A Process-Analysis Microsystem Based on Density Gradient Centrifugation and its Application in the Study of the Galvanic Replacement Mechanism of Ag Nanoplates with $HAuCl_4$

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Supporting materials:

Experimental details

Materials: All the chemicals were A. R. grade, bought from Beijing Chemical Reagent Co., Inc., and used as received without further purification.

Preparation of Triangular Silver Nanoplates[1]: An aqueous solution of $AgNO_3$ (0.1 mM, 25 mL), trisodium citrate (TSC, 30 mM, 0.3 mL), PVP ($Mw \approx 58000\ gmol^{-1}$, 1.75 mM, 1.5 mL), and aqueous H_2O_2 (30 wt%, 60 μL) were mixed and vigorously stirred in the dark at room temperature in air. $NaBH_4$ (100 mM, 250 μL) was then rapidly injected into this mixture. Ag nanoplates were obtained after approximately 30 min as the solution color turned to blue. After washing with deionized water, the sample was stored in the dark.

DGUR Separation of Triangular Silver Nanoplates Employed as a Process-Analysis System: We chose EG-water solutions with a suitable density distribution to prepare the density gradient. In a typical procedure, 20%-70% (v/v) EG solutions were made with E-pure water and the reactant $HAuCl_4$ was dissolved to the 30% of EG to get the final concentration of $AuCl_4^-$ in reaction zone would be 0.243mM. A six-layer gradient (20%+30%+40%+50%+60%+70%) was created directly in Beckman centrifuge tubes (polycarbonate, inner diameter 11 mm, length 60 mm) by adding layers (0.4 mL, 0.4mL, 0.6mL, 0.6mL, 0.6mL, 0.6mL, respectively) with increasing density (i.e., increasing EG concentration) to the bottom of the tube. After the as-prepared Ag NPTs suspension (0.3 mL, 3.33mM) was layered on top of the multilayer EG-water solutions density gradient and centrifuged at 23,000 rpm for 7 min. Fractions (250μl each) were obtained by orderly manual extraction along the centrifuge tube after ultracentrifugation. The fractions were centrifuged and washed with distilled water again. After that, the products were characterized by TEM and EDS.

Traditional Method in the Reaction between Silver Nanoplates and Chlorauric Acid: An aqueous $HAuCl_4$ solution (0.111mL, 0.9mM) was added rapidly into a stirred Ag NPTs suspension (0.3 mL, 3.33mM). The molar ratio of Ag to Au (Ag/Au = 10:1) and the final concentration of $AuCl_4^-$ (0.243 mM) in the reaction system were identical to those used in the DGUR separation system. After the $HAuCl_4$ was added and the mixture stirred for a few seconds, the products were centrifuged and washed with distilled water in a process which lasted ~5 minutes.

Estimation of Reaction Time

The net density (ρ_p) of an Ag nanoplate depends on both the plate size (edge size (a) and thickness (h)) and the hydration layer thickness (t). A model of the Ag nanoplate with its solvation shell is shown in Scheme 1. For the nanoplates in fraction f9, TEM shows that a is about 69 nm, and the average thickness h is about 7 nm. The hydration layer thickness (t) can be assumed[2–4] to be between 3.3 nm and 20 nm. The net density (ρ_p) of the Ag nanoplate is given by formula I:

$$\rho_p = \frac{\rho_{Ag}V_{Ag} + \rho_{H_2O}(V_p - V_{Ag})}{V_p} \tag{I}$$

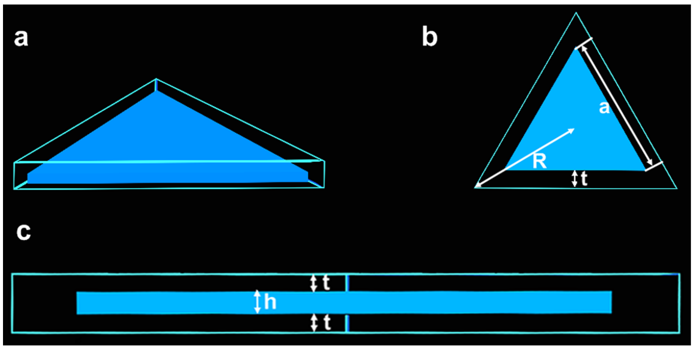
Here, V_p denotes the net volume of the particle and V_{Ag} is the volume of the Ag plate without its hydration layer. The density of Ag (ρ_{Ag}) and the hydration layer (ρ_{H2O}) are 10.5×10^3 kg/m^3 and 1×10^3 kg/m^3, respectively.

