

## *Supporting information*

### **High-yield halide-free synthesis of biocompatible Au nanoplates**

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## **Materials and Methods**

### **Chemicals and apparatus**

Hydrogen tetrachloroaurate (III) ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) was purchased from Acros Organics. Polyvinylpyrrolidone (PVP, M.W. 40000) was obtained from Fluka. Sodium citrate tribasic dehydrate and sodium borohydride ( $\text{NaBH}_4$ ) were purchased from Sigma-Aldrich. Hydrogen peroxide aqueous solution ( $\text{H}_2\text{O}_2$ , 30 wt%) was bought from Fisher Scientific. DNA strands were synthesized by Tsukuba Oligo Service. Citric acid-coated Au nanoparticles of 15nm in diameter were purchased from BBI Solutions.

The morphology of Au nanostructures was characterized by using either a Tecnai T12 or a JEOL JEM-1230 transmission electron microscope (TEM). Long-range optical spectra were measured on a Varian Cary 50 UV/vis spectrophotometer. A probe-type Ocean Optics

HR2000CG-UV-NIR spectrometer was used to measure short-range spectra. Atomic force microscopy (AFM) images were collected on a Veeco nanoscope-IIIa equipment. The surface charge of nanostructures in solution were measured on a zeta potential and particle size analyser (ELSZ-12PL, Otsuka Electronics). Surface-enhanced Raman scattering (SERS) detection was carried out on a Jobin Yvon Laser spectrometer (model LabRAM 010).

### **Synthesis of Au nanoplates**

Firstly, 1 mL of  $\text{HAuCl}_4$  (10 mM) and 0.2 mL of trisodium citrate (10 mM) were mixed with 18.5 mL of ultra-pure water. Immediately after the addition of 0.5 mL of  $\text{NaBH}_4$  (0.1 M) under vigorous stirring (800 rpm), the color of the pale yellow solution turned to red, and then orange within a few seconds. Stirring was stopped after reaction for 5 min. The resulting solution was left for aging for over 3 hrs without any disturbance, and then stored as the seeds at 4 °C for future use. In the growth step, 1 mL of  $\text{HAuCl}_4$  (10 mM) and 2 mL of PVP (2 mM, M.W. 40000) were firstly introduced into 19 mL of ultra-pure water, after which 200  $\mu\text{L}$  of the above seed solution was injected. Finally,  $\text{H}_2\text{O}_2$  (30 wt%) was introduced to trigger seeded growth of Au nanoplates. The mixture was reacted at room temperature for 3 hr when the volume of  $\text{H}_2\text{O}_2$  is equal to or more than 5  $\mu\text{L}$ ; while the reaction was left overnight if less than 5  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$  was added.

The cetyltrimethylammonium (CTA) chloride-capped Au nanoplates with similar size were prepared and purified according to the previous literature (L. Scarabelli, M. Coronado-Puchau, J. J. Giner-Casares, J. Langer and L. M. Liz-Marzán, *ACS Nano*, 2014, **8**, 5833). To calculate the concentration of the Au nanoplates, an estimated extinction coefficient obtained by finite-difference time domain (FDTD) simulation was used for the both types of Au nanoplates because of the similar size.

### **Numerical simulations**

FDTD simulations were conducted with Lumerical FDTD v8. The in-plane dipolar plasmon resonance spectra of an Au nanotriangle in water were calculated, and model structures is shown in Fig. S9. Illumination with a polarized plane wave was performed at an angle normal to the triangle surface to gain its in-plane dipolar plasmon resonance absorption and scattering.

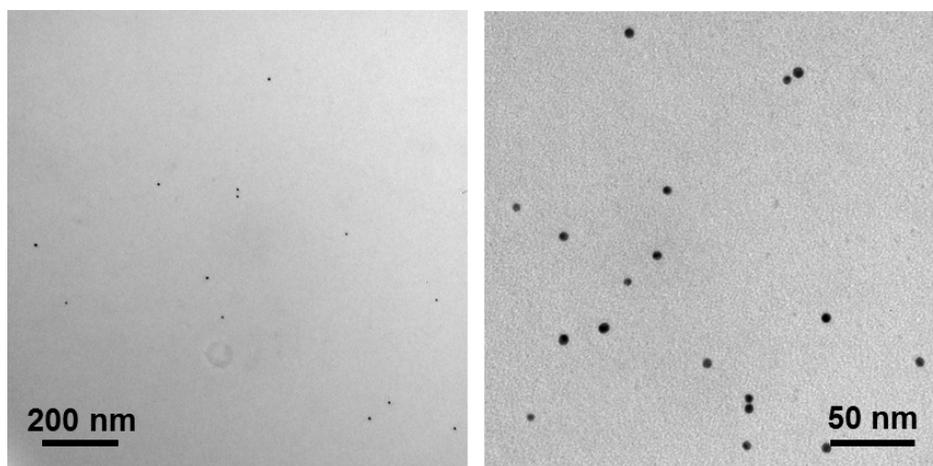
## **DNA-functionalization of Au nanoparticles and nanoplates and DNA-directed hetero-assembly**

