Supporting Information

From a Precursor to an Etchant: Spontaneous Inversion of the Role of Au(III) Chloride for One-pot Synthesis of Smooth and Spherical Gold Nanoparticles

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Chemicals and materials

Gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$), cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC, 25 wt% in water), L-ascorbic acid (AA), sodium borohydride ($NaBH_4$), were purchased from Sigma-Aldrich (St Louis, MO, USA). Deionized water (18.2 MΩ cm) was prepared using a Sartorius Arium®Pro Ultrapure water system and was used for all the experiments. The 20 mL syringe (Kovax-syringe) and syringe pump (NE-300) were used so that gold source can be injected slowly. All the reagents were used without further purification. All glasswares were cleaned using aqua regia. Special care must be taken when researchers handle aqua regia.

AuNP synthesis

For the feasibility of the synthesis, we conducted the whole process at room temperature (~25 °C). A 10 mL of 100 mM CTAB solution was prepared in water and 250 μL of 10 mM $HAuCl_4$ solution was added into it. A 600 μL of reducing solution containing 10 mM $NaBH_4$ dissolved in fresh ice-cold water was added to above solution under vigorous stirring (700 rpm). After stirring for 2 min, we obtained brownish Au-cluster solution. The solution was aged at 27°C for 1 h. In this experiment, $HAuCl_4$ was used instead of $HAuBr_4$. Because bromide ion has strong binding affinity with Au atoms and ions, surface diffusion of gold

atoms and gold deposition on the AuNP surface will become slower when $HAuBr_4$ were used instead of $HAuCl_4$.

To prepare primary AuNPs with 9 nm in size, we grew Au-clusters using AA. A fresh 15 mL of 100 mM AA was added into 20 mL of 200 mM CTAC solution containing 500 μL of Au-cluster. After stirring for 2 min, 20 mL of 0.5 mM $HAuCl_4$ solution was added and aged for 15 min under vigorous stirring. Final primary AuNP solution was washed once by centrifugation (20,000 rcf, 60 min) and redispersed in 20 mM CTAC solution. For the synthesis of size tunable secondary AuNPs with smooth spherical shape, 110 μL of AA was added into the mixture of 20 mL of 100 mM CTAC solution and 500 μL of primary AuNPs. After aging for 2 min under 500 rpm stirring, 20 mL of 0.5 mM $HAuCl_4$ solution was injected slowly into aforementioned mixture solution using syringe pump (20 mL/h). A nanoscale size tunability was obtained by regulating reaction time. The size controlled secondary AuNPs were prepared by washing secondary AuNP solution with 10 min interval after completing $HAuCl_4$ solution injection. Each of extracted sample was washed by centrifugation (20,000 rcf, 10 min) and redispersed in 20 mM CTAC solution.

Characterization

Extinction spectra of AuNPs were obtained using an UV-vis spectrophotometer (Agilent 8453). TEM images were obtained using a JEM-2100F instrument (JEOL) operating at 200 kV. SEM mages were taken using JSM-7600F (JEOL) operating at 15 kV, working distance was 8.0 mm. Dynamic light scattering (DLS) was measured using a Malvern Zetasizer Nano-ZS90 (UK) with a 3 mW He-Ne laser operating at 633 nm. The unit collects light back-scattered at an angle of 90°. For the diameter measurement of AuNPs, we averaged the diameters of at least 200 AuNPs at each condition from TEM images.

