Supplementary Information

Ultrasound Assisted Interfacial Synthesis of Gold Nanocones

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1. Materials.

2-ethoxy aniline (EOA), gold (III) chloride hydrate ($HAuCl_4$, 99.999%), 4-mercaptopyridine (MPy), hexane, octane, decane and hexadecane were purchased from Sigma-Aldrich and used as received. Deionized water (Millipore Milli-Q grade) with resistivity of 18.0 MΩ was used in all the experiments.

2. Synthesis of Au nanocones (AuNCs).

In a typical synthesis procedure, a solution of 20 mM EOA in hexane solvent was gently placed in a 5ml aqueous solution of 0.8 mM $HAuCl_4$ preheated at 45 ^oC. The two-phasic solution was immediately kept under ultrasonication condition at 45 ^oC. After reacting for 90 min, the product is washed with water for 3 times and ready for further characterization.

3. Characterizations.

The AuNCs 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 nanocones aqueous solution on silicon wafers, and dried at room temperature. TEM samples were prepared on 300 mesh copper grids covered with carbon film.

Before doing the surface-enhanced Raman scattering (SERS) measurement, AuNCs are washed with N, N-dimethylformamide (DMF) for 5 times to dissolve free polymer and then washed with water for 3 times. 10 μL of the naked AuNCs aqueous solution was cast on the substrate of 0.5×0.5 cm^2 silicon wafer and dried at room temperature. Subsequently, the silicon wafers with dried AuNCs were dipped in 1 mL of 4-MPy water solution with different concentrations for 1 hr. The samples were then rinsed with pure water and dried. The Raman spectra were recorded on a Horiba LabRAM confocal Raman microscope equipped with a He-Ne laser (632 nm). The laser spot was focused with a spot of 1 μm^2. Raman scattering intensity was collected with the accumulation time of 3 s for 2 cycles. For each measurement, three points were selected to average the final Raman intensity.

4. Calculation of Raman scattering enhancement factor (EF).

SERS enhancement factor (EF) is defined as, $EF=(I_{SERS}/N_{SERS})/(I_{Bulk}/N_{Bulk})$, where I_{SERS} and I_{Bulk} are the Raman scattering intensity of MPy obtained with AuNCs and bulk MPy, respectively; while the N_{SERS} and N_{Bulk} are the number of MPy molecules within the SERS detecting spot (1×1 μm^2) for AuNCs system and bulk system, respectively. The absolute Raman scattering intensity for AuNCs and bulk systems are 5000 and 100 at 1093 cm^{-1}, respectively.

N_{SERS} is the average number of absorbed MPy molecules on the surface of AuNCs. Based on the dimension of AuNCs (the diameter of circular base is ~143.9 nm and the height is ~108.8 nm) we calculated that the surface area of each Au nanocone is 1.2×10^{-13} m^2. With the packing dencity

of MPy on metal surface is 6.8×10^{18} molecules per m^2, the number of AuNCs in 1×1 μm^2 is about 50 we have N_{SERS} $=4.2\times10^7$. N_{Bulk} is the average number of packed MPy molecules in the measured area of bulk MPy, and can be calculated according to the bulk density of MPy used for Raman samples. N_{Bulk} $=6.5\times10^{14}$.

Thus, it gives EF=$7.7*10^8$.

