Electronic Supplementary Material (ESI) for Chemical Communications.

SUPPORTING INFORMATION

Synthesis of Circular and Triangular Gold Nanorings with Tunable Optical Properties

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I. Materials

Silver Nitrate ($AgNO_3$, 99%), sodium citrate tribasic dihydrate ($C_6H_5Na_3O_7$, 99%), L-ascorbic acid ($C_6H_8O_6$, 99%), tetrachloroauric acid (HAuCl4, 99.9%), hydroxylamine hydrochloride (99%), sodium borohydride ($NaBH_4$, 99%), sodium hydroxide (99%), ammonium hydroxide solution (28.0-30.0% NH_3 basis), 4-mercaptobenzoic acid (4-MBA, 99%) were supplied by Sigma-Aldrich. Hydrogen peroxide (H_2O_2, 30%) was from EMD Millipore Corporation. Acetonitrile (C_2H_3N, HPLC Grade) was purchased from Fisher Chemical. Ethyl alcohol (absolute, 200 proof) was received from Pharmco-Aaper. Deionized water (Millipore Milli-Q grade) with resistivity of 18.0 MΩ was used in all the experiments.

II. Experimental Sections

Synthesis of Ag nanoplates with rounded and triangular shapes

Ag seeds were prepared by one-shot injection of 1.2 ml $NaBH_4$ solution into a mixture of ultrapure water (200 ml), $AgNO_3$ (200 μL, 0.1 M), TSC (12 mL, 75 mM), and H_2O_2 (480 μL). The solution was gently stirred for 5 min before aging at least 2 h. The seeds were collected by centrifugation and then dispersed in 6 mL water.

A growth solution was prepared by adding acetonitrile (20 mL), TSC (200 μL, 75 mM), ascorbic acid (300 μL, 0.1 M), and $AgNO_3$ (240 μL, 0.1 M) into water (44 mL).

The shape of Ag nanoplates was controlled by different stirring methods and rates. Magnetic stirring with moderate rate (~350 rpm) was used to produce rounded Ag nanoplates, while mechanical stirring with high rate (~700 rpm) produced triangular Ag nanoplates. The diameter/edge length of Ag nanoplates was controlled by varying the ratio of Ag seeds to $AgNO_3$ in the growth solution. For a better control over the growth kinetics, we varied the dose of Ag seeds, while keeping the amount of $AgNO_3$ and volume of growth solution as constant. The addition of more seeds led to the formation of smaller Ag nanoplates (**Fig. 1e**, **S4**). After 30 min of growth, products were collected by centrifugation and then redispersed in 24 mL of 0.3 mM trisodium citrate aqueous solution.

Synthesis of Ag@Au nanostructures

A mixture (volume ratio 50:1) of hydroxylamine hydrochloride solution (3 mM) to sodium hydroxide (0.2 M) and a $HAuCl_4$ solution (0.30 mM) were infused into a 75 ml Erlenmeyer flask containing 4 mL of Ag@Au solution via two syringes under vigorous stirring. The infusion rate was set as 2 mL/h. After 20 min of infusion, the solution was centrifuged, and the products were redispersed into 6 mL of 0.3 mM trisodium citrate.

Etching of Ag@Au nanoplates to produce Au Nanorings (thin)

The wet etchant solutions (50 mM H_2O_2 and 50 mM $NH_3{\cdot}H_2O$) was introduced into a 6 mL of as-synthesized fresh Ag@Au nanostructure solution in a 50 mL Erlenmeyer flask under steady stirring by using a syringe pump (flow rate: 3 mL/h). After the solution became transparent, the thin AuNRs were collected by centrifugation and redispersed in a 1 mL of 0.3 mM trisodium citrate aqueous solution.

Multiple metal deposition for the preparation of thick/rough AuNRs

Thick AuNRs with smooth surface were synthesized by another round of Au deposition onto the thin AuNRs at the same infusion rate (2 mL/h) of $HAuCl_4$ and basic HyA solution. After 1.5 h, the solution was centrifugedand the products were redispersed in 1 mL of 0.3 mM trisodium citrate.

