

## A Facile Synthesis of Asymmetric Hybrid Colloidal Particles

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### Experimental

**Chemicals and Materials.** Potassium persulphate (KPS, 99.99%, Sigma-Aldrich), gold colloids (50 nm, Ted Pella), 4-styrenesulfonic acid sodium salt hydrate (NaSS, Aldrich), styrene ( $\geq 99\%$ , Sigma-Aldrich), divinylbenzene (DVB, 80%, Aldrich), ethanol (100%, AAPER Alcohol and Chemical) were all used as received. Deionized water having a measured resistivity of 18 M $\Omega$  cm was prepared using an ultrapure water system (Aqua Solutions) and referred to as “water” throughout the manuscript.

**Synthesis of Asymmetric Au-PS Particles.** In a typical synthesis, 50 mg of KPS, 4.5 mL of water, 6 mg of NaSS, and 16.5 mL of ethanol were added into a 25-mL three-neck flask equipped with a reflux condenser and a Teflon-coated magnetic stirring bar. This system was heated to 70 °C under magnetic stirring. When the temperature reached 70 °C, 0.2 mL of a styrene-DVB mixture (99:1, wt/wt) was added to the flask, and 2 min later, 3.0 mL of the Au colloids was introduced. The reaction system was continued with heating at 70 °C for another 4 h before the product was collected by centrifugation and washed with a mixture of ethanol and water (60:40, wt/wt) three times and then ethanol one time.

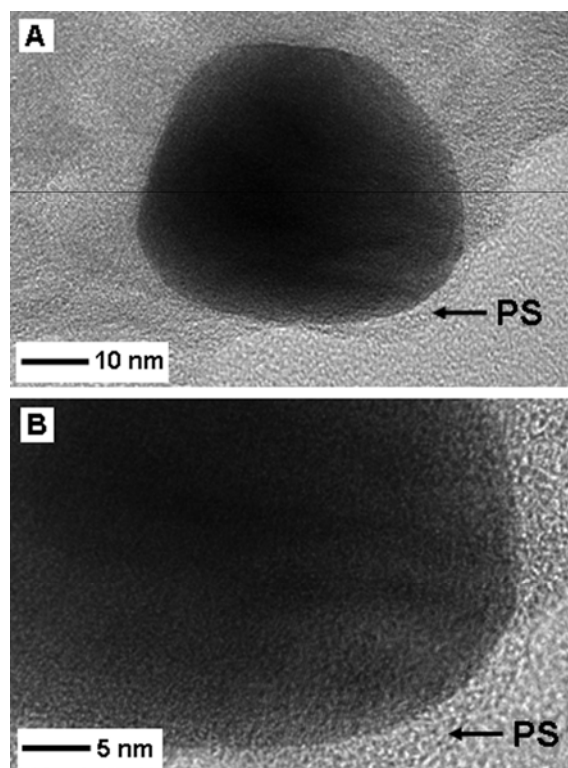
**Instrumentation.** Scanning electron microscopy (SEM) studies were performed with a FEI Nova NanoSEM 2300 operated at 10 kV. Transmission electron microscopy (TEM) studies were conducted with a FEI Tecnai G<sup>2</sup> Spirit operated at 120 kV. High-resolution TEM

(HRTEM) images were taken using a JEOL 2100F microscope operated at 200 kV. The samples for SEM studies were prepared by drying drops of the particle suspensions (in ethanol) on silicon substrates and then dried under ambient conditions. The samples for TEM or HRTEM studies were prepared by drying drops of the particle suspensions on copper grids coated with formvar/carbon (Ted Pella).

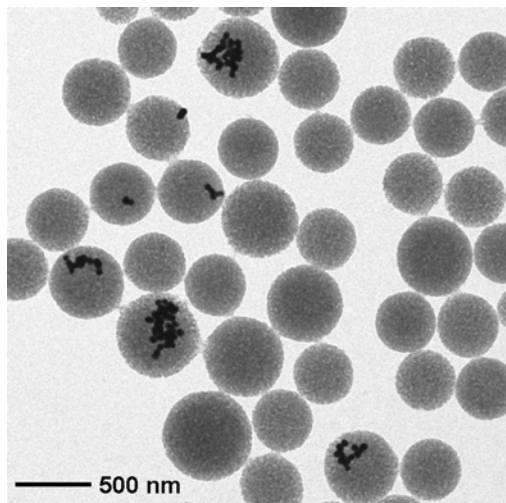
### **Notes**

We did an experiment without using NaSS while keeping other conditions the same, and we found that hybrid particles were obtained at a slightly lower yield (90%). The incorporation of NaSS unit into the oligomers might facilitate their nucleation on the surface of Au nanoparticles.