For DNA functionalization of the Au nanoplates produced using 5  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$ , a thiolated DNA strand (HS-5'-TAC TCC TTA TTA CGC CAC CAG CTC C-3', DNA1) was mixed with the Au nanoplates at a ratio of 6000 in PB buffer (10 mM, pH 7.3) solution, followed by incubation for 3 hours. After centrifugation to remove excess DNA, the Au nanoplates were re-dispersed in PB buffer (10 mM, pH 7.3). The other thiolated DNA strand (HS-5'-TTT TTT TTT GGA GCT GGT GGC GTA A-3', DNA2) were densely grafted onto the Au nanoparticles by following a well-established protocol with minor modification (See references: K. Sato, K. Hosokawa and M. Maeda, *J. Am. Chem. Soc.*, 2003, **125**, 8102; K. Sato, K. Hosokawa and M. Maeda, *Nucleic Acids Res.*, 2005, **33**, e4), where the final salt concentration for incubation DNA with Au nanoparticles was set to 300 mM. To facilitate hetero-assembly of the DNA-functionalized Au nanoplates (1 nM) and Au nanoparticles (10 nM) by DNA hybridization, the both nanostructures were mixed at different ratios, and then incubated in PB buffer (20 mM, pH 7.3) solution containing 50 mM of NaCl. Note that the concentrations of the nanostructures were calculated using corresponding extinction coefficients at their extinction peak positions ( $1.19 \times 10^{11} \text{ M}^{-1} \cdot \text{cm}^{-1}$  for the nanoplate, and  $4.05 \times 10^8 \text{ M}^{-1} \cdot \text{cm}^{-1}$  for the nanoparticle, respectively).

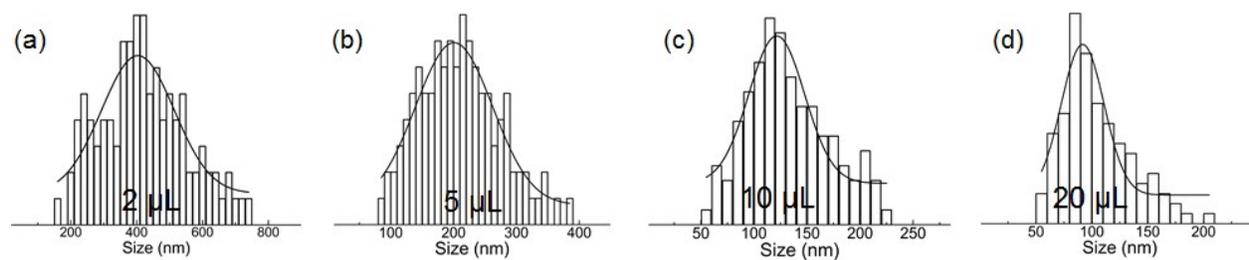
## **Raman scattering measurements**

For surface-enhanced Raman scattering (SERS) measurements, a He-Ne laser operating at a wavelength of 632.8 nm was used as the excitation source with a laser power of approximately 15 mW. Each sample was collected in a using a capillary tube (inside diameter  $\sim 1.2$  mm, Fisher), and a 10 $\times$  objective lens was manipulated to focus a laser spot on the microtube. All of the Raman spectra were collected with an exposure time of 20 seconds.