Rough AuNRs were synthesized by the same method but at a faster infusion rate (5 mL/h) of Au precursor and reducing agent. The solution was then centrifuged after 1 h, and the products were redispersed into 1 mL of 0.3 mM trisodium citrate.

Characterizations

SEM/TEM imaging. The Au NRs were imaged using a Hitachi SU-70 Schottky field emission gun Scanning Electron Microscope (FEG-SEM) and a JEOL FEG Transmission Electron Microscope (TEM). Samples for SEM were prepared by casting a 5 μL of aqueous solution on silicon wafers, and dried at room temperature. TEM samples were prepared on 300 mesh copper grids.

SERS measurement. For the surface-enhanced Raman scattering (SERS) measurement, silicon wafer was treated in plasma cleaner for 60 s. A 20 μL of an aqueous solution of the AuNR (3 mg/mL) was cast on the substrate of 0.2×0.2 cm^2 Si wafer and dried at room temperature. 4-MBA was dissolved in ethanol at concentration of 10 mM. Subsequently, a 20 μL of the 4-MBA solution was cast on the substrate. The samples were then rinsed with pure ethanol and dried. The Raman spectra were recorded using a Horiba LabRAM confocal Raman microscope equipped with a He-Ne laser (633 nm). The laser spot was focused with a spot of 1 μm^2. Raman scattering intensity was collected with the accumulation time of 5 s for 5 cycles. For each measurement, three points were selected to average the final Raman intensity.

Calculation of Enhancement Factors (EFs)

We estimated the SERS enhancement factors (EFs) of 4-mercaptobenzoic acid (4-MBA) at 1590 cm^{-1} using the following formula:

$$EF = \frac{I_{SERS}}{I_{Bulk}} \times \frac{N_{Bulk}}{N_{SERS}},$$

where I_{SERS} and I_{Bulk} are the Raman scattering intensities of 4-MBA obtained with Au NRs and bulk 4-MBA (without Au NRs), respectively; while N_{SERS} and N_{Bulk} are the numbers of 4-MBA molecules for SERS and bulk measurement, respectively.[1,2]

For bulk and SERS samples, 20 μL 10 mM 4-MBA ethanol solution is cast on substrates. Assume that 4-MBA molecules evenly form thin layer on substrate and metal surface of a footprint $A_{molecule} \approx$ 0.54 nm^2. Surface occupied factor $f \approx 0.32$, for Au NRs. Detection spot $A_{focal} = 1 \times 1\ \mu m^2 = 10^{-12}\ m^2$.

$$N_{Bulk} = \frac{V \times C \times N_{Av} \times A_{focal}}{A_{Substrate}} = 3.01 \times 10^{10}$$

$$N_{SERS} = \frac{f \times A_{focal}}{A_{molecule}} = 6 \times 10^{5}$$

Raman scattering intensities for bulk 4-MBA and rough triangular Au NRs are 50 and 8577, respectively.

$$EF = \frac{I_{SERS}}{I_{Bulk}} \times \frac{N_{Bulk}}{N_{SERS}} = \frac{8577}{50} \times \frac{3.01 \times 10^{10}}{6 \times 10^{5}} = 8.6 \times 10^{6}$$

EFs for other Au NRs can be calculated in same approach.

