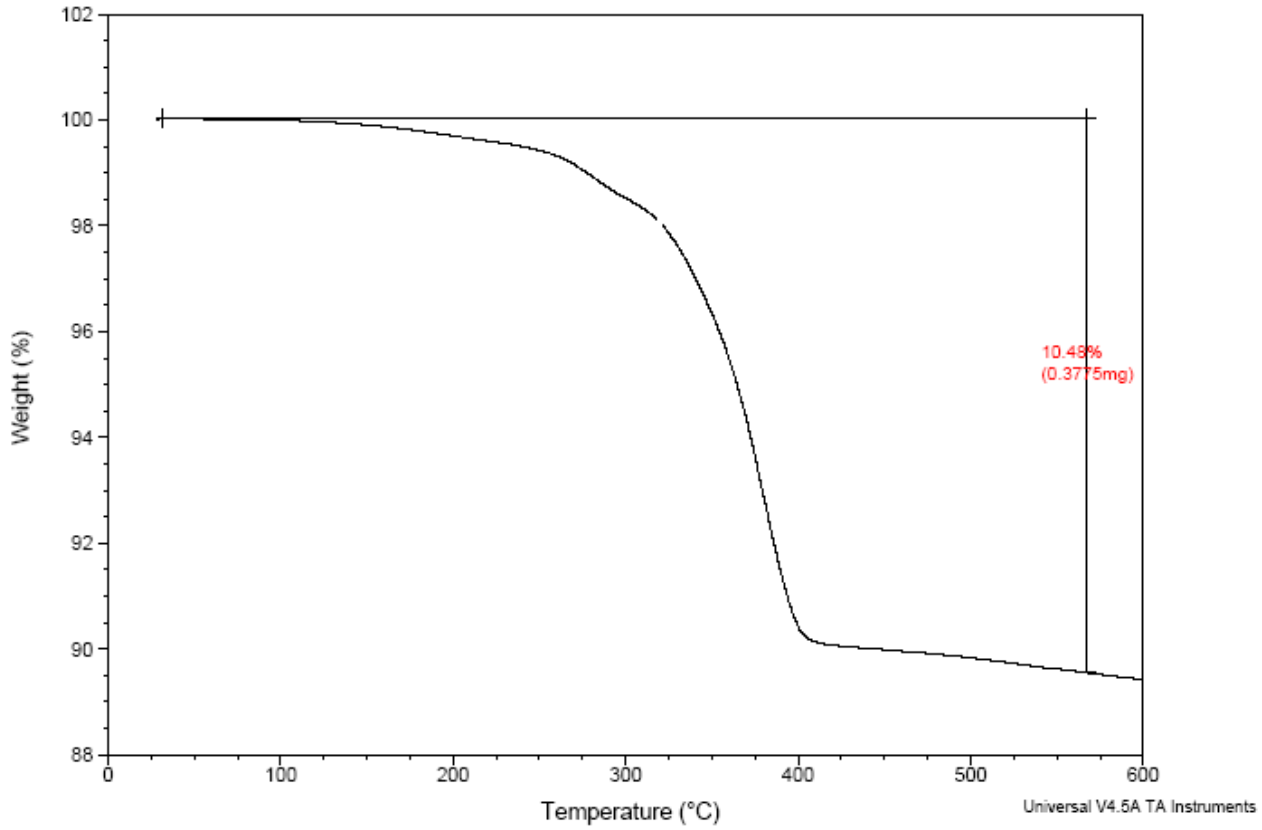
S9A: DSC - TritonX-100 only. The pink arrow evidences the temperature of the Triton X-100 peak



S9B: DSC - $PEG_{2000}SH$-coated GNS, after *two* centrifugation/redissolution cycles: a trace of adsorbed TX100 is remained, and the pink arrow evidences the temperature of the relative peak (same as in S9A). The blue arrow evidences the temperature of the PEG*2000*-SH peak



