SUPPORTING INFORMATION

Facile synthesis of functional Au nanopatchies and nanocups

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1. Materials.

2-Methoxy aniline (MOA), 2-ethoxy aniline (EOA), gold(III) chloride hydrate ($HAuCl_4$, 99.999%), 4-mercaptopyridine (MPy) and hexane 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 PPs.

In a typical synthesis, a 1.02 mg of $HAuCl_4$ (3 μmol) was dissolved in 5 mL of deionized water. After vortexing for 10 s, the solution was then placed into a pre-heated water bath at 45 ^oC for 10 mins to reach thermal equilibrium. Subsequently, 0.8 mL of EOA in hexane solution (20 mM) was carefully added on the top of the $HAuCl_4$ aqueous solution. The mixture was then incubated overnight at 45 ^oC leading to the further growth of PPs. After the solution was cooled down to room temperature, the top hexane phase was discarded. The aqueous solution containing PPs was centrifuged, and then the sediment was collected and washed three times with deionized water to remove the PEOA, the above PPs were concentrated by centrifugation, and then dispersed in DMF for overnight. The PPs were further washed five times by DMF and three times by water until the supernatant had showed no UV absorption peak corresponding to PEOA.

3. Characterizations.

The PPs 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 PP aqueous solution on silicon wafers, and dried at room temperature. TEM samples were prepared on 300 mesh copper grids covered with carbon film. The X-ray diffraction (XRD) diffraction pattern of AMNPs were recorded on a Bruker D8 Advance powder diffractometer equipped with a Cu K(alpha) radiation and LynxEye PSD detector. The XRD samples were prepared by casting the solution samples on a 2.5×2.5 cm^2 glass substrate, and then dried under vacuum for overnight. The size of patchy particles was measured by a Photocor-FC dynamic light scattering (DLS) at a scattering angle of 90^o, equipped with a 633 nm laser (5 mW).

For the surface-enhanced Raman scattering (SERS) measurement, PPs after the remove of PEOA by DMF were dispersed in water. 20 µL of the nanocup solution was cast on the substrate of 0.5×0.5 cm2 silicon wafer and dried at room temperature. 4-MPy was dissolved in ethanol at a predesigned concentration from 100 µM to 1 nM. Subsequently, the silicon wafers with dried Au nanocups were dipped in 2 mL of 4-MPy solution with different concentrations for 1 hr. The samples were then rinsed with pure ethanol 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 and the laser power was set at 76 µW. Raman scattering intensity was collected with the accumulation time of 20 s for 3 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 Au nanocups 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 nanocup system and bulk system, respectively. The absolute Raman scattering intensity for nanocup and bulk systems are 5000 and 60 at 1098 cm^{-1}, respectively.

N_{SERS} is the average number of absorbed MPy molecules on the surface of Au nanocups. Based on the dimension of Au nanocups (diameter of 220 nm) that composed of Au protrusions (diameter of 14 nm), we assumed that the each nanocup is approximately composed of 50 Au protrusions with the length of 100 nm, and the total number of nanocups in 1×1 μm^2 is about 100, considering the aggregation of Au nanocups. The packing density of MPy on the metal surface is 6.8×10^{14} molecules per cm^2. Thus gives $N_{SERS}=1.5*10^8$.

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 smaples. $N_{Bulk}=6.5*10^{14}$.

Thus, it gives $EF=4.1*10^8$.

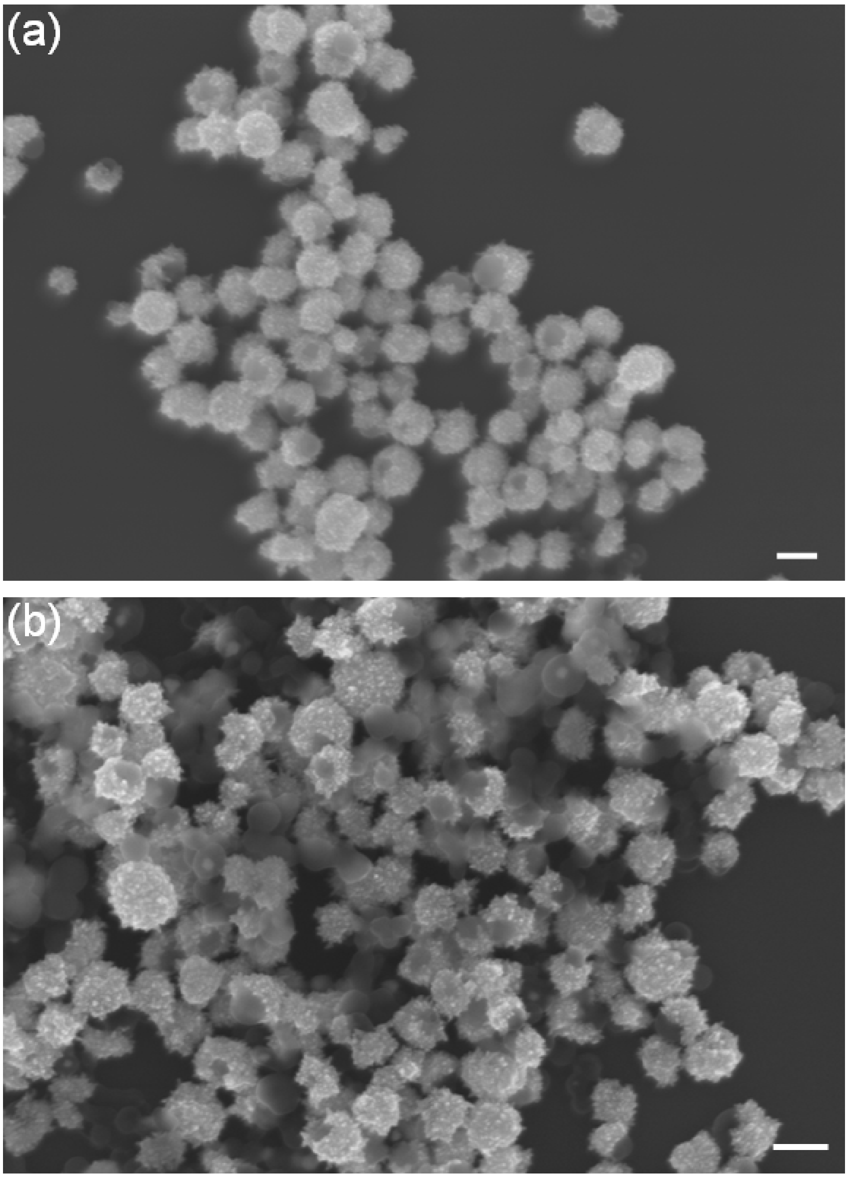

Figure S1. Low magnification SEM images of PPs composed of PEOA and Au nanocups. Synthesis conditions: 5 mL of 0.6 mM $HAuCl_4$ aqueous solution and 0.8 mL of 20 mM EOA hexane solution. Reaction was performed at 45 ^oC for 12 hr. Scale bars are 200 nm.

