Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information for

Experimental approach to the fundamental limit on the extinction coefficients of the ultra-smooth and highly spherical gold nanoparticles†

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I. Zeta-potential of super-spherical AuNPs.

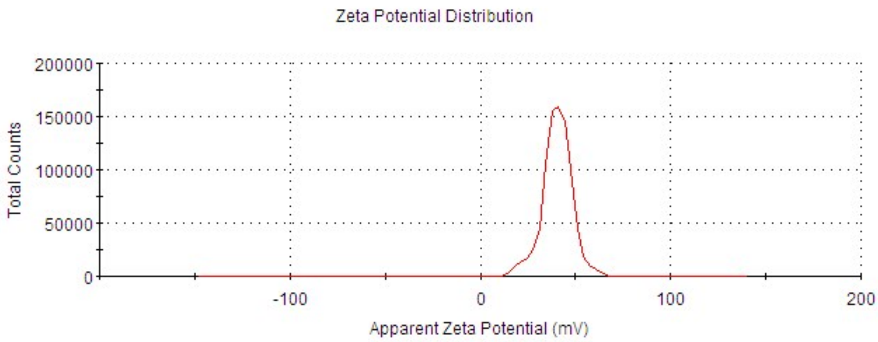

Fig. S1. the zeta potential of the gold nanospheres (d=40nm) in water was 40.4 mV with 7.74 mV of standard deviation, which was measured by Laser Doppler Micro-electrophoresis using MALVERN Zetasizer Nano ZS90.

II. Dimension of Au octahedra

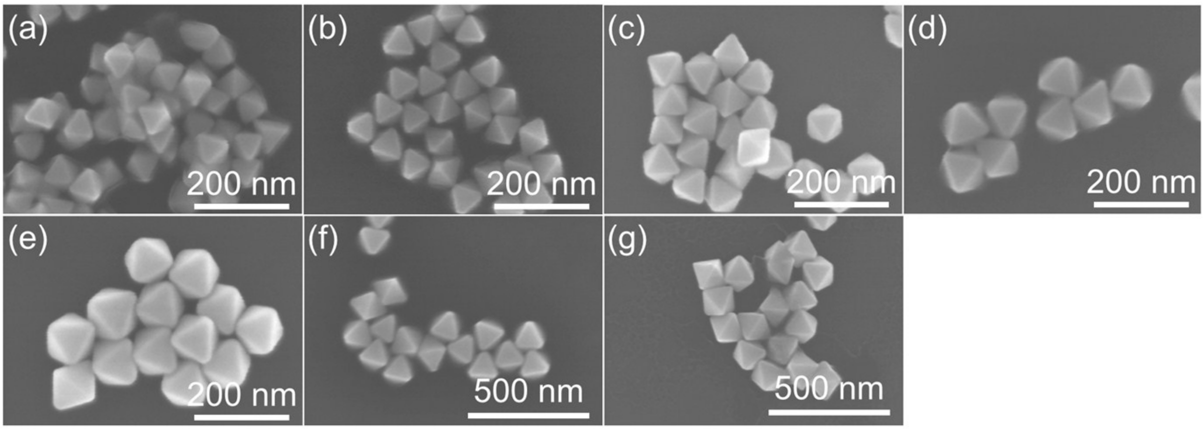

Fig. S2. Scanning electron microscope (SEM) images of Au octahedra (pristine motifs for highly spherical AuNPs) with different sizes of (a) 54 nm, (b) 60 nm, (c) 72 nm, (d) 80 nm, (e) 92 nm, (f) 116 nm, and (g) 125 nm

III. ICP-MS Analysis of supernatant of gold octahedron suspension

Table S1. Measured concentration of unreacted Au atom in Au octahedron suspension by ICP-MS. Calculated amount of unreacted Au atoms based on the total amount of Au atom (1.97 mg) and yield of Au ion reduction in Au octahedron formation.

