Electronic Supplementary Information (ESI)

Insights into polythiol-assisted AgNP dissolution induced by bio-relevant molecules

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1. Materials and Methods

1.1. Samples

Ligand (L)	Sample	[L] (µM)	[Ag] (µM)	Ratio Ag/Ligand	Ratio thiol groups / Ag
-	AgNP		370	-	-
GSH	AgNP + GSH	370	370	1	1
PC2	AgNP + PC2	185	370	2	1
PC3	AgNP + PC3	123.3	370	3	1
PC6	AgNP + PC6	61.7	370	6	1
P^2	AgNP + P^2	185	370	2	1
Atx1	AgNP + Atx1	185	370	2	1

Table S1. List of samples with their concentration as used in this study.

1.2. DLS measurements

At the desired time-point, the sample was diluted five times in HEPES-Citrate buffer (10 mM HEPES, 2 mM sodium citrate pH 7) and 100 µL were transferred to a UVette (Eppendorf). DLS signal was measured 10 times (each measurement consisting of 10 acquisitions of five seconds). Using the Wyatt software package, the autocorrelation function of the scattered intensity was determined by the Brownian motion. This relationship is characterized by the intensity of the autocorrelation function defined as:

$$G(\tau) = \int_{-\infty}^{\infty} I(t)I(t-\tau)dt$$

Where I(t) is the detected intensity as a function of time, and τ is a delay time. Then, the Stoke-Einstein relationship was used to define the hydrodynamic radius (r_K), equivalent to the size of a sphere that diffuses at the same velocity as the measured particle. This is determined as:

$$r_k = \frac{k_b T}{6\pi\eta D_T}$$

Where k_b is the Boltzman's constant, T is the absolute temperature, η is the solvent viscosity and D_T is the diffusion coefficient.

1.3. AF_4-UVD-MALLS-ICP-MS measurements

A metal free HPLC (1260 Infinity, Agilent Technologies, Santa Clara, USA) was used to inject 50 µL of samples that were pre-diluted 20 times in NaOH 10^{-4} M pH 9, solution also used as eluent for the separation of the nanoparticles inside the trapezoidal channel (Wyatt technology, Goleta, USA) and using a 1 kDa cut-off regenerated cellulose membrane (Postnova analytics) as accumulation wall. The flow controller (Eclipse, Wyatt technology) was set to perform an exponential decrease of the cross flow from 1 $mL.min^{-1}$ to 0 $mL.min^{-1}$ over 20 min allowing the efficient separation of AgNPs ranging from 20 to 180 nm.[1] Absorbance detector was tuned near the maximum absorbance of citrate-coated 20 nm AgNPs SPR signal at λ = 402 nm (UV detector VWD-G1314B, Agilent Technologies). The outlet of the multi angle laser light scattering detector (MALLS, Dawn Heleos II, Wyatt technology) was connected to inductive coupled plasma mass spectrometer (ICP-MS 7700x, Agilent Technologies) using a peek T connector, without addition of acidified internal standard. The Ag signal recorded was related directly to Ag concentration using an external calibration done with ionic standards in HNO_3 2 %. Under these conditions, the Ag recovery of citrate-coated 20 nm nanoparticles used as reference herein was of R ≈ 80 % and indicated a limited but existing loss of the AgNPs during the elution procedure. UVD and MALLS were used here as online indicators of the presence of AgNPs and their potential dissolution or aggregation respectively.

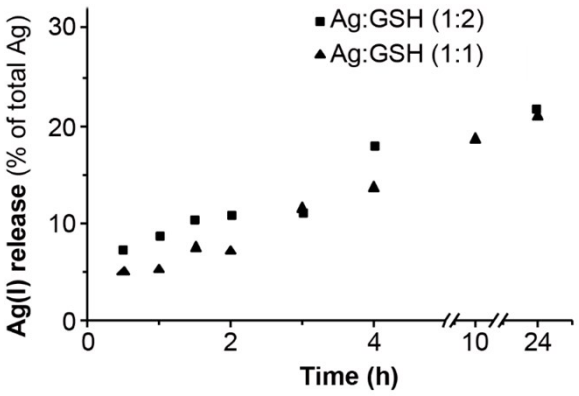

Fig. S1 AgNP dissolution at two different Ag:S ratios. Fraction of Ag(I) released from AgNPs determined by ICP-AES in presence of 1 or 2 molar equivalent of GSH compared to total Ag in solution. The fraction of Ag(I) released corresponds to the amount of Ag recovered in the supernatant of the sucrose centrifugation divided by the total amount of Ag recovered in both fractions (supernatant + pellet).

