

Synthesis of Colloidal Metal Nanocrystals in Droplet Reactors: The Pros and Cons of Interfacial Adsorption

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Experimental Section

Fabrication of the fluidic device used for the generation of droplets. As shown in Figure 1a, the fluidic device was typically constructed from two silica capillaries (O.D. = 164 μm , Polymicro Technologies) and a PTFE tube (I.D. = 500 μm , length = 6 m, Sigma) aligned in a parallel configuration. For the silica capillaries, their tips were leveled up by pushing them against a glass slide and subsequently cut at the same position with a razor blade, followed by fixing with a commercial fast adhesive (Super Glue Liquid, Loctite). The silica capillaries were then inserted into the PTFE tube and fixed with an adhesive (Epoxy Quick Set, Loctite) after alignment. To improve the mixing efficiency in the droplets, a 100-mm long mixing zone was fabricated by physically clamping the PTFE tube with a precision-tip tweezers every 2 mm. The clamping force was adjusted until the inner diameter of the PTFE tube was reduced to *ca.* 250 μm .

To perform synthesis at the water-oil interface, a modified device was fabricated as shown in Figure 2a. Firstly, a silica capillary (O.D. = 164 μm , Polymicro Technologies) was inserted into a PTFE tube (I.D. = 500 μm , length = 6 m, Sigma) from a bending position and aligned in a parallel configuration. Another silica capillary (O.D. = 164 μm , Polymicro Technologies) was inserted into the center of the PTFE tube in a perpendicular configuration. The silica capillaries were then fixed with an adhesive (Epoxy Quick Set, Loctite) after alignment. The length of the PTFE tube between the two silica capillaries was set to 3 m.

Preparation of the 22-, 40-, and 90-nm Ag cubes. The 22-nm Ag cubes were prepared using our recently reported protocol with diethylene glycol (DEG) as the solvent/reductant.¹ In a standard synthesis, 5 mL of DEG was added into a flask and heated under magnetic stirring in an oil bath set to 150 $^{\circ}\text{C}$ for 30 min. Other reagents were separately dissolved in DEG and sequentially introduced into the flask using pipet. Specifically, 0.06 mL of NaSH solution (3 mM) was added first. After 4 min, 0.5 mL of HCl (3 mM) was added, followed by 1.25 mL of PVP (20 mg/mL). After another 2 min, 0.4 mL of CF_3COOAg solution (282 mM) was introduced. The synthesis

was quenched by placing the flask in an ice-water bath when the major localized surface plasmon resonance (LSPR) peak reached 402 nm. After centrifugation and washing with acetone and DI water three times, the nanocubes were dispersed in DI water at a concentration of 1.5×10^{13} particles/mL and used as seeds for the growth. The particle concentration of Ag seeds was determined using an inductively coupled plasma mass spectrometry (ICP-MS, NexION 300Q, Perkin-Elmer). The sample for ICP-MS analysis was prepared by dissolving 10 μ L of the suspension of Ag seeds with 30 μ L of concentrated HNO_3 . The resultant solution was further diluted to a level of 100 ppb for ICP-MS analysis.

The 40-nm Ag cubes were prepared using the same protocol as for the 22-nm Ag cubes, except for the use of ethylene glycol (EG) as a solvent/reductant.² The product was obtained by quenching the reaction with an ice-water bath when the major LSPR peak reached 438 nm. After centrifugation and washing with acetone and DI water three times, the cubes were then dispersed in DI water and EG at a concentration of 1.1×10^{12} particles/mL to be used as templates for the galvanic replacement reaction with HAuCl_4 and as seeds for the synthesis of the 90-nm Ag cubes, respectively.