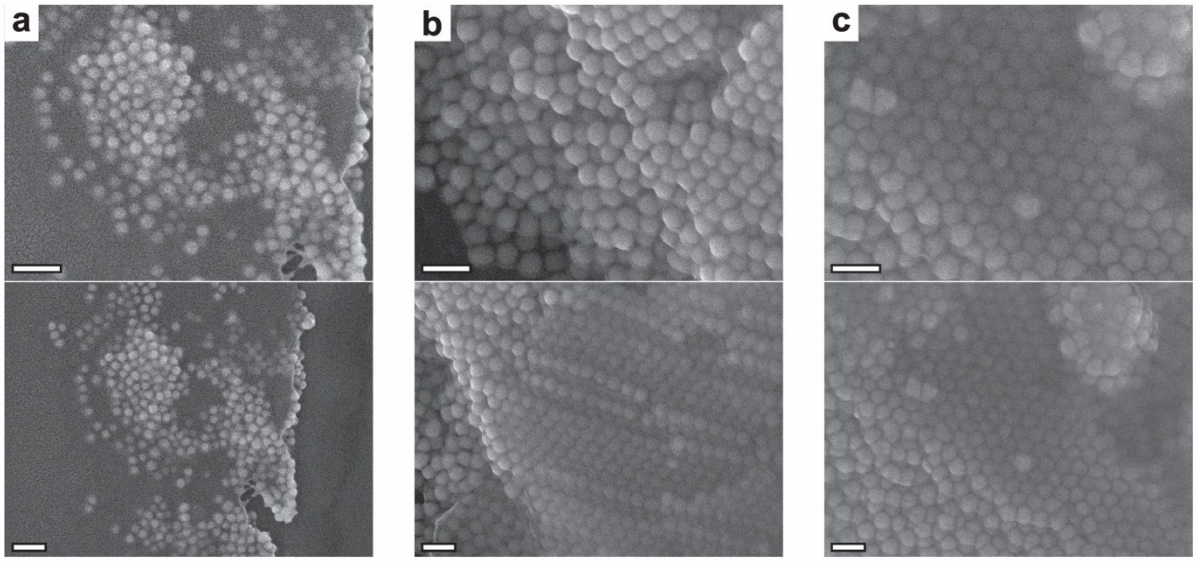

Figure S1. SEM images of secondary AuNPs synthesized using (a) 60, (b) 110, (c) 160 µL of AA. Scale-bar: 100 nm, (upper low images: 15k magnification, lower low images: 10k magnification)

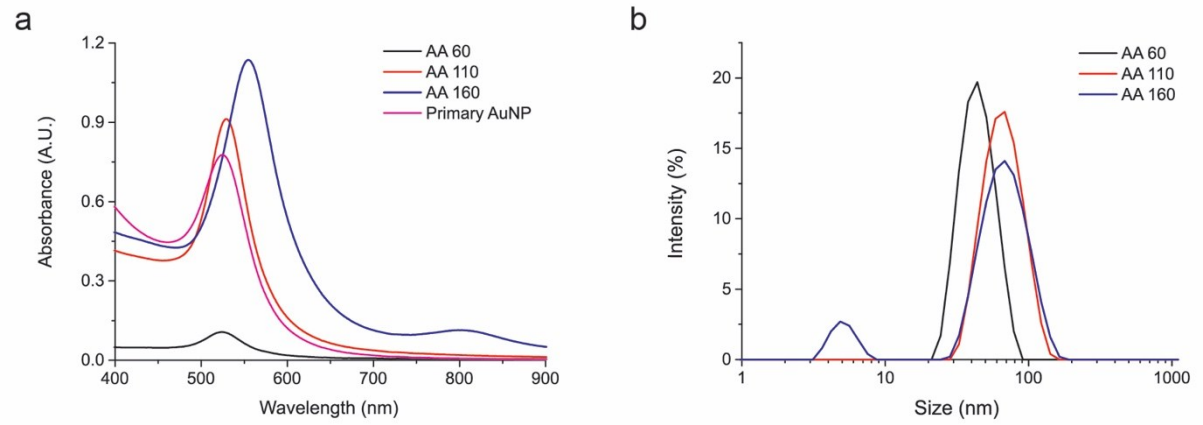

Figure S2. (a) UV- visible spectra of secondary AuNPs synthesized using different amount of AA solution. (b) DLS spectra of secondary AuNPs synthesized using different amount of AA solution.

