Electronic Supporting Information

Intrinsic and Well-defined Second Generation of Hot Spots in Gold Nanobipyramids versus Gold Nanorods

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Materials

All chemicals were used as received from the commercial suppliers unless otherwise stated. Gold (III) chloride trihydrate ($HAuCl_4$), 4-aminothiophenol (4-ATP, 97%), silver nitrate ($AgNO_3$, ≥ 99%), sodium borohydride ($NaBH_4$, 98%), cetyltrimethylammonium bromide (CTAB, ≥ 98%), benzyldimethylhexadecylammonium chloride (BDAC), L-ascorbic acid (AA, 99%), sodium citrate (≥ 98%), and copper chloride ($CuCl_2$, 99%) were purchased from Sigma-Aldrich. Freshly prepared *aqua regia* (HCl: HNO_3 in a 3: 1 ratio by volume) was used to clean all glassware followed by rinsing with copious amounts of ultrapure water (18.2 Milli-Q).

Experimental procedures

Synthesis of gold nanorods: Gold nanorods were synthesized through seed-mediated method reported in the literature.[1] To make the seeds, ice-cold freshly-prepared $NaBH_4$ (600 µL, 1 mM) was added into the mixture of $HAuCl_4$ (5 mL, 0.5 mM) and CTAB solution (5 mL, 0.2 M) under vigorously stirring continuing for 2 min, then the solution was kept at 30 °C for 2 h. The growth solution was prepared by adding $AgNO_3$ (1.2 mL, 4 mM) into the solution containing $HAuCl_4$ (25 mL, 1 mM) and CTAB (25 mL, 0.2 M). The reaction continued by injecting freshly made ascorbic acid (380 µL, 78.8 mM) which caused an immediate color change from yellow to colorless. Finally, the seed solution (40 µL) was added to growth mixture and the reaction allowed to be completed at 30 °C overnight. The as-synthesized gold nanorods were purified by two steps of centrifugation (13000 *g*, 35 min) and redispersed in CTAB solution (1 mM).

Synthesis and purification of gold bipyramids: Gold bipyramids were prepared and purified following the literature procedures.[2] Briefly, seed solution was first synthesized by adding $NaBH_4$ solution (300 µL, 10 mM) to a mixture of Milli-Q water (18.95 mL), $HAuCl_4$ (250 µL, 10 mM) and freshly prepared sodium citrate (500 µL, 10 mM), followed by 2 h of incubation at room temperature. Then 110 µL of the seeds was introduced to a growth solution containing CTAB (10 mL, 0.1 M), $HAuCl_4$ (500 µL, 0.01 M), $AgNO_3$ (100 µL, 0.01 M), HCl (200 µL of 1 N) and ascorbic acid (80 µL, 0.1 M) and the reaction was allowed to proceed at 30 °C for 2 h. The obtained colloid was centrifuged twice (15000 *g*, 13 min) and redispersed in CTAB solution (3 mL, 1 mM). Afterward the purification step was performed by adding the particles solution (3 mL) to BDAC (7 mL, 0.5 M) followed by incubated at 30 °C overnight. The supernatant was carefully removed and resultant precipitate was centrifuged twice (8000 *g*, 8 min) and redispersed in CTAB (3 mL, 1 mM).

Tip-modification and end-to-end assembly process: selective surface modification was conducted by adding 4-ATP (1.5 µL, 2 mM) to 100 µL of the CTAB-capped particles solution (OD ~ 10), the mixture was stirred at 25 °C for 2 h, followed by 3 times centrifugation to remove excess amount of 4-ATP. End-to-end assembly was further performed by adding an aqueous solution of Cu^{2+} (0.2 μM) to tip-modified gold bipyramids and nanorods. The solution was left to react for 1 h before performing SERS measurement.

Finite element method simulation: Electric field modeling was performed using finite element method under COMSOL Multiphysics 5.1 software. The domain was surrounded by perfectly matched layer (PML) for the absorption of the propagating wave. The frequency-dependent dielectric constant was applied based on Johnson and Christy experimental data.[3] Gold bipyramids and nanorods were modeled as being composed of two circular cones, and one cylinder respectively, with spherically rounded tips in accordance to their electron microscopy images. The average diameters and lengths were determined from the TEM images using Image J software (the dimensions were estimated over average of 150 particles).

