Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Surface area-dependent second harmonic generation from silver nanorods

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A – Characterization of nanoparticles

A.1 – UV-Vis spectra and electronic microscopy

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.

A.2 – Harmonic Light Scattering experiment

SHG measurements of AgNRs are performed by Harmonic Light Scattering[(i)] (HLS) at 1.064 μm. The approach followed here relies on HLS as initially proposed and developed by Terhune and Maker[(i)] and Clays and Persoons[(ii)]. A transverse single mode Nd^{3+}:YAG laser (SAGA from Thales Laser) is used as the fundamental source, consisting of 10 MW peak power, 3 ns duration IR pulses at a 10 Hz repetition rate). 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 extracted from the main beam at a 45° incidence by a glass plate and sent onto a highly nonlinear NPP (N-4-nitrophenyl-prolinol) [(iii)] 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 a 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 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 (home made software) by a computer. The 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 as the square of the incoming fundamental intensity. The signal is then detected, sampled, averaged and 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 powder used as a frequency doubler. The variation of the SH intensity scattered from the solution is recorded as a function of the reference SH signal provided by the NPP powder, both signals scaling as the square of the incoming fundamental intensity.

The scattered harmonic signal from a solution is given by[ii]:

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

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. The g factor includes local field factors and transmission coefficients at ω and 2ω (these terms depending on the refractive indices n^{ω} and $n^{2\omega}$ of the solution), and spatial average values of the direction cosines between the incident electric field E^{ω} and the spherical components of the β tensor, as expressed in eqn 40 and 41 of ref.[iv]. The concentration in AgNR in water being very low, n^{ω} and $n^{2\omega}$ of their aqueous solution are very close (the difference being lower than 10^{-3} refractive index units) to those of pure water.

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 $I_{NNP}^{2\omega}$ (the SHG intensity from a reference NLO material (NPP) sample which is proportional to I_ω^2), we can infer the $<\beta^2>$ and β (defined as $\sqrt{\left\langle \beta^2 \right\rangle}$) values of the nanoparticles. Calibrations are made with respect to the pure water solvent.