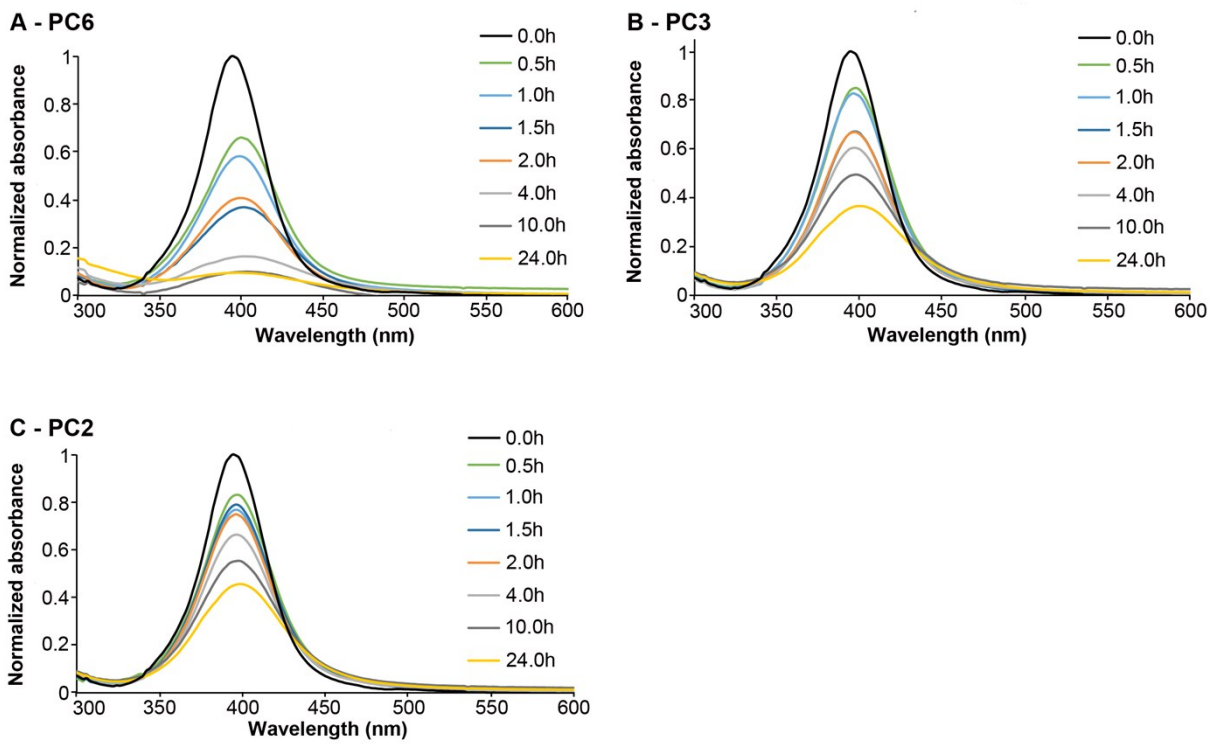

Fig. S2 Analysis of AgNP SPR spectra in presence of phytochelatins. Time-dependent analysis of AgNP SPR spectra in presence of PC6 **(A)**, PC3 **(B)** and PC2 **(C)** between 0 and 24-hour incubation.

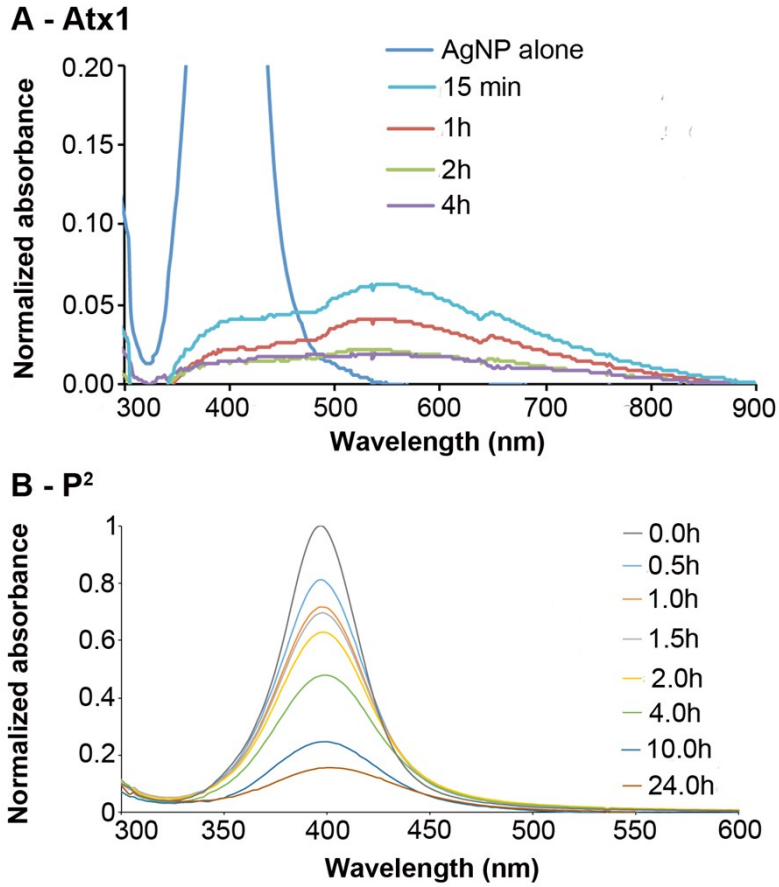

Fig. S3 Analysis of AgNP SPR spectra in presence of chelating molecules. Time-dependent analysis of AgNP SPR spectra in presence of Atx1 between 0 and 4-hour incubation **(A),** and P^2 between 0 and 24-hour incubation **(B)**.