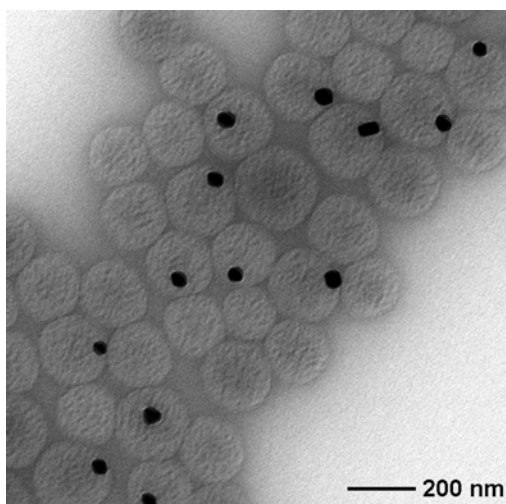
We did a set of experiments to investigate the role of ethanol as a solvent in forming the hybrid particles. In summary, we found that the yield of hybrid particles increased as the concentration of ethanol increased to 60% (wt.). When we used only water as a solvent, the Au nanoparticles were observed to be separated from PS beads. The ethanol seems to play a pivotal role in enhancing the wetting of Au colloid surface by PS oligomers and thus improving heterogeneous nucleation.



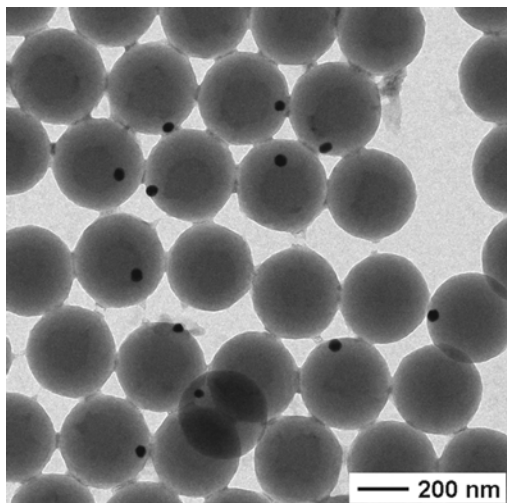
**Figure S1.** HRTEM images taken from the edge of an asymmetric Au-PS particle where the Au nanoparticle was 50 nm in size. There seems to be a very thin layer of polymer on the surface of Au nanoparticle, but it could also be caused by the polymer particle underneath it due to the orientation of the hybrid particle relative to the electron beam.



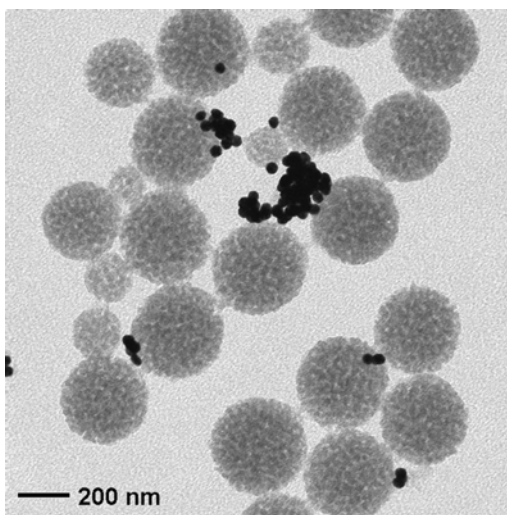
**Figure S2.** TEM image of the product when Au colloids were added right before the polymerization. The PS bead might contain a large number of Au nanoparticles which were formed due to agglomeration. The PS bead might contain no Au nanoparticle at all due to a homogeneous nucleation and growth pathway in the absence of enough Au nanoparticles in the solution (due to agglomeration). The Au nanoparticles were 50 nm in size.



