

Supporting Information

Optimization of second harmonic generation of gold nanospheres and nanorods in aqueous solution: the dominant role of surface area

*Hoang Minh Ngo, Phuong Phong Nguyen, Isabelle Ledoux-Rak**

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A - Characterization of nanoparticles

UV-Vis absorption spectra of the obtained solutions were recorded by UV-Vis spectroscopy (Lambda 950). Particles sizes were determined by TEM using a JEOL Model JEM-1400 at 100kV.

The measurement of SHG from AuNPs was done by Harmonic light scattering at 1.064 μ m from a Q- switched Nd³⁺: YAG nanosecond laser (SAGA from Thales Laser) at a 10 Hz repetition rate. The detected signal is then sampled, averaged processed by a computer. A low intensity reference beam is extracted from the main beam at a 45° incidence angle by a glass plate and focused onto a highly nonlinear NPP (N-4-nitrophenyl-prolinol) powder used as a frequency doubler. The variation of the second harmonic intensity scattered from the solution is recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder, both signals scaling as the square of the incoming fundamental intensity I_ω .

The scattered harmonic signal $I^{2\omega}$ from a solution is given by:

$$I^{2\omega} = g \left(N_s \langle \beta_s^2 \rangle + N \langle \beta^2 \rangle \right) I_\omega^2$$

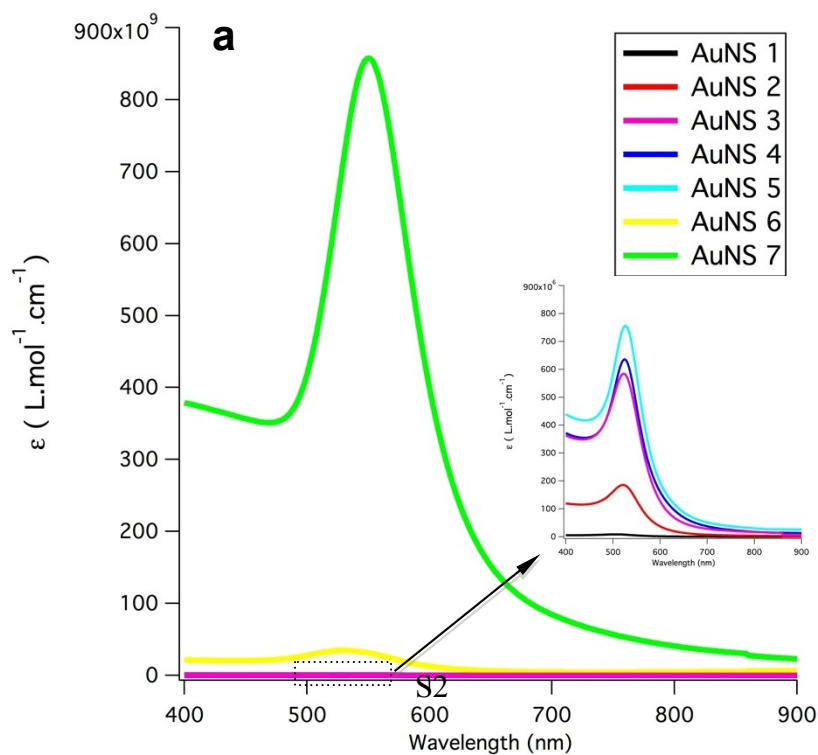
where g is a geometry factor, N_s and N are the number of solvent molecules and nanoparticles per unit volume respectively; β_s and β are the molecular hyperpolarizability of the solvent and nanoparticle, respectively. From the slopes P (respectively P_0) of the lines obtained for the solution (respectively solvent) by recording the variation of $I^{2\omega}$ as a function of $I_{NPP}^{2\omega}$ (the SHG intensity from a reference NLO material (NPP) sample which is proportional to I_ω^2), we can infer the β values of the nanoparticles.^{17,26,27}

UV-Vis spectra

In order to optically characterize the AuNPs solutions, their UV–Vis absorption spectra were recorded. These spectra are given in Table 1, Figure S1 and Figure S2.