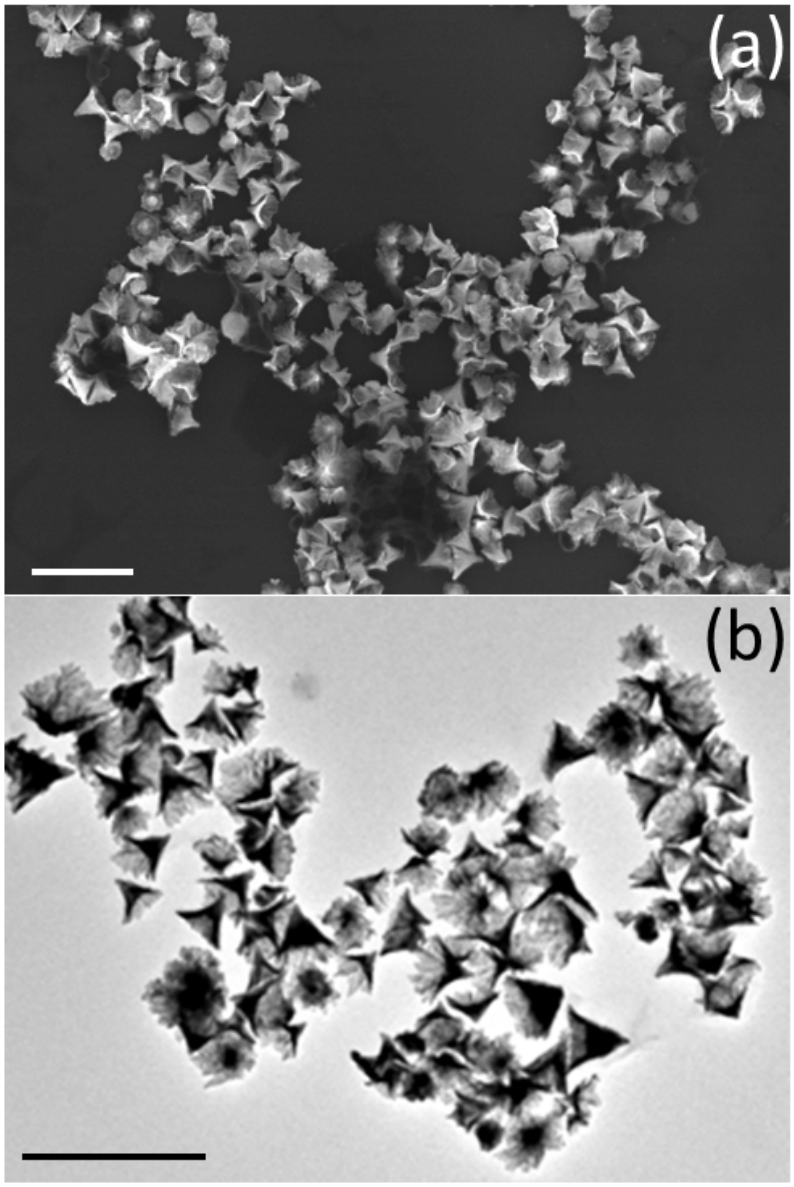

Figure S1. Low magnification SEM (a) and TEM (b) images of AuNCs. The AuNCs were synthesized by adding 2.5 ml 20 mM EOA hexane solution into 5 ml 0.8 mM $HAuCl_4$ aqueous solution *under sonication*.

