Electronic Supplementary Information

Quantitative resolution of nanoparticle size using single particle inductively coupled plasma mass spectrometry (spICP-MS) assisted with the K-means clustering algorithm

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A. Converting spICP-MS raw data to sample concentration and size distribution.

After differentiation from background noise, the particle signals were further converted to sample concentration and size distribution on the basis of existing methodologies[1].

Briefly, the transport efficiency (fraction of analyte passing through the nebulizer and entering the plasma) was first determined using reference nanoparticles with known size as standards. The number concentration of particles can then be related to the pulse frequency by:

$$C_N = \frac{f_p}{q\eta_t} \qquad (1)$$

where C_N is the number concentration of nanoparticles in L^{-1}, f_p is the pulse frequency of particle signals in min^{-1}, q is the sample flow rate into the instrument in $L \cdot min^{-1}$, and η_t is the transport efficiency. The number concentration of particles can be further converted to mass concentration on the basis of the geometry and density of the particles.

Based on Pace et al.'s computational approach[1], by incorporating the transport efficiency into the calibration curve obtained from ionic element standards, the magnitude of each particle signal (pulse) can be related to the mass of a single particle by:

$$m_{p,i} = f_a^{-1}\left[\frac{\left(I_{p,i} - I_b\right) - b}{k / \eta_t}\right] \qquad (2)$$

where $m_{p,i}$ is the mass of the i^{th} particle (corresponding to the i^{th} pulse) in g, $I_{p,i}$ is the signal intensity of the i^{th} pulse in cps, I_b is the average background noise intensity in cps, k and b are the slope and intercept of the calibration curve obtained by plotting the instrument response intensity as a function of mass per dwell time for the ionic element standards, and f_a is the mass fraction of the analyte element in the particle. This computation assumes 100% ionization efficiency of the nanoparticles.

Geometric assumptions are used to convert the mass of each particle to size. For example, if the nanoparticles are assumed to have a spherical geometry, the diameter is determined by:

$$d_{p,i} = \left(\frac{6m_{p,i}}{\pi\rho} \right)^{\frac{1}{3}} \qquad (3)$$

where $d_{p,i}$ is the diameter of i^{th} particle in nm and ρ is the density of the nanoparticles.

B. Characterization of gold nanoparticles.

To quantify the concentration of Au in the stock solution, aqua regia (HCl:HNO3 3:1 v/v) was used to digest gold nanoparticles, and the resulting gold ions were measured using ICP-MS (Thermo X series II) to obtain the accurate mass concentration of gold nanoparticles.

Dynamic light scattering (DLS) analysis was carried out on a Brookhaven ZetaPals Analyzer (Brookhaven Instruments, Holtsville, USA) using the particle sizing function. The wavelength was 660 nm, and the scattering angle was set at 90°. A multimode size distribution (MSD) algorithm was used to characterize the particle size distribution. The MSD output format was set as intensity, which the instrument measures directly. Refractive indexes of 1.33 and 2.30 were used for Au and CeO_2, respectively.

Transmission electron microscopy (TEM) was conducted on Philips CM200-FEG high resolution TEM/STEM. Over 100 nanoparticles were sized under the TEM image to obtain TEM-based nanoparticles size distribution.

Size distributions of AuNPs obtained by different techniques are shown in Figure S1.