Diameter of Au nanospheres (nm)	Concentration of unreacted Au atom in Au octahedron suspension (ppb)	Calculated total amount of unreacted Au atom (mg)	Yield of Au ion reduction in Au octahedron formation (%)
40	10 <	0.0002 <	99.99 >
50	10 <	0.0002 <	99.99 >
60	22.7	0.000454	99.98
70	10 <	0.0002 <	99.99 >
80	10 <	0.0002 <	99.99 >
90	10 <	0.0002 <	99.99 >
100	40.8	0.000816	99.96

IV. Size distribution of highly spherical AuNPs

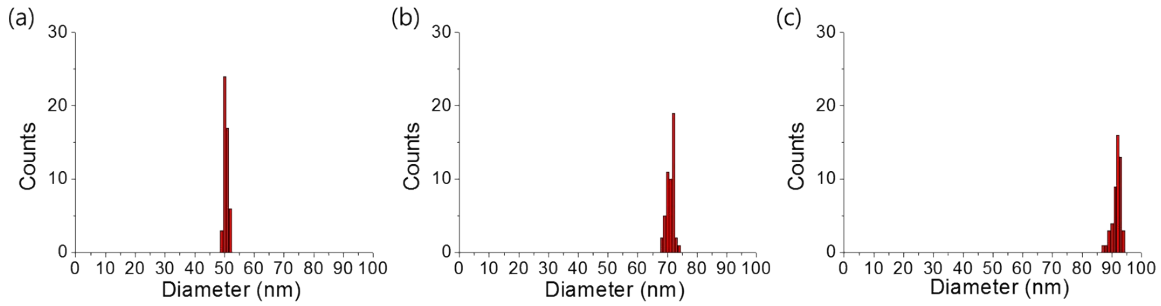

Fig. S3. Size distribution histograms of highly spherical AuNPs of (a) 50 nm, (b) 70 nm, and (c) 90 nm-sized AuNPs, which were analyzed by ImageJ software.

V. Detailed descriptions for Mie theory

Total extinction cross section of a spherical AuNPs can be analytically addressed by solution of Maxwell′s equations, which were firstly found by Mie:[S1]

$$\sigma = \frac{\lambda_m^2}{2\pi}\sum_{l=1}^{l=\infty}(2l+1)[Im\{t_l^E\} + Im\{t_l^M\}]$$

where t_l^E, t_l^M, and l refer respectively to electric, magnetic scattering coefficients, and number of nodes (l =1 means a fundamental dipole oscillation); both t_l^E and t_l^M can be analytically calculated by Bessel and Hankel functions (for homogeneous sphere), as follows:[S2]

$$t_l^E = \frac{-\varepsilon_m j_l(\rho_m)\left[j_l(\rho) + \rho j_l'(\rho)\right] + \varepsilon[j_l(\rho_m) + \rho_m j_l'(\rho_m)]j_l(\rho)}{\varepsilon_m h_l^{(+)}(\rho_m)[j_l(\rho) + \rho j_l'(\rho)] - \varepsilon[h_l^{(+)}(\rho_m) + \rho_m h_l^{(+)'}(\rho_m)]j_l(\rho)}$$

$$t_l^M = \frac{-\rho j_l(\rho_m)J_l'(\rho) + \rho_m j_l'(\rho_m)j_l(\rho)}{\rho h_l^{(+)}(\rho_m)j_l'(\rho) - \rho_m h_l^{(+)'}(\rho_m)j_l(\rho)}$$

where $\rho=(2\pi R/\lambda)\sqrt{\varepsilon}$, $\rho_m=(2\pi R/\lambda)\sqrt{\varepsilon_m}$, and the primes stand for derivatives; herein, R indicates the a radius of a spherical AuNP. The complex dielectric constants of Au was obtained by Drude model with the variables including plasma frequency of 14.3×10^{15} rad/s, epsilon infinity of 11.85, and collision frequency of 1.12×10^{13} THz.