According to the classical theory of colloids, the sedimentation rate of colloidal particles in a given medium with density ρ_m and viscosity η_m, in a centripetal force field of g', can be described as

$$v = 2(\rho_p - \rho_m)R^2(g'/9\eta_m) \tag{II}$$

where R denotes the radius of the Ag nanoplate coated with a solvation shell several nanometers thick. The density (ρ_m) of 30% ethylene glycol (EG) is 1.035×10^3 kg/m^3 and the viscosity (η_m) of 30% EG is 2.089×10^{-3} Pa·s. We centrifuged at 23,000 rpm, so the centripetal force field of g' is equivalent to an acceleration of 4.87×10^5 m/s^2.

The distance (l) of the reaction zone through which the nanoplates have to pass is 5 mm. Using the above formulae and data, the time spent by the nanoplates of sample f9 in the reaction zone can be estimated to be 13 s when using the minimum value of t (3.3 nm) whilst for the maximum value of t (20 nm), the estimated reaction time is 47 s. Thus, we can conclude that the reaction time of sample f9 was in the range between 13 s and 47 s (30 ± 17 s).



Scheme 1. Illustrations of the hydrated colloidal Ag NPT used in the model. (a) side view; (b) view along the direction perpendicular to the *xy*-plane; (c) view along the direction perpendicular to the *z*-axis of the Ag NPT.

Instrumentation

TEM images were obtained using a Hitachi H-800 TEM with an accelerating voltage of 200 kV. High-resolution TEM (HRTEM) images and EDS were measured with a FEI Titan 80–300 instrument operating at 300 kV. Specimens for TEM and HRTEM analysis were prepared by depositing a drop of colloidal solution onto holey carbon-coated Cu grids and drying in air at room temperature. The optical properties of samples were characterized by UV-vis absorbance spectroscopy (UV-2501PC, Shimadzu, working in the range 300–1100 nm).

Supplementary Figures

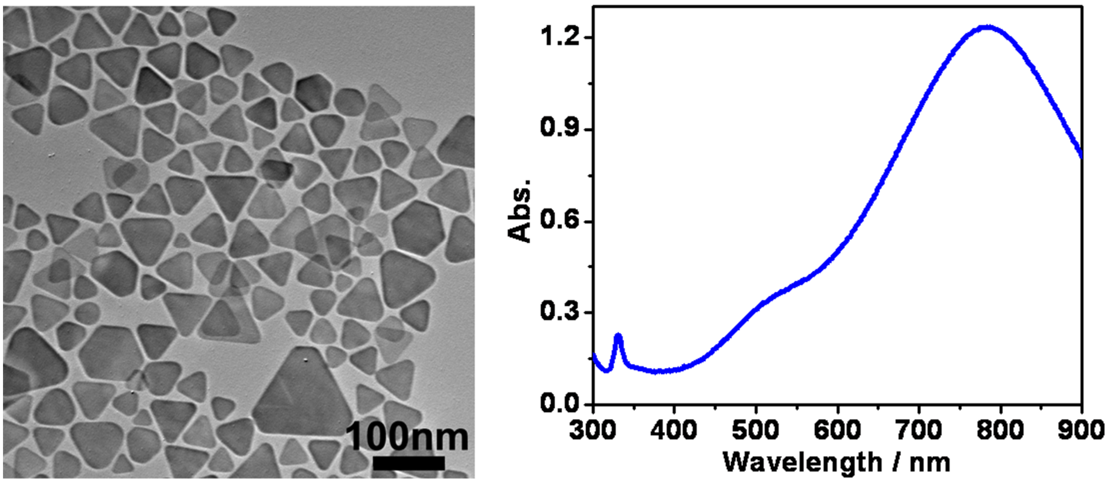


Figure S1. TEM image (left) and UV–vis absorption spectrum (right) of the original Ag NPTs before separation.