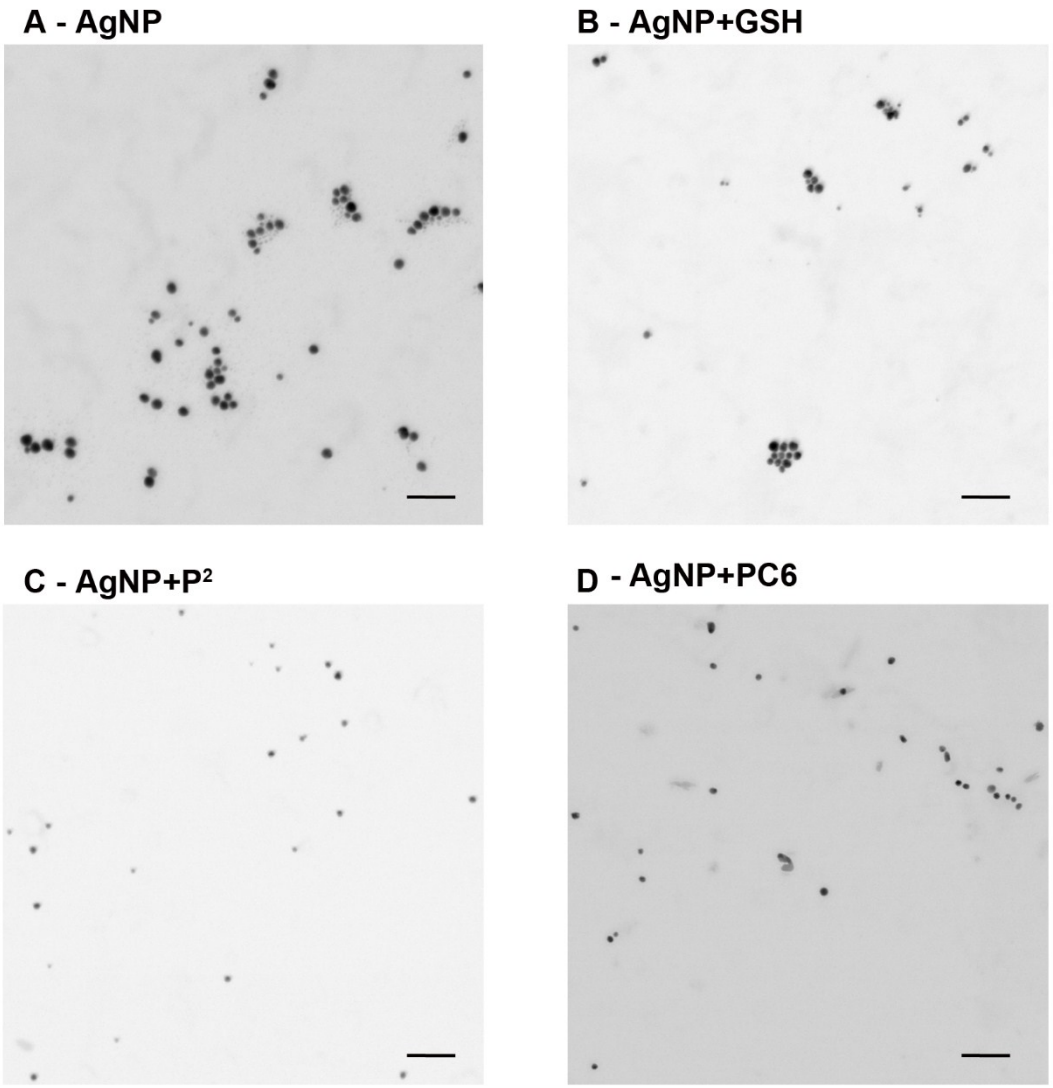

Fig. S4 STEM analysis of AgNPs incubated in presence of thiol-containing molecules. Representative STEM micrographs of pristine citrate-coated AgNPs (**A**); AgNPs incubated for 24-hour with GSH (**B**); AgNPs incubated for 24-hour with P^2 (**C**) and AgNPs incubated for 24-hour with PC6 (**D**). Scale bars are 100 nm.

REFERENCES

1. S. Motellier, N. Pelissier and J. G. Mattei, Contribution of single particle inductively coupled plasma mass spectrometry and asymmetrical flow field-flow fractionation for the characterization of silver nanosuspensions. Comparison with other sizing techniques, *Journal of Analytical Atomic Spectrometry*, 2017, **32**, 1348-1358.