

## Supporting information

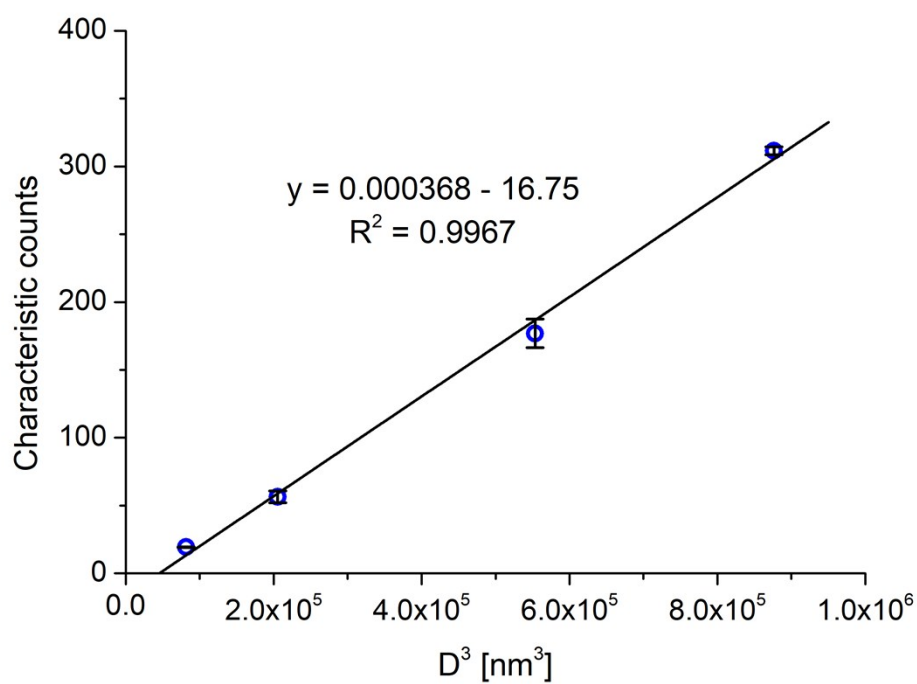
### Porosity determination of nano- and sub-micron particles by single particle inductively coupled plasma mass spectrometry

#### Single particle ICP-MS data evaluation

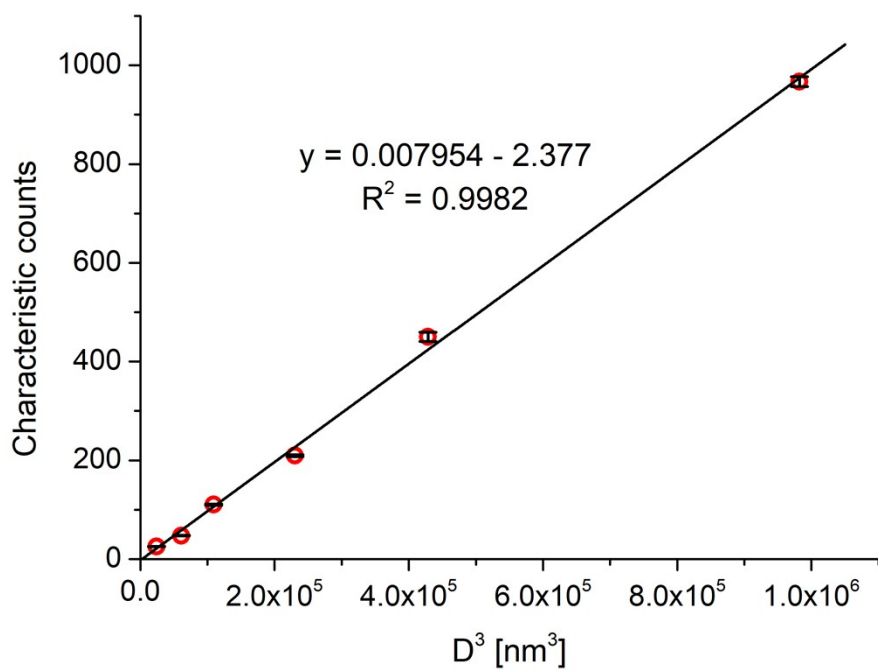
Data evaluation in spICP-MS uses the histograms (frequency–count diagrams) produced from the time-resolved signal traces. In histograms from correctly set-up experiments, the background signal shows up as a peak at a low count position, fittable by a symmetric, Poisson function. The histograms can be directly used for qualitative purposes, but for quantitative analysis (size calibration or concentration determination), it is needed to correct the background. It can be done by either of two equivalent approaches: the finding and subtraction of the background directly in the time resolved signal trace, or the manipulation of the histogram. As the reliable performance of the former approach requires a significantly longer acquisition time, here we adopted the latter, simpler approach: the mode of the background peak was subtracted from the mode of the particle peak (fittable by a lognormal function). Thus, the characteristic intensities (counts) of the particles are obtained. All data shown in the present study were background corrected.