Characterization: Cary 60 single-beam UV-Vis spectrophotometer was used to measure absorption spectra of gold bipyramids and nanorods at room temperature. Transmission electron microscopy (TEM) images were recorded on the FEI TECNAI G2 microscope at an acceleration voltage of 200 kV. The TEM sample was prepared by drop casting the nanoparticles solution on carbon coated copper grids followed by air-drying overnight. Raman spectra were measured using a Renishaw inVia confocal Raman microscope with excitation laser wavelengths of 785 nm and the diffraction grating of 1200 g/mm. Raman measurements were recorded on colloidal sample in capillary tubes with the laser power of ~ 2.01 mW, accumulation time of three and exposure time of 10 s. The average of 3 times measurement was used to present in SERS spectra. The concentration of gold nanorods and bipyramids were determined using inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer, NexION). X-ray photoelectron spectroscopy was applied for surface analysis of nanoparticles using an ESCALab 250 Xi (Thermo Scientific) spectrometer equipped with a monochromatic Al Kα source (1486.6 eV) hemispherical analyzer. The sample was made by placing nanoparticles solution on clean indium substrate followed by air-drying. The XPS data fitting was done using Avantage 4.73 software.

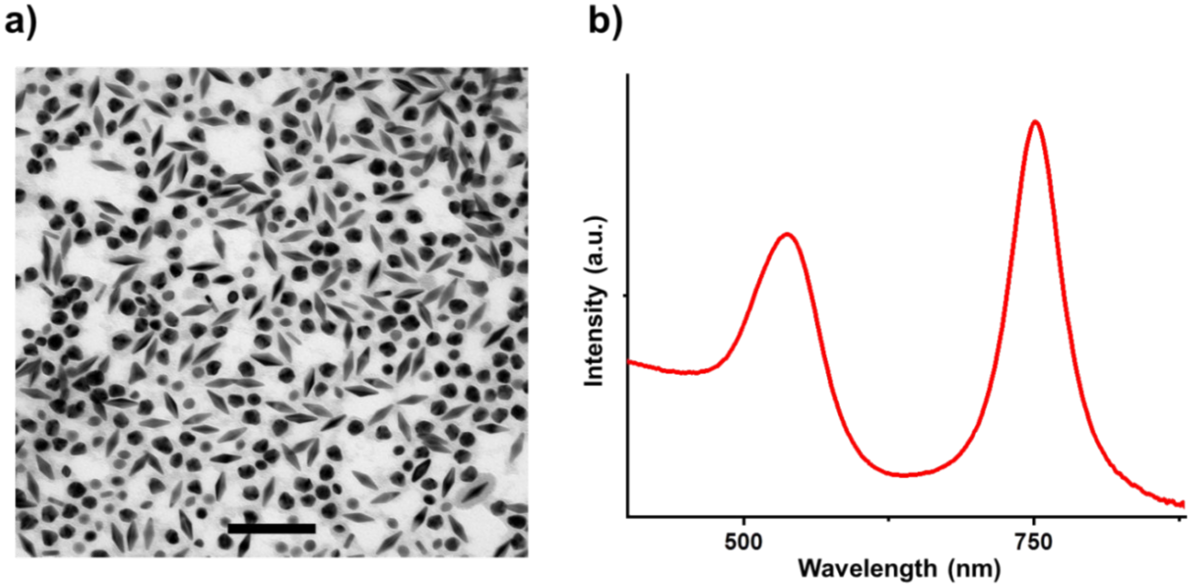

Fig. S1 (a) TEM micrograph and (b) UV-Vis spectrum of as-synthesised gold bipyramids by following the seed-mediated method reported by Guyot-Sionnest *et al.*[2]