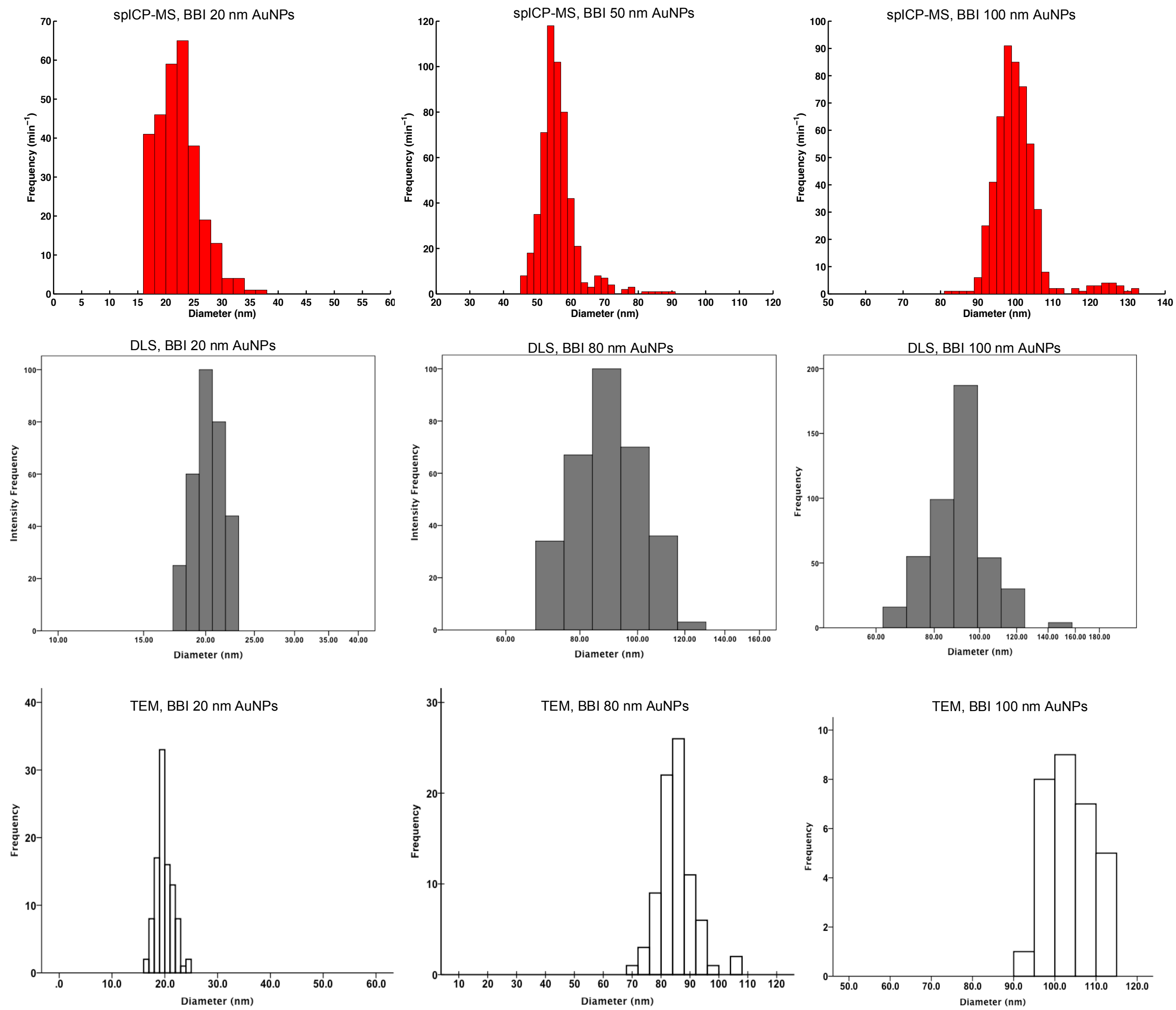
