

Supporting Information

Identification of a source of size polydispersity and its solution in Brust-Schiffrin metal nanoparticle synthesis

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Synthesis and Preparation

Didodecyl disulfide was synthesized according to a modified literature approach.^{1,2} 15 mg NaI was added to the solution of 2.4-mL C₁₂H₂₅SH and 30-mL ethyl acetate. After the addition of 1.1 mL of 30 wt% H₂O₂, the mixture was stirred at room temperature for 30min, which led to a clear yellowish solution. 15-mL Na₂S₂O₃ (3.13 g) aqueous solution was then poured in. The color of the solution then faded. The two-phase mixture was transferred to a separatory funnel. After removing the solvent from the top solution, the desired product was obtained as white crystal powder.

[TOA][AuBr₄] was prepared following the reported approach.^{1,3,4} TOAB (1.26 g) and KAuBr₄·H₂O (1.37 g) were mixed with 60 mL of anhydrous EtOH. After 1-h stir and 10-min sonication, the mixture was stored in a freezer overnight. The product, dark red crystals, was collected through vacuum filtration.

[TOA][AuBr₂] was synthesized according to a revised literature approach.^{1,3,4} The mixture of [TOA][AuBr₄] (0.88 g) and 8.8-mL anhydrous EtOH was heated in water bath up to 70°C, by which [TOA][AuBr₄] was completely dissolved in EtOH. Once the temperature of water bath reached 70°C, 0.88-mL acetone was added. After that, the solution turned to white cloudy in a short time and then heating was stopped. When the mixture was cooled down, vacuum filtration was performed to remove the white insoluble byproduct. The clear colorless filtrate was stored in a freezer overnight. The product, colorless crystals, was collected by vacuum filtration.

BSM synthesis of Au Nanoparticles. A typical Brust-Schiffrin two-phase method⁵ was used. 0.21 mL of 0.1421M HAuCl₄ (0.025 mmol) aqueous solution was mixed with 10 mL of TOAB (0.025 mmol) toluene solution. After 1-h vigorous stirring, the

top wine-red solution was collected and then the ligands (0.075 mmol C₁₂H₂₅SH or 0.0375 mmol didodecyl disulfide) were added dropwise. After stirring for 1h, 1 mL of fresh NaBH₄ (0.25 mmol) aqueous solution was poured in. The mixture was stirred for 3h and then transferred to separatory funnel. The organic phase was rinsed with water three times and was put through a vacuum filter. After the removal of most solvent by rotary evaporation with pump, ~50 mL of EtOH was added to black slurry. The mixture was sonicated for couple of minutes and then stored in a freezer overnight. The desired product was the filter cake after filtering with microfilter system.

Characterization

UV-vis spectroscopy. Solid samples were first dissolved in toluene to make a dilute solution. They were then transferred into a 1-cm path length quartz cuvette and the measurements were done on a HP 8453 diode array UV/Vis spectrometer. A typical experiment scanned the wavelength from 300 to 800 nm. Background adjustments were made using toluene as blank.

NMR. ¹H NMR spectra were recorded on a Bruker AM 300 MHz spectrometer that was interfaced with a Tecmag DSPECT acquisition system. Deuterated benzene was used as a solvent, whose ¹H (7.16 ppm) and ¹³C (128.39 ppm) peaks were used as references.

TEM. The TEM characterization was performed on JEOL JEM-2100 LaB₆ transmission electron microscope at 100 kV. The samples were prepared by placing two or three drops of the dilute nanoparticle dispersion in toluene on carbon-coated copper grids (400 mesh, Electron Microscopy Science). Nanoparticle sizes were measured using ImageJ.

IR. The IR spectra were obtained using a Bruker Vector-22 infrared spectrometer. The NPs were crushed out with EtOH (in details, after the removal of most solvent by rotary evaporation with pump, ~50 mL of EtOH was added to black slurry. The mixture was sonicated for couple of minutes and then stored in a freezer overnight. The nanoparticles were filtered out as filter cake through the microfilter system.) A small amount of NP powder was mixed with KBr powder as a solid support and ground to an even mixture with a pestle. The mixture was pressed into a wafer for IR measurement. All measurements were performed in the transmittance mode at 2 cm⁻¹ resolution. The spectra were background subtracted with respect to KBr and subjected to baseline correction and smoothing.

