Electronic Supplementary Information

Hydrothermal Synthesis of Gold Nanocrystals by Varying Surfactant Concentration and Their LSPR and SERS Properties

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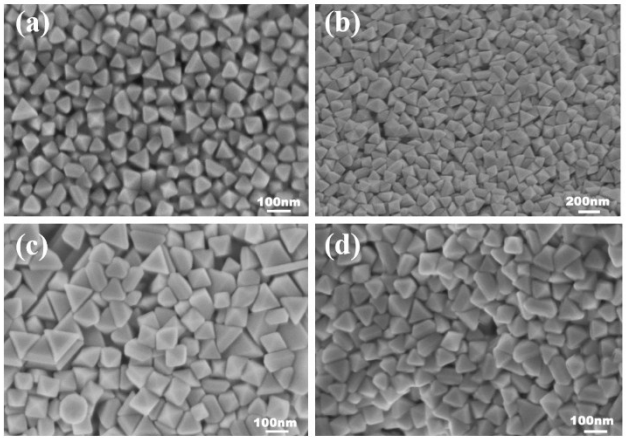

Fig. S1 SEM images of the Au NCs synthesized with the concentrations of CTAB: (a) 10.5 mM, (b) 9 mM, (c) 7.5 mM and (d) 6 mM.

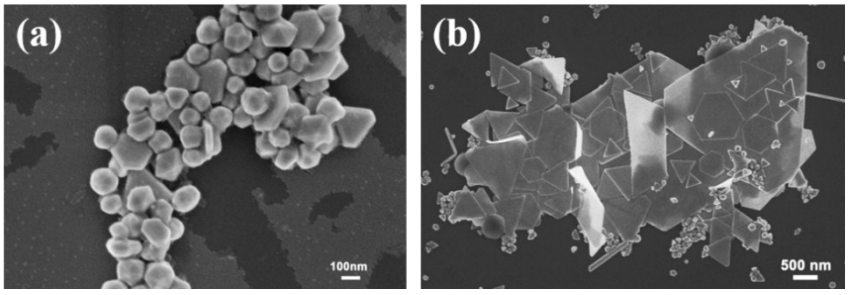

Fig. S2 SEM images of Au NCs synthesized with extremely low concentrations of CTAB: (a) small triangular plates (3 mM, CTAB /Au = 15) and (b) large triangular and hexagonal plates (1.5 mM, CTAB /Au = 7.5)

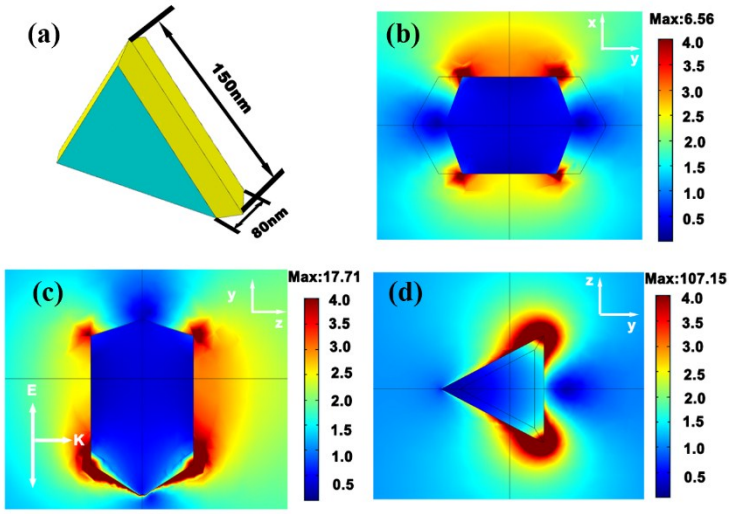

Fig. S3. (a) 3D model of the truncated Au bitetrahedron and the corresponding distributions of near-field enhancement in the tangent planes along (a) x-y plane, (b) x-z plane and (c) y-z plane.