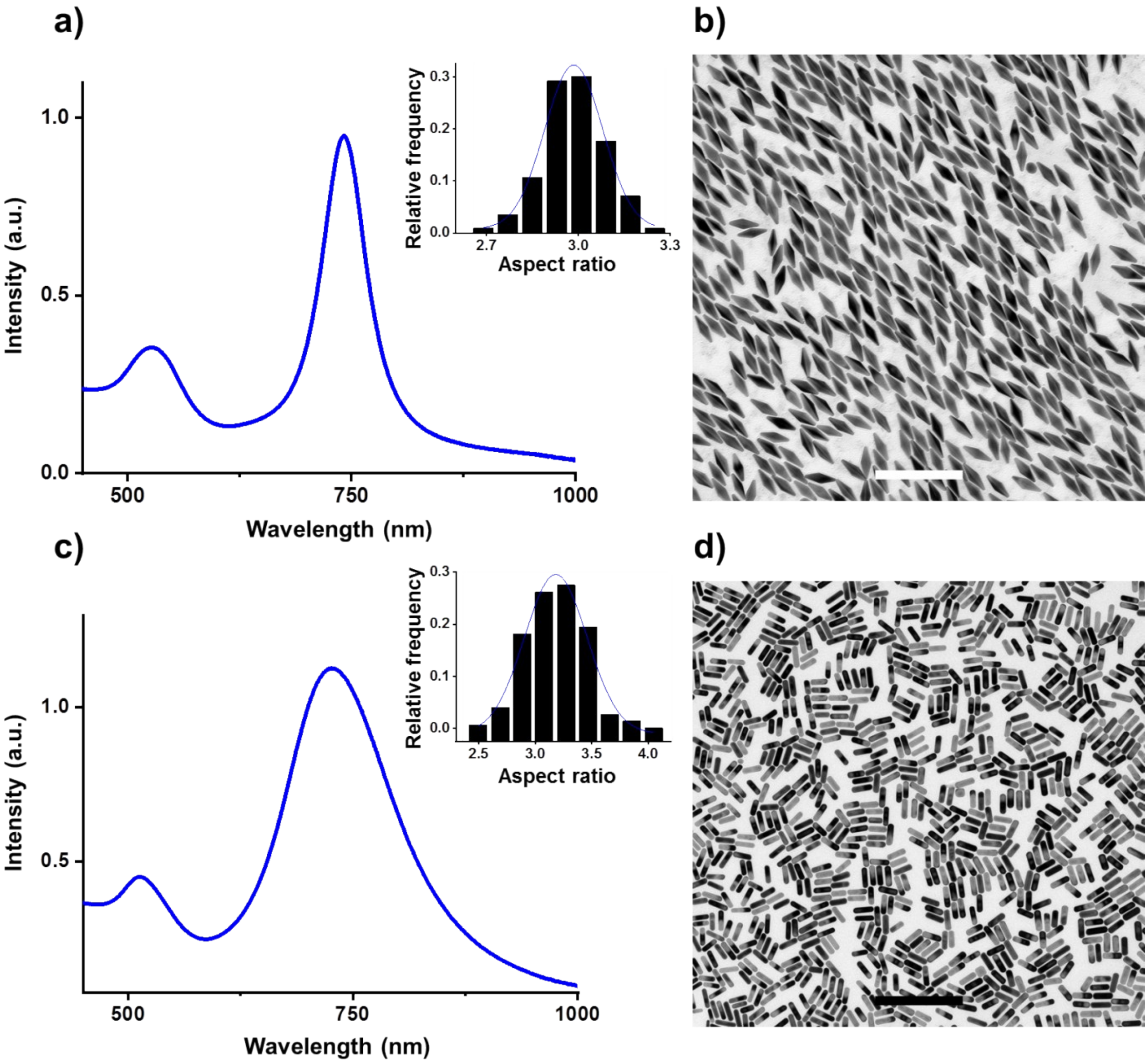

Fig. S2. (a) UV−Vis absorption spectra, corresponding aspect ratio distribution and (b) TEM micrograph of purified gold bipyramids by following the method reported by Weizmann *et al,*[4] (c) UV−Vis absorption spectra, corresponding aspect ratio distribution and (d) TEM micrograph of gold nanorods synthesised by the seed-mediate method developed by El-Sayed *et al*,[1] the scale bars represent 200 nm.

