ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

ESI1. Justification for negligible NP degradation with low laser fluence

Our work assumes that at the lowest fluence of 0.43 J cm^{-2} only a negligible amount of NP degradation occurs. In order to justify this assumption, we used our earlier developed LA-sp-ICPMS simulation algorithm (available at http://193.2.14.6:9988/webapps/home/) and derived theoretical size distribution histograms using the data from the manufacturer's technical reports. The simulation input parameters were tuned so that simulated and experimental histograms would contain the same number of NPs. A comparison of the simulated and experimental histograms is given in Figure S1, from which a slight broadening of the NP size distribution can be observed.

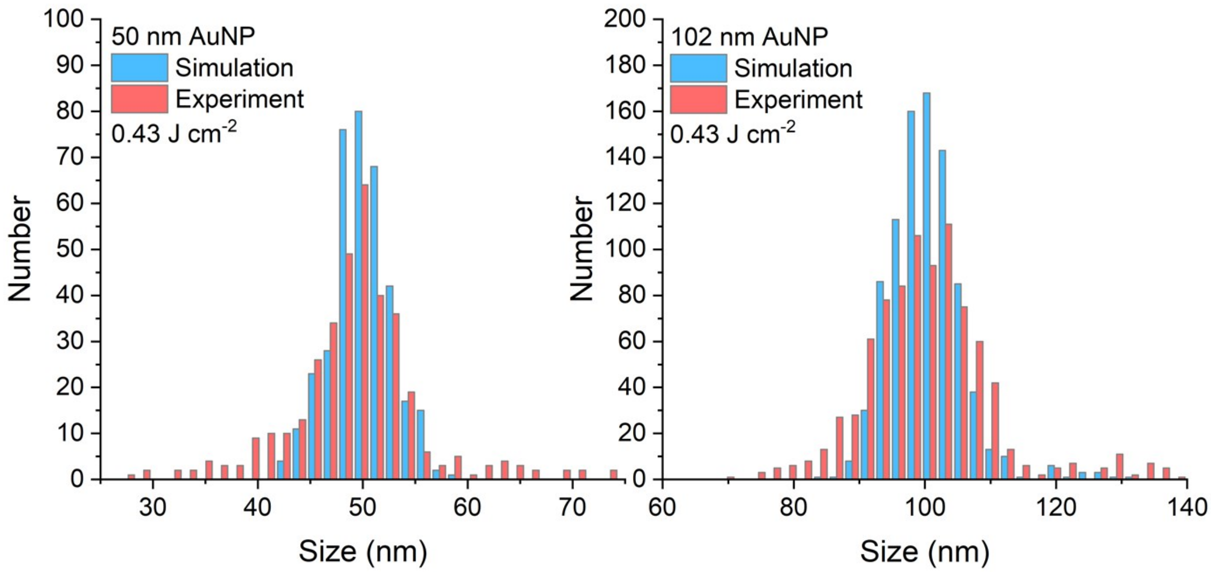

Figure S1. Comparison of simulated and experimental NP size histograms for the lowest fluence of 0.43 J cm $^{-2}$.

For added perspective, Figure S2 shows how the simulation histograms compare to the experimental histograms in 3D bar plots (shown in the same fashion as Figure 2a and b in the main text). These results show that, strictly speaking, it cannot be claimed that there is no NP degradation occurring even for the lowest stable fluence used, even though it may be regarded as negligible for the purposes of NP sizing.