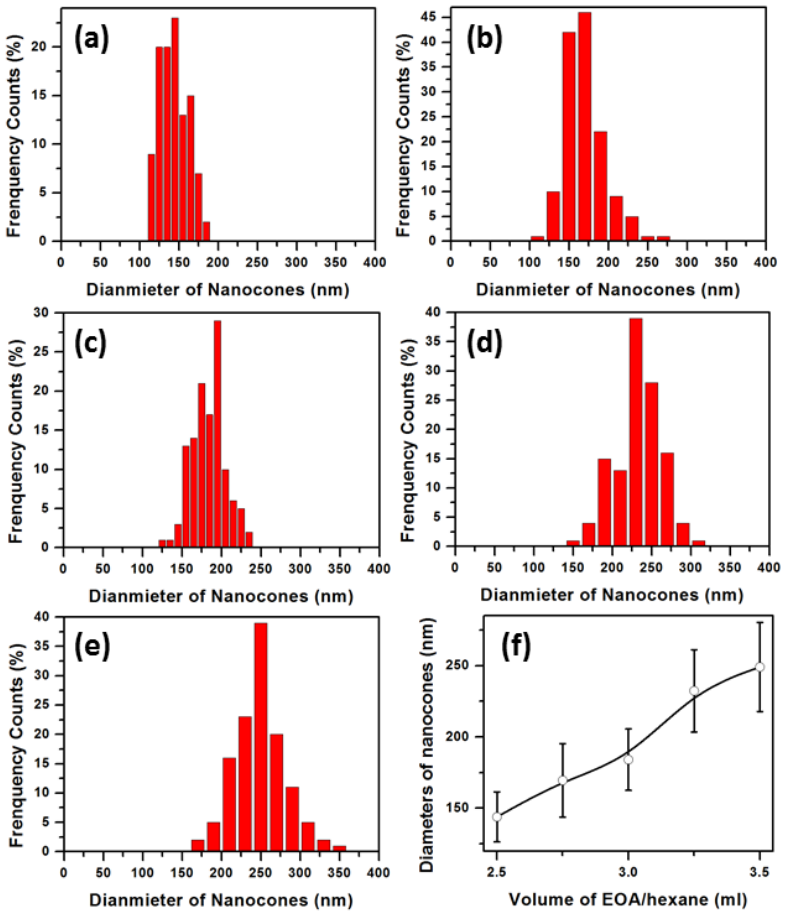

Figure S2. Diameter and diameter distribution of AuNCs synthesized by adding 2.50 (a), 2.75 (b), 3.00 (c), 3.25 (d) and 3.50 (e) ml of 20 mM EOA hexane solution into 5ml 0.8 mM $HAuCl_4$ aqueous solution *under sonication*. (f) The diameter of NCs as a function of volume of EOA hexane solution.

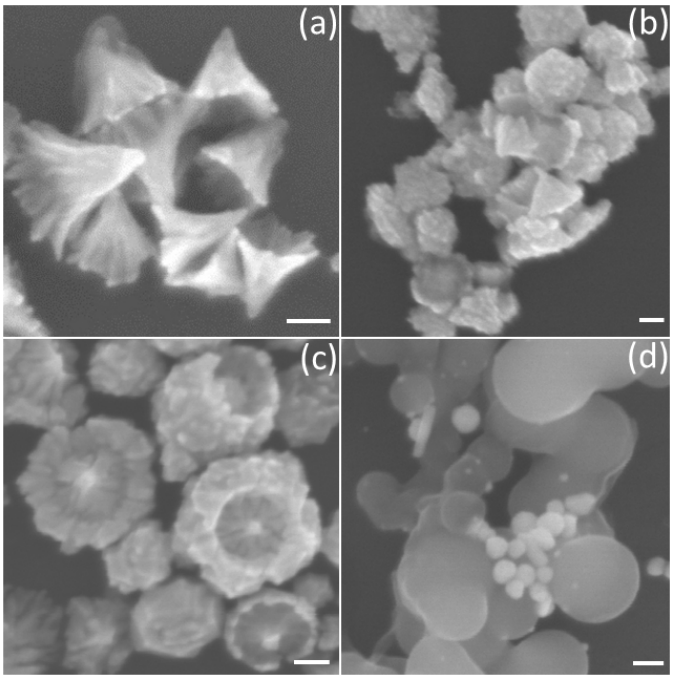

Figure S3. The effect of boiling point (B.P.) of the organic phase on the ultrasound assisted synthesis. SEM images of Au nanoparticles obtained by adding 2.5 ml 20 mM EOA hexane solution (a), octane solution (b), EOA decane solution (c) and EOA hexadecane solution (d) into 5 ml 0.8 mM $HAuCl_4$ aqueous solution *under sonication*. The scale bars are 50 nm.

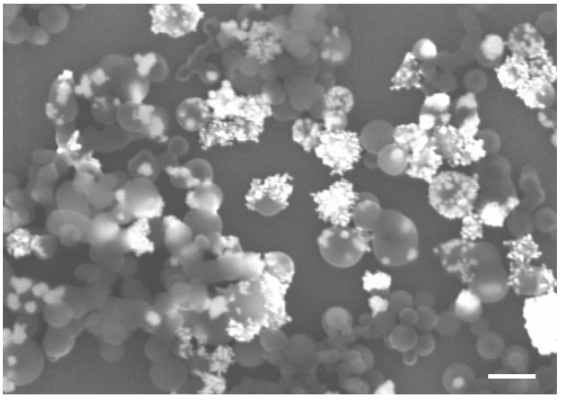

Fig. S4. SEM image of Au nanoparticles obtained by adding 2.5 ml 20 mM EOA hexane solution into 5 ml 0.8 mM $HAuCl_4$ aqueous solution *without sonication*. The scale bar is 200 nm.