B – Results

B.1 – Histogram of AgNR's lengths

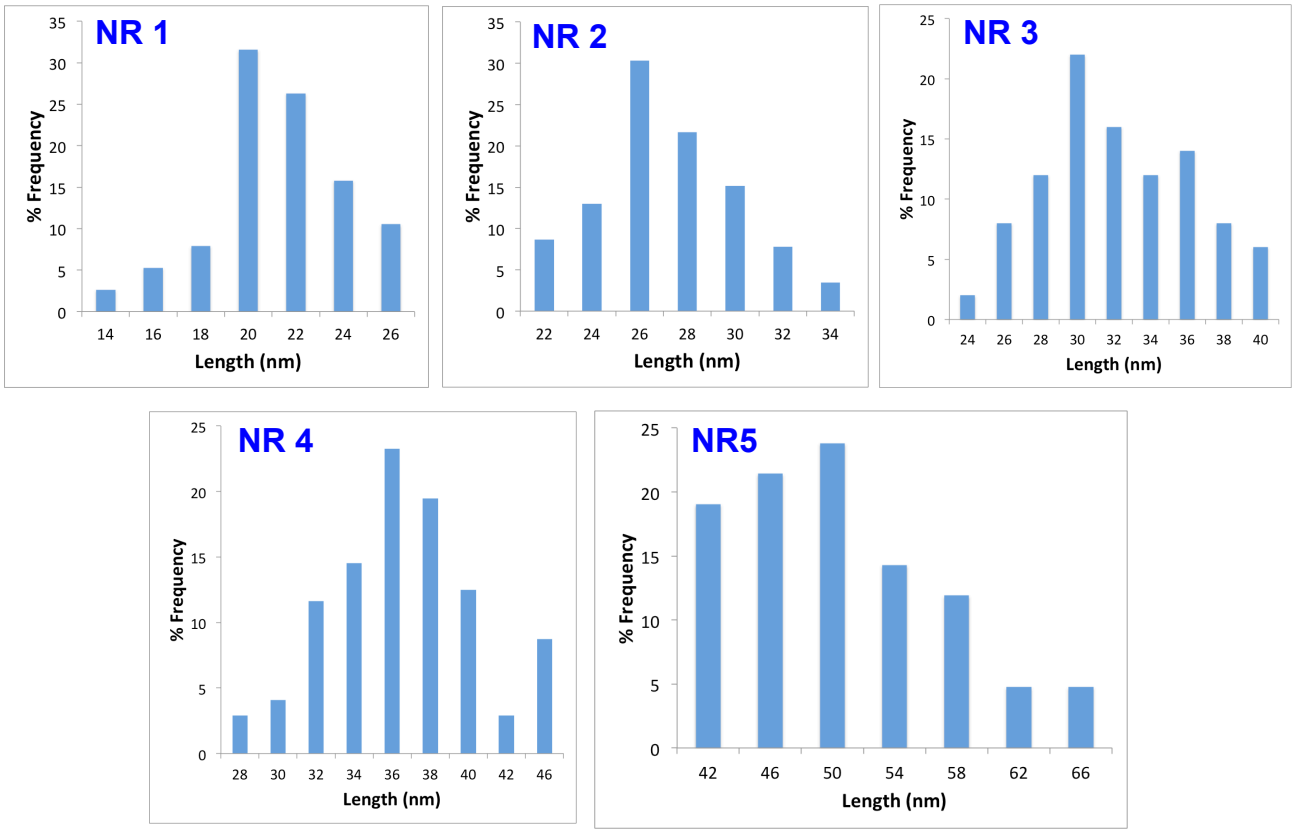

Figure S1. *The histogram of lengths of silver nanorods (corresponding to Figure 2). The average lengths are found to be 20.1 ± 3.0; 25.7 ± 4.9; 31.4 ± 6.5; 36.0 ± 4.4 and 49.6 ± 8.7 nm for (NR1-NR5), respectively.*

B.2 – Standard deviation on Aspect ratios (ARs):

Rule: $(L \pm \varepsilon_L) / (W \pm \varepsilon_W) = (L / W) \pm (\varepsilon_L + \varepsilon_W)$

where L (nm) : length

W (nm) : width

$\varepsilon_{L,W}$ (%): the relative uncertainly on L and W

For example with AgNR 1:

L = (20.1 ± 3.0) nm = (20.1 nm ± 14.9%)

W = (4.0 ± 0.9) nm = (4.0 nm ± 22.5%)

$$\Rightarrow AR_{AgNR1} = \frac{L}{W} = \left(\frac{20.1}{4.0}\right) \pm (14.9\% + 22.5\%) = 5.0 \pm 37.4\% = 5.0 \pm 1.9$$

The calculation is similar to AgNR2 - AgNR5

Sample	Length (nm)	Width (nm)	Aspect ratio
AgNR 2	25.7 ± 19.1%	4.1 ± 12.2%	6.3 ± 31.3% = **6.3 ± 2.0**
AgNR 3	31.4 ± 20.7%	4.2 ± 16.7%	7.5 ± 37.4% = **7.5 ± 2.8**
AgNR 4	36.0 ± 12.2%	4.4 ± 18.2%	8.2 ± 30.4% = **8.2 ± 2.5**
AgNR 5	49.6 ± 17.5%	5.1 ± 19.6%	9.7 ± 37.1% = **9.7 ± 3.6**

C – Stability of AgNRs

The stability of the silver colloidal solutions can be easily checked by recording their UV-Vis spectra[v]. Results are shown in Figure S2.

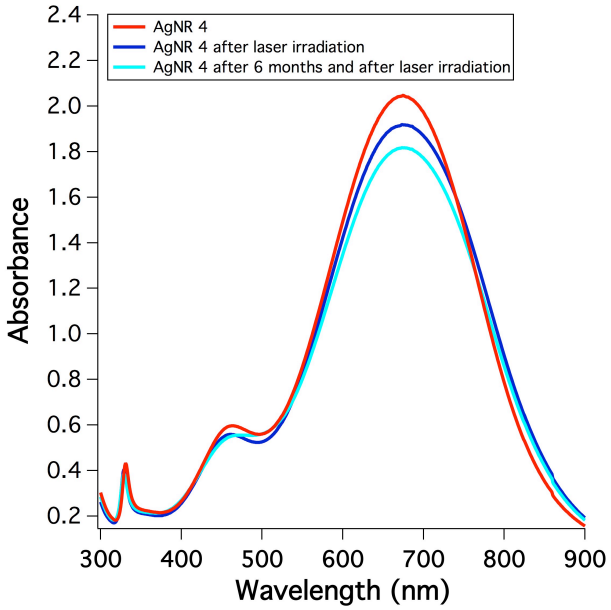

Figure S2. *UV-Vis absorption spectra of AgNR 4. Red: spectrum recorded just after AgNR synthesis. Dark blue: spectrum recorded after laser irradiation (10 minutes) a few days after synthesis. Pale blue: spectrum of the same (laser irradiated) sample recorded after a 6 months storage.*

In Fig. S2, the maximal peak intensity decreases of 6% and 11% after irradiation with the laser and a further 6 months storage, respectively. The position of λ_1 and λ_2 is almost unchanged only the absorbance is slightly modified. It means that silver colloidal solutions are relatively stable in shape and size.

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[v] Y. Takeuchi, T. Ida, and K. Kimura, *J. Phys. Chem. B* **1997,** *101*, 1322-1327.