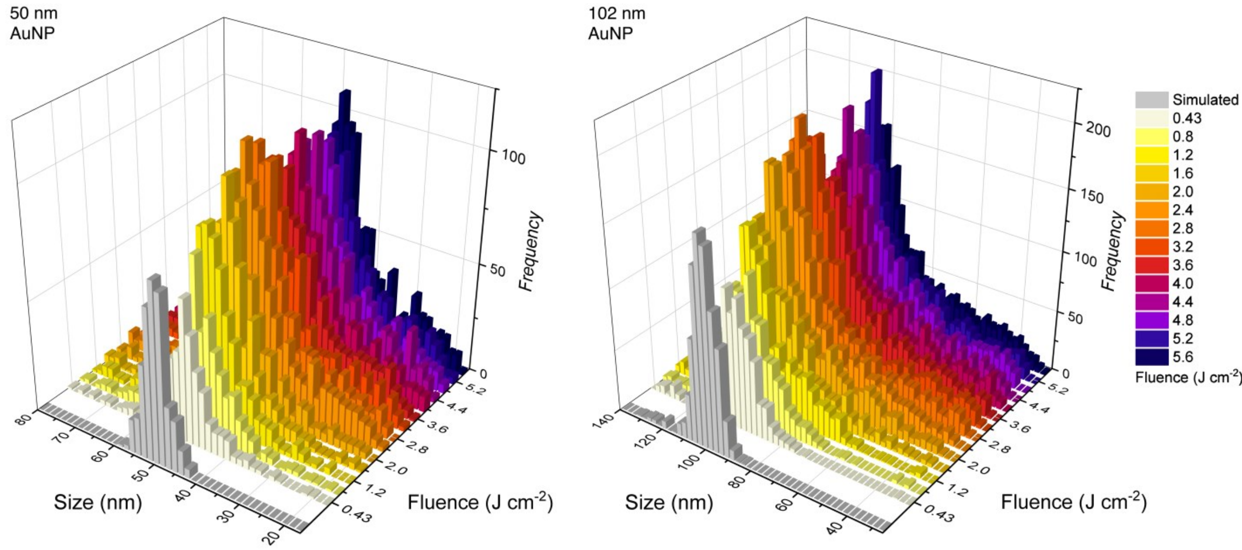

Figure S2. Comparison of simulated and experimental NP size histograms for the entire fluence range tested.

ESI2. Lognormal fitting and size calibration

Size calibration associated with a fluence of 0.43 J cm^{-2}, the alleged negligible NP degradation condition, was performed by conducting laser ablation line scans on dried gelatine containing 20, 50 and 102 nm AuNPs, followed by data processing based on our earlier established protocols in which the cubic root of the integrated NPs was sorted by incidence (see the histograms in Figure S3). The histograms were fitted with a lognormal distribution, whereupon the median (μ) value of the fit was taken as the reported NP size. The median values of the lognormal fits were used to construct a two-point size calibration graph (Figure S4).

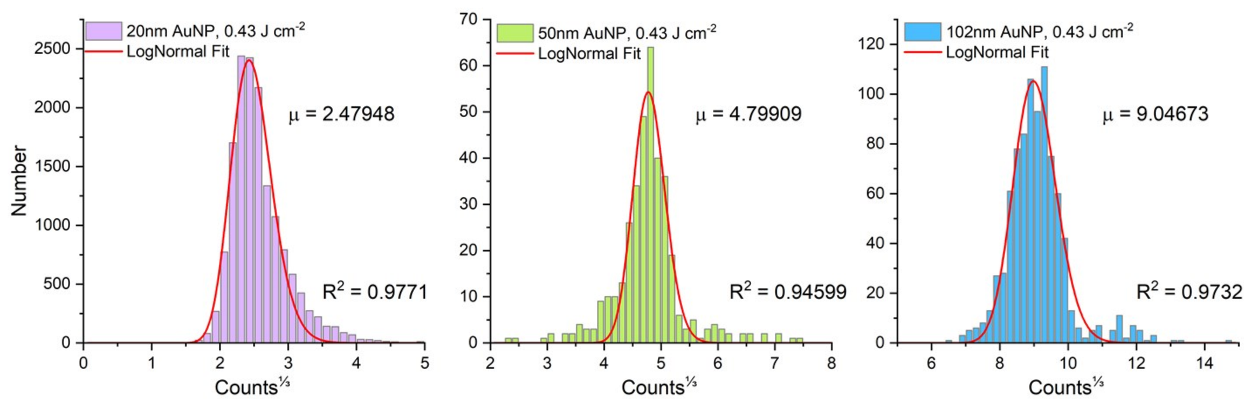

Figure S3. Histograms of 20 nm (purple bars), 50 nm (green bars) and 102 nm (blue bars) AuNPs detected in the gelatine standards upon LA-sp-ICPMS at a fluence of 0.43 J cm^{-2}, including fits with a lognormal distribution (red line).