The calibration of spICP-MS was carried out by using standard particle dispersions where the particle sizes were certified. The size calibration curve is obtained by plotting the characteristic counts as a function of the third power of the particle diameter, which is proportional with the volume or mass of the particles. During these calibrations, the “compactness” of the calibrating particles assumed to be full (in other words: their porosity was 0). These calibration graphs were fitted with a straight line. The “volume of analyte” in the investigated porous nanoparticles were then calculated from the equation of the fitted line.

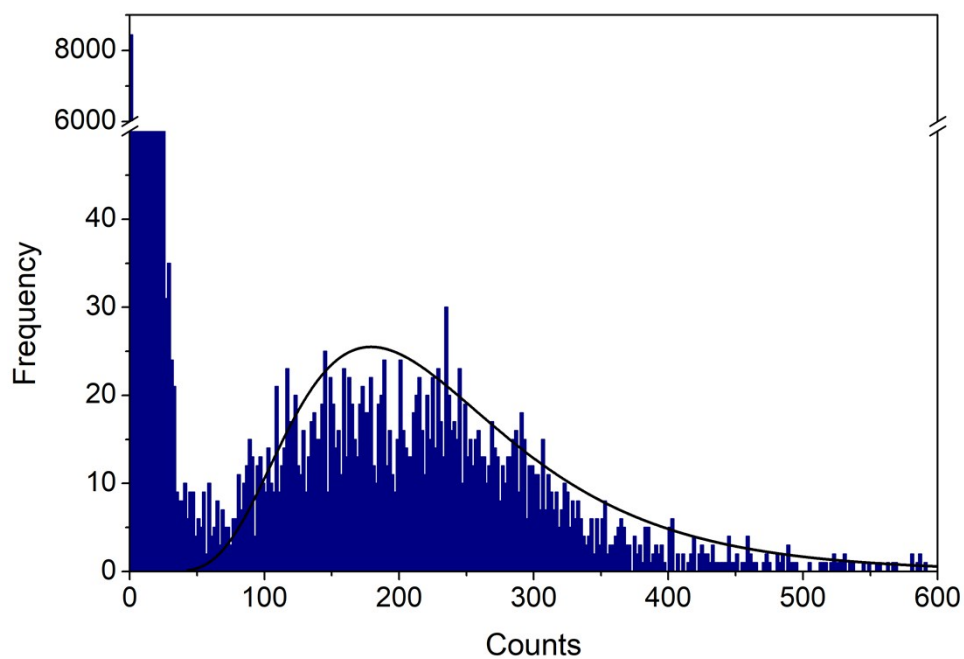
The following graphs show all calibration plots used as well as illustrative signal histograms for each of the particle types studied.