The 90-nm Ag cubes were prepared using a seeded growth approach.³ In a standard synthesis, 1.25 mL of EG was held in a 20 mL glass vial and heated in an oil bath at 150 °C under magnetic stirring. After 1.5 min, 0.3 mL of a PVP solution in EG (20 mg/mL) was added. After another 1.5 min, 50 μ L of the as-prepared 40-nm Ag cubes (1.1×10^{12} particles/mL) in EG solution was introduced, followed by the addition of 200 μ L of silver nitrate (AgNO_3 , Aldrich) solution in EG (282 mM). The product was obtained by quenching the reaction with an ice-water bath when the major LSPR peak reached 485 nm. After centrifugation and washing with acetone and DI water three times, the cubes were then dispersed in DI water for characterizing the adsorption of nanocrystals at the interface.

Synthesis of asymmetric nanocrystals at the water-oil interface of droplets. To synthesize 1/6 truncated Ag octahedra, 0.01 mL of the as-prepared 40-nm Ag cubes in an aqueous solution, 0.99

mL of aqueous Na_3CA (50 mM, Aldrich), and 1.0 mL of aqueous AA (1.0 mM, Aldrich) were mixed together to produce the reagent R1; 1.0 mL of aqueous CF_3COOAg (0.3 mM, Aldrich) was used as R2. To synthesize Au-Ag nanocups, 0.01 mL of the as-prepared 40-nm Ag cubes in an aqueous solution, 0.1 mL of aqueous PVP (20 mg/mL, MW \approx 55,000, Aldrich), and 1.89 mL of DI water were mixed together to form the reagent R1; 1.0 mL of aqueous HAuCl_4 (0.08 mM) was used as R2. The flow rates for R1 and R2 were set to 20, and 10 $\mu\text{L}/\text{min}$, respectively, while the flow rate for silicone oil was 120 $\mu\text{L}/\text{min}$. The output of the PTFE tube was collected by a 20-mL glass vial, and the products were concentrated at the water-oil interface due to adsorption.

Collection of the products adsorbed at the water-oil interface. When no Triton X-100 was used in the control experiments, most of the products were concentrated at the water-oil interface. To transfer the products from the interface into an aqueous phase, most of the silicone oil was sucked out from the 20 mL glass vial using a pipet and 0.2 mL of aqueous Triton X-100 (5% by wt.) was added, followed by sonication for 5 min. The aqueous suspension of products was then transferred into a 1.5 mL centrifuge tube and centrifuged at 8000 rpm for 10 min, followed by washing with DI water three times. The sample was finally dispersed in DI water prior to TEM characterization.

Galvanic replacement reaction in the droplet reactors. In a typical process, 0.1 mL of the as-prepared 40-nm Ag cubes in an aqueous solution and 4.9 mL DI water were mixed together to produce the reagent R1; 0.5 mL of aqueous HAuCl_4 (0.05-0.45 mM), 0.2 mL of aqueous Triton X-100 (5% by wt.), and 0.55 mL DI water were mixed together to produce the reagent R2. The reaction was performed at 60 $^\circ\text{C}$ by immersing a 6-m long PTFE tube in a water bath. The output of the PTFE tube was collected with a 20 mL glass vial, and the aqueous suspension of Au-Ag nanoboxes or nanocages was then transferred into a 1.5 mL centrifuge tube and centrifuged at 8000 rpm for 10 min, followed by washing with DI water three times. The sample was finally dispersed in DI water prior to TEM characterization.

Seeded growth of Ag nanocrystals in the droplet reactors with different capping agents. In a standard synthesis, 0.01 mL of the 22-nm Ag cubes (1.5×10^{13} particles/mL) in DI water, 0.5 mL of aqueous PVP (20 mg/mL) or 0.5 mL of aqueous Na_3CA (50 mM), 0.05 mL of aqueous AA (50 mM), 0.2 mL of aqueous Triton X-100 (5% by wt.), and 0.15 mL DI water were mixed together to produce the seed solution (R1); 0.5 mL of aqueous CF_3COOAg (0.3 mM) and 0.41 mL of DI water were mixed together to produce the precursor solution (R2). The reaction was allowed to proceed at room temperature (22 °C). The output was collected with a 20 mL glass vial, and the aqueous suspension of nanocrystals was then transferred into a 1.5 mL centrifuge tube and centrifuged at 10000 rpm for 10 min, followed by washing with DI water twice. The sample was finally dispersed in DI water prior to TEM characterization.