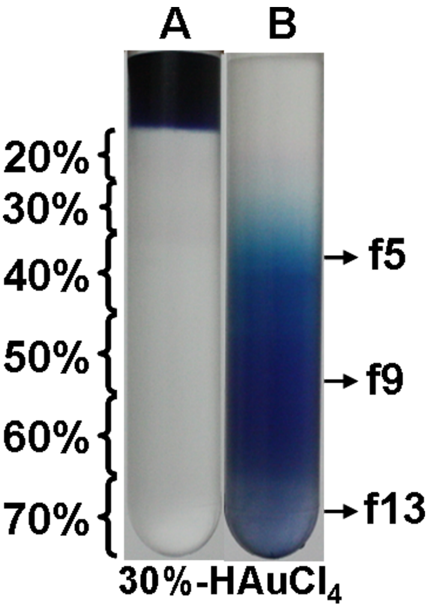


Figure S2. Digital camera images of the ultracentrifuge tubes after separation at 23,000 rpm: (A) before separation; (B) after separation for 7 min.

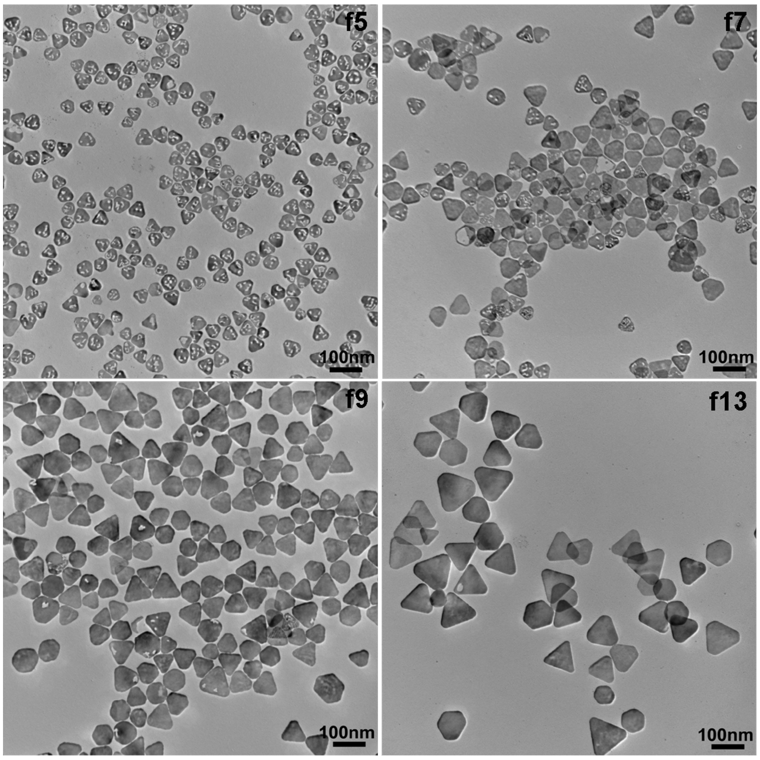


Figure S3. TEM panoramas of the samples in different fractions.