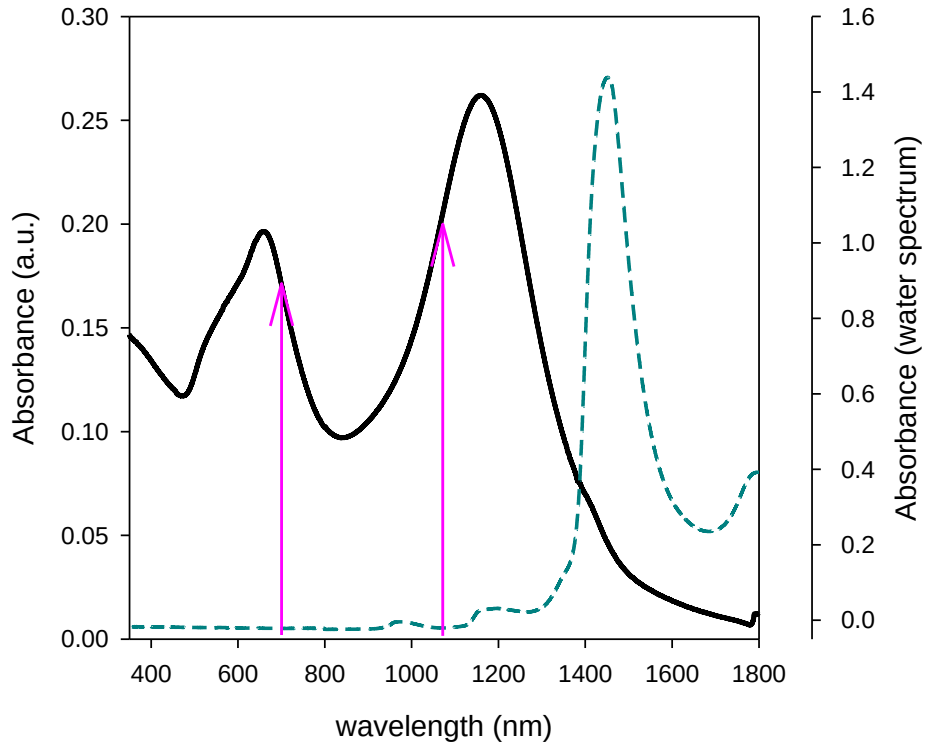
S9C: DSC- PEG2000SH-coated GNS, after four centrifugation/redissolution cycles: in this case, the peak relative to TX100 is disapperared. Only the peak of PEG_{2000}-SH is observed



S9D: TGA – GNS coated with PEG_{2000}-SH. Sample weight = 3.6010 mg. Total weight lost = 0.3775 mg (10.48% = PEG_{2000}-SH). Gold = 3.6010 – 0.3775 = 3.2235 mg.
PEG_{2000}-SH = 0.3775/3.2235 = 0.117mg/mgAu

S10 – Photothermal behaviour

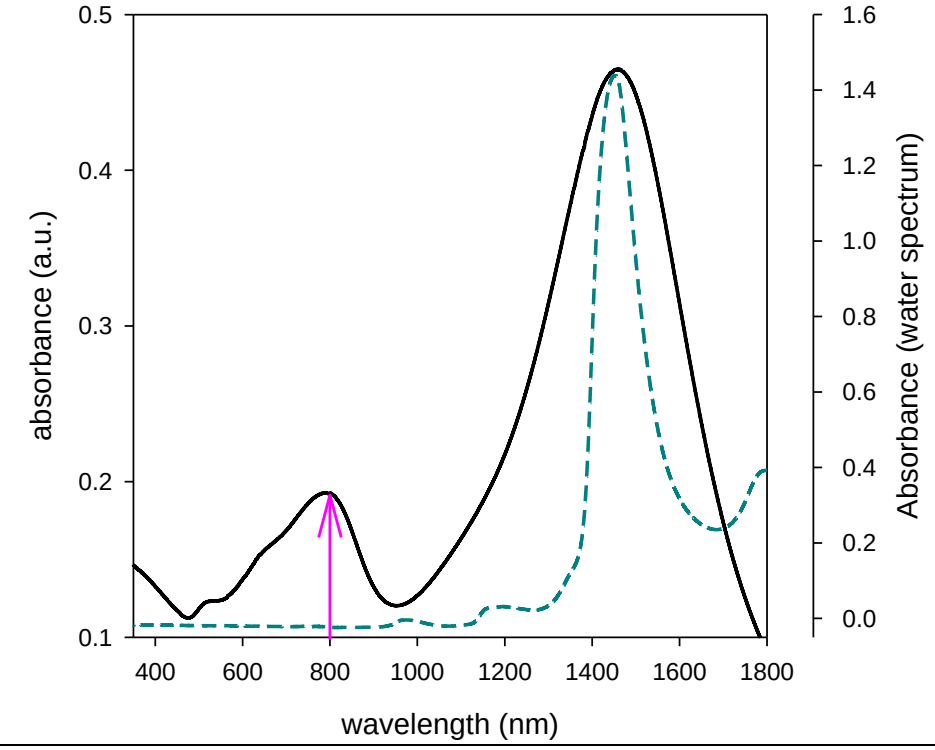
A: absorption spectra of the three solutions used



Type (**a**) solution (see main text).
LSPR at 670 and 1150 nm, black solid spectrum.

