Electronic Supplementary Material (ESI) for RSC Advances.

Ligand exchange for TEM imaging:

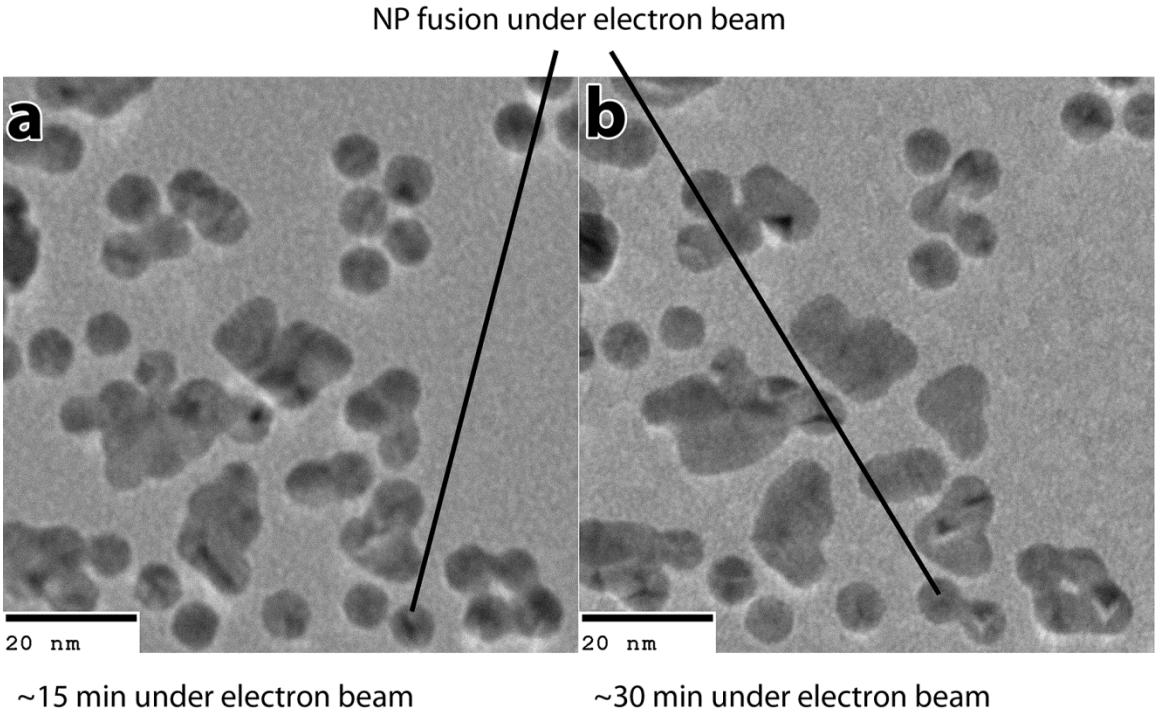


Fig. S1 (a) NPs with dodecylamine ligands after exposure to a TEM electron beam for 15 minutes; (b) same NPs as in (a) after 30 minutes under the electron beam.

As can be seen from TEM images above, Au NPs with dodecylamine (DDA) ligands undergo fusion under the electron beam, making NP size analysis difficult. To overcome this problem, DDA ligands were exchanged with dodecanethiol (DDT) for amine-capped NPs obtained from size-selective precipitation (SSP). A typical precipitate collected from the SSP procedure was first dispersed in 3 mL of toluene. 0.075 mL of a DDT solution (0.25 mL DDT + 5 mL toluene) was then added to the NP solution, and 20 minutes was elapsed to ensure ligand exchange. A drop of NP solution was then cast on a TEM grid for imaging, and NP fusion was no longer observed.