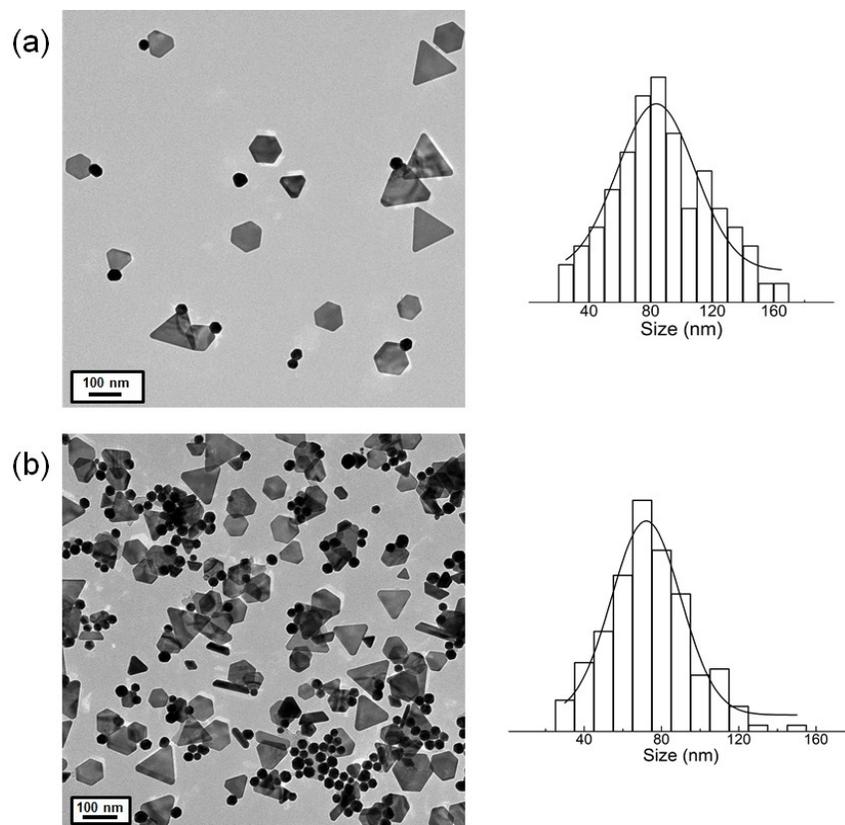
## Supplementary Figures



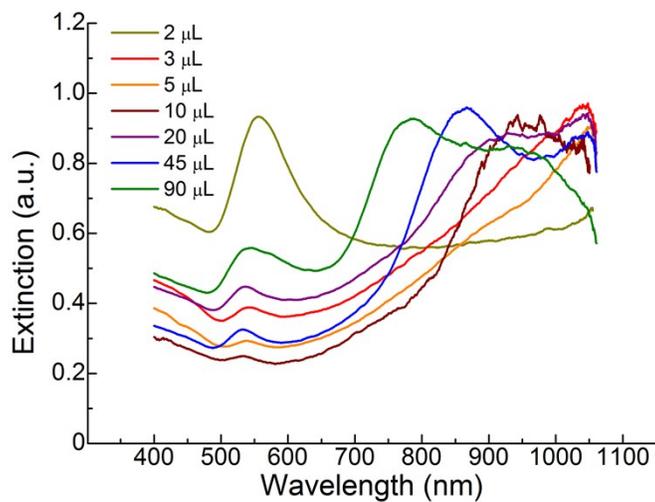
**Fig. S1** TEM images of the seeds used for growth of the Au nanoplates.



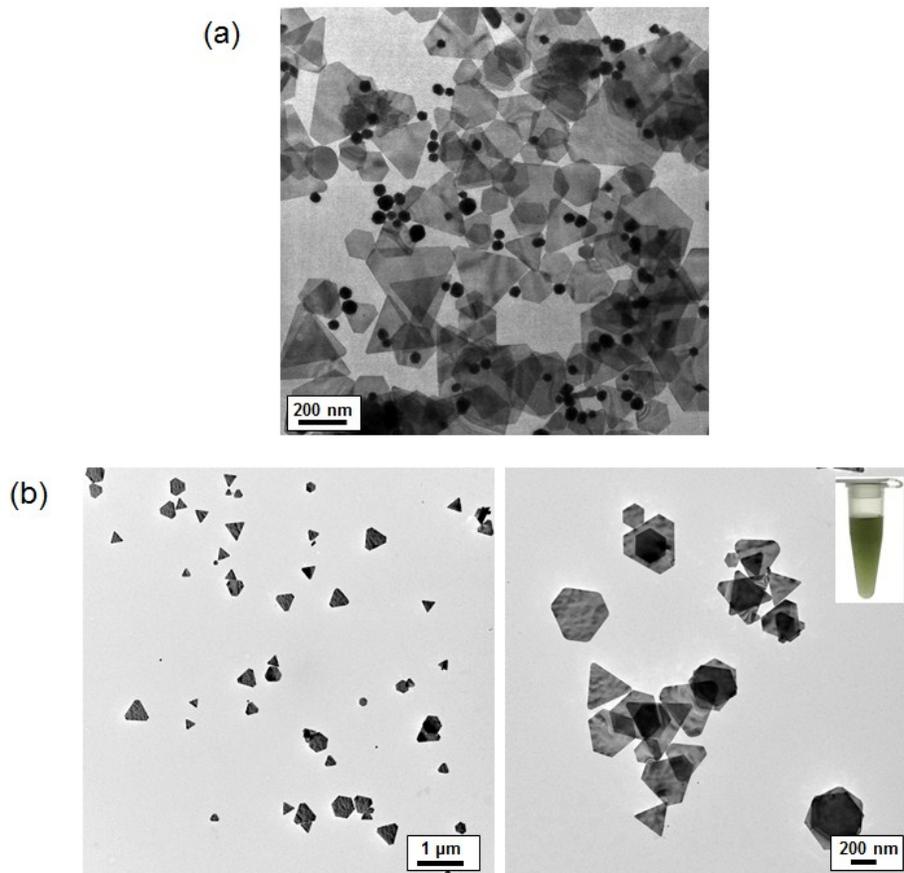
**Fig. S2** The size distributions of Au nanoplates prepared in the presence of 2  $\mu\text{L}$  (a), 5  $\mu\text{L}$  (b), 10  $\mu\text{L}$  (c), and 20  $\mu\text{L}$  (d) of  $\text{H}_2\text{O}_2$ , respectively.