Table S1. UV-Vis maximum absorption wavelengths λ_1 (AuNSs, AuNRs) and λ_2 (AuNRs) of the AuNPs solutions. For AuNRs, L is the length and W the diameter of the rods

sample	λ_1 (nm)	λ_2 (nm)	diameter (nm)	aspect ratio (AR)
AuNS 1	505		3.0	1
AuNS 2	522		11.6	1
AuNS 3	524		15.8	1
AuNS 4	525		17.4	1
AuNS 5	527		20.0	1
AuNS 6	530		43.0	1
AuNS 7	550		80.0	1
AuNR 1	549	634	20.6(L) - 14.0(W)	1.47
AuNR 2	543	637	20.4(L) - 12.5(W)	1.63
AuNR 3	539	639	20.4(L) - 8.9(W)	2.30



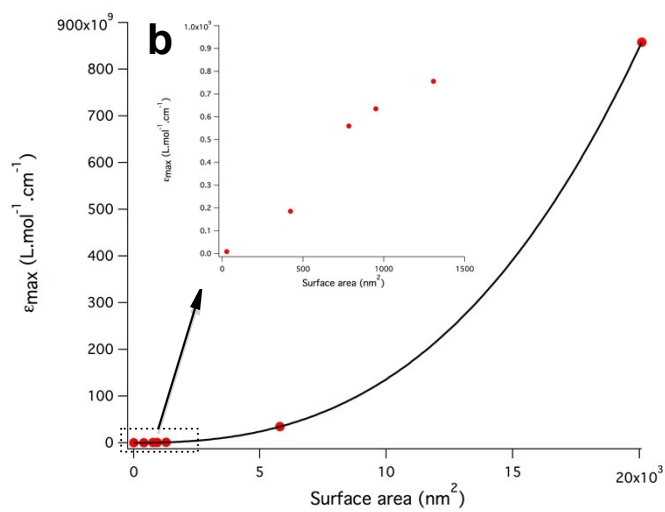


Figure S1. Molar absorptivity (ϵ) spectra of AuNSs solutions

(a) The insert shows magnified spectra for small NP's.

(b) Plot of ϵ_{\max} (as measured at λ_1) as a function of the surface area of NP's. Insert: magnification for small particles.

It can be easily inferred from the red shift of the position of the peak maxima (from 505 to 550nm) that the size of AuNSs increases (from 3.0 to 80.0nm) in Figure S1. The role of the surface area is exemplified in Figure S1b, the molar extinction coefficient at the peak maximum, ϵ_{\max} , displaying a quasi linear dependence with surface area in the case of small particles, with a faster growth rate for the largest ones.

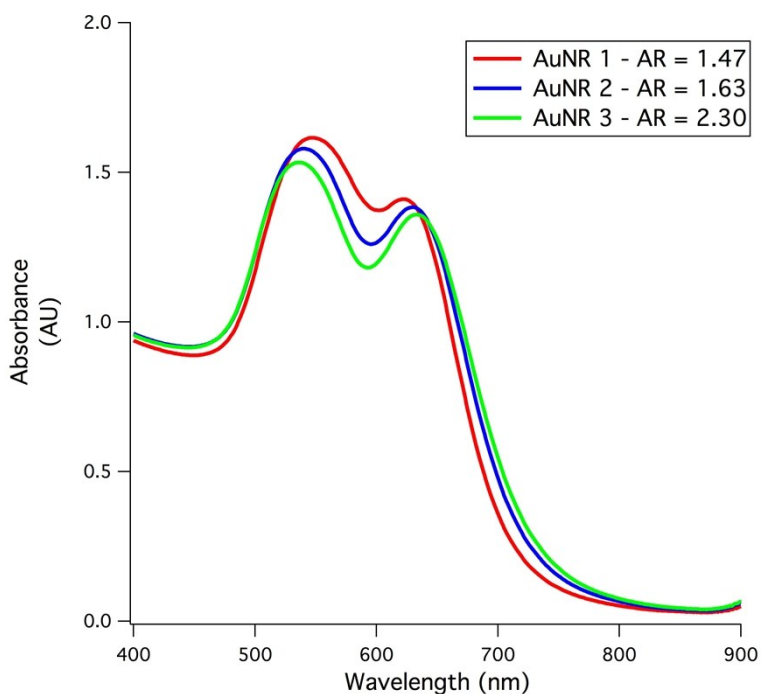


Figure S2. UV-Vis absorption spectra of the AuNRs solutions.