Measuring the percentage of Ag nanocubes adsorbed by the water-oil interface. The percentage of Ag nanocubes adsorbed by the water-oil interface of droplets was obtained by measuring the LSPR peak intensity of the Ag nanocubes collected from the output of the PTFE tube. Typically, 10 μL of the as-obtained Ag nanocubes (22-, 40-, and 90 nm in edge length) in DI water and 1.0 mL DI water were mixed together and used as reagent R1 while the reagent R2 was DI water, aqueous PVP solution (11 mg/mL), aqueous Na_3CA solution (27.8 mM), a aqueous solution of PVP (11 mg/mL) and Triton X-100 (1.1% by wt.), and an aqueous solution of Na_3CA (27.8 mM) and Triton X-100 (1.1% by wt.), respectively. The flow rates of R1 and R2 were set to 20 $\mu\text{L}/\text{min}$ while the flow rate of silicone oil was set to 200 $\mu\text{L}/\text{min}$. PTFE tubes of three different lengths (2, 4, and 6 m) were used to study the interfacial adsorption. To obtain a calibration curve, 0.5 mL of R1 and 0.5 mL DI water were mixed together to produce a stock solution, and then, 25, 50, 75, and 100 μL of this stock solution were diluted to 0.6 mL with DI water for the measurement of UV-vis spectra. To obtain the LSPR peak intensity of individual sample collected from the output of the PTFE tube, 100 μL of the aqueous suspension of Ag nanocubes was diluted into 0.6 mL for the measurement of UV-vis spectrum.

Characterization. TEM images were taken using an H-7700 microscope operated at 120 kV (Hitachi, Tokyo, Japan). Samples were prepared by drop-casting aqueous suspensions of the nanocrystals on carbon-coated Cu grids (Electron Microscope Science, Hatfield, PA) and dried in air under ambient conditions. All UV-vis extinction spectra were recorded using a Lambda 750 UV-vis-NIR spectrometer (Perkin-Elmer, Waltham, MA).

References

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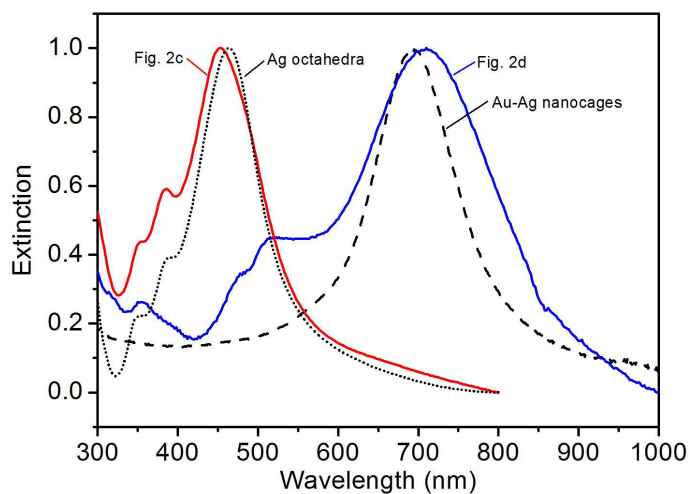


Figure S1. Normalized UV-vis spectra recorded from aqueous suspensions of the 1/6-truncated Ag octahedra (in Figure 2c), the Au-Ag nanocups (in Figure 2d), and the corresponding normal Ag octahedra (*ca.* 65 nm in size) and Au-Ag nanocages that were prepared using 40-nm Ag cubes as seeds and templates, respectively.

