

Supporting Information for

PEG-POSS Assisted Facile Preparation of Amphiphilic Gold Nanoparticles and Interface Formation Janus Nanoparticles

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Experimental details

Materials. Tetrachloroaurate trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.99%), sodium citrate dehydrate (99%), sodium borohydride (NaBH_4 , 98% min), and L-(+)-ascorbic acid (99+%), hexadecyltrimethylammonium bromide (CTAB, 99.9%), tetraethyl orthosilicate, 3-Aminopropyltriethoxysilane, and ascorbic acid were all purchased from Sigma-Aldrich. PEG-POSS was purchased from Hybrid Plastics. All chemicals were used without further purification.

Synthesis of Au NPs stabilized with citrate

Citrated stabilized Au NPs were obtained by injecting 5 ml of 38.8 mM sodium citrate solution to a boiling tetrachloroauric acid (20 mg dissolved in 50 ml DI water) solution.¹ Continue reflux for 30 min and cool down to room temperature. The obtained Au NPs was characterized by TEM shows an average diameter of 17 ± 2.5 nm. (ref: K. C. Grabar, R. Griffith Freeman, M. B. Hommer and M. J. Natan, *Anal. Chem.* 1995, **67**, 735–743.)

Synthesis of Au NPs stabilized with oleylamine

Au NPs stabilized with oleylamine were prepared by quick injection of a solution of 1.5 ml of 0.125 M of tetrachloroauric acid solution in oleylamine to a boiling solution containing 3 ml of oleylamine and 48 ml of toluene. The solution color changes from light yellow to colorless and finally to red. Continue refluxing for about 2 hours and then cool down to room temperature. TEM results shows the formation of the Au NPs with sizes of 20 ± 2 nm. (ref: Hiramatsu, H.; Osterloh, F. E. *Chem. Mater.* **2004**, *16*, 2509 - 2511.)

Synthesis of Au NPs stabilized with PEI

In a 50 ml flask was added 25 ml of the 100 mM PEI solution and 10 mM of formaldehyde in water. To this solution, was added 5 ml of the 5 mM of tetrachloroauric acid solution and slow increase the temperature to about 100 °C and keep at this temperature for 5 min. Stop the reaction by cooling down to room temperature. TEM measurement shows the formation of Au NPs with sizes of 20 ± 4.5 nm.

Synthesis of Au NRs stabilized with CTAB

First, the seed solution was prepared by addition an aqueous HAuCl_4 solution (0.125 mL, 0.01M) into an aqueous CTAB solution (3.75 mL, 0.1M) in a plastic tube. After the solution was mixed by gentle inversion, an ice-cold, freshly prepared aqueous NaBH_4 solution (0.3 mL, 0.01M) was added all at once, followed by rapid inversion mixing for 2 min. The solution was left stand at room temperature for 2 hours before use.

The growth solution was prepared by mixing 15 ml of 0.2 M hexadecyltrimethylammonium bromide and 15 ml of 0.5 mM of HAuCl_4 . To this solution, 0.05 ml of 0.1 M ascorbic acid was added and the color changed to colorless immediately. To the growth solution, 400 μl of the seed solution was added and shake up and down for 10 s, then left stand at room temperature for overnight. TEM images show the formation of Au NRs with length of 75 ± 5 nm and diameter of 12 ± 1.5 nm. (ref: Nikoobakht, B.; El-Sayed, M. A. Chem. Mater. 2003, 15, 1957–1962.)

Synthesis of silica NPs

To a 100 ml flask was added 50 ml anhydrous ethanol and 1.5 ml of tetraethyl orthosilicate. Under stirring, 3 ml 28% ammonia was added quickly and keep stirring at room temperature for 24 hours in dark. Then the particles were separated out by centrifugation and wash with ethanol for 3 time. SEM images show the formation of the silica particles with diameter of 80 ± 5 nm.