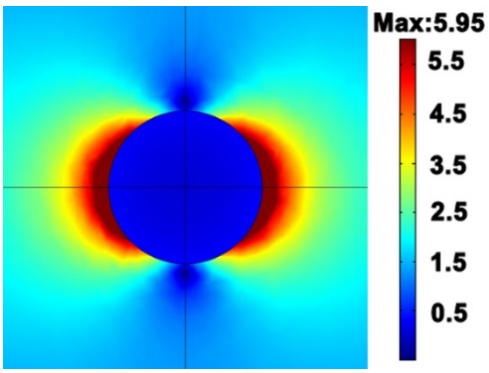

Fig. S4 Calculated near-field distributions in the central tangent plane of Au nanosphere with diameter 80nm

Analytical SERS enhancement factors (EFs) calculation

The calculation of SERS enhancement factors is followed the equation: $EF = (I_{SERS}/I_{bulk}) \times (N_{bulk}/N_{SERS})$ where I_{SERS} and I_{bulk} are the integrated intensities of a characteristic band from SERS and from bulk Raman , respectively; N_{bulk} is the number of bulk molecules probed in the bulk sample; and N_{SERS} is the number of excited molecules adsorbed on the SERS substrate. The Raman spectrum of the 4-MBA solution (10 mM) was used to estimate the "bulk" values in the EF equation. The diameter of illumination focus of the 2.39 μm was first calculated using the following formula: $D_{diameter} = (\lambda/NA) \times 1.22$, in which the NA = 0.4 for the 20×objective lens of the Raman spectrometer at the 785 nm wavelength. Moreover, the penetration depth of laser beam is about 6.86 μm in the solution. Then, the effective excitation volume was 64.5 μm^3 and the $N_{bulk} = 3.89\times10^8$. Next, with regard to the calculation of N_{SERS}, the excitation light of 785-nm wavelength was directly irradiated on the Au colloidal solution, so the effective excitation depth was assumed as a monolayer of NC in the Au colloidal solution. The effective excitation volume is:

$$V_{SERS} = \pi\left(\frac{D_{diameter}}{2}\right)^2 R,$$

where R represents the dimension of NCs. In our calculation, the polyhedral Au NC was assumed as a

nanosphere with radius of 43 nm. The number of absorbed 4-MBA molecule was estimated through the initial concentration of 4-MBA solution (20 μl, 1mM). And 1 ml solution of the 4-MBA-labeled polyhedral Au NCs was transferred to a 2 mm quartz cuvette for SERS measurement. Therefore, the number of excited molecules equals to the effective excitation volume multiplies the initial volume density of molecular, i.e. $N_{SERS} = V_{SERS} \times N_{Initial}/V_{Initial}$. Then, $N_{SERS} = 1.34\times10^3$ was obtained.

However, the above calculation process ignores the different surface areas between the polyhedral Au NCs samples. Hence, it is necessary to add a corrected factor to modify the N_{SERS} of nanosphere for the different kinds of polyhedral Au NCs. The corrected factor *f* is strongly dependent on the surface area of polyhedral Au NC and defined as follows[S1, S2]:

$$f = [\frac{Spolyhedron}{Ssphere}]^2,$$

where $S_{polyhedron}$ is the surface area of polyhedral Au NCs, and S_{sphere} the surface area of nanosphere. For high degree Au polygon, the corrected factor is calculated as $f_1 \approx 0.91$; (2) For Au truncated cuboctahedron, $f_2 \approx 0.82$; (3) For Au cuboctahedron, $f_3 \approx 0.74$. (4) For Au truncated octahedron, $f_4 \approx 0.68$; (5) For Au truncated bitetrahedron and tetrahedron, $f_5 \approx 0.53$. Consequently, the number of excited molecules of the polyhedral Au NCs colloidal samples are given as $N_1 = f \times N_{SERS} = 1.22\times10^3$, $N_2 = 1.10\times10^3$, $N_3 = 9.90\times10^2$, $N_4 = 9.11\times10^2$ and $N_5 = 7.78\times10^2$, respectively. In addition, the values of I_{bulk} is 4.87×10^4 and the values of I_{SERS} are $I_1 = 8.25\times10^5$, $I_2 = 1.29\times10^5$, $I_3 = 1.31\times10^5$, $I_4 = 1.34\times10^5$, and $I_5 = 1.67\times10^5$, respectively. Thus, the EF values of the polyhedral Au NCs colloidal samples are given as $EF_1 = 7.51\times10^5$, $EF_2 = 9.15\times10^5$, $EF_3 = 1.01\times10^6$, $EF_4 = 1.10\times10^6$, $EF_5 = 1.29\times10^6$.

Reference:

[S1] Q. Zhang, N. Large and H. Wang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 17255–17267.

[S2] V. S. Tiwari, T. Oleg, G. K. Darbha, W. Hardy, J. P. Singh and P. C. Ray, *J. Phys. Chem. Lett.*, 2007, **446**, 77–82.