Histograms for reported results in figure 2:

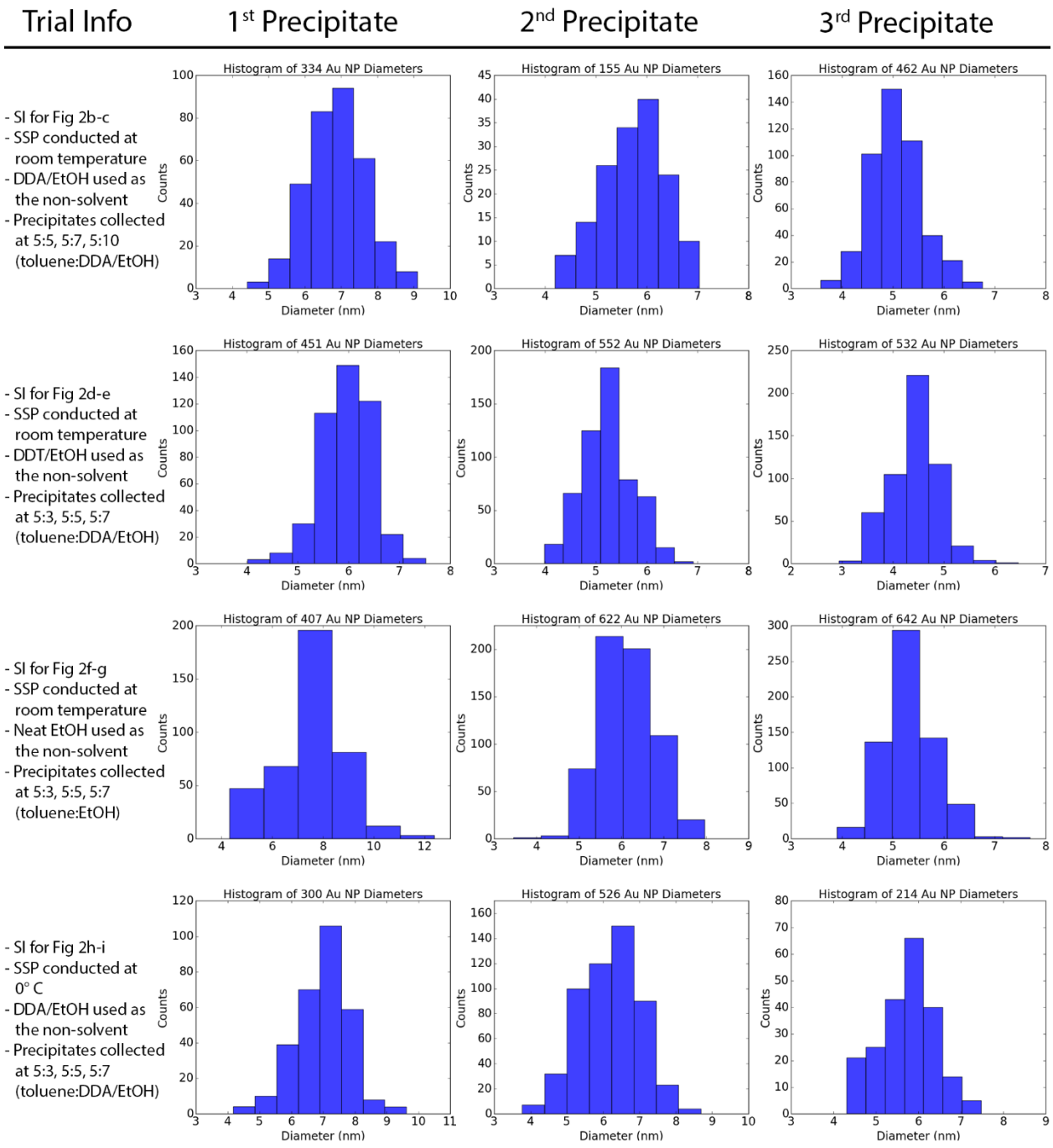


Fig. S2 Histograms for corresponding Gaussian fits to NP size distributions of precipitates characterized in figure 2.