VI. FDTD-simulated extinction coefficients of spherical AuNPs

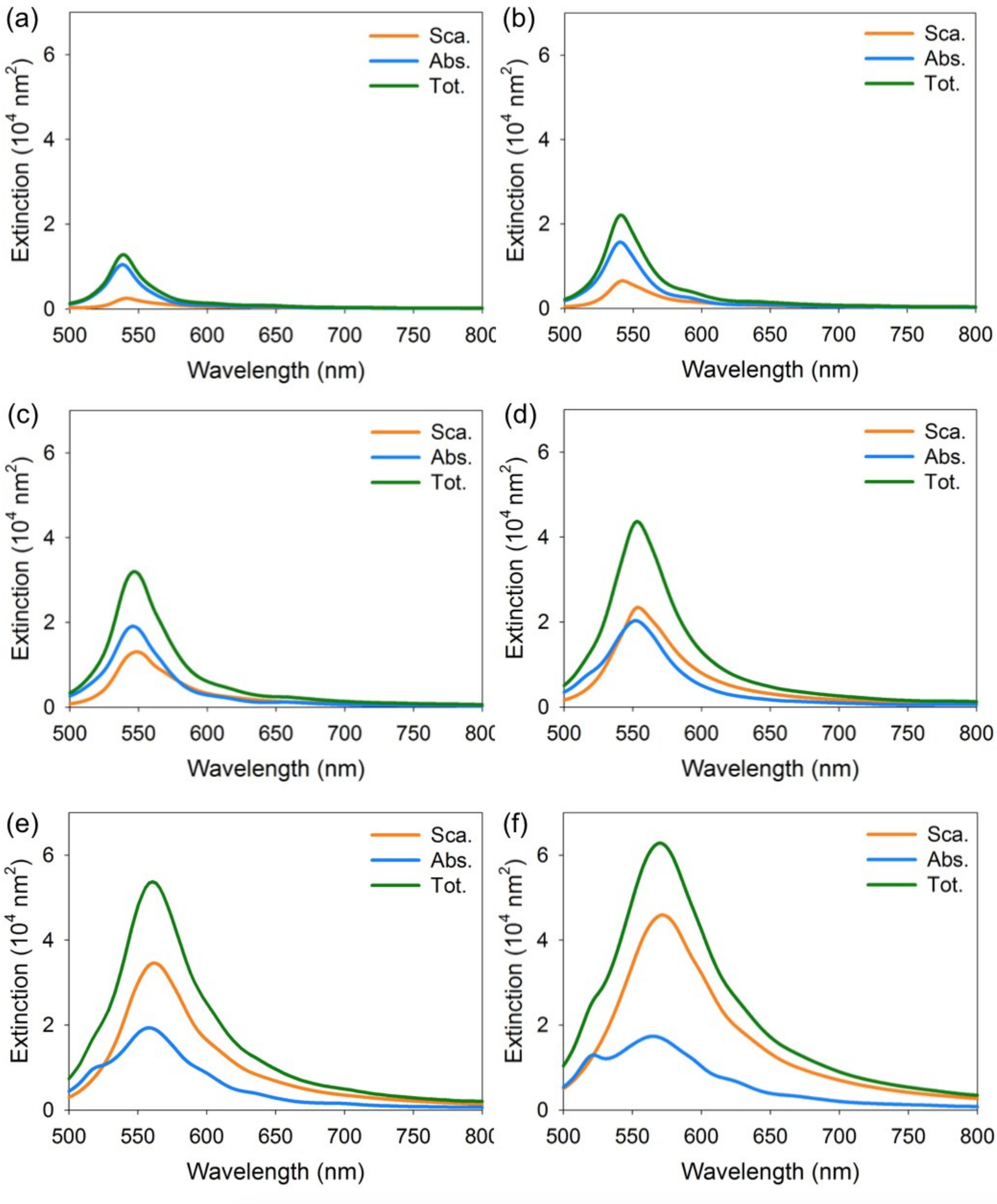

Fig. S4. FDTD-simulated extinction cross sections of highly spherical AuNPs with sizes of (a) 40 nm, (b) 50 nm, (c) 60 nm, (d) 70 nm, (e) 80 nm, and (f) 90 nm.

VII. References

S1. Mie, G. Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen. *Ann. Phys. (Leipzig)* **1908**, *25*, 377.

S2. van de Hulst, H. C. *Light Scattering by Small Particles*, Dover, New York, **1981**.