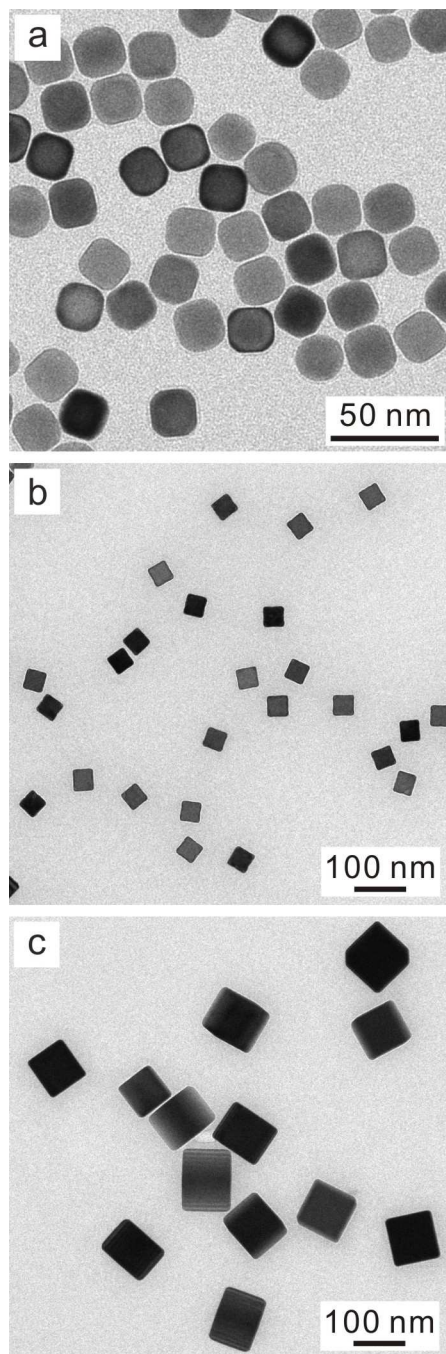


Figure S2. TEM images of Ag nanocubes with different edge lengths used for measuring the adsorption of nanocrystals to the water-oil interface: (a) 22 nm, (b) 40 nm, and (c) 90 nm. The 22- and 40-nm Ag cubes were also used as seeds and templates for the overgrowth and the galvanic replacement reaction with HAuCl_4 , respectively.