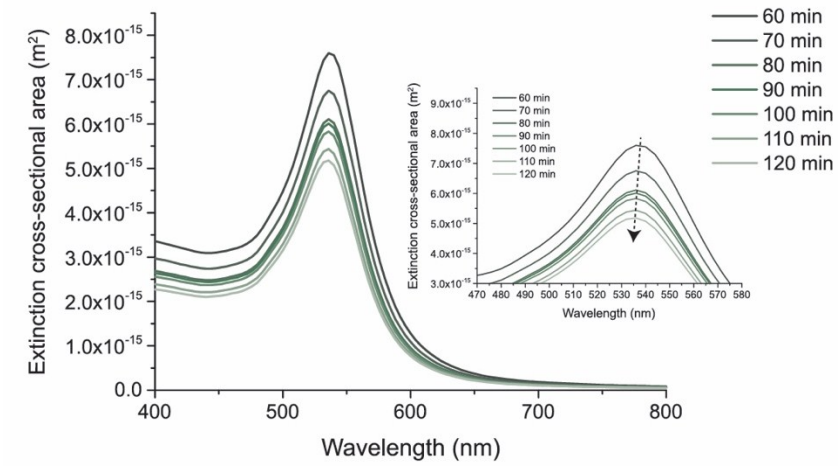

Figure S3. Calculated UV-visible spectra of secondary AuNPs in Fig. 3a based on Mie theory. Extinction shows blue-shift and decrease of intensity consistent with experimental spectra in Fig. 3c in the manuscript.

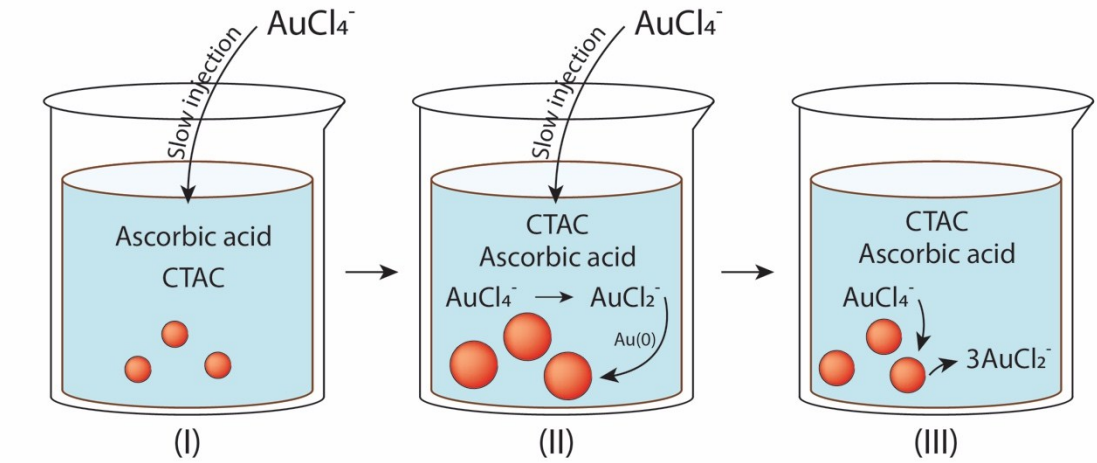

Figure S4. Schematic of suggested mechanism of the etching process of secondary AuNPs. At the stage (I), $AuCl_4^-$ solution is injected slowly into the reaction solution containing AA, CTAC and primary AuNPs. At the stage (II), slowly injected $AuCl_4^-$ is reduced by AA into $AuCl_2^-$, Au(0) and being deposited on the primary AuNPs. At the stage (III), the [AA]/ [$AuCl_4^-$] ratio is relatively smaller than stage (II). Thus, reduction reaction is retarded generating unreduced $AuCl_4^-$ which acts an Au etchant.