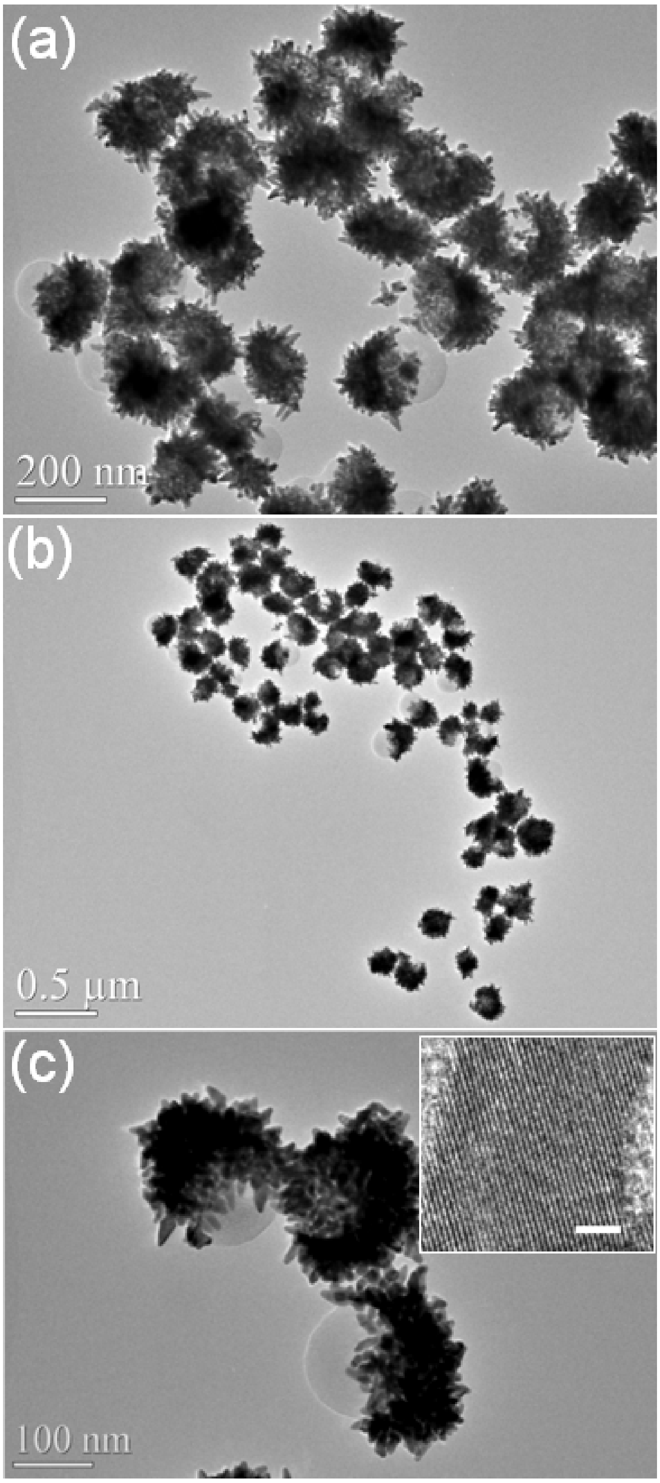

Figure S2. TEM images of PPs composed of PEOA and Au nanocups. Synthesis conditions: 5 mL of 0.6 mM $HAuCl_4$ aqueous solution and 0.8 mL of 20 mM EOA hexane solution. Reaction was performed at 45 ^{o}C for 12 hr. Scale bar is 2 nm in the inset of (c).

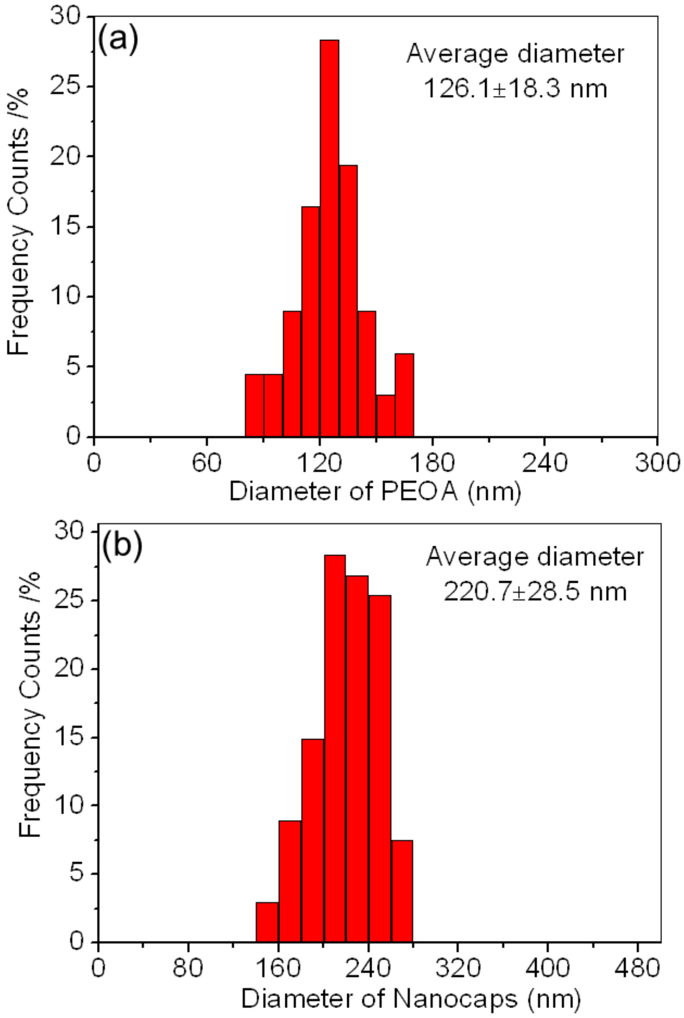

Figure S3. Size and size distribution of PEOA NPs (a) and nanocaps (b), showing in Figure S1 and 2. The diameters of NPs are the average values obtained from >100 NPs.