Supplementary Material (ESI) for Chemical Communications

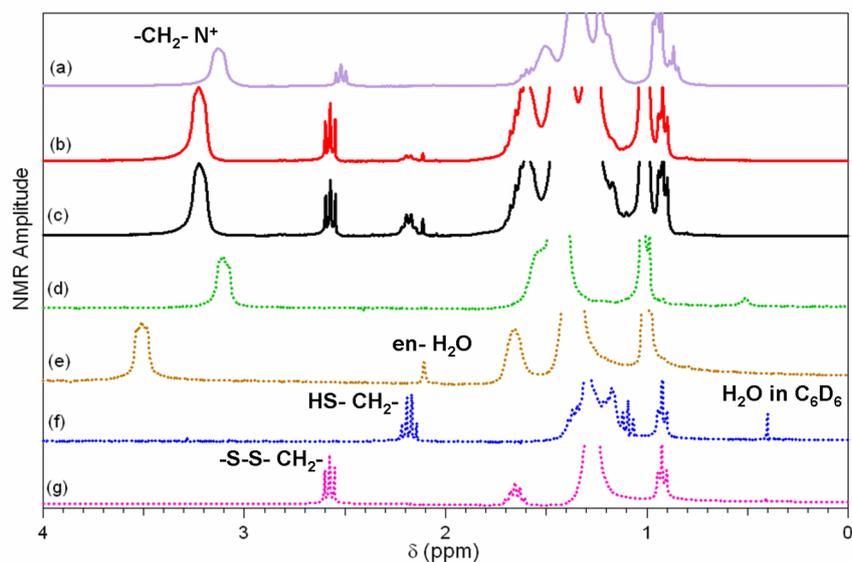


Figure S1. ^1H NMR spectra of the intermediate obtained after the addition of (a) 1, (b) 2, (c) 3 equiv of dodecanethiol to TOAB-plus-Au(III) (TOAB: Au = 2:1) C_6D_6 layer, (d) of synthesized $[\text{TOA}][\text{AuBr}_2]$ complex, (e) TOAB, (f) dodecanethiol, and (g) synthesized didodecyl disulfide, all in 0.80 mL C_6D_6 . (Note: en-H₂O means the water encapsulated by the inverse micelles of TOAB.^{1,6})

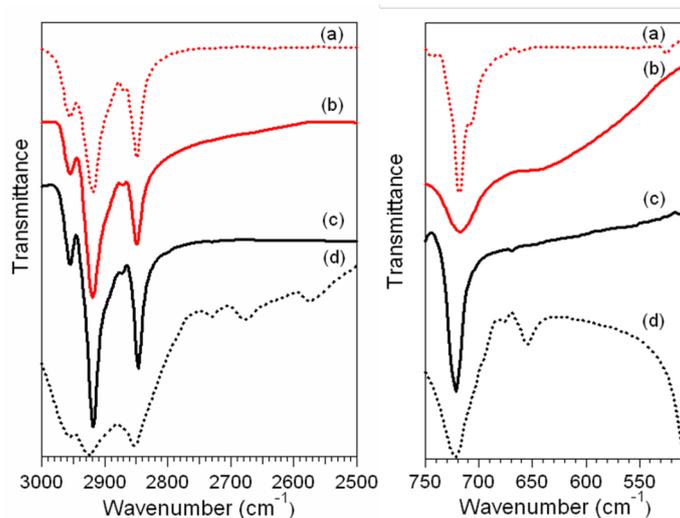


Figure S2. IR spectra of (a) pure didodecyl disulfide, (b) Au NPs protected with the ligands originally from didodecyl disulfide, (c) Au NPs protected with the ligands originally from dodecanethiol, (d) pure dodecanethiol.

Supplementary Material (ESI) for Chemical Communications

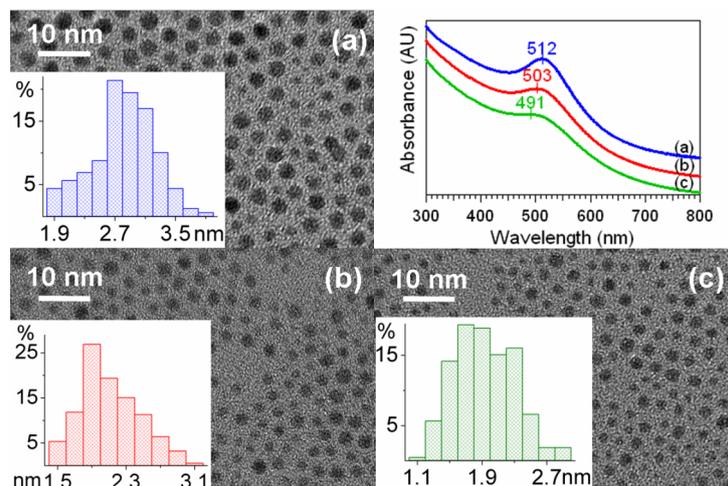


Figure S3. TEM images with size distribution and UV-visible spectra of the Au nanoparticles formed from [TOA][AuBr₂] (0.025 mmol) toluene solution (1.0 mL) (no addition of 0.2-mL water) with (a) 3 equiv of dodecanethiol (2.81 ± 0.42 nm), (b) a mixture of 1 equiv of dodecanethiol and 1 equiv of didodecyl disulfide (2.11 ± 0.38 nm), (c) 1.5 equiv of didodecyl disulfide (1.93 ± 0.36 nm).

References

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