Synthesis of silica NPs with positive charged surface

The synthesis of the silica nanoparticles with positive charged was achieved by refluxing the formed 80 nm sized silica nanoparticles with 400 μl of 3-Aminopropyltriethoxysilane in 50 ml of ethanol at 80 °C overnight with protection of nitrogen flow.

Characterization and Techniques

The DLS study was performed using a Brookhaven (BI-200 SM) light scattering instrument. The light source was a 35-mW He-Ne laser emitting vertically polarized light of 632.8 nm wavelength. The sample cells were mounted in a temperature-controlled, refractive index matched bath filled with decahydronaphthalene (decalin). In the DLS measurements, the intensity correlation function was measured at 25 °C with a maximum number of 256 channels using a BI-9000AT digital autocorrelator. The calibration of the spectrometer was carried out using a polystyrene standard solution with a size of 97 ± 3.2 nm. UV-vis spectra were recorded on a Shimadzu 3600 UV-VIS-NIR Spectrophotometer.

TEM micrographs were obtained using a JEOL 2100TEM operating at an accelerating voltage of 200 kV. A drop of sample solution was cast onto a 200-mesh carbon-coated copper grid. The samples were dried at room temperature prior to measurement.

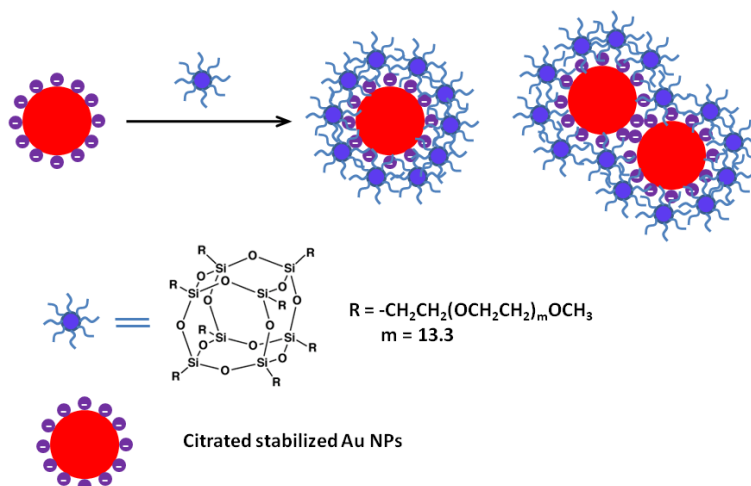


Figure S1. Schematic showing the interaction of POSS-PEO with citrated stabilized Au NPs.