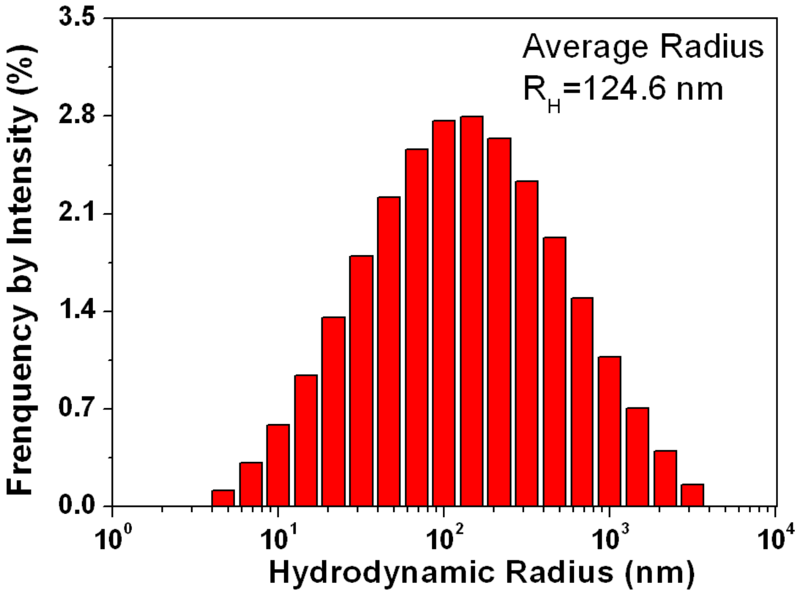

Figure S4. Average radius and distribution of PPs (shown in Figure S1) measured from DLS. The average size is consistent with the measurements from SEM images.

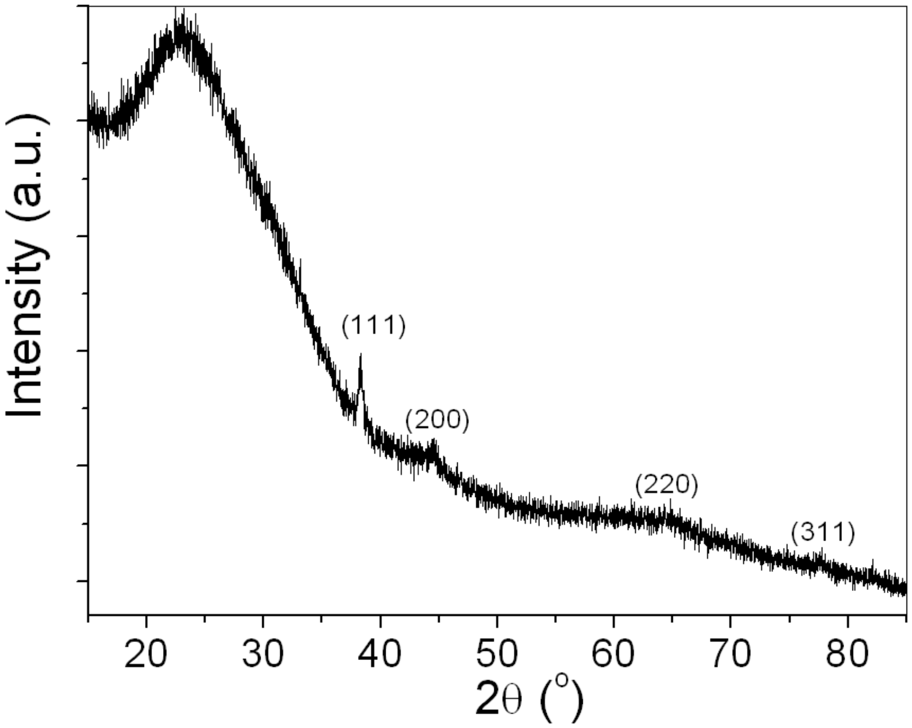

Figure S5. XRD patterns of PPs composed of PEOA and Au nanocups before the removal of PEOA. The typical diffraction peaks from (111), (200), (220), and (311) reveal the typical face center cubic crystallization of Au. The hump between 20° to 30° is possibly attributed to the amorphous PEOA.