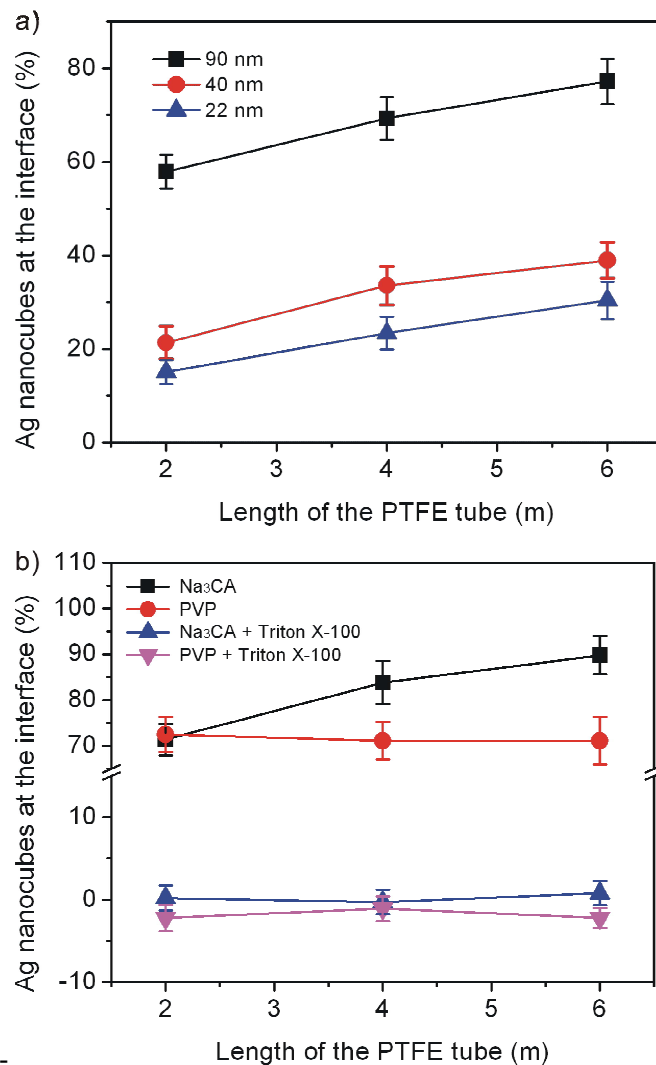


Figure S3. The percentages of Ag nanocubes adsorbed at the water-oil interface of droplets as a function of the length of the PTFE tube. The flow rates for the aqueous suspension of Ag nanocubes and silicone oil were set to 40 and 200 $\mu\text{L}/\text{min}$, respectively. (a) The Ag nanocubes with different sizes were dispersed in DI water. (b) The 22-nm Ag cubes were dispersed in Na_3CA (13.9 mM) and PVP (5.5 mg/mL) aqueous solutions, with and without the addition of Triton X-100 (0.55% by wt.), respectively.

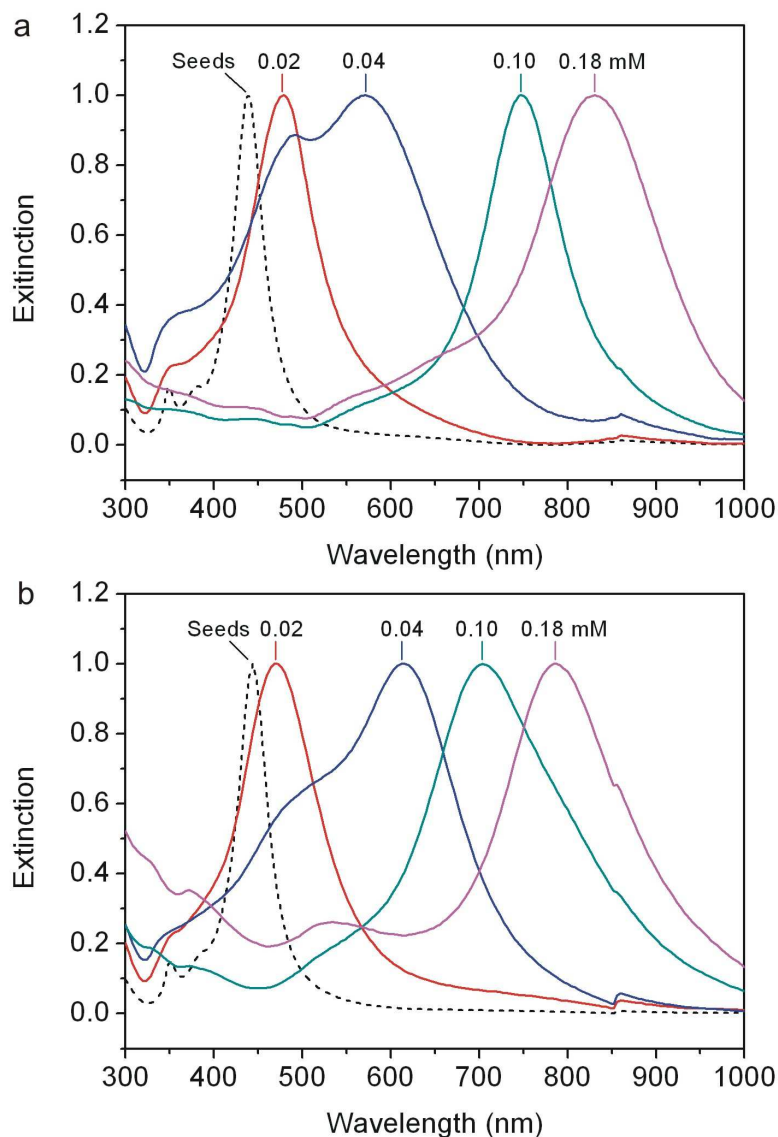


Figure S4. Normalized extinction spectra taken from aqueous suspensions of samples shown in Figure 3, which were prepared in the (a) presence and (b) absence of Triton X-100, respectively. The concentration of H_{AuCl}₄ in the reagent R2 is labeled on each spectrum. Dashed curves correspond to the UV-vis spectra of the 40-nm Ag cubes serving as the templates.