Supplementary Figures

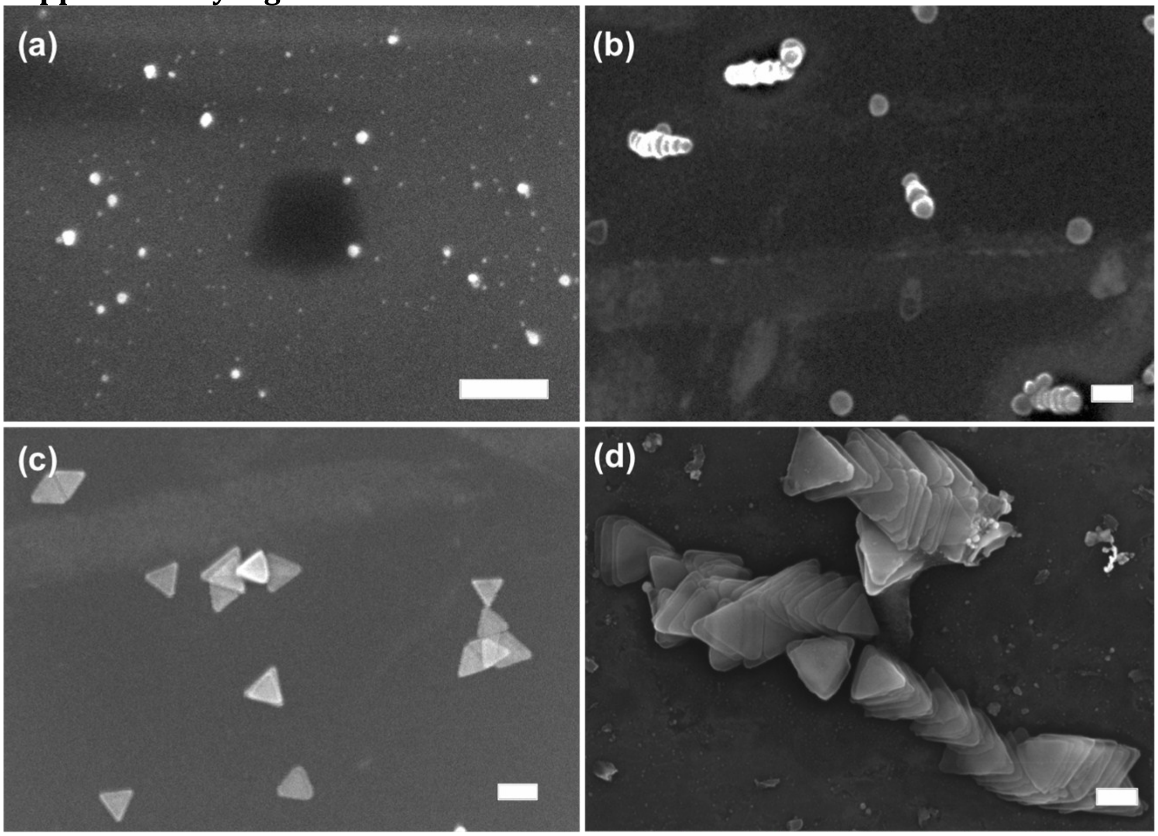


Fig. S1 SEM images of (a) Ag seeds, (b) rounded Ag nanoplates, and triangular Ag nanoplates with edge length of (c) 100 nm and (d) 250 nm. Scale bars are 100 nm.