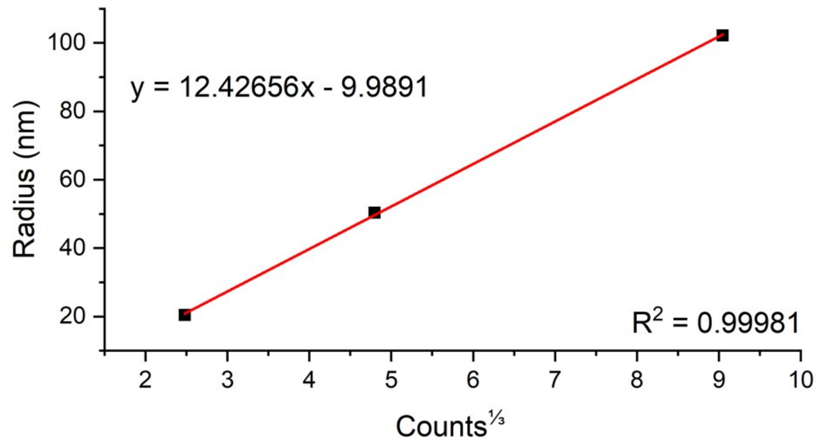

Figure S4. Calibration graph derived from the fitted histogram positions in Figure S3.

ESI 3. Retrieval of histograms and histogram subtraction residuals from the raw LA-sp-ICPMS data

Although a quick look at the NP size distribution histograms in Figures 2a and b in the main text is enough to illustrate LA-induced NP degradation, the degree to which this process is occurring is more difficult to evaluate as there is a significant amount of non-NP related background signal (S_B) present in the raw data**.** To this end we devised a way to show the degree of degradation based on the use of two correction factors (R_0 and F):

From the raw time-resolved line scan data for the lowest fluence of 0.43 J cm^{-2} (Figure S5a) and the higher fluences (an example is given for a fluence of 5.6 J cm^{-2}, Figure S5b), the accumulated NP signals (S_{NP}) and total accumulated signals (S_T) in the line scans were calculated. From the line scans conducted with the lowest fluence of 0.43 J cm^{-2}, the ratio R_0 was calculated:

$$R_0 = {S_{NP(0.43)}} / {S_{T(0.43)}} \tag{1}$$

We assume that this ratio is representative for an "ideal" NP to total signal ratio where the least amount of NP degradation is expected. For the samples with the 50 and 102 nm NPs, the R_0 values were 0.65 and 0.83, respectively. Multiplying R_0 with the total signal from line scans conducted at higher fluences, $S_{T(>0.43)}$, yields a predicted (non-degraded) NP signal, $S_{NP,predict(>0.43)}$, for that fluence:

$$S_{NP,predict(>0.43)} = R_0 \cdot S_{T(>0.43)} \tag{2}$$

Comparing the predicted (non-degraded) NP signal for a given fluence, $S_{NP,predict(>0.43)}$, with the actual NP signal for the lowest fluence, $S_{NP(0.43)}$, gives the following NP signal scaling factor, $F_{(>0.43)}$:

$$F_{(>0.43)} = {S_{NP,predict(>0.43)}}/{S_{NP(0.43)}} \qquad (3)$$

In parallel, a NP size distribution histogram associated with the lowest fluence of 0.43 J cm^{-2} was created, followed by fitting to a lognormal function (Figure S5c). Multiplying this "ideal" (non-degraded) NP size histogram with the NP signal scaling factor, $F_{(>0.43)}$, allows for the creation of the predicted size distribution histograms for higher fluence values (Figure S5d). Finally, subtracting the predicted NP size histograms from the experimental size histograms results in histogram subtraction residuals as shown in Figure S5e. Here, the negative values represent a deficit in experimentally observed NPs as opposed to predicted, whereas positive values represent a surplus.

This data processing procedure was conducted for all measurements, with fluences ranging from 0.43 to 5.6 J cm^{-2}, and the resulting histogram subtraction residuals are shown in the main article (Figures 2c and d).

