Table S1: Sedimentation (Centrifugal) FFF channels dimensions

System	Channel thickness (cm)	Channel volume (mL)	Channel radius (cm)
A	0.0165	2.90	15.1
B	0.0200	2.26	10.2

Table S2: Run parameters used to analyze TiO_2 and CeO_2 nanoparticle suspensions

Method	Initial RPM	Final RPM	t_1 (min)	t_a (min)	Channel flow rate (mL/min)	Relaxation time (min)	Injection volume (µL)	Carrier
I	1800	100	5.6	-45.0	1.00	10	100	0.05% CTAB
II	2200	57	10.0	-80.0	1.00	10	100	0.05% FL-70 De-ionized water
III	3000	57	10.0	-80.0	1.00	3	100	0.05% FL-70 De-ionized water

Table S3. SP-ICP-MS general method parameters.

Sample flush time (sec)	Sample flush speed (rpm)	Read delay time (sec)	Delay and analysis speed (rpm)	Analysis flow rate (mL/min)	Analyte dwell time (ms)	Readings per run
50	24	20	20	0.974	10	20000

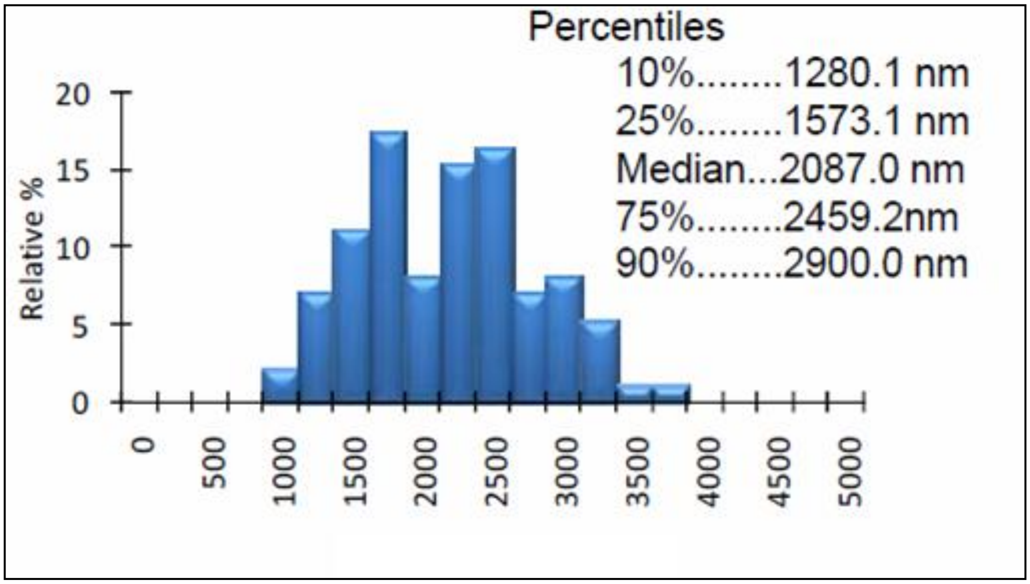

Figure S1. Manufacturer size distribution for Ag nanowires

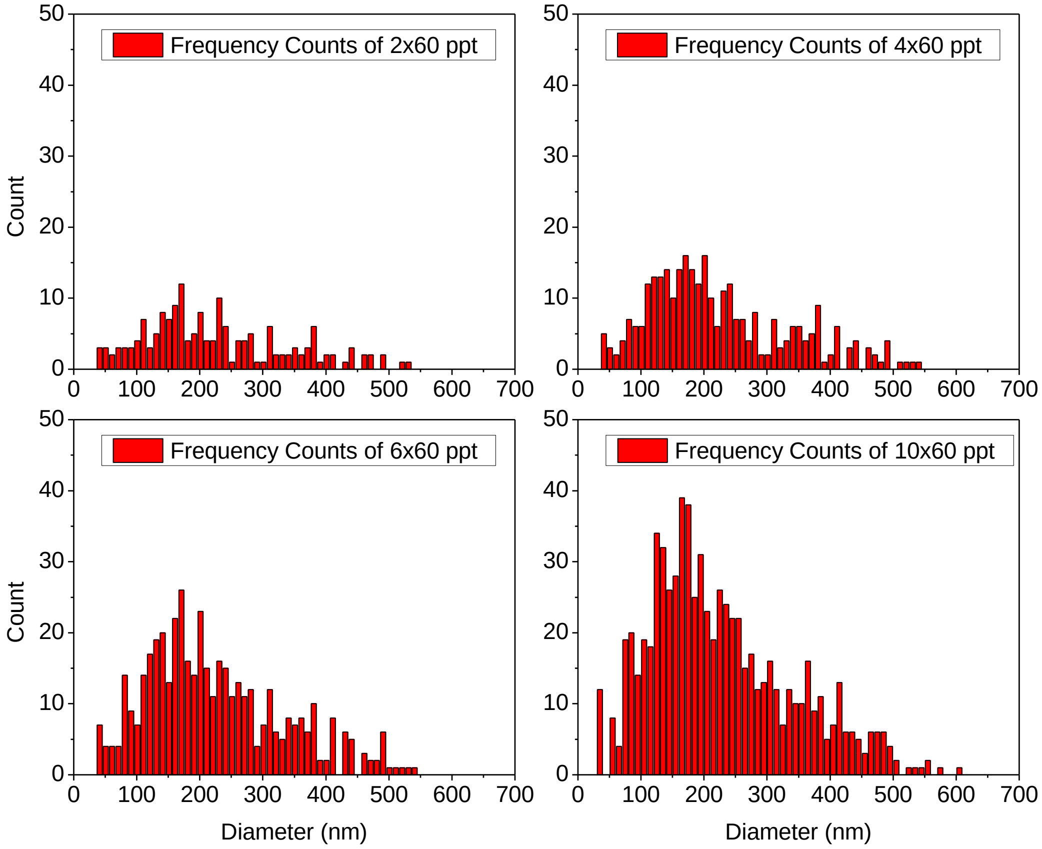

Figure S2. Combinations of size distribution data for 60 ppt TiO_2. Emergence of a well-defined size distribution is seen with increasing number of replicates.