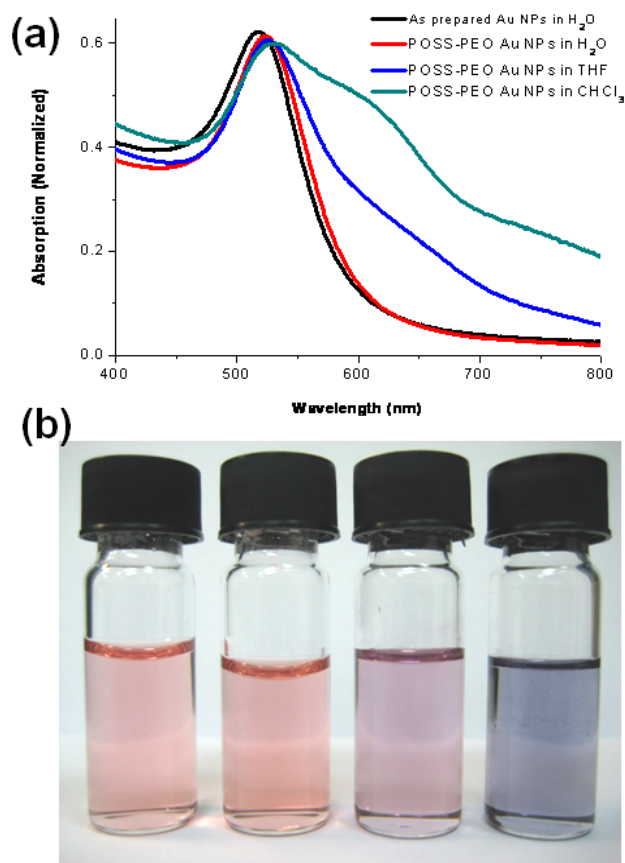


Figure S2. UV-vis spectra (a) and photos (b) of Au NPs in different solvent assisted with POSS-PEO. In Figure (b), the Au NPs solutions from left to right are as synthesized Au NPs dispersed in water, POSS-PEO coated Au NPs in water, POSS-PEO coated Au NPs in THF, and POSS-PEO coated Au NPs in chloroform.

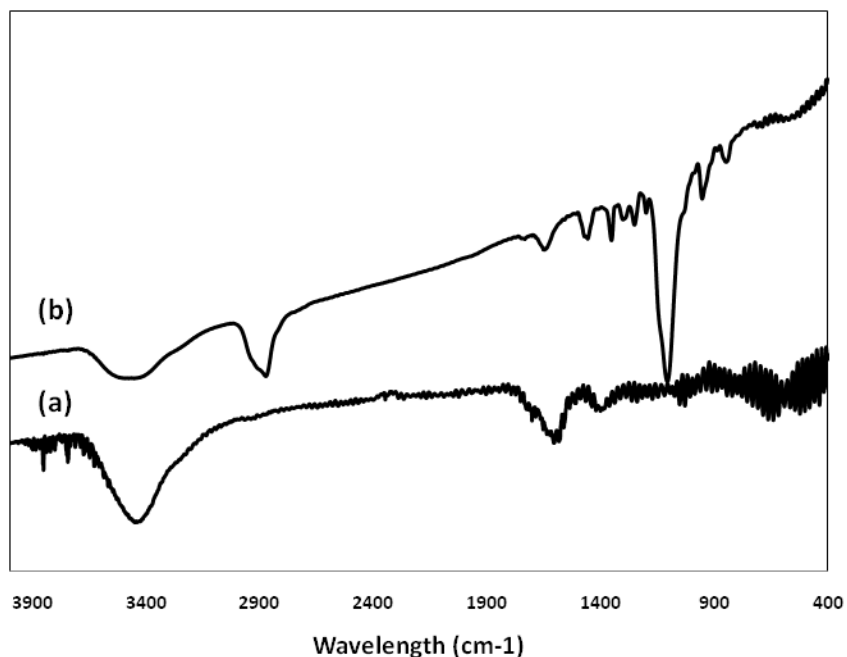


Figure S3. FT-IR spectra of citrate stabilized Au NPs (a) and PEG-POSS coated Au NPs (b). The shift of –C=O peak from 1637 cm⁻¹ in the citrate stabilized Au NPs to 1790 cm⁻¹ was attributed to the hydrogen bonding between the PEG-POSS and the citrate ligands.