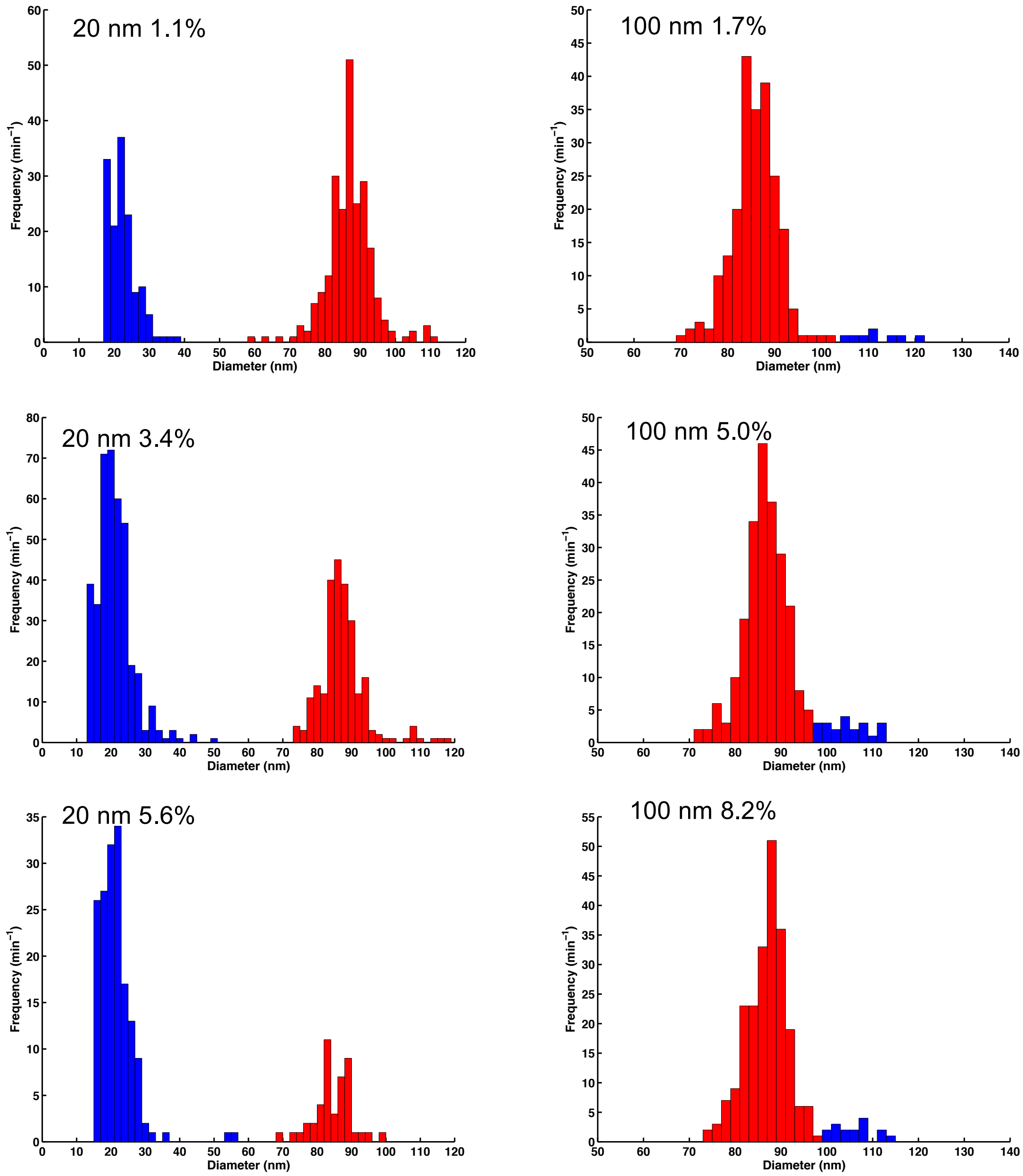