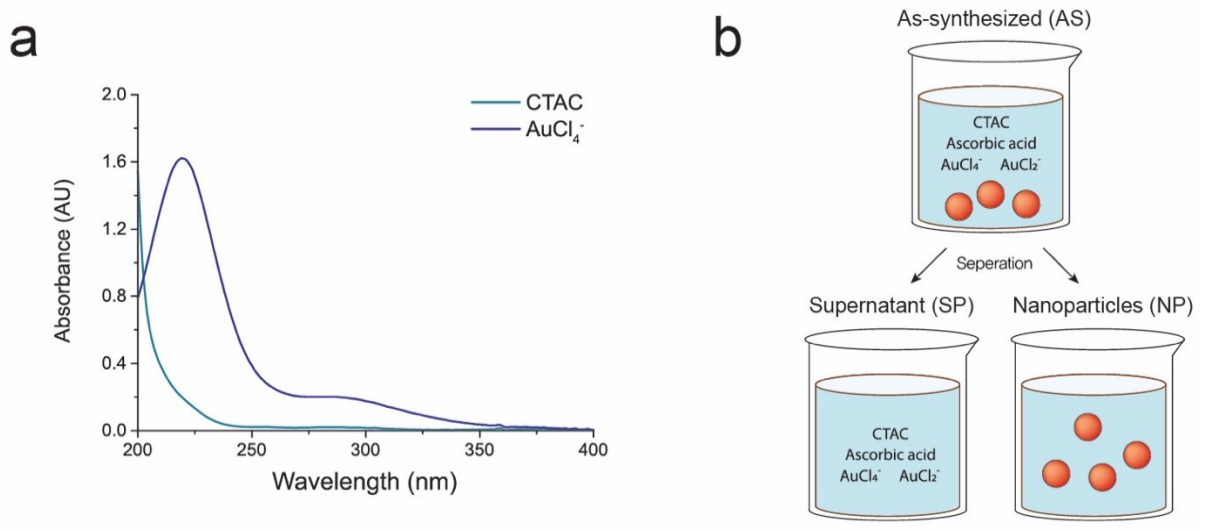

Figure S5. (a) UV-visible spectra of CTAC and $AuCl_4^-$ solution. (b) As-synthesized secondary AuNP(AS) was separated into supernatant(SP) and nanoparticle(NP) solution using centrifugation for precise measurement of $AuCl_4^-$–CTAC and $AuCl_2^-$–CTAC complexes.

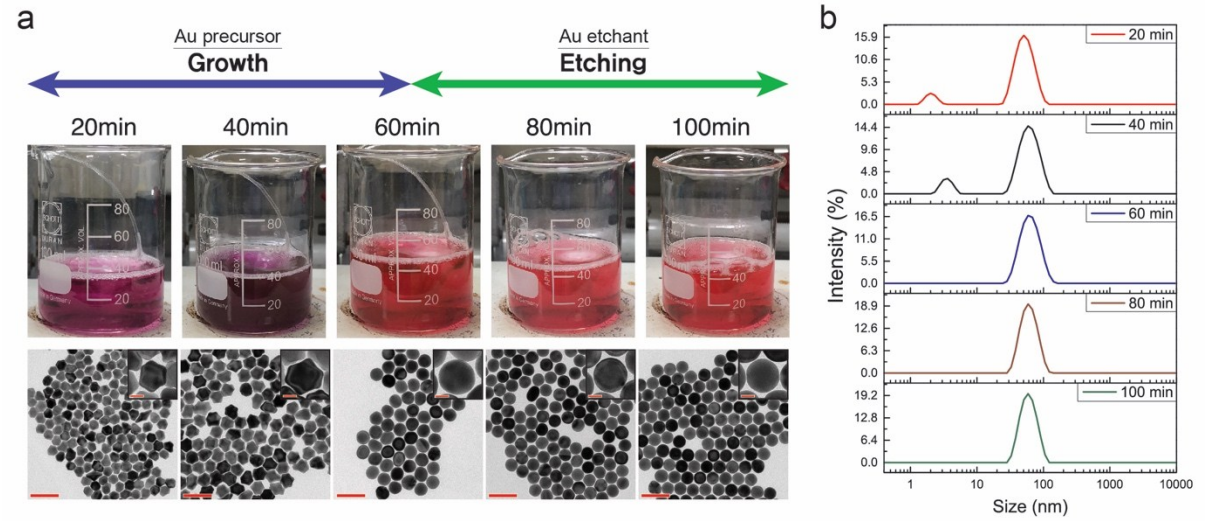

Figure S6. (a) Pictures obtained under ambient light and TEM images of secondary AuNPs after time interval of 20 min. The total volume of secondary AuNP increased due to slow injection of gold source. Up to 60 min of reaction, secondary AuNP was under growth stage. However, it went through etching stage after 60 min with smooth, spherical shape. (b) DLS spectra of secondary AuNPs collected after different reaction time. At the initial stage of reaction (20, 40 min), two peaks were shown due to the rotational diffusion mode resulted from anisotropic shape of secondary AuNPs. Once AuNPs have isotropic shape, DLS data shows single peak (60, 80, 100 min).