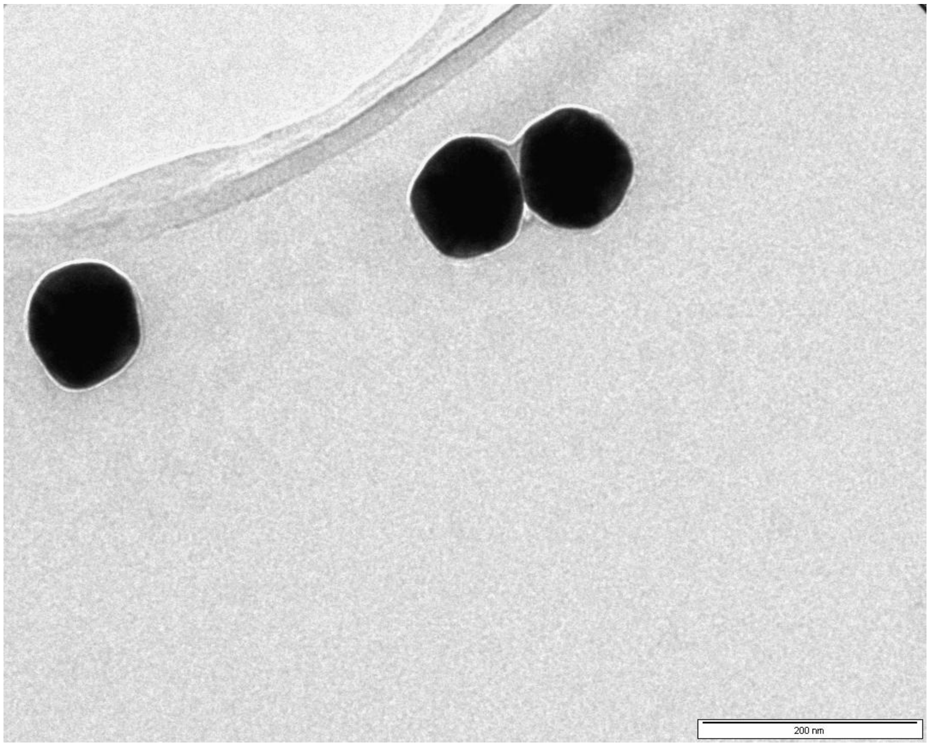

Figure S3. BBI Au ENPs TEM image

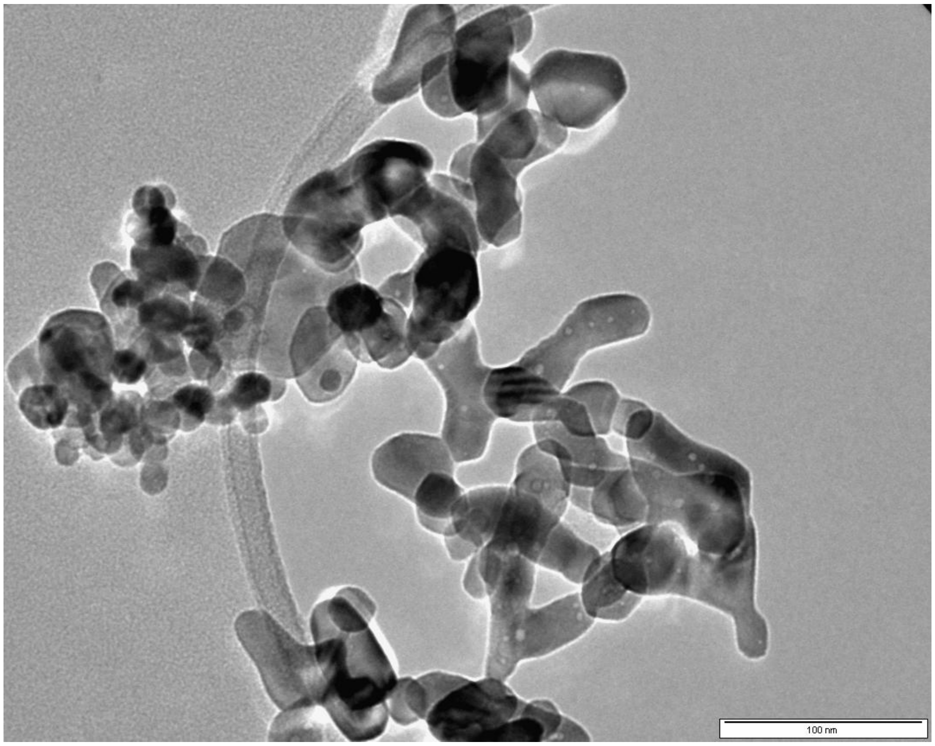

Figure S4. Inframat CeO_2 ENPs TEM image

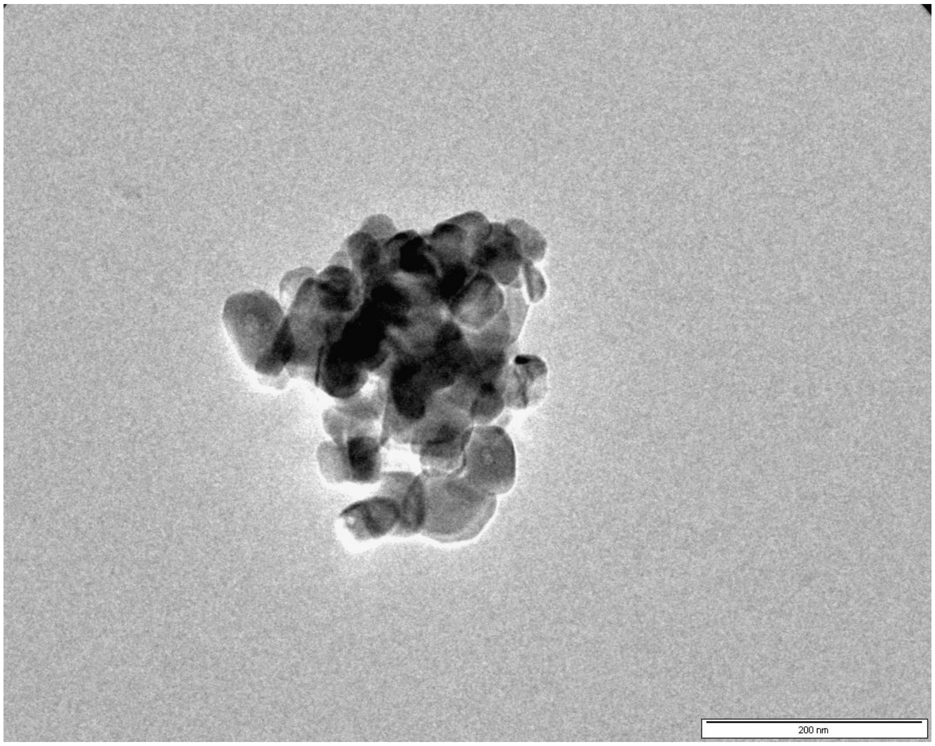

Figure S5. Aldrich TiO_2 ENPs TEM image

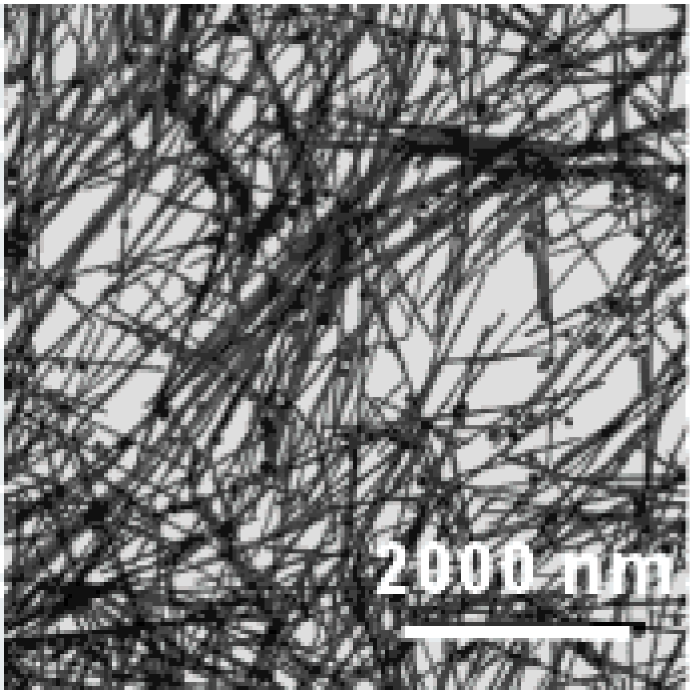

Figure S6. NanoComposix Ag nanowires TEM image (from manufacturer spec sheet)

Size Calculation Approaches

During ICP-MS operation, the majority of liquid sample flows to waste, while a small fraction is aerosolized, reaches the plasma, and is ionized for detection by the mass spectrometer. Ascertaining the fraction of sample that is analyzed is crucial for quantitative analysis of ENP size and number concentration. Well-characterized Au ENPs of a narrow particle size distribution (British Biocell International [BBI], 100 nm) were used to assess sample transport efficiency during SP-ICP-MS analysis by two different methods (*1*). The first method, based on particle number in solution, compares the number of observed pulses in a given run to the theoretical particle number in solution. The theoretical particle number at a given concentration is calculated assuming a spherical particle of known size (100nm for the Au NP used) and a density of 19.3 g/cm^3. Dividing the observed particle number/min by the theoretical particle number/min yields a transport efficiency for the instrument under a given set of flow parameters and sample introduction devices. Table S4 shows values obtained for this approach to efficiency determination.