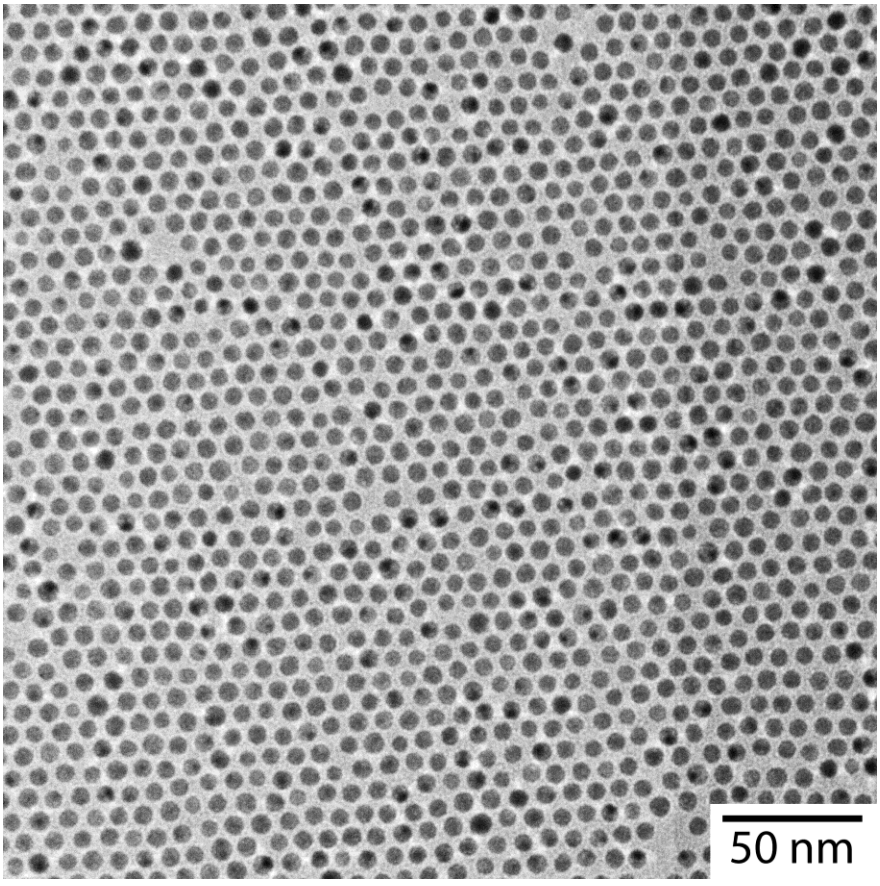
Average particle sizes and standard deviations can be found directly in figure 2 in the manuscript. Above are the corresponding raw histograms of NP diameters for various trials.

Film assembly on a water surface contained within a 5 cm^2 Teflon ring:

Au NPs are fist capped with DDT ligands. For DDA-ligated NPs obtained from SSP, precipitates were first redispersed in 3 mL of toluene and then 0.075 mL of a DDT solution (0.25 mL DDT + 5 mL toluene) was added and 20 minutes was elapsed to ensure ligand exchange. NP solutions were then dried under vacuum until the solvent volume was less than ~0.5 mL, and then washed 4 times with ethanol to remove excess DDT. NPs are then redispersed in hexane and the solvent volume is adjusted to normalize NP concentration, which is confirmed with a UVVIS spectra. A ten-fold diluted NP solution exhibits an absorbance of ~0.1 at 400 nm through a path length of 1 cm. 0.9 mL of NP solution is then deposited on the water surface within the Teflon ring, which evaporates over a period of ~20 minutes forming a densely-packed monolayer. Portions of the resulting film were then sampled with TEM grids via the Langmuir-Schaefer technique and imaged by TEM.

Details of the Teflon ring apparatus can be found in previous works.[a,b] In short, the water surface is pinned by the inner bottom edge of the Teflon ring, resulting in a convex-up geometry. Thus, when a hydrophobic solution of NPs is dropped on the water surface, a thin film is deposited and grows radially outward as the solvent evaporates. Using the above sample preparations, extensive monolayers of NPs can be produced.

313 nm x 313 nm region of a monolayer formed with NPs with a standard deviation of 6.9%:



The above image was used to calculate the 2D FFT in figure 4 in the manuscript.

References:

a) S. Gravelsins, M. Hasham, Y. Lin, K. Yu, M. Tie, C. Goh and A.-A. Dhirani, *Soft Matter*, 2017, **13**, 2437.
b) V. Santhanam, J. Liu, R. Agarwal and R. P. Andres, *Langmuir*, 2003, **19**, 7881.