The svailable laser sources used for this solution are at 700 and 1064 nm. Their wavelength is evidenced by the pink arrows.

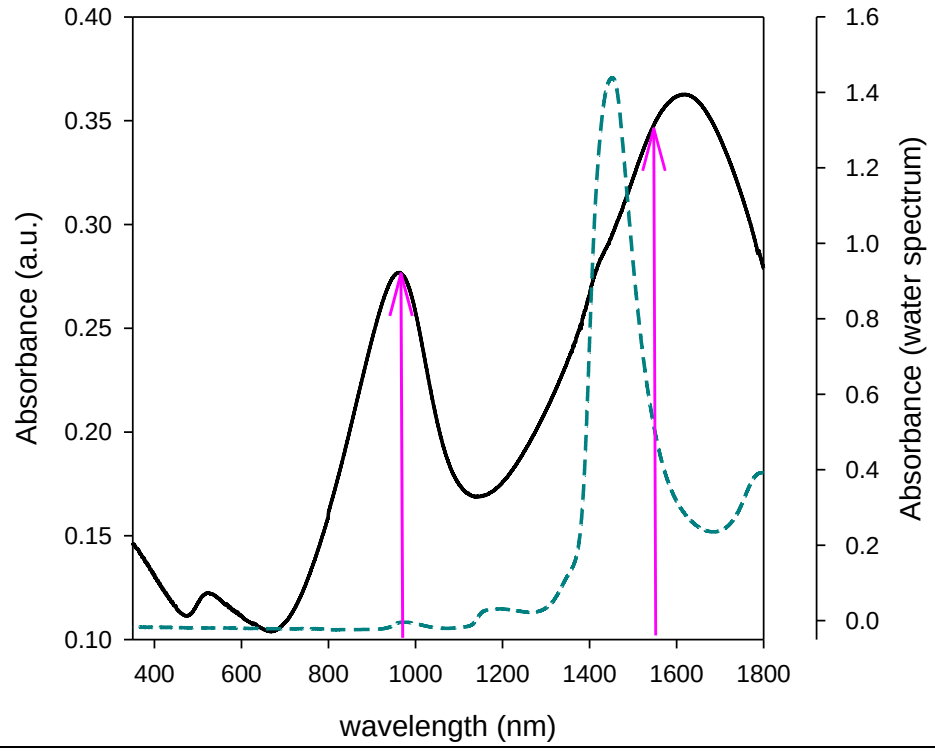
The azure dashed spectrum is that of water, reported for comparison



Type (**b**) solution (see main text)
LSPR are at 795 and 1450 nm.

The available laser source used for this solution is at 800nm.
Its wavelength is evidenced by the pink arrows.

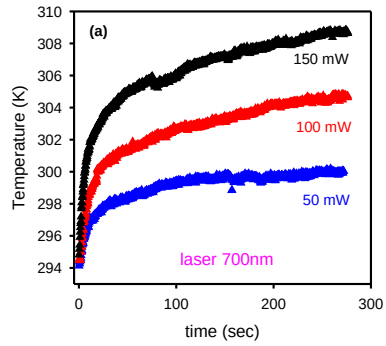
The azure dashed spectrum is that of water, reported for comparison.



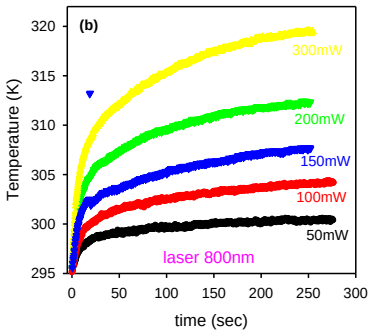
Type (**c**) solution (see main text) LSPR are at 960 and 1590 nm.

The available laser sources used for this solution are at 970nm and 1550 nm. Their wavelength is evidenced by the pink arrows.