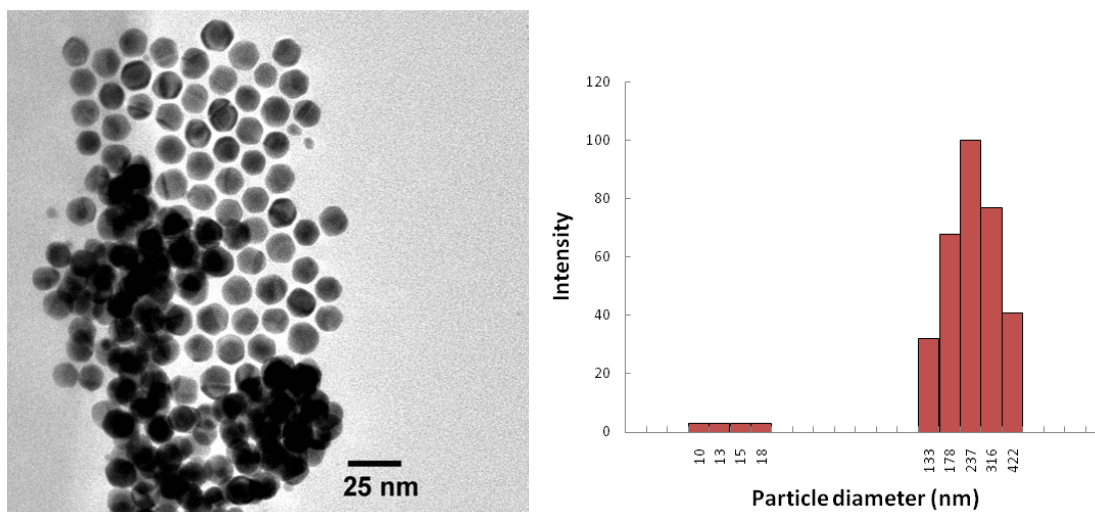


Figure S4. TEM images of amphiphilic Au NPs assisted with POSS-PEG from chloroform and DLS results of Au NPs in chloroform.

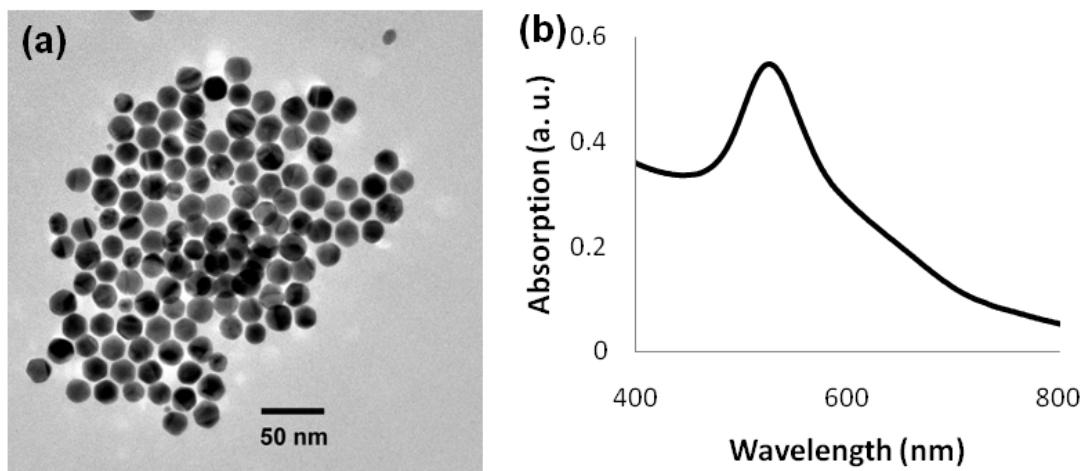


Figure S5. TEM and UV-vis spectra of amphiphilic POSS-PEG coated PEI stabilized Au NPs in THF.