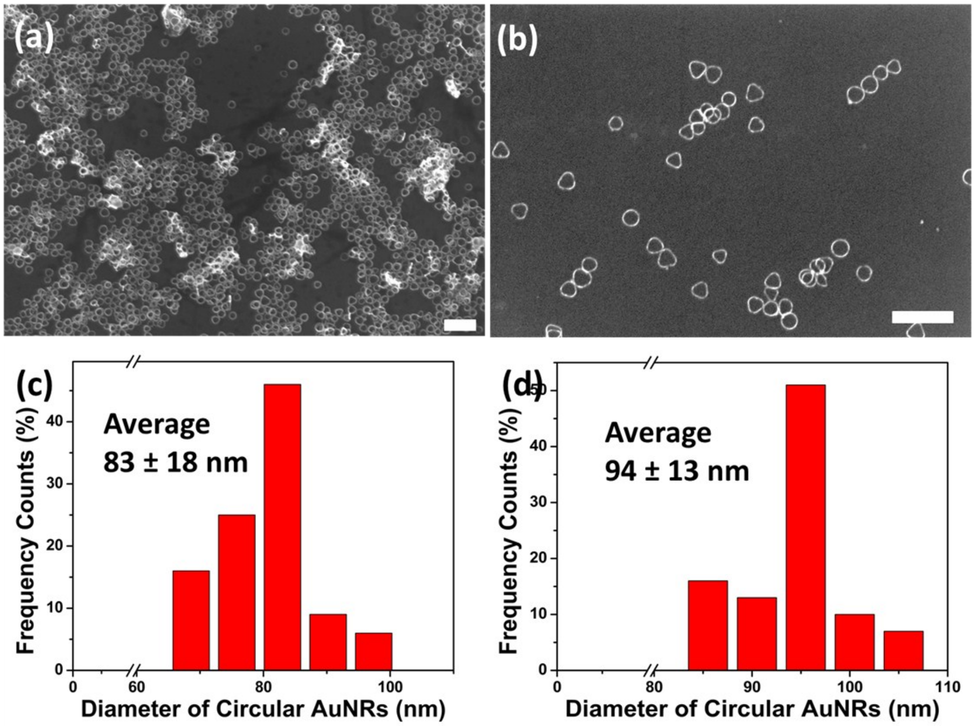


Fig. S2 Large-scale SEM images of circular AuNRs (a,b) and their corresponding size distribution (c,d), respectively. Scale bars are 300 nm.

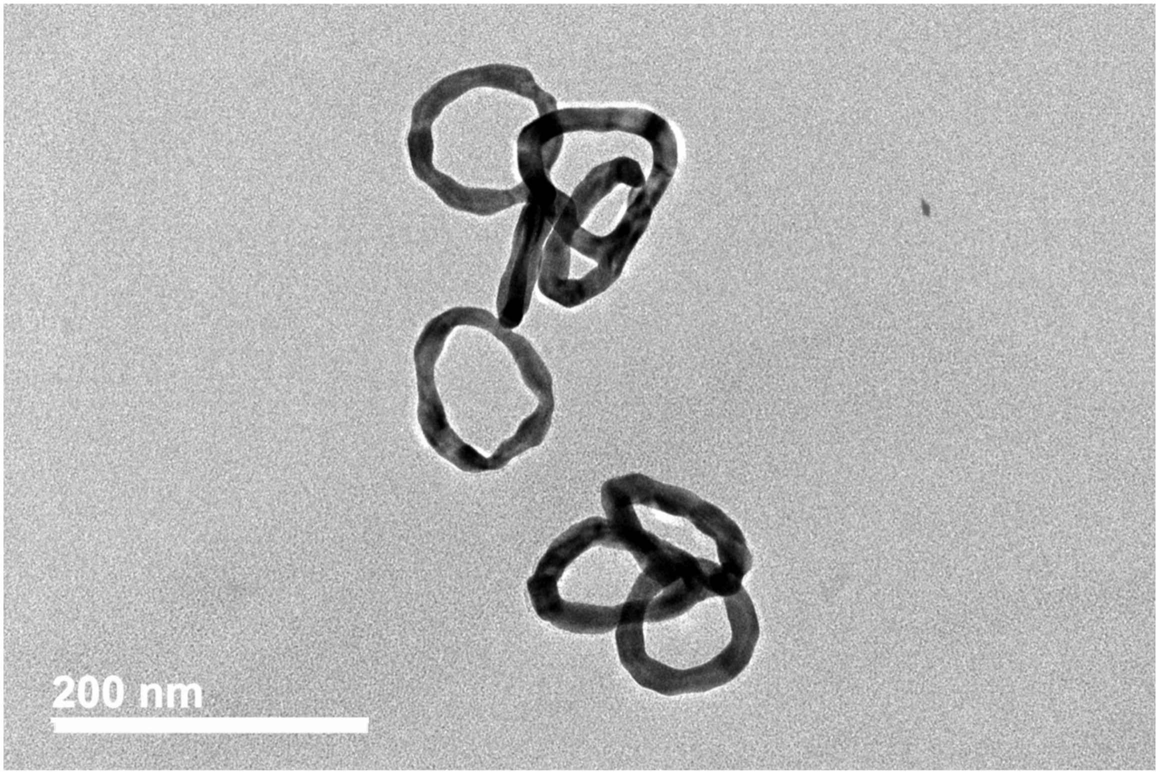
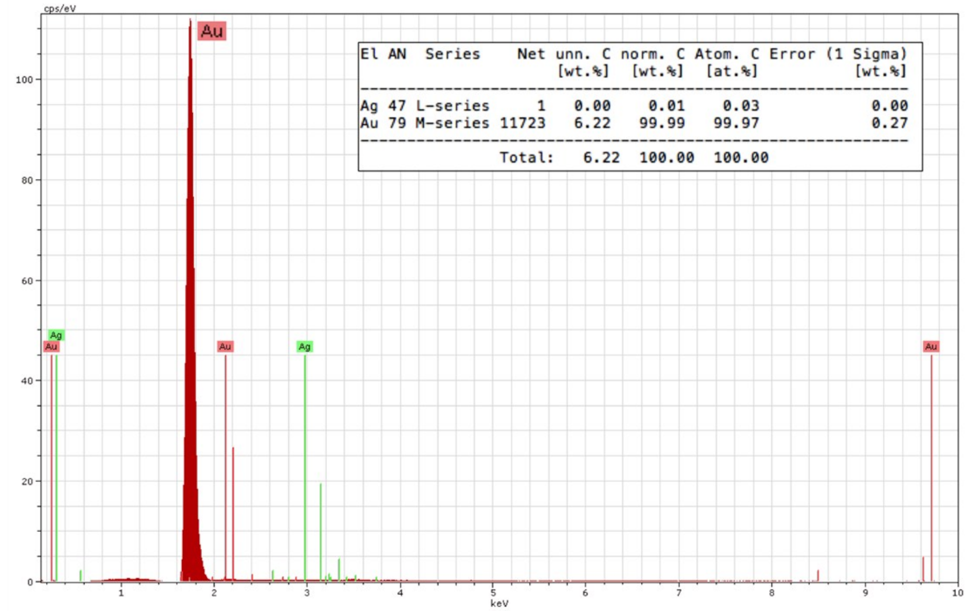