For nanorods, the expected two distinct surface plasmon resonances (SPR) are clearly observed from Figure S2: one (λ_1) is associated with a transverse SPR mode and the other one (λ_2) associated with a longitudinal SPR mode. In Figure S2, while the transverse band is insensitive to the size of the nanorods, the longitudinal band is significantly red shifted when increasing the aspect ratio AR ($AR=\text{length}/\text{width}$).^{14,16,17}

B - Nonlinear optical (NLO) properties of various AuNPs

Table S2. First hyperpolarizability (β) of Au per atom and per particle

sample	diameter (nm)	surface area (nm ²)	volume (nm ³)	N _{Au} per particle	particle conc.	β per particle (β) (10 ⁻²⁶) esu	β per atom (β') (10 ⁻³⁰) esu	β_R (10 ⁻²⁰) esu
AuNS 1	3.0	30	15	800	8.80E-08	0.4	130	1
AuNS 2	11.6	420	820	48000	3.04E-09	3.4	160	0.56
AuNS 3	15.8	780	2100	120000	9.06E-10	6.5	190	0.57
AuNS 4	17.4	950	2800	160000	9.02E-10	8.3	210	0.61
AuNS 5	20.0	1300	4200	240000	5.94E-10	13	270	0.72
AuNS 6	43.0	5800	42000	2400000	4.0E-11	58	370	0.69
AuNS 7	80.0	20100	270000	16000000	1.28E-12	260	660	0.9
AuNR 1	20.6(L) - 14.0(W) <i>AR</i> = 1.47	1200	3200	190000	3.11E-09	6.6	150	
AuNR 2	20.4(L) - 12.5(W) <i>AR</i> = 1.63	1050	2500	150000	1.99E-09	4.7	120	
AuNR 3	20.4(L) - 8.9(W) <i>AR</i> = 2.30	700	1300	73000	3.96E-09	2.9	110	