Table S4. Instrument transport efficiency from comparing observed pulse number and theoretical particle number for Au ENPs. [*]Theoretical particle number per minute is based on calculated particles/mL and measured at 0.974 mL/min sample flow rate.

Au ENP concentration (ppt)	Theoretical particle number/min*	Observed pulse number/min	Efficiency (%)
10	963.8	30.0	3.11
25	2409.6	78.2	3.25
50	4819.2	76.2	3.16
100	9638.4	150.9	3.13
150	14457.5	145.0	3.01
200	19276.7	317.0	3.29
		Average:	3.15

These data are based on Au ENP runs from a single day. Figure S7 shows the reproducibility of Au ENP analyses on four different days. Although for this data set results are quite reproducible, instrument performance can vary day-to-day, even with proper optimization, and thus the transport efficiency will vary as well. It is recommended that transport efficiency be determined each day of analysis.

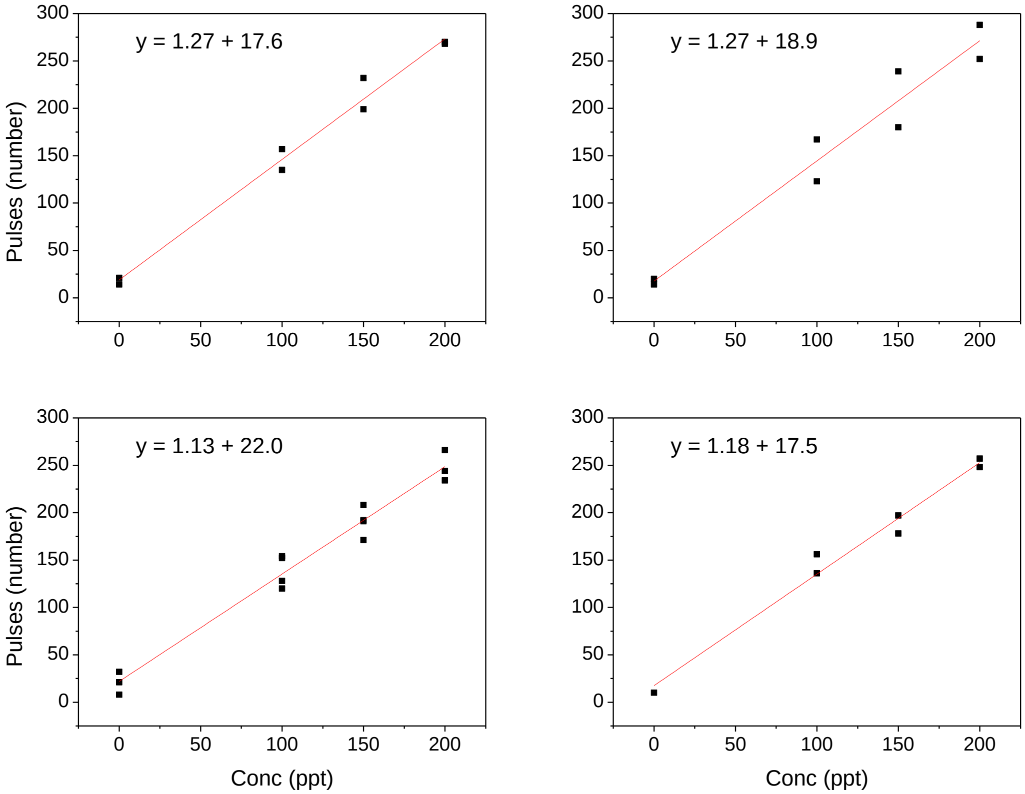

Figure S7. Observed number of pulses vs. concentration for four separate analyses of Nanocomposix 100 nm Au ENPs. Although the slope is reproducible within ~10%, including a standard monodispersed ENP in each SP-ICP-MS analysis is recommended for evaluating day-to-day variation in instrument efficiency.