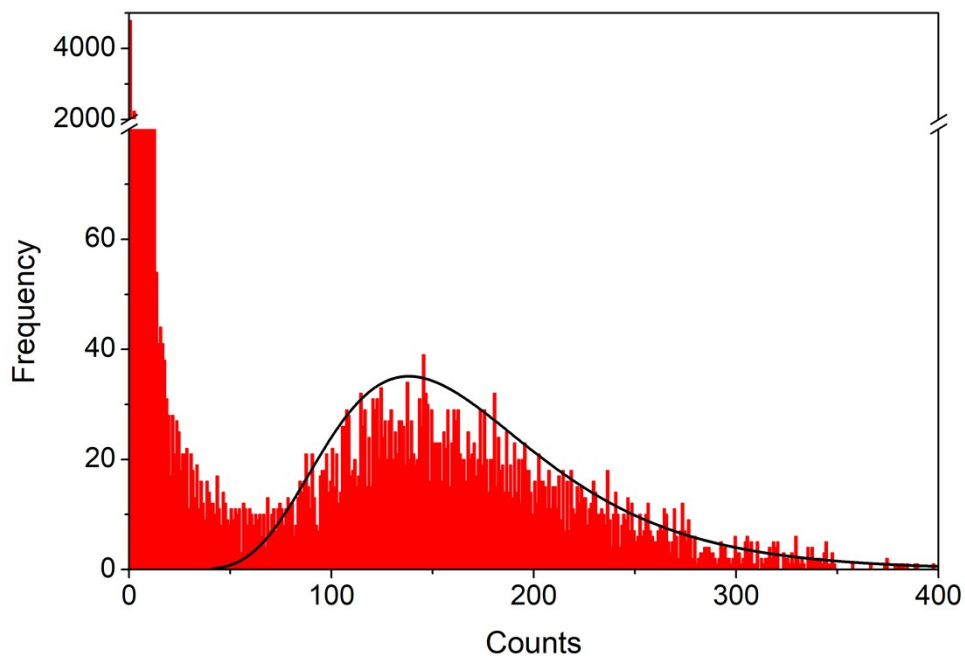
**Figure S1.** sp-ICP-MS size calibration graph for Ag nanoparticles (error bars are calculated from three repeated measurements)



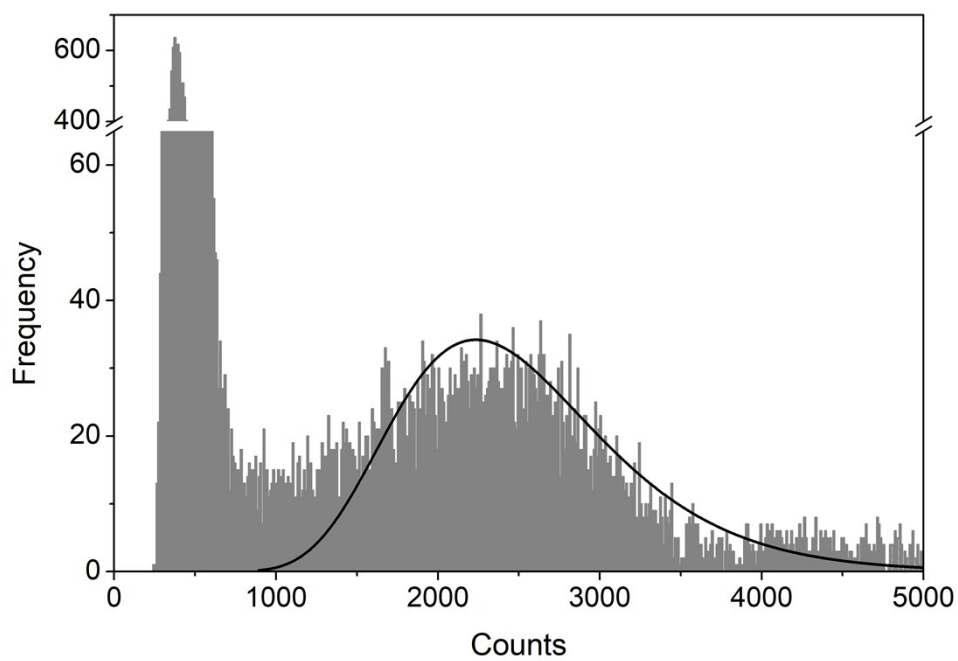
**Figure S2.** spICP-MS size calibration graph for Au nanoparticles (error bars are calculated from three repeated measurements)



**Figure S3.** sp-ICP-MS signal histogram for the  $^{107}\text{Ag}$  signal from 79 nm Au-Ag core-shell NPs. The curve shows the lognormal fit.



**Figure S4.** sp-ICP-MS signal histogram for the  $^{197}\text{Au}$  signal from 77.9 nm hollow Au NPs. The curve shows the lognormal fit.



**Figure S4.** sp-ICP-MS signal histogram for the  $^{28}\text{Si}$  signal from 447 nm porous  $\text{SiO}_2$  particles. The curve shows the lognormal fit.