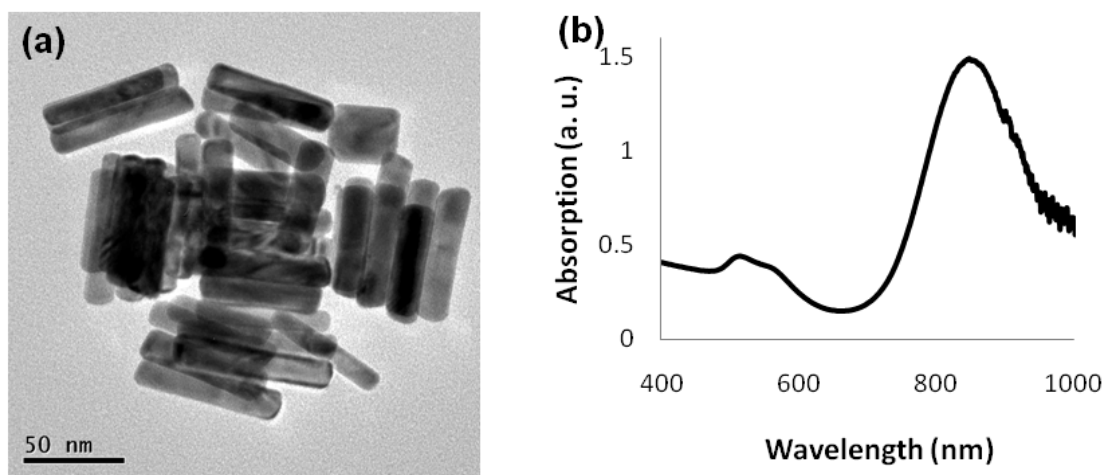


Figure S6. TEM and UV-vis spectra of amphiphilic POSS-PEG coated cetyltrimethylammonium bromide (CTAB) stabilized Au NRs in THF.

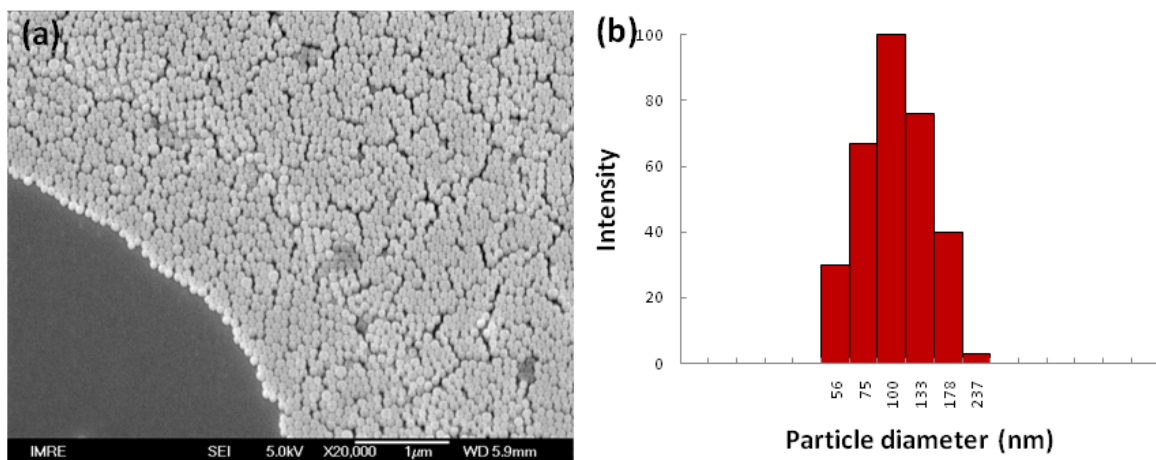


Figure S7. SEM and DLS of amphiphilic POSS-PEG coated silica NPs in THF.

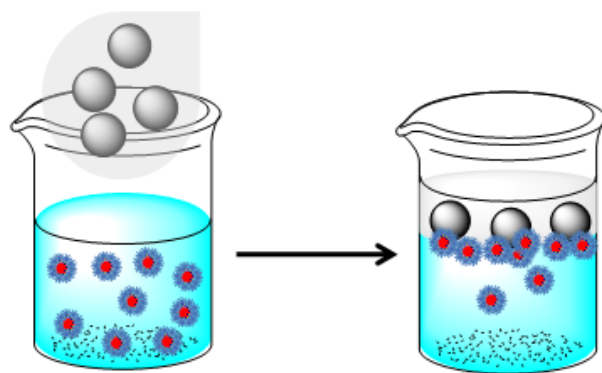


Figure S8. Schematic illustrates the formation of hybrid polar Janus particles at the organic/aqueous interface.