C- The dipolar response

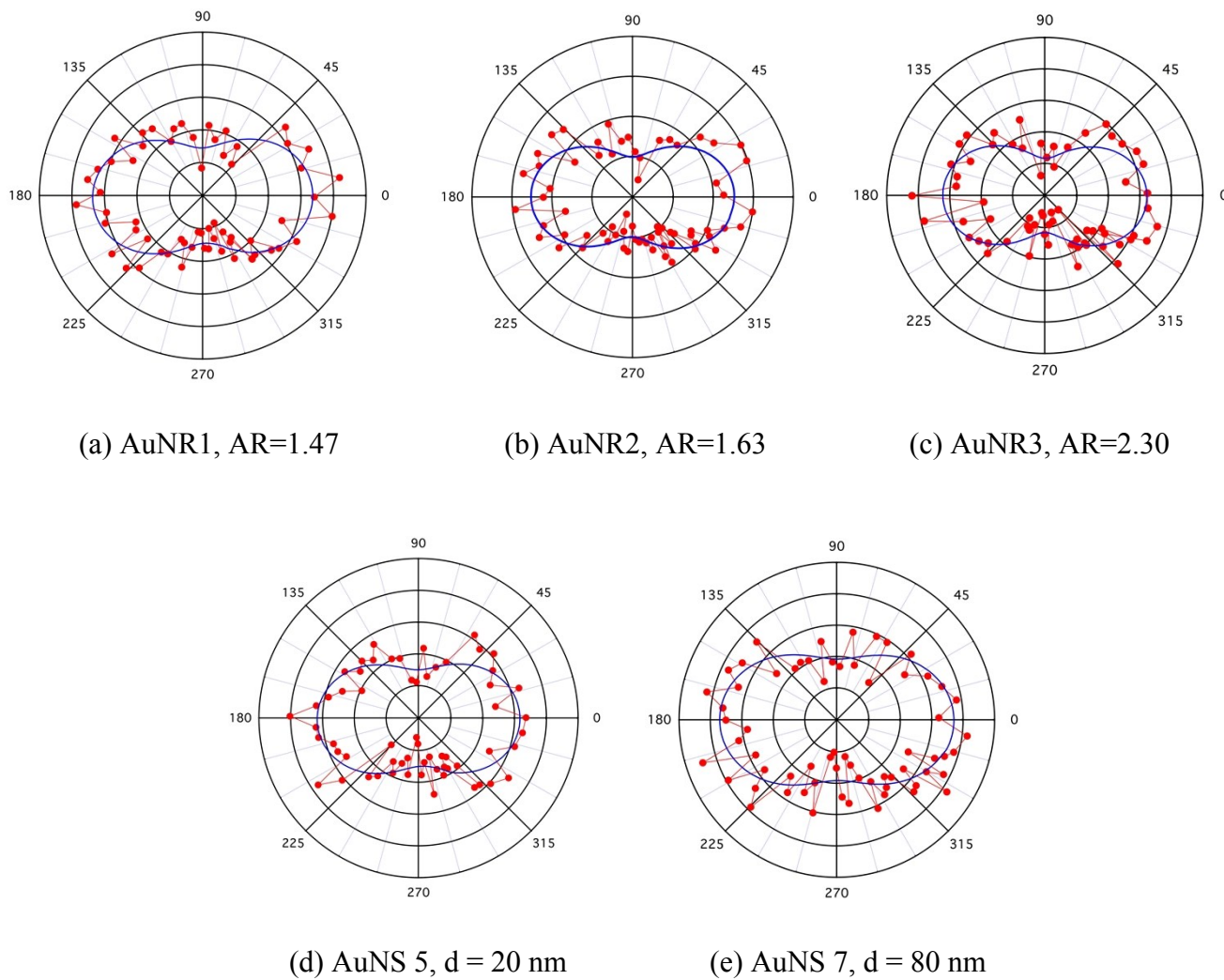


Figure S3. Polar plot of the polarization resolved HRS intensity as a function of the input polarization recorded for the AuNRs and AuNSs at 1064 nm.

D - Harmonic Light Scattering experiment

The approach followed here relies on Harmonic Light Scattering (HLS) as initially proposed and developed by Terhune and Makerⁱ. A transverse single mode Nd³⁺:YAG laser is used as the fundamental source, consisting of 10 MW peak power, 3 ns duration IR pulses at 1.064 μm repetition rate 10 Hz). The incident IR intensity can be continuously monitored by a half-wave plate rotated between two crossed Glan polarizers. A small part of the incident beam is removed at a low reflection angle by a glass plate and sent onto a highly nonlinear NPP (N-4-nitrophenyl-prolinol)⁽ⁱⁱ⁾ powder used as a reference frequency doubler. The emitted second harmonic signal is detected by a photomultiplier. The main fundamental beam (vertically polarized) is focused into the sample using a 8 cm focal length converging lens. The sample consists in an adequately designed parallelepipedic spectrophotometric cell presenting four polished windows so as to allow for simultaneous longitudinal illumination and transverse collection of the scattered emission. Collection of the HLS photons at 532 nm is performed in the transverse off-axis 90° direction, using a large (diameter 50 mm) and short focal distance ($f = 50$ mm) spherical lens in order to focus the light onto the photocathode of a photomultiplier tube. The numerical aperture of the optical collection system is low so as to avoid the depolarizing contribution of the off-axis beams. The detected reference and scattered harmonic signals, after spectral selection through an interference filter with 5 nm spectral resolution, are then sampled and averaged using a home-made acquisition card and processed by a computer. Variation of the scattered second harmonic intensity from the solution is recorded on the computer as a function of the reference second harmonic signal provided by the NPP powder, which scales like the square of the incoming fundamental intensity. Then $\langle\beta^2\rangle$ and β (defined as $\sqrt{\langle\beta^2\rangle}$) values are inferred from the slopes of the resulting lines. Calibrations are made with respect to the pure water solvent.

HLS depolarization measurementsⁱⁱⁱ are made by varying the angle ϕ of the linearly polarized beam using the rotation of a second half-wave plate set after the glass plate, in order to keep its reflectivity from being polarization dependent.

ⁱ Terhune, R.W. ; Maker, P.D. ; Savage, C.M. *Phys. Rev. Lett.* **1965**, *14*, 681 ; Maker, P.D. *Phys. Rev. A*, **1970**, *1*, 923.

ⁱⁱ Zyss, J.; Nicoud, J.F.; Coquillay, M. *J. Chem. Phys.***1984**, *81*, 4160 .

ⁱⁱⁱ Brasselet, S.; Zyss, J. *J. Opt. Soc. Am.B* **1998**, *15*, 257.