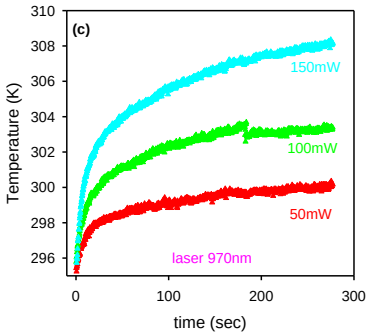
The azure dashed spectrum is that of water, reported for comparison



solution (a)



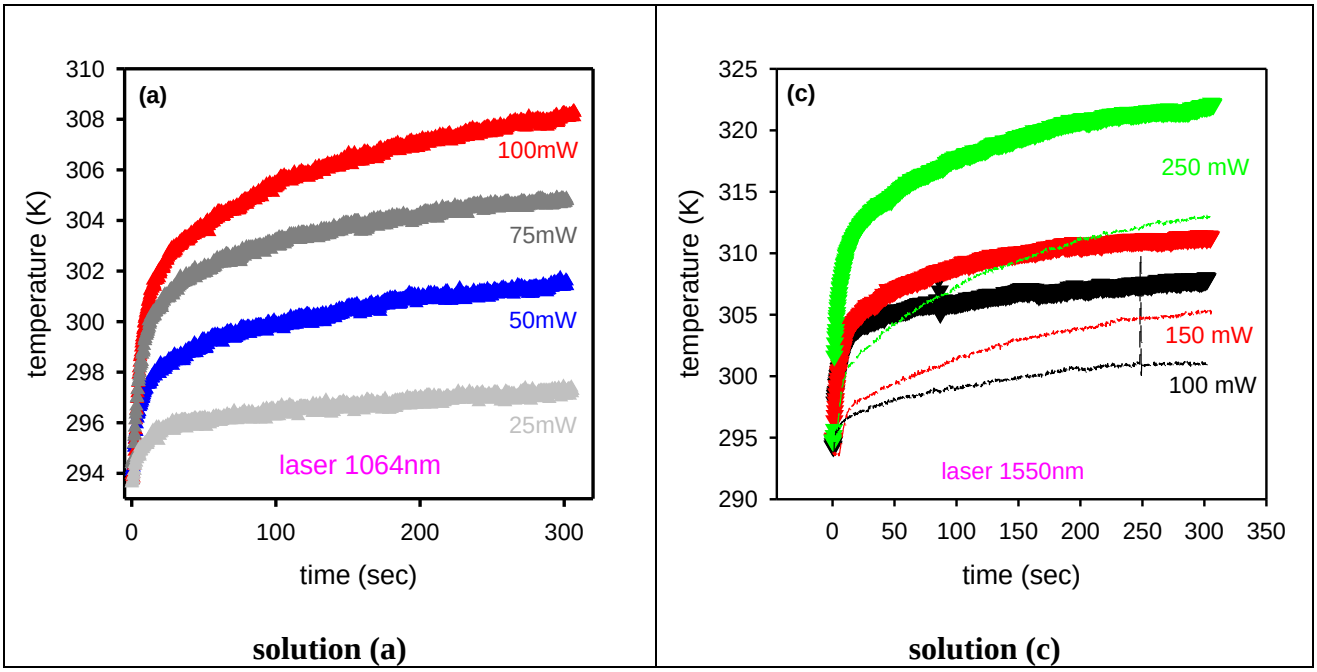
solution (b)



solution (c)

B – Irradiation on the INTERMEDIATE LSPR.

T increase vs time for samples of solutions (a), (b) and (c). Laser wavelengths were 700, 800 and 970 nm, respectively. Measurements were carried out on solutions containing ~ 0.6 mg/mL GNS, volume = 250 μL, in 1 cm^3 plastic wells (Nunc, Labtek, D), using a ThermaCAM SC 3000 (FLIR Systems). Blank experiments were carried out on the same volume of water, at the same wavelengths, in the same wells, at the same laser powers, not observing any temperature increase.



C – Irradiation on the LONG LSPR

T increase vs time for samples of solutions (a) and (c), laser = 1064 and 1550nm, respectively). Measurements were carried out on solutions containing ~ 0.6 mg/mL GNS, volume = 250 μL, in 1 cm^3 plastic wells (Nunc, Labtek, D), using a ThermaCAM SC 3000 (FLIR Systems).

Blank experiments were carried out on the same volume of water, at the same wavelengths, in the same wells, at the same laser powers. While with the 1064nm laser blank experiments did not give T increase, with 1550 nm laser (solution c), the shoulder of the water absorption at 1460nm was hit. A T increase for water only was thus observed. Results for water are included in the figure (solution c) as thin dashed lines. Data for GNS solutions = large triangles. Same color indicates same power. The GNS solutions always gave a much larger T increase, at any laser power.