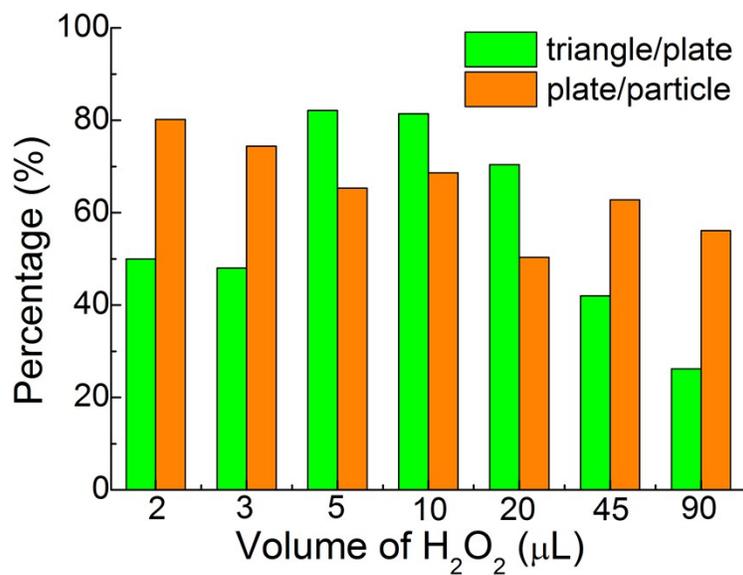
**Fig. S3** Typical TEM image (left) and size distribution (right) of Au nanoplates synthesized in the presence of 45  $\mu\text{L}$  (a) and 90  $\mu\text{L}$  (b) of  $\text{H}_2\text{O}_2$ , respectively. The Au nanoplates were centrifuged twice to remove excess PVP prior to TEM measurement.



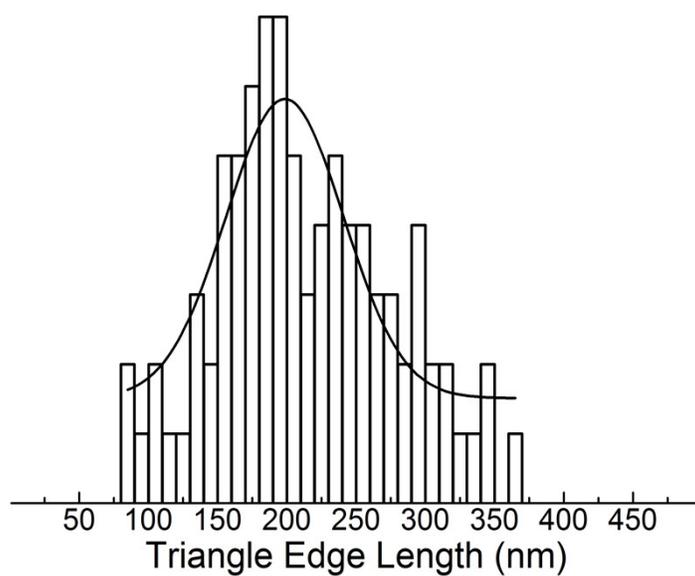
**Fig. S4** Extinction spectra of the different Au nanoplates after twice centrifugation. Most of the spectra indicate relative decrease in the bands centered at around 519–540 nm.