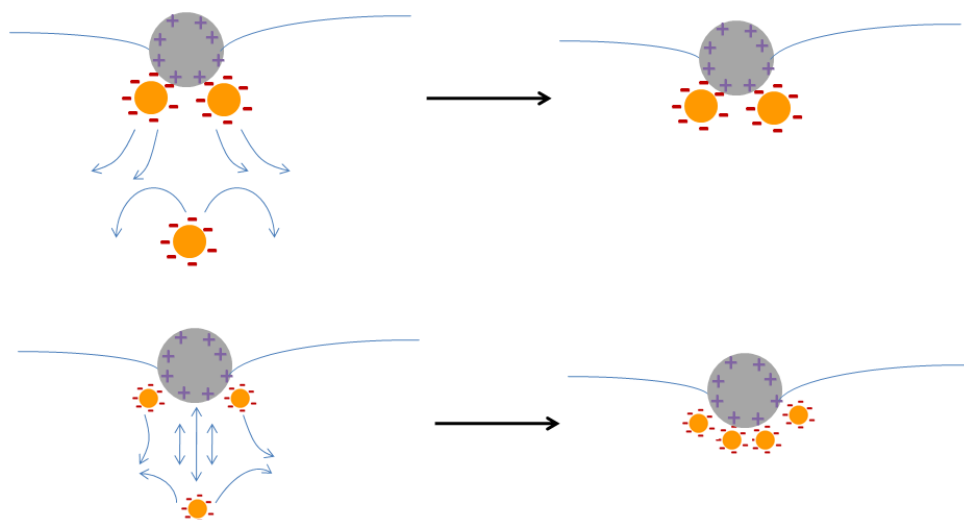


Figure 9. Schematic illustration of the formation of Janus particles and why the snowman shaped and patchy Janus particles were formed.

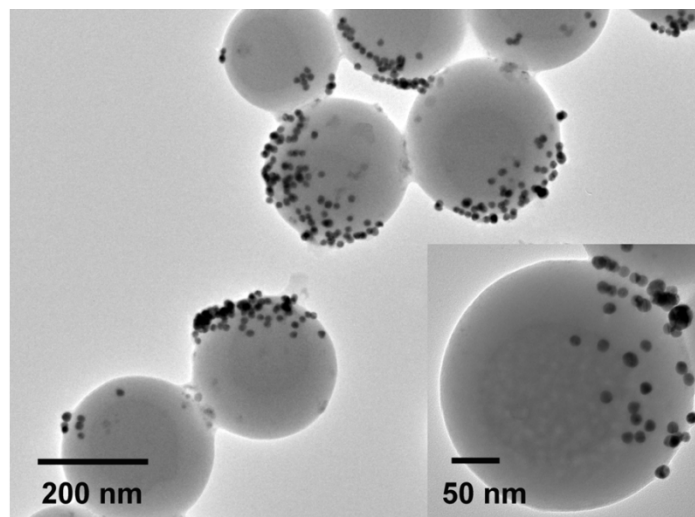


Figure 10. TEM images of patchy Janus particles formed by binding of negatively charged Au NPs ($d = 17$ nm) and positively charged silica NPs ($d = 250$ nm).

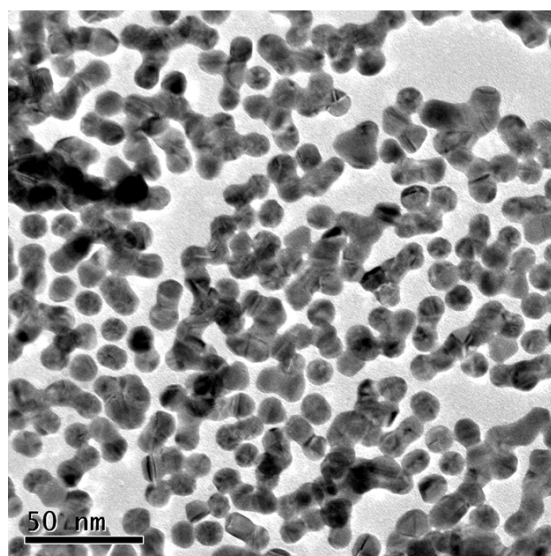


Figure S11. The formed gold nanostructures such as dumbbell, tripod, tetrapod, and nanowires.