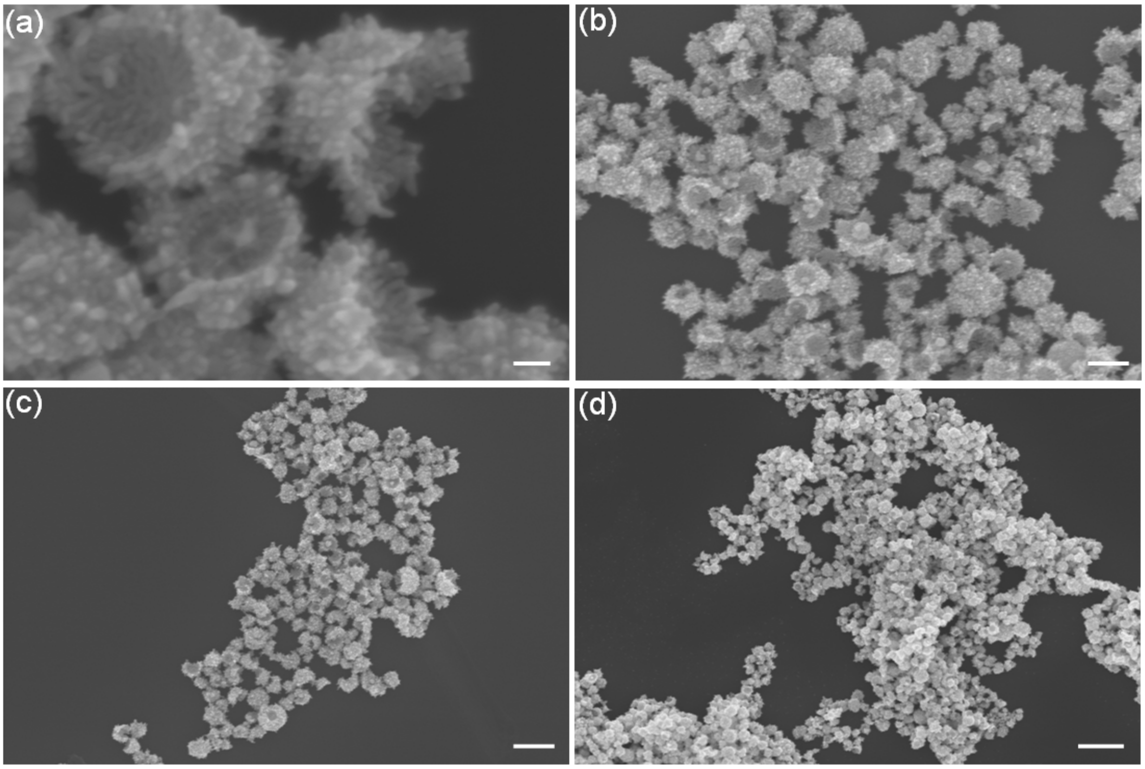

Figure S6. Representative SEM images of Au nanocups from Figure S1 after the removal of PEOA. The PEOA was etched by DMF. Scale bars are 40 nm (a), 200 nm (b), 400 nm (c) and 800 nm (d), respectively.

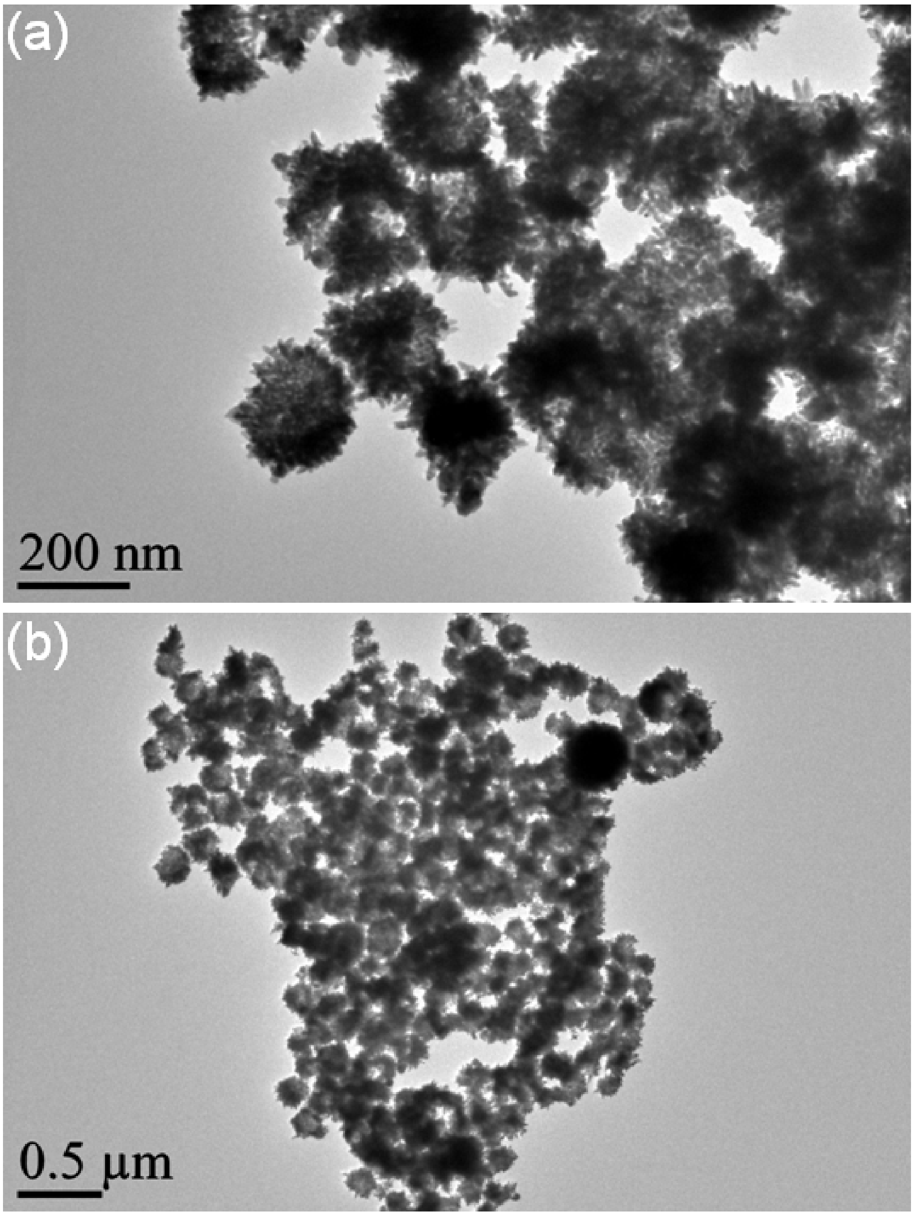

Figure S7. TEM images of Au nanocups after removing PEOA of PPs in Fig S1. The PEOA was etched by DMF.

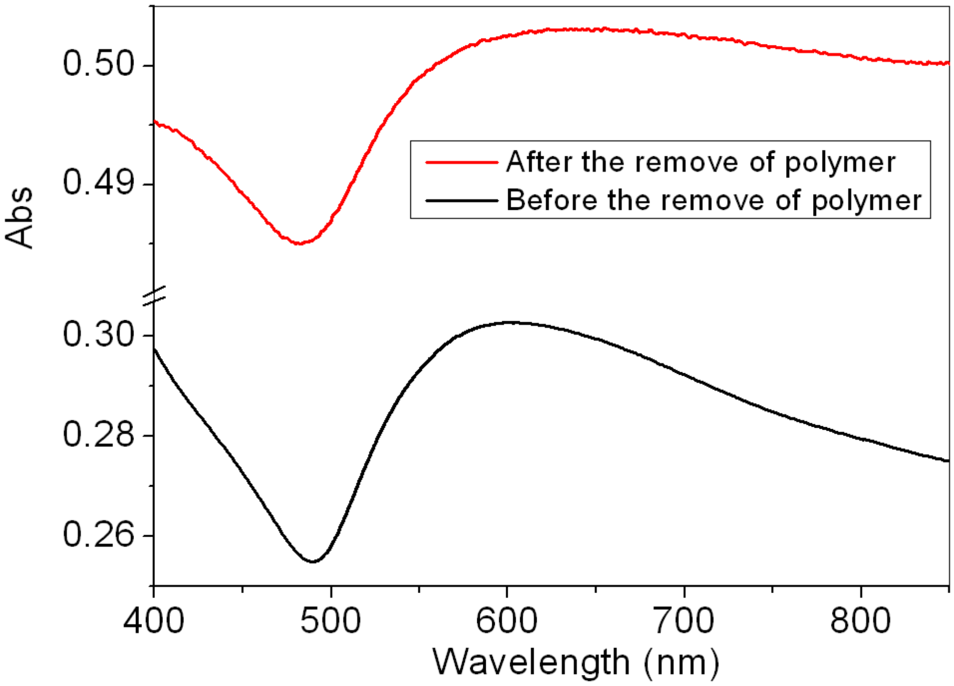

Figure S8. UV-vis spectra of PPs composed of PEOA and Au nanocups in solutions before and after the removal of PEOA. The UV-vis absorption of Au nanocups covered the whole range from 500 to 1000 nm.