Fig. S3 TEM image of circular AuNRs with different angles of view. Scale bar is 100 nm.



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El AN  Series     Net unn. C norm. C Atom. C Error (1 Sigma)
                      [wt.%]  [wt.%]  [at.%]           [wt.%]
--------------------------------------------------------------
Ag 47 L-series      1   0.00    0.01    0.03             0.00
Au 79 M-series  11723   6.22   99.99   99.97             0.27
--------------------------------------------------------------
                Total:   6.22  100.00  100.00
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Fig. S4 Energy-dispersive X-ray spectra of Au (red) and Ag (green) on the ridge of AuNR.

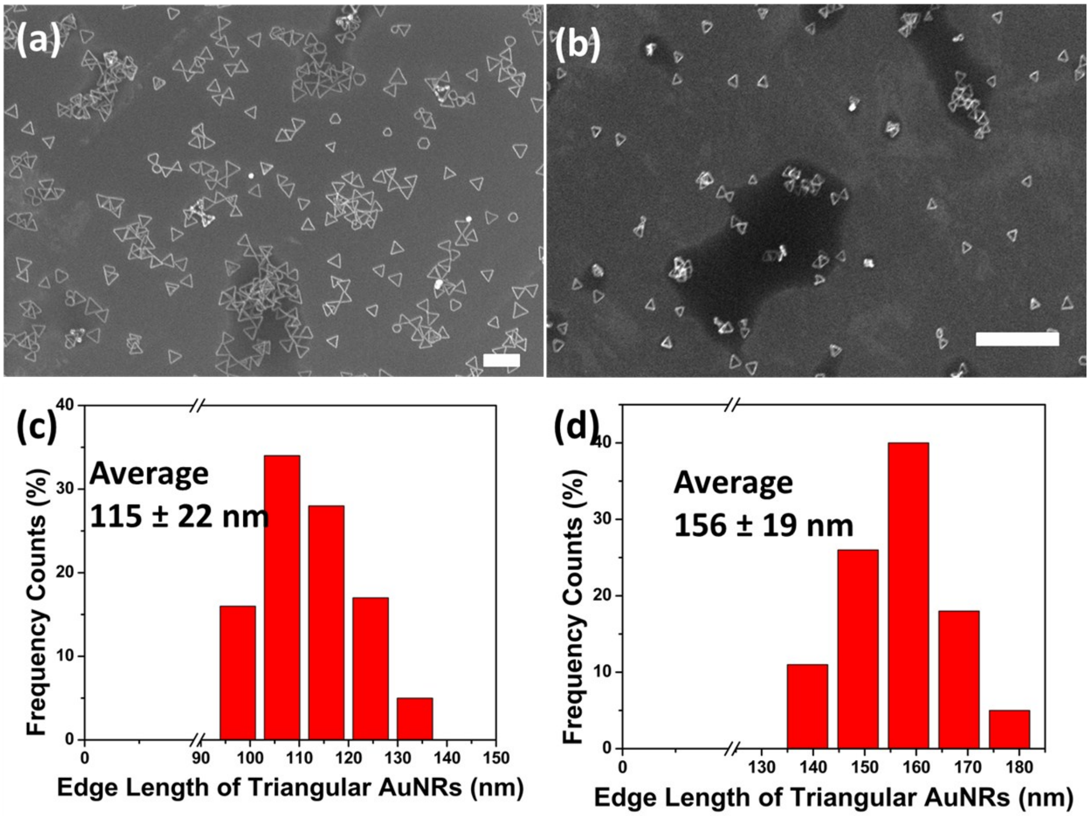

Fig. S5 Large-scale SEM images of triangular AuNRs (a,b) and their corresponding size distribution (c,d), respectively. Scale bars are 300 nm in (a) and 1000 nm in (b).

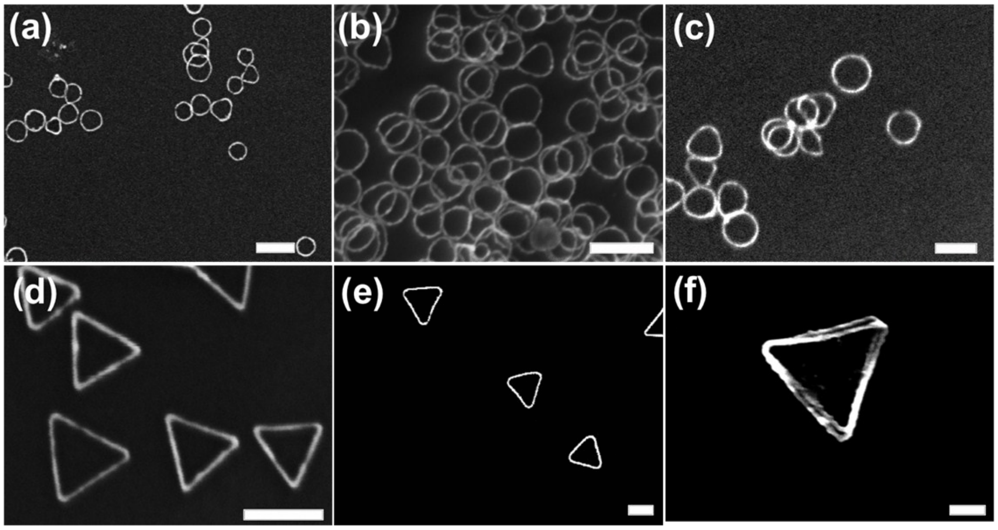

Fig. S6 (a-c) Circular AuNRs with different diameters synthesized with the addition of (a) 4 mL, (b) 3 mL, and (c) 2 mL of Ag seed solutions. The diameter of AuNRs are 50 nm (a), 70 nm (b) and 90 nm (c). (d-f) Triangular AuNRs with different edge lengths synthesized with the addition of (d) 2 mL, (e) 1 mL, and (f) 0.125 mL of Ag seed solutions. The edge length of triangular AuNRs are 90 nm (d), 150 nm (e), and 350 nm (f). Scale bars are 100 nm.