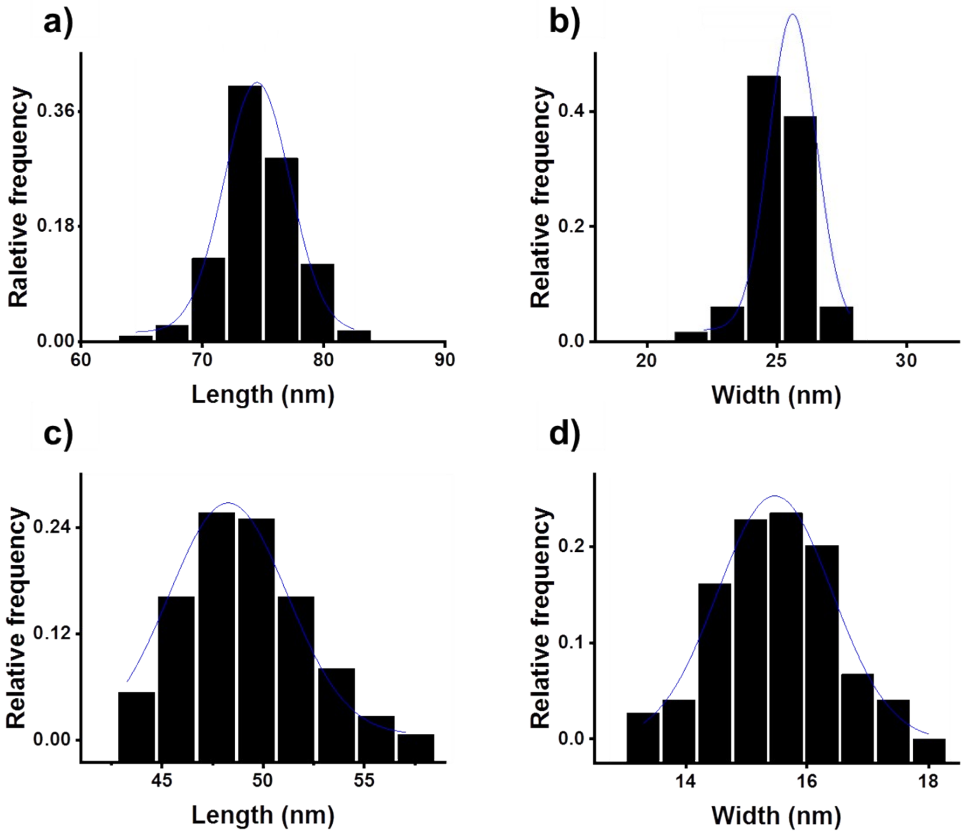

Fig. S3. TEM-based length and width distribution histogram of (a, b) bipyramids and (c, d) gold nanorods, the statistic distributions have been done for 150 nanoparticles.

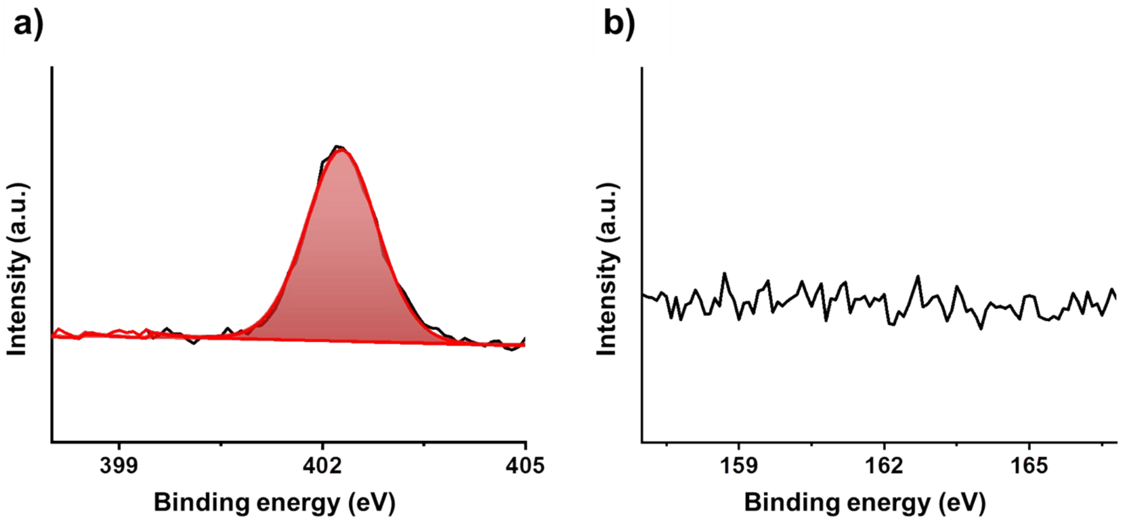

Fig. S4. High resolution (a) N 1s and (b) S 2p XPS spectra of CTAB capped gold nanorods.

