

Supplementary Information for

# Topographically Directed Self-Assembly of Gold Nanoparticles

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## EXPERIMENTAL METHODS

**Materials.** HAuCl<sub>4</sub> and sodium citrate were obtained from Sigma-Aldrich. Propylene glycol methyl ether acetate (PGMEA) was obtained from Ultra Pure Solution Inc. Tetramethylammonium hydroxide (TMAH) developer solution was purchased from FujiFilm Electronic Materials Inc. Thiol-terminated polystyrene (Mn=6,500; PDI=1.18) was obtained from Polymer Source. All chemicals were used as received.

**Synthesis of Citrate-protected AuNPs:** All glassware was cleaned with 1% HCl diluted solution three times, rinsed with Nanopure H<sub>2</sub>O, and then oven dried prior to use. Colloidal AuNPs with an average diameter of 20 nm were prepared by rapidly injecting a sodium citrate solution (1.5 mL, 38.8 mM) into a boiling aqueous solution of HAuCl<sub>4</sub> (100 mL, 0.35 mM) with vigorous stirring. After boiling for 20 min, the reaction flask was removed from the heat to allow the reaction solution to cool to room temperature.

**Polystyrene-coated AuNPs.** In a typical preparation, thiol-terminated polystyrene (5 mg) was dissolved in 10 mL of THF and then mixed with 50 mL of citrate-coated gold nanoparticles in aqueous solution in a 250 mL separatory funnel. Chloroform (25 mL) was then added, resulting in immediate separation of the organic and aqueous phases. The red-purple colored organic layer containing the polystyrene-coated AuNPs was isolated, and the organic solvents removed under reduced pressure. The polystyrene-coated AuNPs were washed with hexane solution twice to remove the residual unreacted polymers,<sup>1</sup> and then characterized in chloroform as the solvent.

**Fabrication of Patterned Substrates.** The patterned substrates were fabricated using either 193nm lithography or e-beam lithography. The positive-tone 193nm photoresist JSR 2928 is coated on the top of antireflection coating (ARC29) on the silicone wafer. Patterned arrays were comprised of features with critical dimensions ranging from 1.0 μm down to 200 nm, and feature

heights of 80 nm. The patterned features were flood exposed to 254 nm irradiation and bake to render the resist insoluble in the coating solvent of the nanoparticle.

**Evaporative Self-Assembly of Polystyrene-coated AuNPs onto Lithographically Patterned Substrates via Spin-coating.** Polystyrene-coated AuNPs (20 nm) in PGMEA (4.5 mg / mL) were spin-coated onto the lithographically defined substrates (2.0 cm × 2.0 cm). In general, the spin-coating protocol was set to 30s at 3000 rpm. The substrates were then irradiated with 254 nm UV lamp for 10 min to crosslink the polystyrene shell onto the particle surface. The substrates were then dipped into TMAH developer aqueous solution (0.2 wt%) for 10 s to remove the photoresist patterns. After rinsing with water three times, the substrates were dried under vacuum for further characterization.

**Characterization Methods.** Transmission electron microscopy (TEM) images were recorded on a Philips CM12 TEM (120 KV). A drop of AuNP solution was placed onto a carbon-coated copper grid and left to dry at room temperature. Scanning electron microscopy (SEM) images were recorded on Hitachi S-4700 instrument. UV-vis absorption spectroscopy was recorded on Varian Cary 50 UV-vis spectrophotometer.

## Reference

1: K. Y. Van-Berkel, A. M. Piekarski, P. H. Kierstead, E. D. Pressly, and C. J. Hawker, *Macromol.*, 2009, **42**, 1425-1427.

**Figure S1.** Top-down FE-SEM images of the evaporative self-assembly of 20 nm polystyrene-coated AuNPs onto the square post-patterned substrates before (a & b) and after (c & d) removing post templates using 0.2 wt% TMAH developer solution.