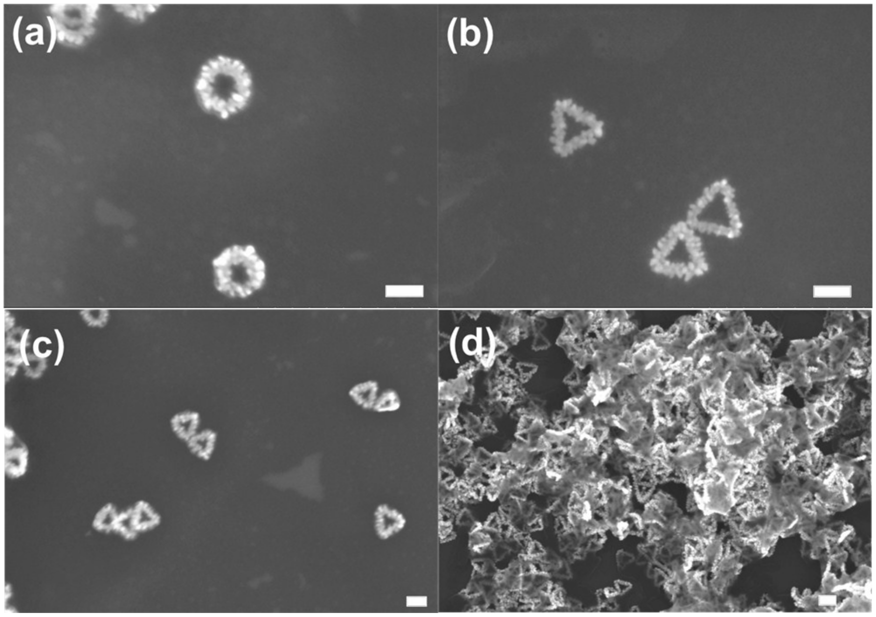

Fig. S7 SEM images of monodispersed circular AuNRs (a) and triangular AuNRs (b-d) with rough surface. The sample in (d) was imaged before washing away trisodium citrate surfactant. Scale bars are 100 nm.

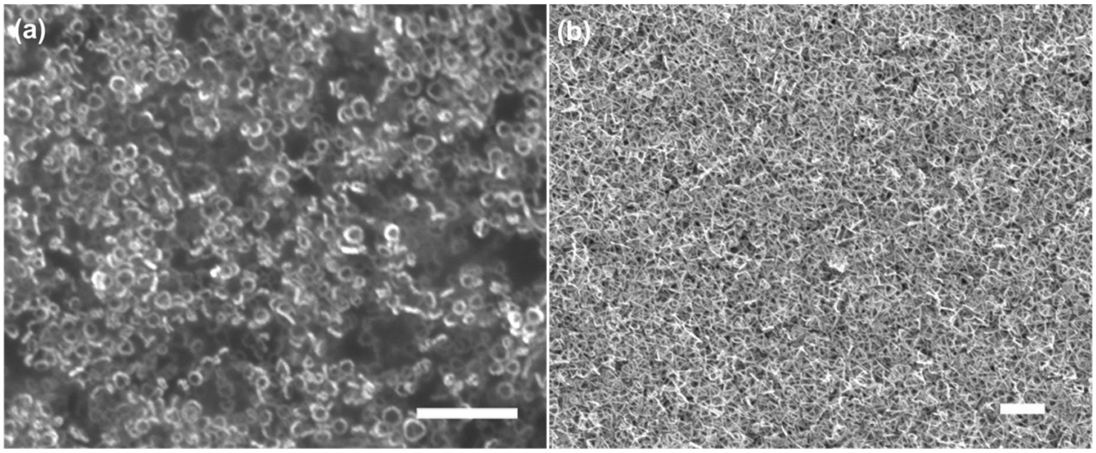

Fig. S7 SEM images of SERS substrates made with (a) thick circular and (b) thick triangular Au NRs. Scale bars are 200 nm.

Reference:

1 A. Michota and J. Bukowska, *J. Raman Spectrosc.,* 2003, **34**, 21–25.
2 E. Le Ru, E. Blackie, M. Meyer and P. G. Etchegoin, *J. Phys. Chem. C*, 2007, **111**, 13794–13803.