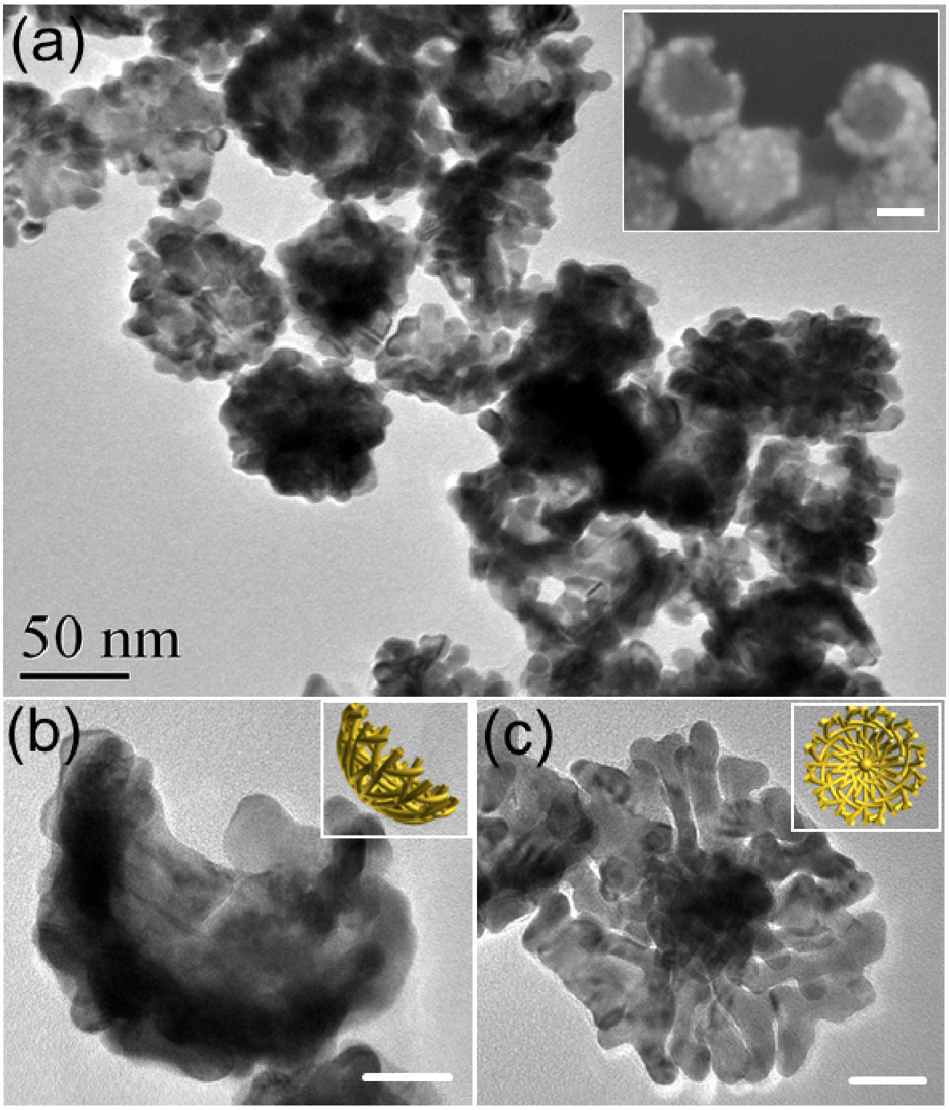

Figure S9. Low (a) and high (b,c) magnification TEM images of sub-100 nm Au nanocups prepared under sonication. Inset shows a SEM image of nanocups. The nanocups are dried on the TEM grid with random orientation. Representative TEM images of nanocups oriented with side (b) and top opening (c) facing the screen. The average diameter of the nanocups is 76.6±12.7 nm. The scale bars are 20 nm (b,c) and 40 nm (inset in a). Synthetic conditions: 5 mL of 0.6 mM $HAuCl_4$ aqueous solution and 0.8 mL of 20 mM EOA hexane solution were sonicated at 45 ^{o}C for 2 hr.