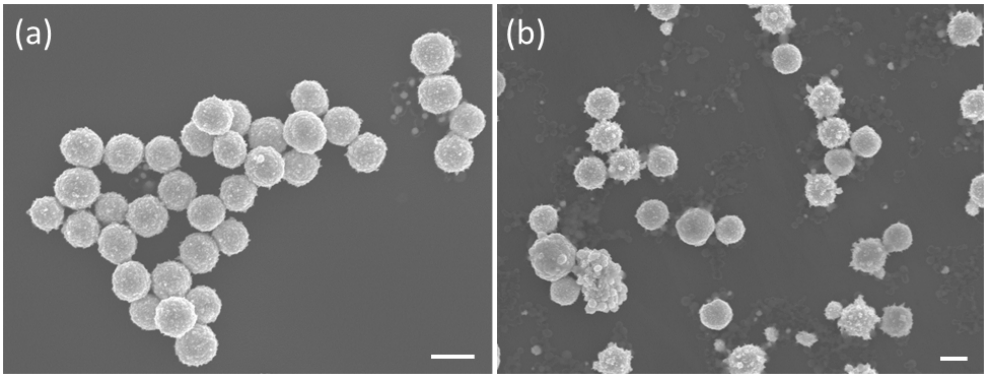

Fig. S5. SEM images of Au nanoparticles obtained by adding 0.5 ml (a), 1.5 ml (b) 20 mM EOA hexane solution into 5 ml 0.8 mM $HAuCl_4$ aqueous solution *without sonication but under shaking* at 45 ℃. The scale bars are 500 nm.

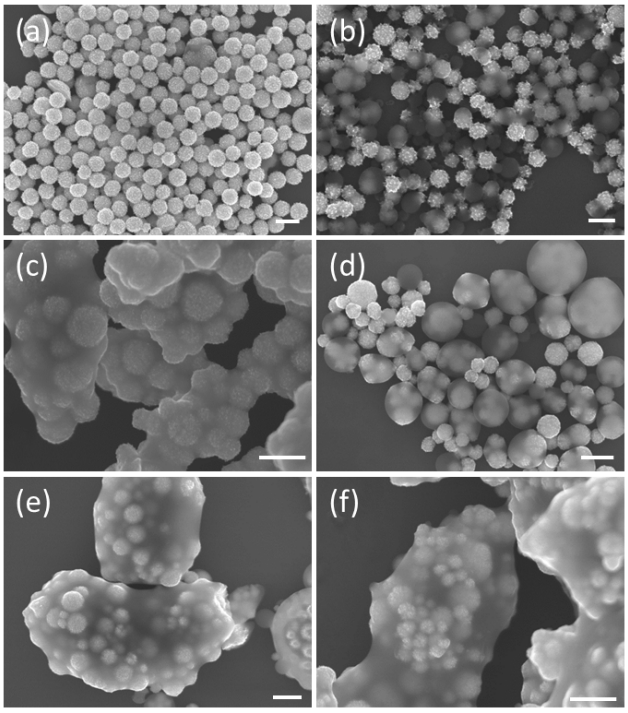

Fig. S6. SEM images of Au nanoparticles synthesized by using *single phase method* (without the organic phase). The Au nanoparticles were obtained by adding 0.5 ml (a), 1.0 ml (b) 2.0 ml (c) 2.5 ml (d) 3.0 ml (e) and 3.5 ml (f) 20 mM EOA aqueous solution into 5 ml 0.8 mM $HAuCl_4$ aqueous solution. The scale bars are 500 nm.

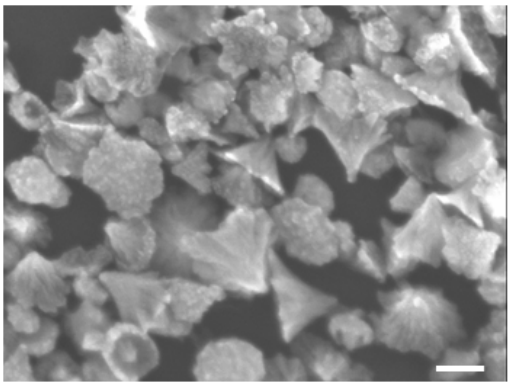

Figure S7. SEM image of samples synthesized by adding 2.5 ml 20 mM EOA hexane solution into 5 ml 0.8 mM $HAuCl_4$ aqueous solution *under sonication at 30 ^oC*. The scale bar is 100 nm.