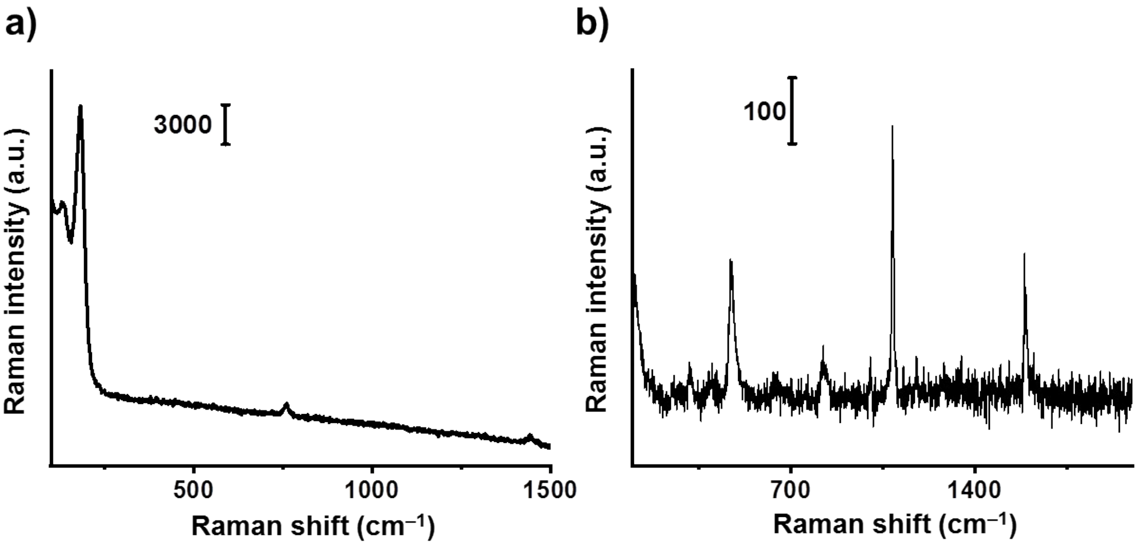

Fig. S5. Raman spectra of (a) CTAB capped gold nanorods and (b) normal Raman spectra of 4-ATP solution (10^{-2} M).

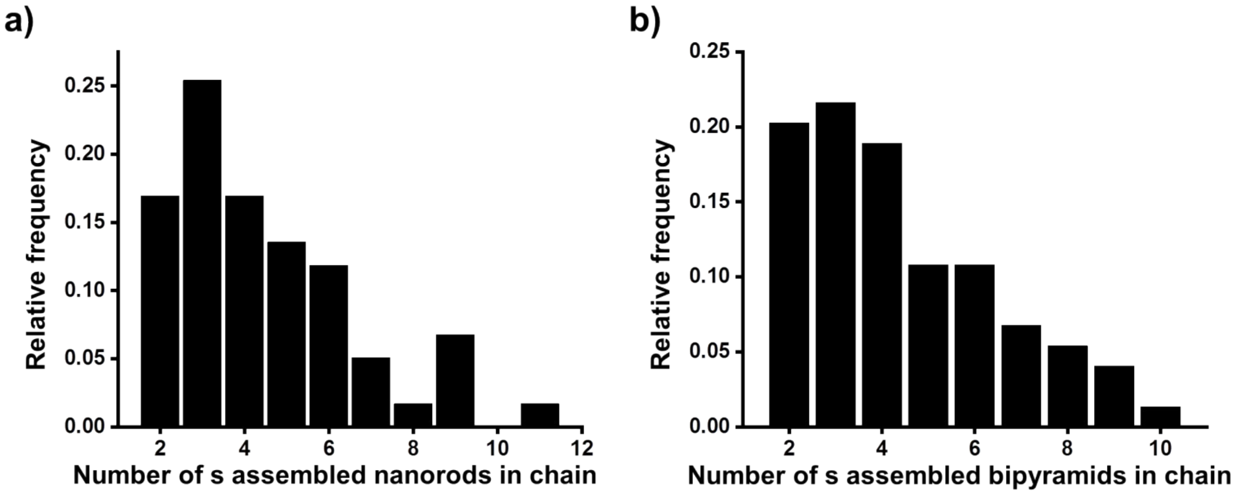

Fig. S6. TEM-based histograms of numbers of (a) gold bipyramids and (b) gold nanorods in end-to-end assembled chains.