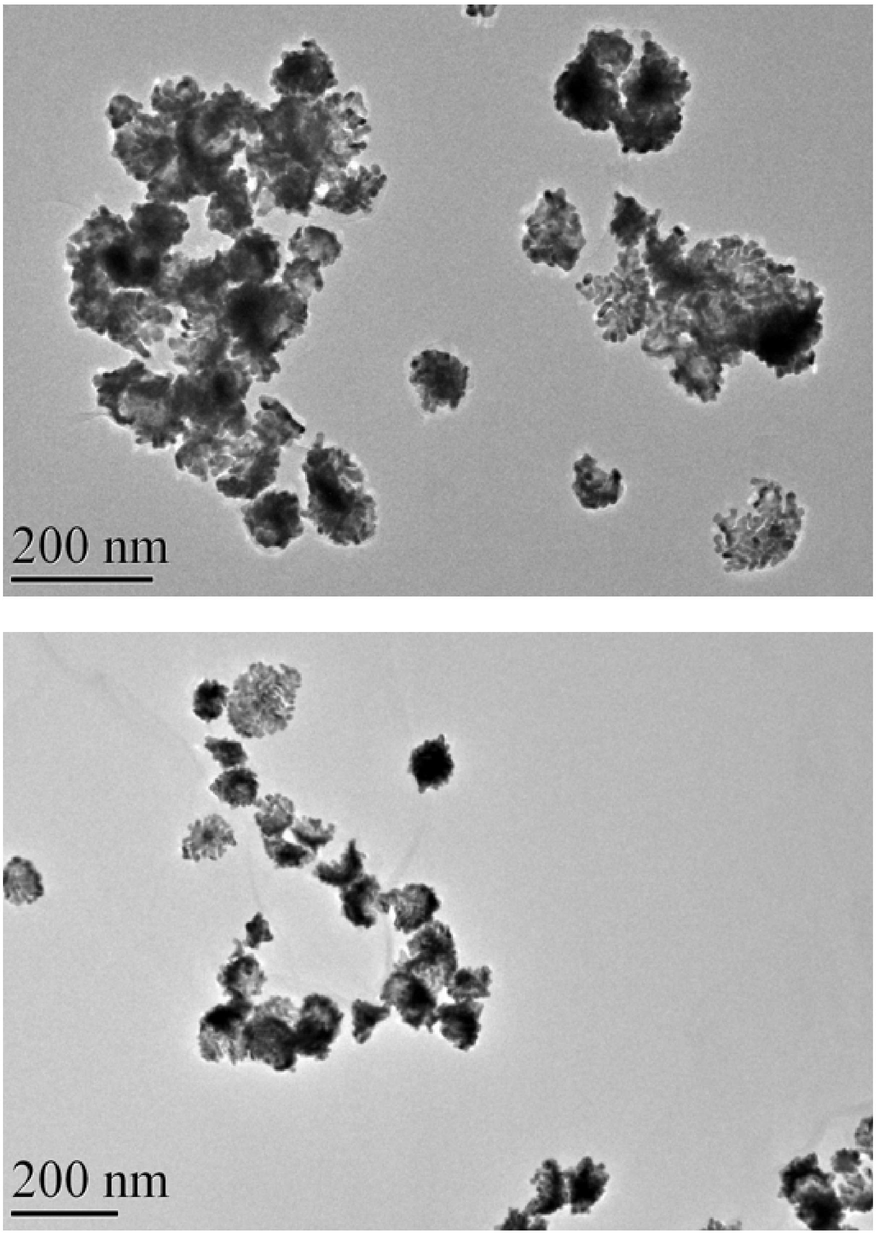

Figure S10. Low magnification TEM images of Au nanocups prepared under sonication. Synthesis conditions: 5 mL of 0.6 mM $HAuCl_4$ aqueous solution and 0.8 mL of 20 mM EOA hexane solution at 45 ^{o}C for overnight.

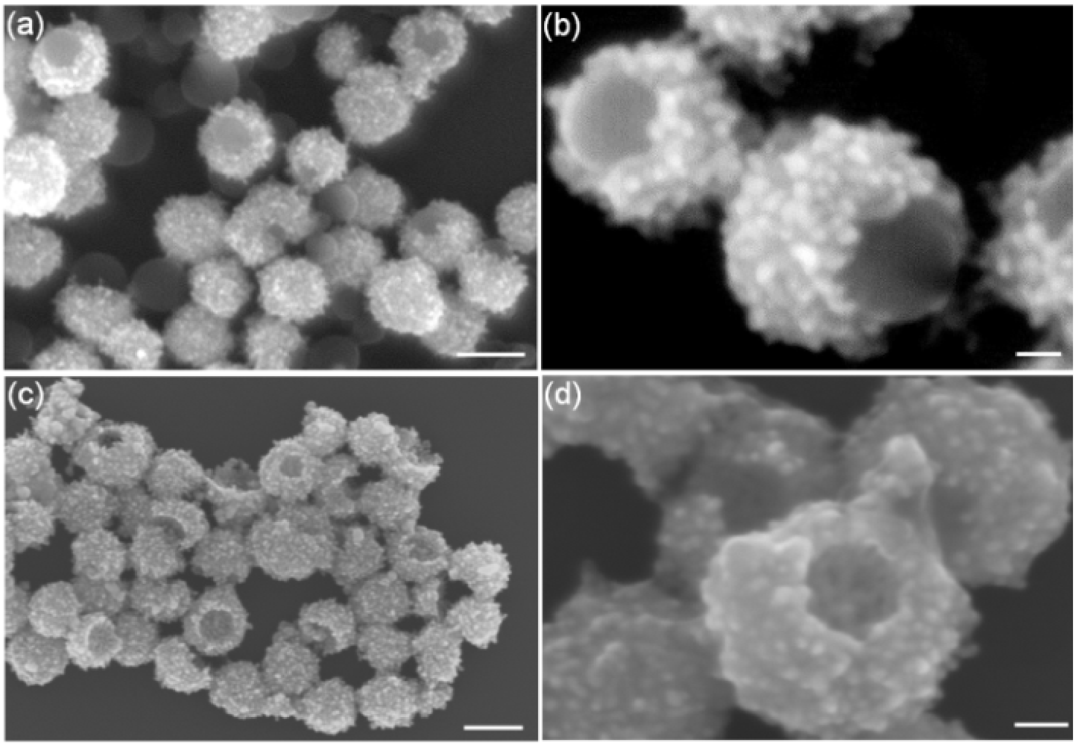

Figure 11. SEM images of PPs prepared from PMOA (a,b) and Au nanocups (c,d) after the remove of PMOA particles. Synthesis conditions: 5 mL of 0.7 mM $HAuCl_4$ aqueous solution and 0.8 mL of 20 mM MOA hexane solution. Reaction was performed at 45 ^{o}C for 12 hr. Scale bars are 200 nm in (a,c) and 50 nm in (b,d).