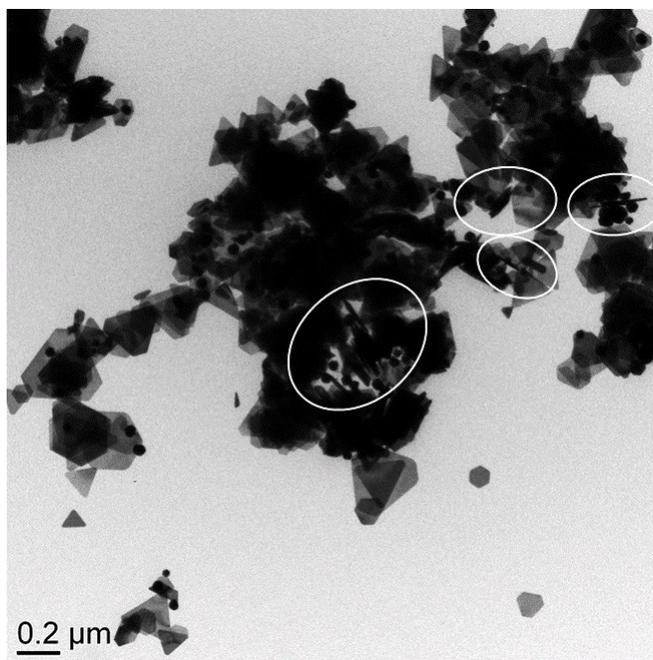
**Fig. S5** (a) A TEM image of a sample used for estimating the yield of Au nanoplates. All nanoplates and nanospheres were precipitated by centrifugation to remove excess PVP for ease of TEM sampling. (b) TEM images of the Au nanoplates after purification by gravitational sedimentation for 2 days. The Au nanoplates were prepared in the presence of 5  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$ . The insert (b) indicates the pure Au nanoplate colloid solution.



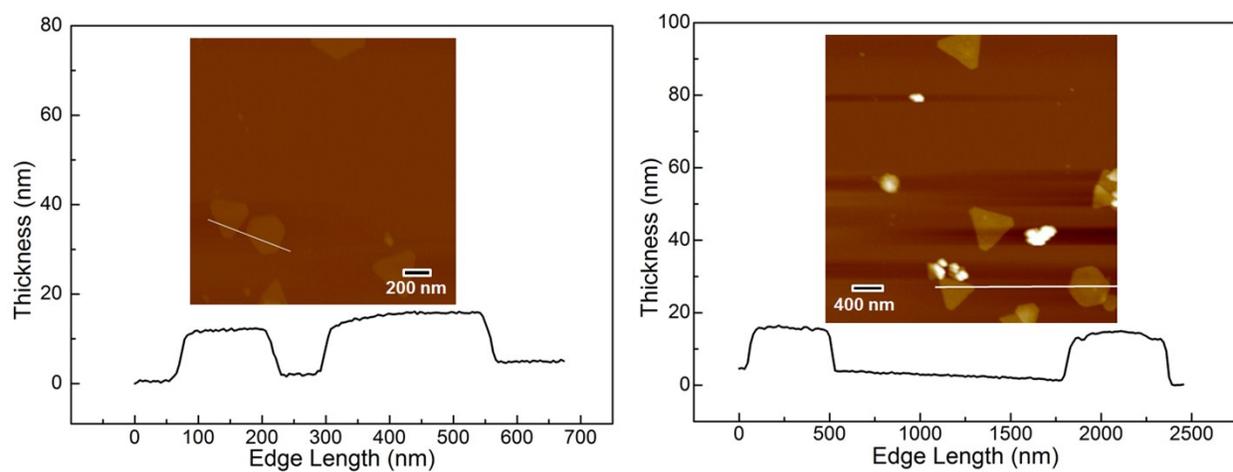
**Fig. S6** Percentages of triangle to plate and plate to particle, respectively, calculated from statistics of TEM analysis.