Figure S1. Particle size distribution histograms of BBI AuNPs determined by spICP-MS, DLS, and TEM.


20 nm 1.1%
100 nm 1.7%
20 nm 3.4%
100 nm 5.0%
20 nm 5.6%
100 nm 8.2%
Frequency (min^{-1})
Diameter (nm)

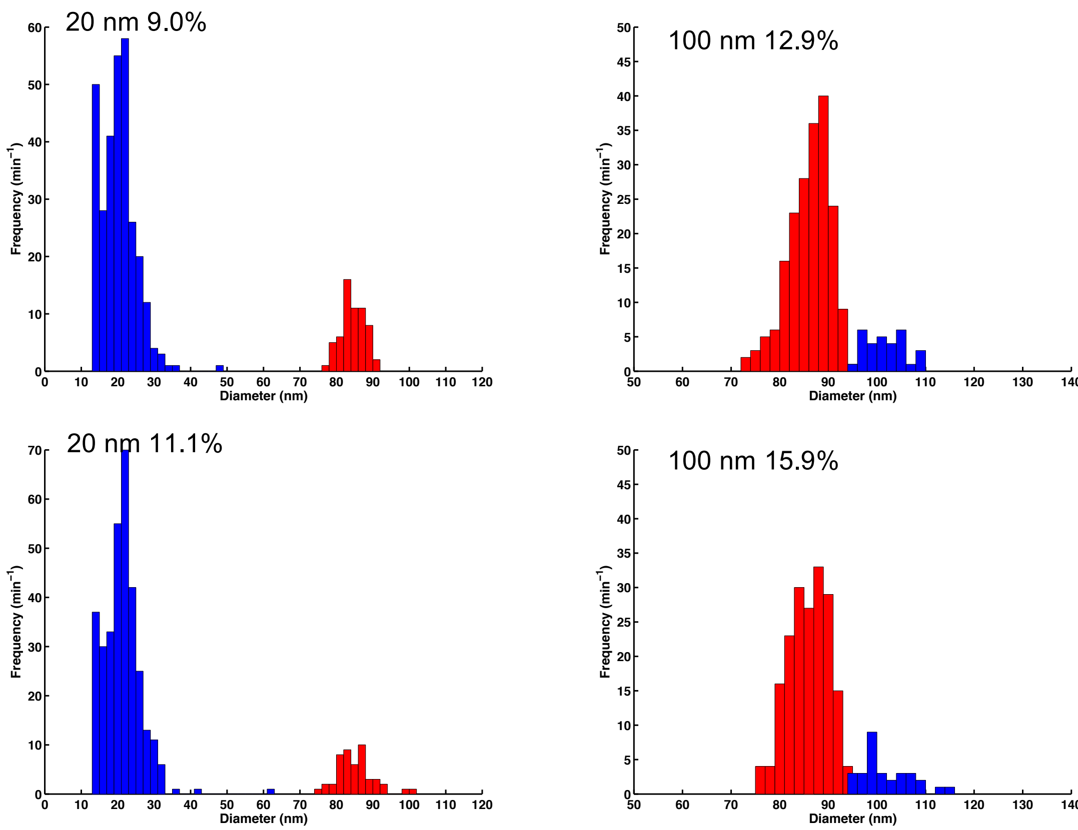


Figure S2. Particle size distribution of AuNP samples with different size constituents. All the percentages in the figure are based on mass.

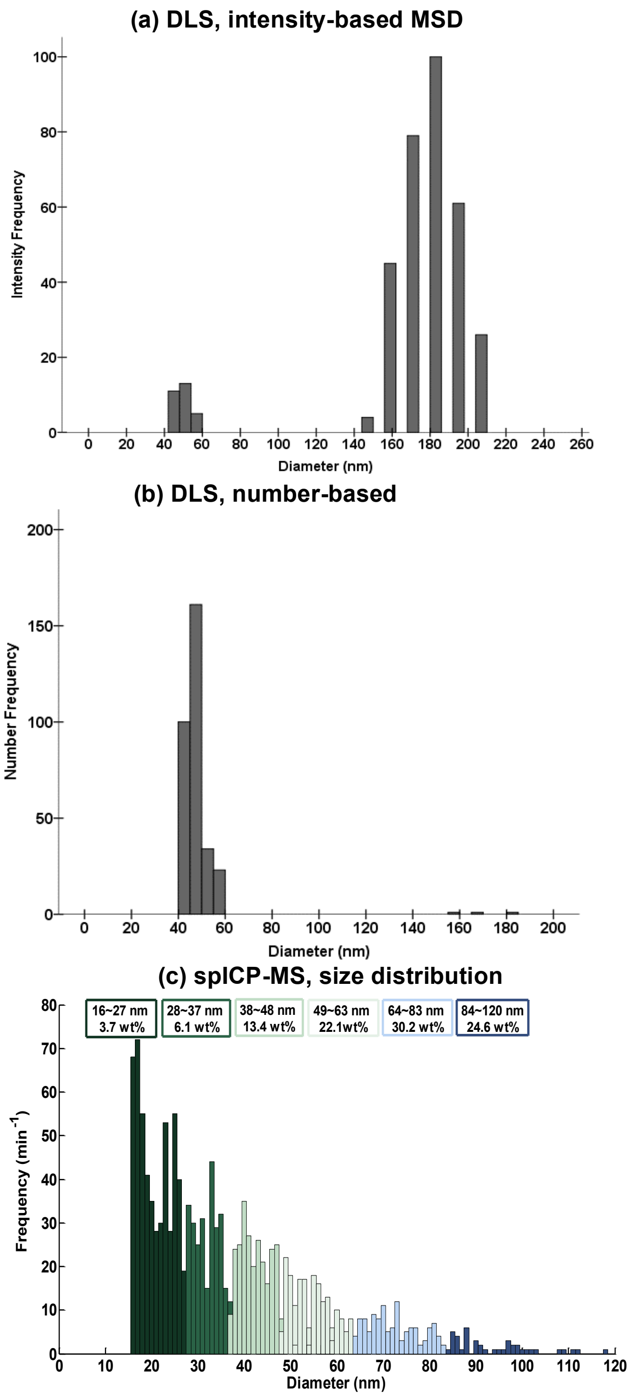


Figure S3. DLS and spICP-MS analysis of a nominal 30-nm CeO_2 nanoparticle sample: (a) intensity-based multimodal size distribution result by DLS; (b) number-based multimodal size distribution result by DLS; (c) size distribution by spICP-MS with the mass of different size ranges quantitatively determined by the K-means algorithm.

Reference

(1) Pace, H. E.; Rogers, N. J.; Jarolimek, C.; Coleman, V. A.; Higgins, C. P.; Ranville, J. F. *Anal. Chem.* **2011**, *83*, 9361-9369.