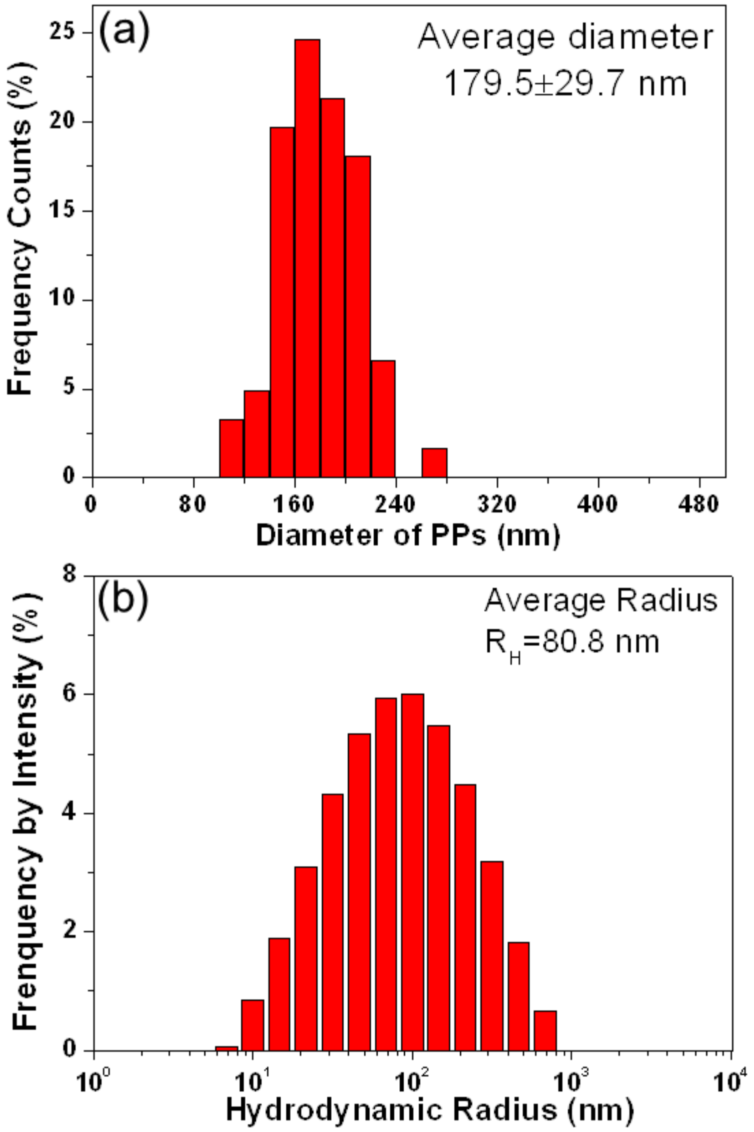

Figure S12. Size and size distribution of PPs synthesised using MOA by SEM measurement (a) and DLS (b). The diameters of NPs obtained from SEM are the average values obtained from >100 NPs.

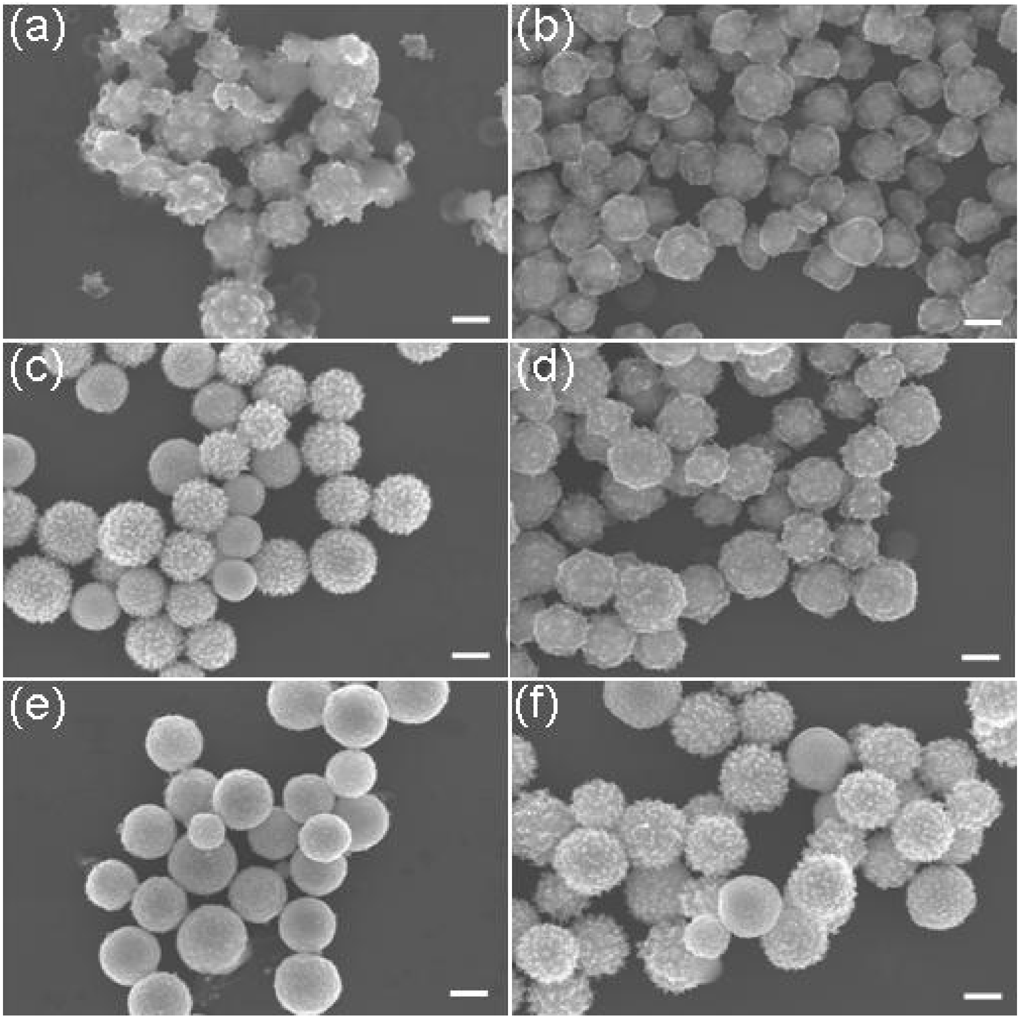

Figure S13. Control experiments of EOA and $HAuCl_4$ reacted in aqueous solution. Synthetic conditions: (a) 0.8 mL of 10 mM EOA and 5 mL of 0.4 mM $HAuCl_4$; (b) 0.8 mL of 20 mM EOA and 5 mL of 0.4 mM $HAuCl_4$; (c) 0.8 mL of 10 mM EOA and 5 mL of 0.6 mM $HAuCl_4$; (d) 0.8 mL of 20 mM EOA and 5 mL of 0.6 mM $HAuCl_4$; (e) 0.8 mL of 10 mM EOA and 5 mL of 0.8 mM $HAuCl_4$; and (f) 0.8 mL of 20 mM EOA and 5 mL of 0.8 mM $HAuCl_4$. All the reactions were preceded at 45 ^{o}C for overnight. Scale bar are 300 nm.