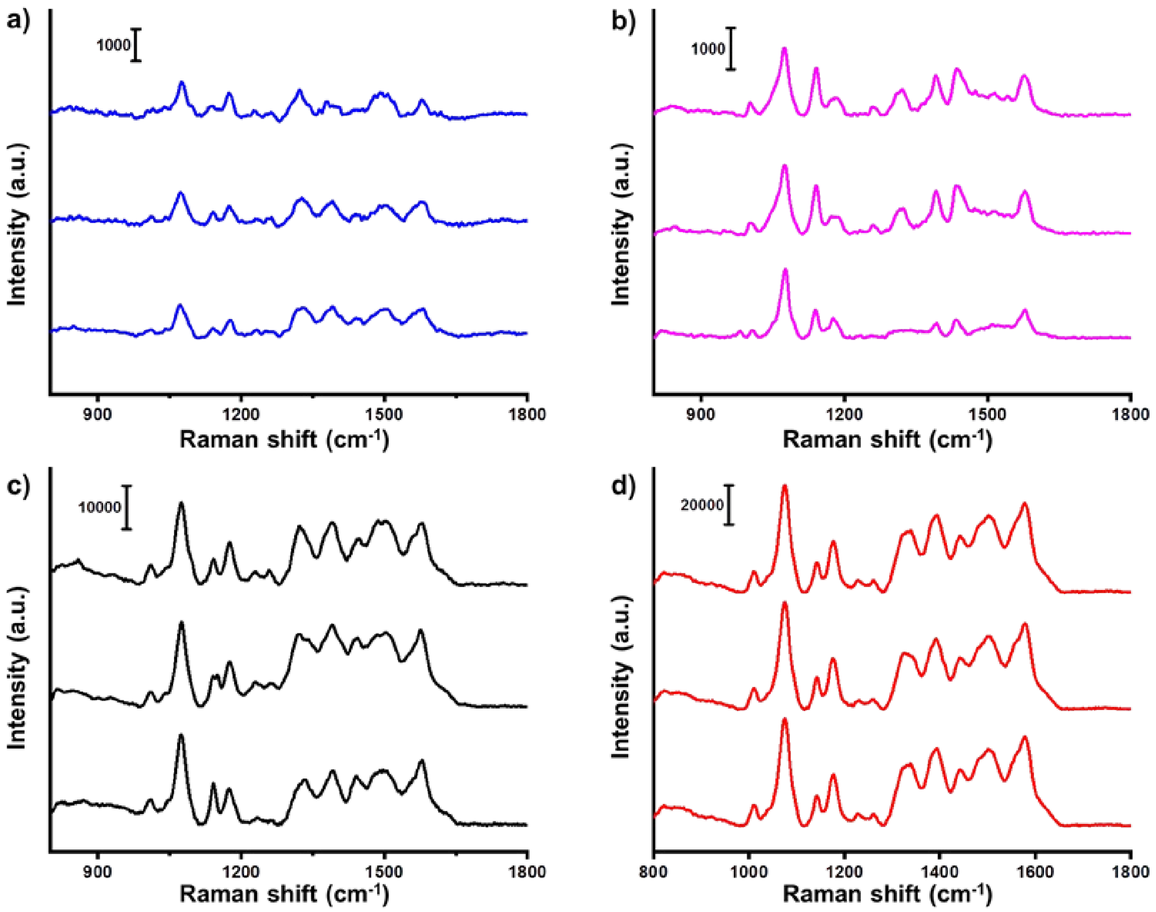

Fig. S7. SERS spectra of individual tip-modified (a) gold nanorods, (b) gold nanobipyramids, (c) end-to-end assembled gold nanorods and (d) end-to-end-assembled gold nanobipyramids collected in three different times.

Enhancement factor calculations

The enhancement factors (EF) associated with the individual and assembled bipyramids and nanorods were calculated through the following equation:

$$EF = (I_{SERS}/N_{SERS}) / (I_{NR}/N_{NR}) \qquad \text{(Equation S1)}$$

Where I_{SERS} and I_{NR} are the Raman intensity of C-S stretching mode of 4-ATP in presence and absence of the gold nanoparticles respectively. N_{NR} and N_{SERS} indicate the average number of 4-ATP molecules dispersed in solution and attached to the surface of gold nanoparticles, respectively.