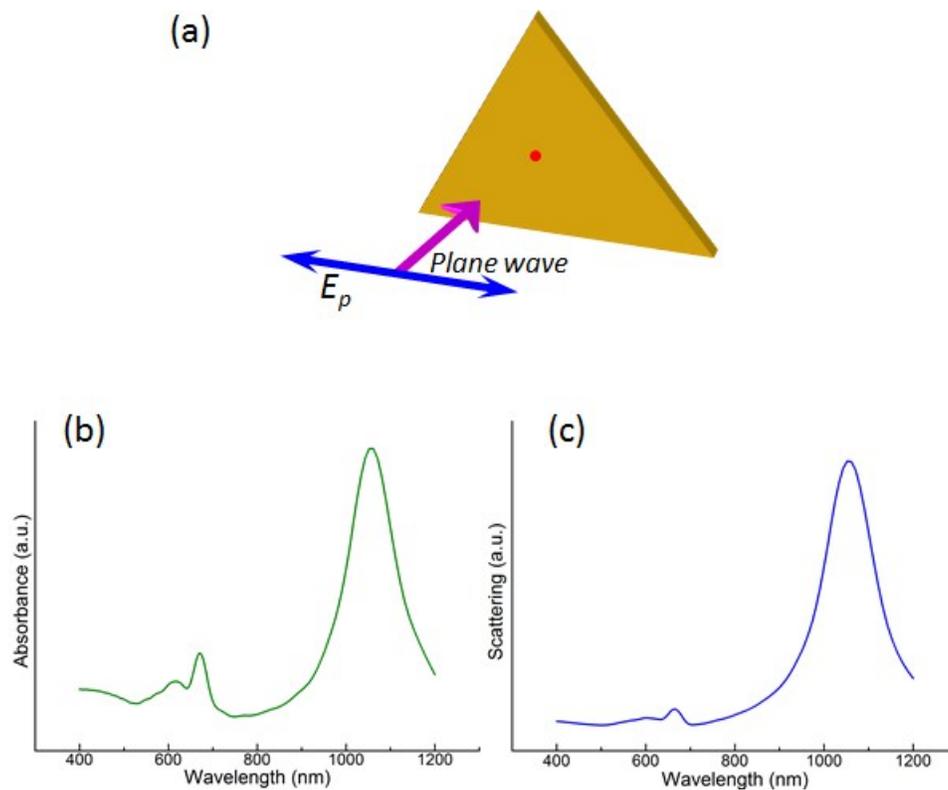
**Fig. S7** The size distribution of the Au nanotriangles produced with 5 μL of H<sub>2</sub>O<sub>2</sub>. The average edge length was estimated to be 198.5 nm.



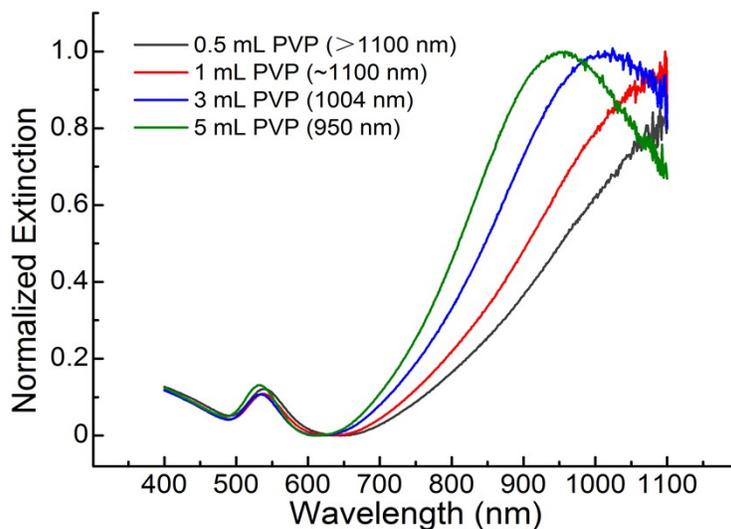
**Fig. S8** A TEM image that show some Au nanoplates stand vertically on the grid up on their edge. The Au nanoplates were prepared in the presence of 5  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$ .