A second method of ascertaining transport efficiency is a particle size-based approach. The number of ions generated by disintegration of an ENP in the plasma is proportional to the ENP size, and can be related to instrument signal intensity via a dissolved metal calibration curve. This has been shown previously by Degueldre et al (*2*) and Pace et al (*1*), who uses Equation 1 to transform a dissolved element calibration curve of instrument signal, I, vs. analyte concentration, C, to instrument signal vs. analyte mass per instrument reading, W.

$$W = \lfloor \eta_n * q_{liq} * t_{dt} * C \rfloor \qquad (1)$$

The instrument dwell time setting, t_{dt}, and flow rate, q_{liq}, are set by the user, and the transport efficiency η_n is adjusted to make a calculated diameter fit the known ENP diameter using the procedure as follows. By using a gold standard of a size sufficient to create a distribution well elevated above the background data, in this study 100 nm, a distribution of intensities is obtained. After transformation of the dissolved metal calibration curve to the desired units of ug/event (W) versus intensity, the intensity of each ENP pulse is used in Equation 2 to calculate the mass of a single ENP, m_{ENP}.

$$m_{ENP} = f_M^{-1} * \left[\frac{(I_{pulse} - I_{Bkgd})/\eta_i}{m} \right] \qquad (2)$$

Where the mass fraction of the analyte metal in the ENP is given by f_M, (1 for Au and Ag, 0.599 for TiO_2, and 0.814 for CeO_2) and m is the slope of W versus intensity. I_{Bkgd} is composed of both the instrumental background, equivalent to the intercept of the dissolved calibration curve (b) and dissolved elemental background in the ENP sample. I_{Bkgd} is subtracted from pulse intensity I_{pulse}, to obtain the intensity due to the ENP (I_{ENP}). The degree to which the ENP is ablated and ionized in the plasma is given by η_i; this is assumed to be 1. The mass of an ENP can be related to a particle diameter (d_{ENP}) via a given density, ρ, and assuming a spherical geometry by Equation 3.

$$d_{ENP} = \left[\frac{6 * m_{ENP}}{\pi * \rho} \right]^{1/3} \qquad (3)$$

The calibration standards and ENPs are both assumed to be atomized and ionized to the same degree in the plasma. Should this not be the case, then different transport efficiencies will be obtained from the two methods. Since we have seen only small differences, we believe the assumption about ionization efficiency is correct for the particles studied here.

For unknown ENPs, in some cases the distribution of pulse intensities are not clearly separated from the background. The situation can arise from the presence of very small ENPs in the distribution and/or from a high dissolved metal background. To extract the intensities due to ENPs from the background instrument response in a given run, iterative calculations are performed using Microsoft Excel. The entire dataset is used for calculation of a mean and standard deviation of measured intensity. Any data points above $\bar{x}$ + 5s are counted as a pulse arising from an ENP, and are removed from the dataset. The resulting new dataset is used to recalculate the mean and standard deviation, any pulses above $\bar{x}$ + 5s are added to the number of pulses from the first calculation and removed from the dataset, and the process is repeated until converging on mean value for the background response. The resulting pulses from the dataset are then processed by Equations 2 and 3. A less conservative approach can use 3s to detect the smaller ENPs in the size distribution. This approach relies on the assumption that the dissolved background signal is normally distributed. This is not always the case, especially with analytes having very low background response on the order of 0-5 counts. This approach has the potential to overestimate particle number concentrations and include “false-positives” in the lowest size range of the distribution, but should not affect the size analysis of the ENPs that are well-resolved from the background.

1. H. E. Pace *et al.*, *Anal Chem* **83**, 9361 (Dec 15, 2011).
2. C. Degueldre, P. Y. Favarger, S. Wold, *Analytica Chimica Acta* **555**, 263 (Jan 12, 2006).