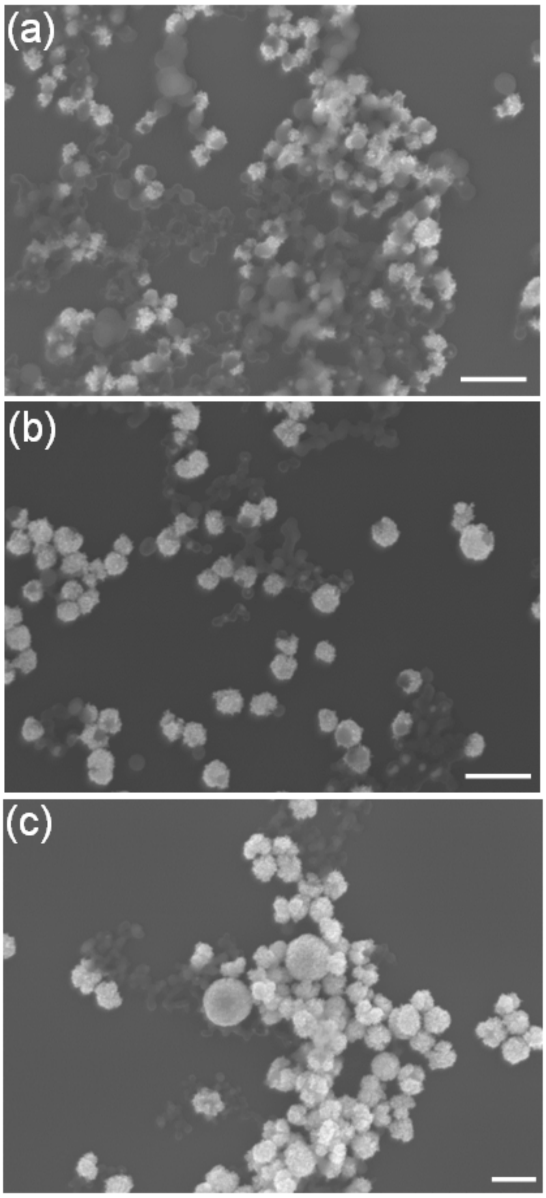

Figure S14. SEM images of NPs synthesized using EOA with various concentration of EOA. Synthesis conditions: (a) 0.8 mL of 10 mM EOA hexane solution; (b) 0.8 mL of 15 mM EOA hexane solution; and (c) 0.8 mL of 25 mM EOA hexane solution. In all the reactions, 5 mL of 0.6 mM $HAuCl_4$ was used at 45 °C for overnight. Scale bars are 500 nm.

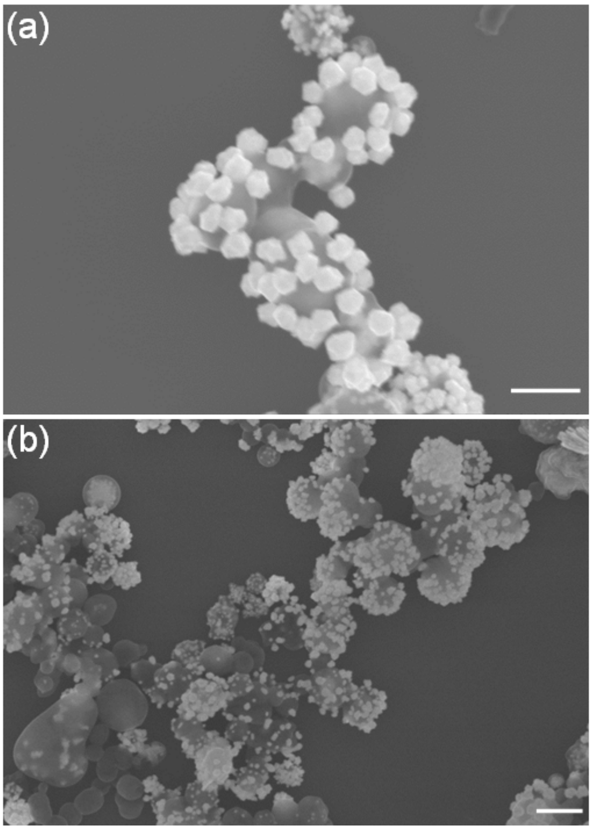

Figure S15. SEM images of NPs synthesized using EOA with various concentration of $HAuCl_4$. Synthesis conditions: (a) 5 mL of 0.4 mM $HAuCl_4$ aqueous solution; and (b) 5 mL of 1.4 mM $HAuCl_4$ aqueous solution. In all the reactions, 0.8 mL of 20 mM EOA hexane solution was used at 45 ^{o}C for 12 hr. Scale bars are 250 nm in (a) and 500 nm in (b).

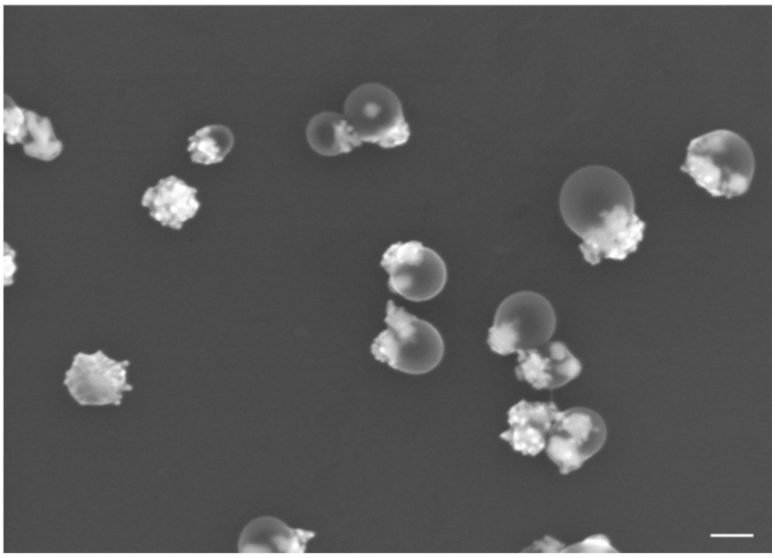

Figure S16. SEM images of NPs synthesized using EOA synthesized at 60 °C. Synthesis conditions: 5 mL of 0.6 mM $HAuCl_4$ aqueous solution and 0.8 mL of 20 mM EOA hexane solution was used. Reaction was performed at 45 °C for 12 hr. Scale bar is 100 nm.