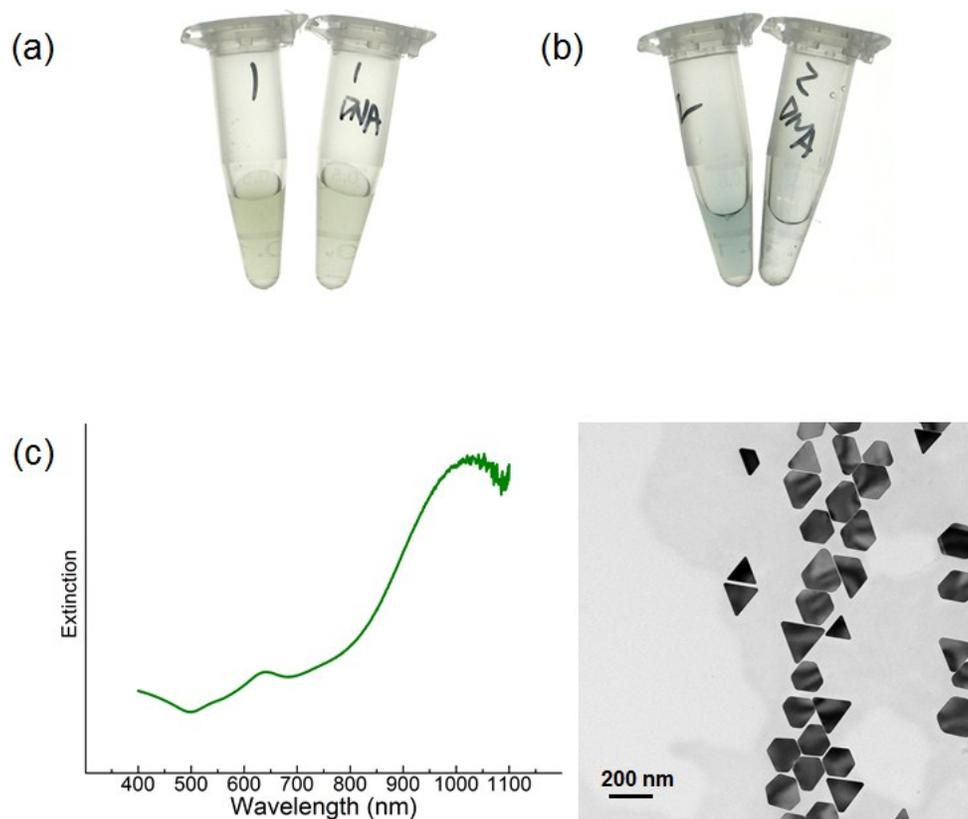
**Fig. S9** AFM images and height profiles of Au nanoplates obtained in the presence of 5  $\mu\text{L}$  of  $\text{H}_2\text{O}_2$ .



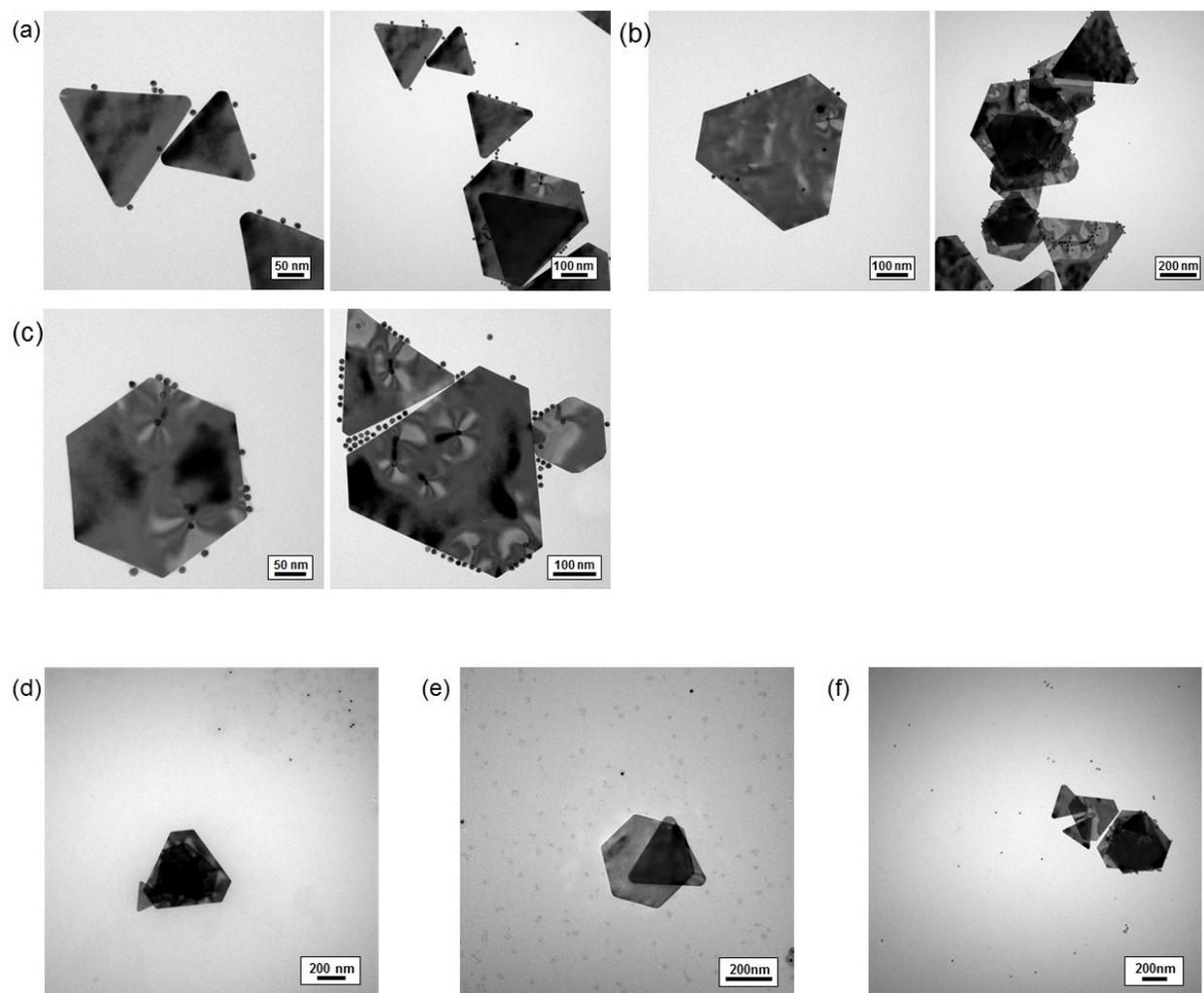
**Fig. S10** (a) Scheme of FDTD simulation setup, and calculated absorption (b) and scattering spectra (c) of an Au nanotriangle with an edge length of 198.5 nm and a thickness of 12.2 nm. The polarizing direction is parallel to one edge of the triangle. The override mesh cell size was set to  $3 \times 3 \times 3 \text{ nm}^3$ .