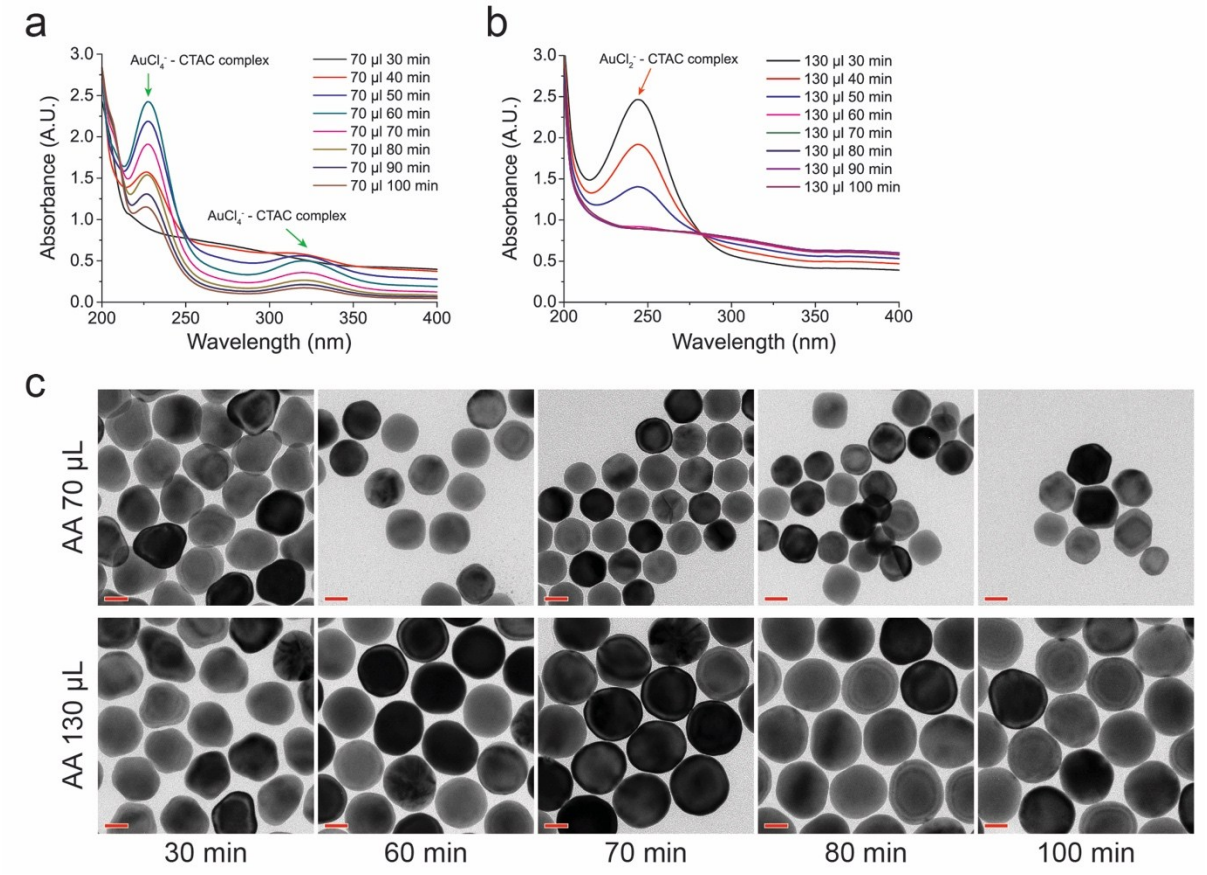

Figure S7. Time resolved UV- visible spectra of secondary AuNPs with (a) less amount of AA (70 µL) and (b) excessive amount of AA (130 µL). (c) TEM images of secondary AuNPs collected after different reaction time and amount of AA (70, 130 µL). Scale-bar: 20 nm