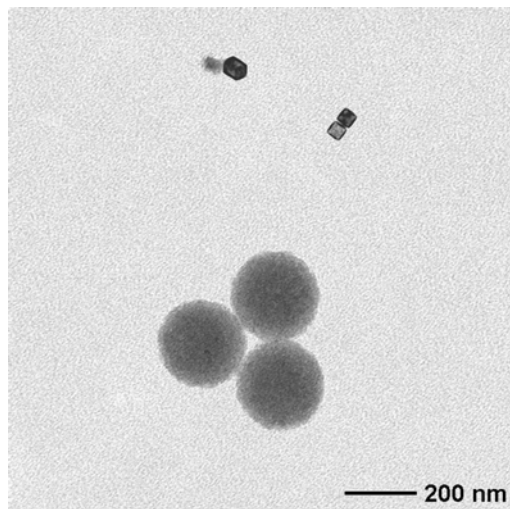
**Figure S3.** TEM image of the product when Au colloids were added 30 min after the polymerization had been initiated. Many of the PS beads contained no Au nanoparticle and the yield of asymmetric, hybrid particles had dropped to ~50%. The Au nanoparticles were 50 nm in size.



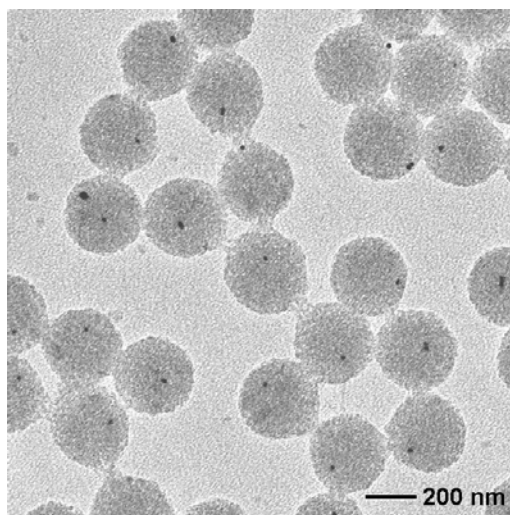
**Figure S4.** TEM image of the product when the amount of styrene monomer was increased to  $\sim 1.5$  times relative to the synthesis shown in Figure 1. Some of the PS beads contained no Au nanoparticle at all due to a homogeneous nucleation and growth pathway in the absence of enough Au nanoparticles in the solution.



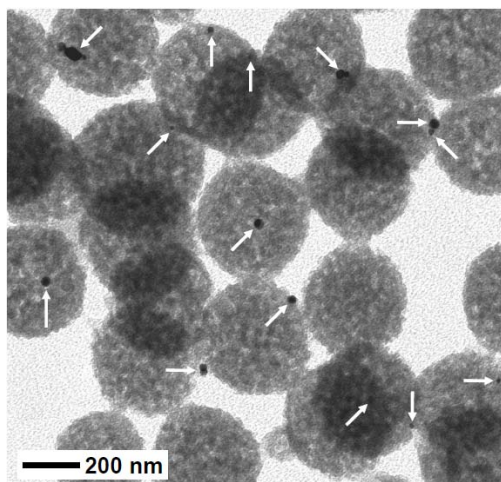
**Figure S5.** TEM image of particles that were prepared with Au nanoparticles whose surface was stabilized by a positively charged polymer, poly(allylamine). The Au nanoparticles tended to agglomerate during the synthesis. The average diameter of the Au nanoparticles was 50 nm.



**Figure S6.** TEM image of particles that were prepared with Au nanocages whose surface was stabilized by a non-ionic surfactant, poly(vinyl pyrrolidone). No asymmetric dimer was observed in this system. Note that the Au nanocages and PS beads seem to be separated from each other during the synthesis. The average diameter of the Au nanocages was 50 nm.



**Figure S7.** TEM image of asymmetric Au-PS particles that were prepared with home-made Au nanoparticles whose surface was only stabilized by citrate. The average diameter of the Au nanoparticles was 20 nm.



**Figure S8.** TEM image of asymmetric Ag-PS particles that were prepared with Ag nanoparticles whose surface was stabilized by citrate. The average diameter of the Ag nanoparticles was 40 nm. White arrows indicate Ag nanoparticles. The yield still needs to be improved by optimizing the reaction conditions.