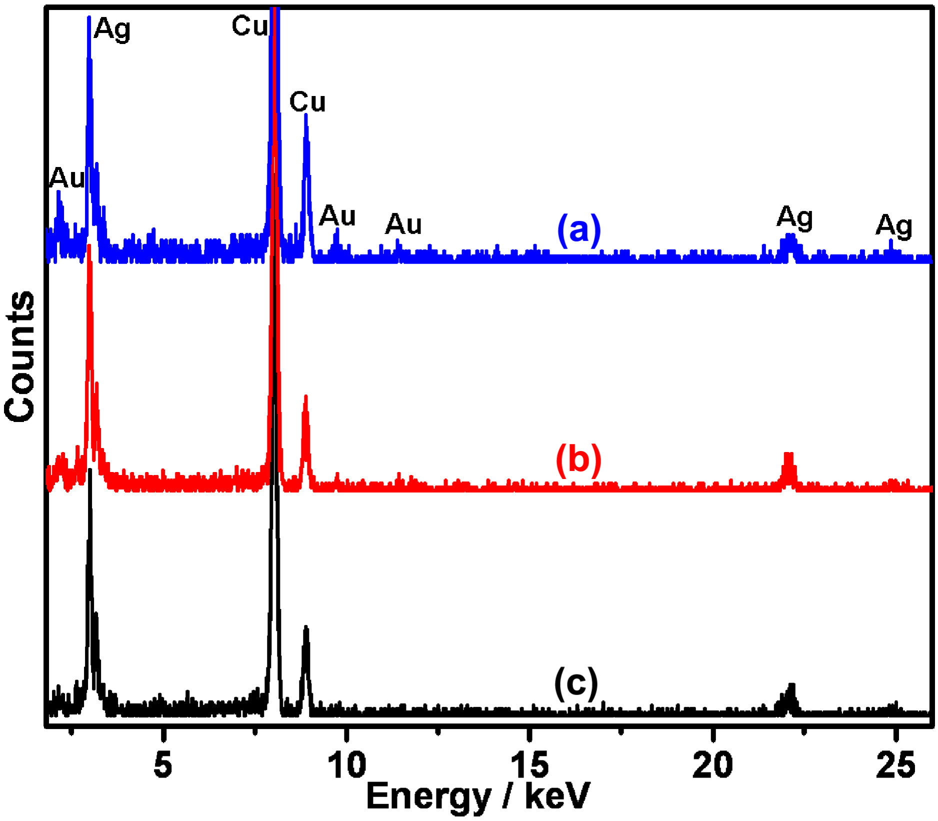


Figure S4. The original EDS data for f9: (a) edge; (b) thick area of basal plane; (c) thin area of basal plane.

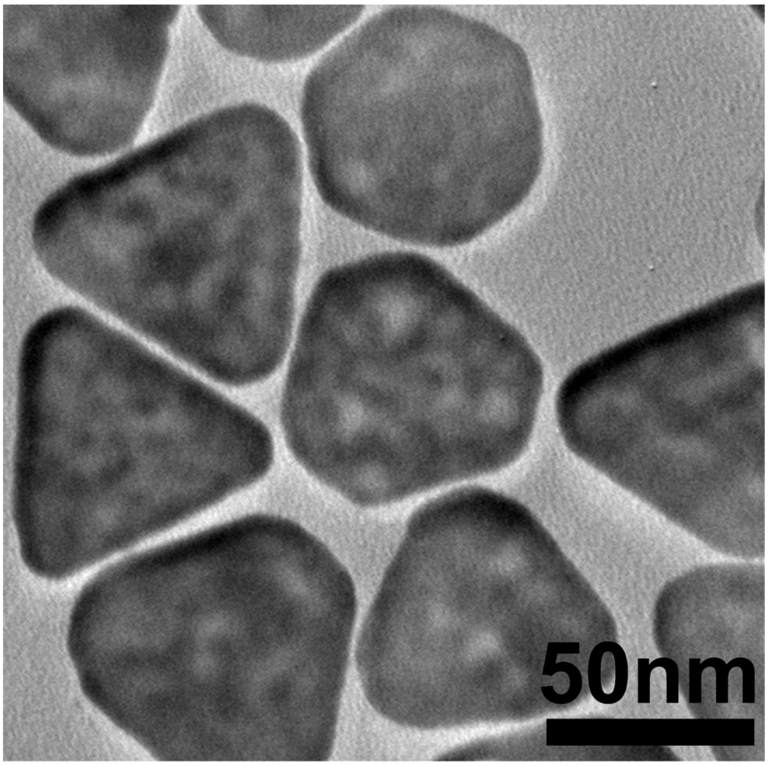


Figure S5. TEM image of the sample in fractions f9.

References

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