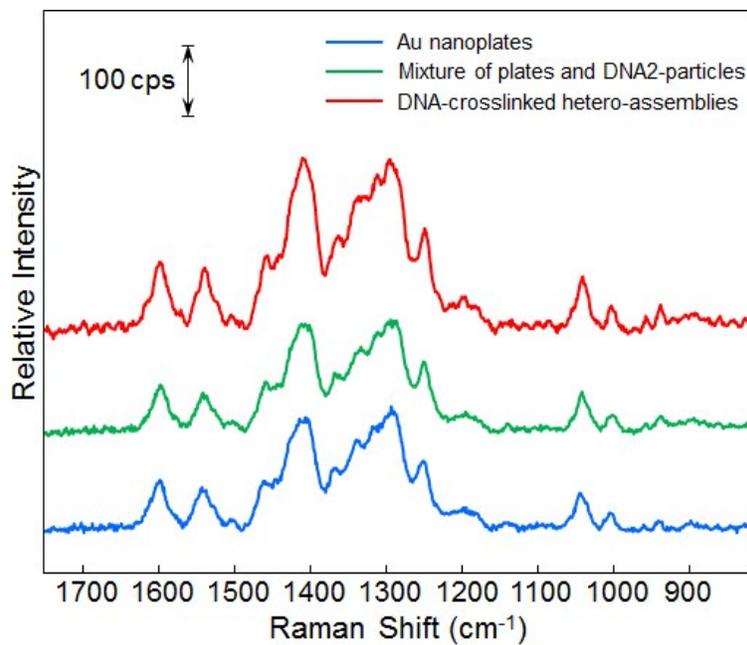
**Fig. S11** Effect of the volume of PVP on the growth of Au nanoplates.



**Fig. S12** Digital photographs of PVP-capped Au nanoplates (a) and CTA chloride capped Au nanoplates before (left) and after (right) DNA modification treatment. (c) showed the characterization results for the CTA chloride-capped Au nanoplates obtained by UV-Vis spectral and TEM, indicative of a similar size to the PVP-capped Au nanoplates produced with 5  $\mu\text{l}$  of  $\text{H}_2\text{O}_2$ .



**Fig. S13** Typical TEM images of nanoplate-nanoparticle hetero-assemblies obtained by introducing DNA2-modified Au nanoparticles to Au nanoplates with (a-c) and without (d-f) DNA1 modification at different ratios (a/d: 5, b/e: 10, and c/f: 20).



**Fig. S14** Comparison among the SERS spectra of 2,2'-dithiodipyridine (DTDP,  $1.0 \times 10^{-5}$  M) adsorbed on Au nanoplates, the mixture of DNA2-modified Au nanoparticles and Au nanoplates (at a ratio of 50), and the DNA-crosslinked hetero-assemblies (prepared at a ratio of 50), respectively.