The surface area of hot spots for both gold nanorods and bipyramids were estimated by considering the tip area as hemispheres (Fig. S8a and b). So by knowing the average dimension from TEM statistic size distribution data, we did the calculation as below:

Surface area of each tip (gold nanorod): $\pi (r^2 + a^2) = ((7.6)^2 + (4.3)^2) \times 3.14 = 239.42$ nm^2, so for single nanorod = 478.85 nm^2

Surface area of each tip (gold bipyramids): $\pi (r^2 + a^2) = ((3.25)^2 + (3.3)^2) \times 3.14 = 67.35$ nm^2, so for single bipyramid = 134.70 nm^2

By knowing 4-ATP fingerprint on gold surface (0.214 nm^2) gold nanorods and bipyramids concentration (2×10^{-10}), the number of molecules attached on the intrinsic hot spot area can be estimated as below:

Number of 4-ATP molecule attached to each nanorod: 478.85 nm^2/0.214 nm^2 = 2237

Number of 4-ATP molecule attached to each bipyramid: 134.70 nm^2/0.214 nm^2 = 629

N_{SERS} (total number of 4-ATP) for the gold nanorods solution: [$C_{nanorods} \times N_A \times N_{4\text{-}ATP}$ (attached to each rod)]:

$2 \times 10^{-10} \times 6.022 \times 10^{23} \times 2237 = 2.694 \times 10^{14}$ mL^{-1}

N_{SERS} (total number of 4-ATP) for gold bipyramids solution: [$C_{gold\ bipyramids} \times N_A \times N_{4\text{-}ATP}$ (attached to each bipyramid)]:

$2 \times 10^{-10} \times 6.022 \times 10^{23} \times 629 = 7.575 \times 10^{13}$ mL^{-1}

N_{NR}: $10^{-2} \times 6.022 \times 1\ 0^{23} \times 10^{-3} = 6.022 \times 10^{18}$ mL^{-1}, $I_{NR} = 437$

Individual tip-modified gold nanorods EF: (1015/2.694× 10^{14} mL^{-1}) / (437/6.022 × 10^{18} mL^{-1}) = 5.19×10^4

Individual tip-modified gold bipyramids EF: (1636/7.575× 10^{13} mL^{-1}) / (437/6.022 × 10^{18} mL^{-1}) = 2.97 × 10^5

Longitudinal assembled gold nanorods EF: (19474/2.694 × $10^{14}$$mL^{-1}$) / (437/6.022 × $10^{18}$$mL^{-1}$) = 9.96 × 10^5

Longitudinal assembled gold bipyramids EF: (56472/7.575 × $10^{13}$$mL^{-1}$) / (437/6.022 × $10^{18}$$mL^{-1}$) = 1.02 × 10^7

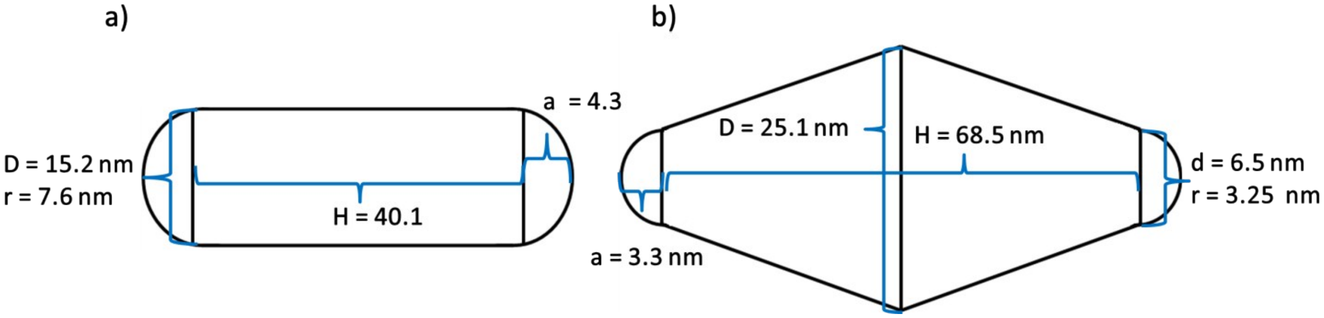

Fig. S7. Schematic representation of (a) gold nanorod and (b) bipyramid dimensions determined by analysing TEM images (average of 150 particles)

References

1. B. Nikoobakht and M. A. El-Sayed, *Chemistry of Materials*, 2003, **15**, 1957-1962.
2. Liu and P. Guyot-Sionnest, *The Journal of Physical Chemistry B*, 2005, **109**, 22192-22200.
3. P. B. Johnson and R. W. Christy, *Physical Review B*, 1972, **6**, 4370-4379.
4. J.-H. Lee, K. J. Gibson, G. Chen and Y. Weizmann, *Nature Communications*, 2015, **6**, 7571.