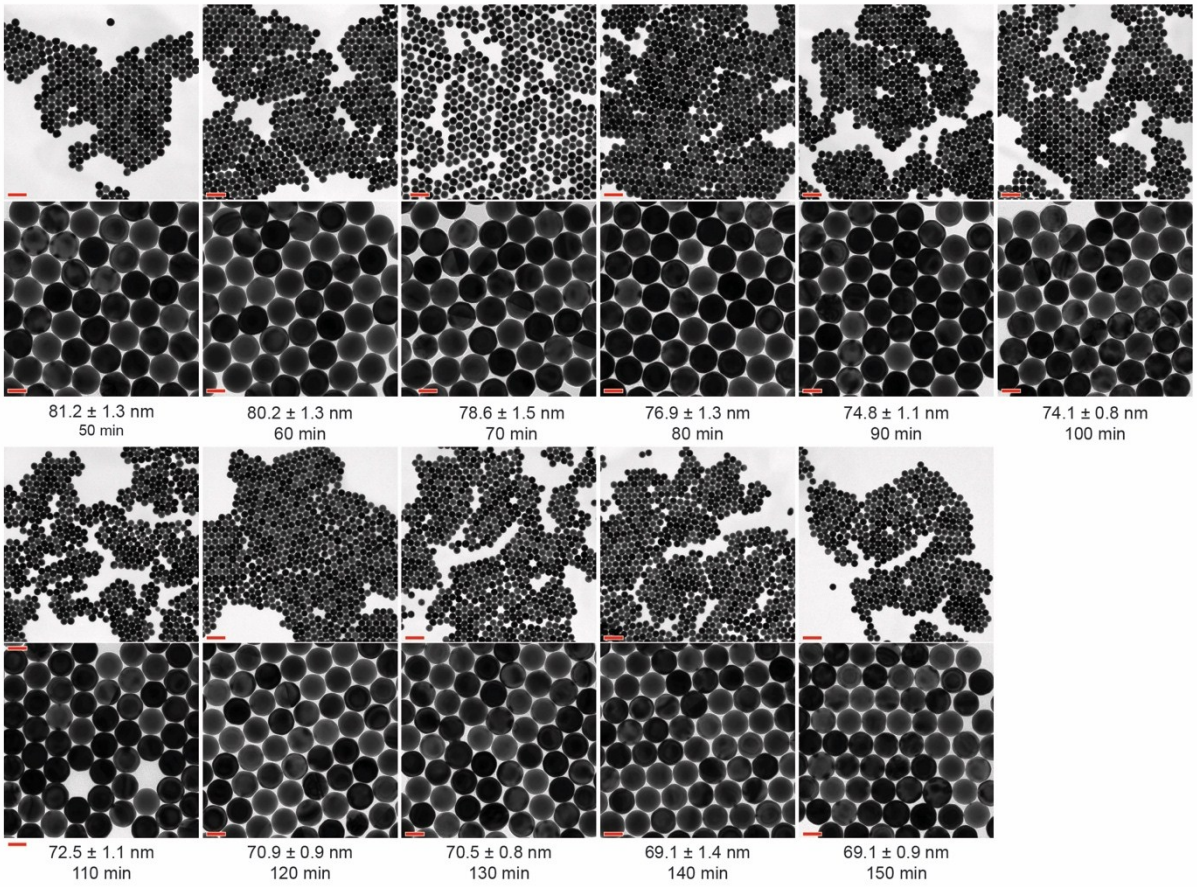

Figure S8. TEM images of secondary AuNPs with different sizes ranging from 69 nm to 81 nm (Upper low magnification image scale bar: 200 nm, lower low high magnification image scale bar: 50 nm).