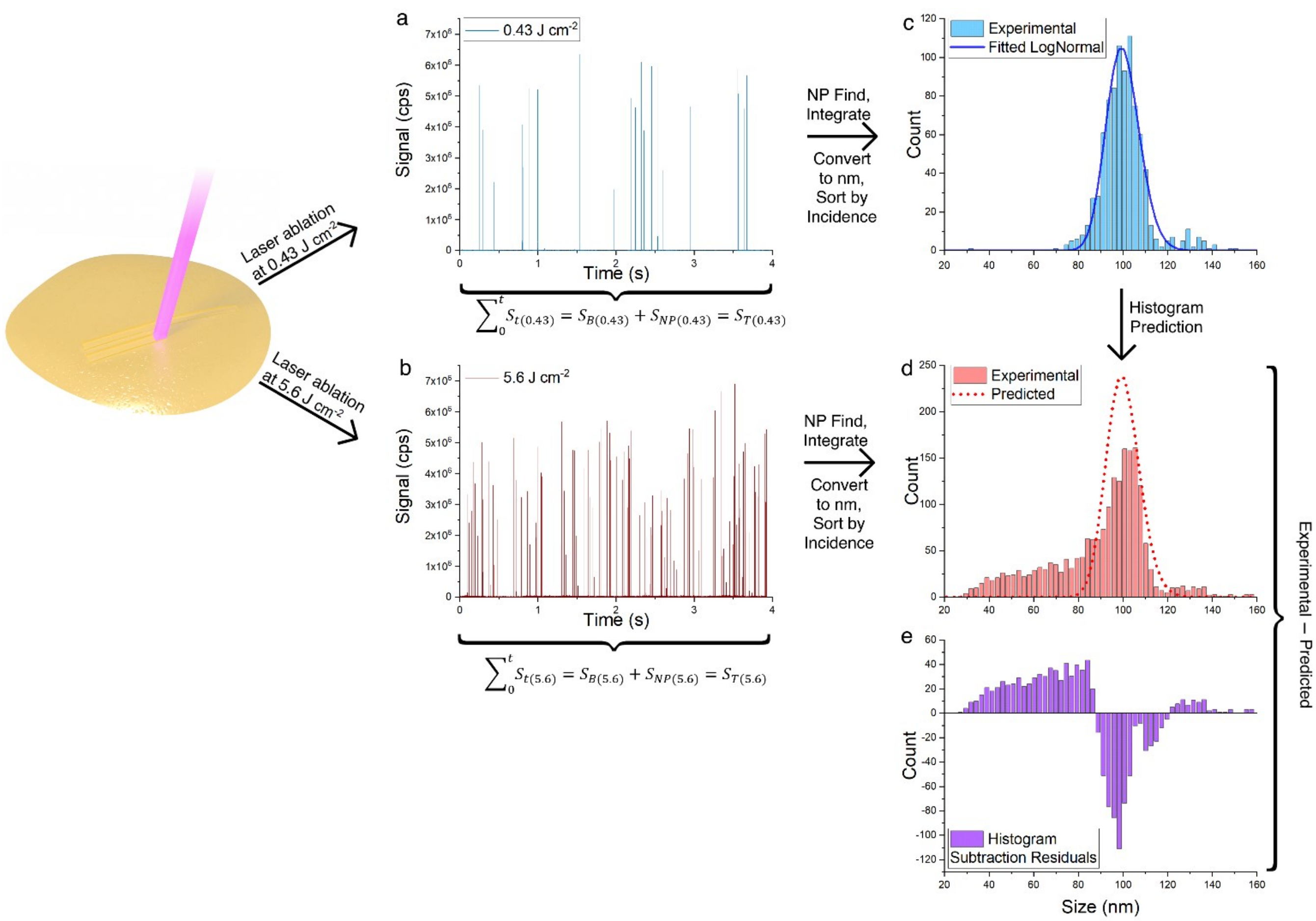

Figure S5. Overview of the measurement and data processing protocol required for the generation of histograms from the raw LA-ICPMS data (a, b, c and d) and histogram subtraction residuals (e).