Electronic Supplementary Information (ESI)

Synthesis of gold nanoparticles in a biocompatible fluid from sputtering deposition onto castor oil

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Detailed Experimental Conditions

TEM was performed with a JEOL JEM 1200-ExII equipment, operating at 80 kV, while HRTEM and EDS was realized in a JEOL JEM 2010 equipment, operating at 200 kV. The samples for TEM were prepared dispersing the Au-deposited castor oil in isopropanol at room temperature and then drop deposited on a carbon-coated copper grid and introduced in TEM after evaporation of isopropanol. UV-Vis spectra were measured in a Varian Cary 100 spectrophotometer by using 1 mm optical path quartz cuvettes at room temperature. Due to high concentrations, the samples sputter deposited at 375 and 405 V were diluted 50 times before UV-Vis measurements. High Performance Liquid Chromatography (HPLC) analysis were performed on a Shimadzu LC-20A Prominence liquid chromatograph equipped with an evaporative light scattering detector (ELSD) and a four-solvent delivery system. The solvents were filtered through a 0.45 mm Millipore filter prior use and degassed by continuous stripping with nitrogen. Injection volumes of 1 mL and a flow rate of 1 mLmin⁻¹ were used in all experiments. All samples were dissolved in 2-propanol-hexane (5:4, v/v). All solvents were of HPLC grade and were used without further purification. A column,
Shim-Pack C-18 (250mm/4.6 mm I.D.), was obtained from Shimadzu. HPLC method: reservoir A contained water, reservoir B contained acetonitrile and reservoir C contained 2-propanol- hexane (5:4, v/v). A 50 min ternary gradient at 35°C with two linear gradient steps was employed: 30% A+70% B in 0 min, 100% B in 15 min, 50% B+50% C in 30 min, followed by isocratic elution with 50% B+50% C for the last 27 min.

SAXS experiments were performed in NPs solutions at the SAXS1 beam line of Brazilian Synchrotron Light Laboratory (LNLS), with \( \lambda = 1.488 \, \text{Å} \) and 0.05 < \( q < 3.33 \) nm\(^{-1} \), where \( q = 4\pi \sin(2\theta) / \lambda \); \( q \) is the scattering vector, \( \theta \) is the scattering angle and \( \lambda \) is the X-ray wavelength. The colloidal solutions were injected by a syringe into a cell with mica windows specially designed for liquids.

**SAXS Analysis**

In a typical scattering of X-rays, the absolute scattering intensity \( I(q) \) (Eq. (S1)) of a multi particle system can be written as:

\[
I(q) = \frac{N}{V} \cdot \Delta \rho^2 \cdot V_p^2 \cdot S(q) \cdot P(q) \quad \text{Eq. (S1)}
\]

In this equation \( N/V \) is the number of dispersed particles per unit volume in the sample. \( \Delta \rho \) is the excess electron density which is defined as the difference between the electron density of the particles and that of the surrounding medium. \( V_p \) is the volume of the particle. \( P(q) \) is the form factor which characterizes the single particle scattering and \( S(q) \) is the structure factor, that describes the interactions between the particles. For highly diluted suspensions of non-aggregated particles, the structure factor can be taken as unity. In practice, most colloidal suspensions are polydisperse and there is the necessity to taken in to account a distribution function. Therefore the measured intensity
represents the sum of the scattering intensity from particles of various sizes. For a sphere the form factor can be calculated as in Eq. (S2), where \( R \) is the radius.\(^1\)

\[
P(q) = \left( \frac{3\sin(qR) - qR\cos(qR)}{(qR)^3} \right)^2
\]

Eq. (S2)

In our case, supposing monodisperse spherical particles with a lognormal distribution (Eq. (S2) and Eq. (S3)) it was possible to fit the experimental SAXS curves using the free software package SASfit, see Fig. S3.

\[
\text{LogNorm}(R) = \frac{N}{R^p} \exp \left( \frac{\ln R - \ln \mu}{2\ln \sigma} \right)^2
\]

Eq. (S3)

In addition, A. Guinier developed a valid approach for dilute and monodisperse systems in small \( q \) regions of scattering curves, as can be seem in Eq. (S4),\(^1,2,3\) where \( R_g \) is the radius of gyration of the particles, defined in analogy with classical mechanics as the mean square distance of electrons with respect to the electronic center of gravity.

\[
I(q) = I(0)e^{-\frac{q^2R_g^2}{3}}
\]

Eq. (S4)

As known, in the Guinier region, the graphical representation of the curve \( \ln I(q) \) versus \( q^2 \) is a straight line whose slope directly provides the turning radius of the particle. For a monodisperse system, the radius of gyration and the radius of the spherical particle are given by Eq. (S5):\(^2\)

\[
R_g = \left( \frac{3}{5} \right)^{\frac{1}{2}} R
\]

Eq. (S5)
Another valid and useful approach, known as Porod’s law, refers to the final part of the curve of scattering and is related to the fine structure of the particle.²⁴ In the Porod region the radius of the particle can be calculated by plotting $I(q).q^4$ versus $q$ limited to the region where $\log I(q) = \text{constant} - 4\log(q)$. The first maximum of the curve ($q_{\text{max}}$) can be directly related to the mean diameter of the particle, Eq. (S6):

$$D_p = \frac{5.5}{q_{\text{max}}} \quad \text{Eq. (S6)}$$

Figures

**Fig. S1** UV-Vis spectra of castor oil after Au deposition at 330 V (13 W) for different sputtering times.
**Fig. S2** Histograms of AuNPs sputter deposited onto castor oil at 330 V (13 W) for sputtering times of (a) 300s and (b) 600 s. This shows that the sputtering time does not influence the AuNPs size.

**Fig. S3** Experimental and calculated SAXS profile of AuNPs sputter deposited onto castor oil at 405 V (37 W) and 280 V (4 W) for 150 s. The fitting was made supposing spherical monodisperse NPs with lognormal size distribution. A fractal aggregate of 30 nm is taken into account to fit the experimental curve of sample sputter deposited at 280 V.
Fig. S4 TEM image of AuNPs sputter deposited onto castor oil at (a) 260 V and (b) 405 V for 150 s. The AuNPs sputter deposited onto castor oil at 260 V present agglomerations as expected for samples sputter deposited below 280 V.

References


