

## Supporting Information

### Unravelling the Shell Growth Pathways of Au-Ag Core-Shell Nanoparticles by *In-Situ* Liquid Cell Transmission Electron Microscopy

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#### 1. Synthesis of Au nanobipyramids (NBPs)

##### 1.1 Materials

CTAB was purchased from Sigma. Hydrogen tetrachloroaurate tetrahydrate ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ), silver nitrate ( $\text{AgNO}_3$ ), sodium borohydride ( $\text{NaBH}_4$ ), trisodium citrate dihydrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), L-ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ ), hydrochloric acid (HCl) and sodium chloride (NaCl) were all purchased from Shanghai Sinopharm Chemical Reagent Co. Ltd. (China). All the chemicals and reagents were used as received. Deionized water with resistance of 18 M $\Omega$  cm was used in all the experiments. All the glassware was cleaned by aqua regia (HCl:  $\text{HNO}_3$  in a 3:1, v/v) and rinsed with deionized water prior to the experiments.

##### 1.2 Synthesis of citrate-capped gold seeds

Tiny gold nanocrystals were synthesized as the seeds for the growth of gold NBPs by reducing  $\text{HAuCl}_4$  with  $\text{NaBH}_4$  in presence of trisodium citrate. To a 40 mL solution containing 0.25 Mm  $\text{HAuCl}_4$  and 0.25 mM trisodium citrate under vigorous stirring, 1.0 mL of 100 mM freshly prepared  $\text{NaBH}_4$  solution was added quickly at room temperature. The orange-red seed solution was aged at room temperature for at least 2 h before use in order to allow the complete hydrolysis of unreacted  $\text{NaBH}_4$ . The sizes of as-produced gold nanocrystals were smaller than 10 nm.

### 1.3 Synthesis of gold NBPs

A 100 mL of growth solution containing 0.5 mM HAuCl<sub>4</sub> and 0.1 M CTAB was prepared. To this solution was added 1 mL of 10 mM AgNO<sub>3</sub>, 2 mL of 1.0 M HCl and 0.8 mL of 0.1 M L-ascorbic acid in turn and the resulting solution as growth solution was stirred gently. The orange color of the gold salt in the CTAB solution disappeared when L-ascorbic acid was added, due to the reduction of Au<sup>3+</sup> to Au<sup>+</sup>. The growth of gold NBPs was initiated by adding 0.8 mL of the seed solution to the growth solution. After the addition, the color of the growth solution changed from clear to violet red. The mixture solution was kept at 30 °C in water bath and left undisturbed overnight. For a typical purification procedure of gold NBPs, the crude gold NBPs solution was firstly centrifuged at 11,000 g/min for 10 min to get rid of the extra CTAB. This treatment is necessary because that CTAB at a high concentration (0.1 M or more) is very easy to crystallize at room temperature. After centrifugation, the precipitates contained most of gold NBPs and byproducts were re-dispersed by the same volume of deionized water. The total concentration of the residual CTAB is ~5 mM. Next, a 20 mL of the NBPs dispersion was placed in a 50 mL plastic centrifuge tube followed the addition of 17.5 mL of 3.44 M NaCl aqueous solution and 2.5 mL deionized water. The mixture solution was then kept at ambient temperature without disturbance. After 24 h, the supernatant was taken and deionized water was added to the tube to disperse the precipitates.

### 2. Supporting Movies

Movie S1: *In-situ* TEM movie (accelerated 15 times) shows the overgrowth of Ag shell via atom deposition corresponding to Figure 2a.

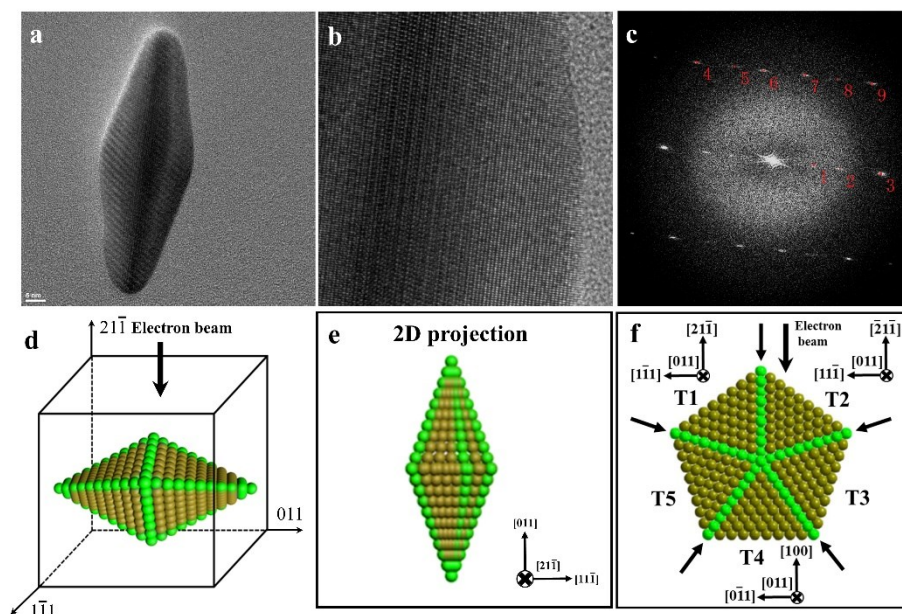
Movie S2: *In-situ* TEM movie (accelerated 20 times) shows Au NBPs in silver precursor solution without AA corresponding to Figure S3.

Movie S3: *In-situ* TEM movie (accelerated 20 times) shows the overgrowth of Ag shell via nuclei

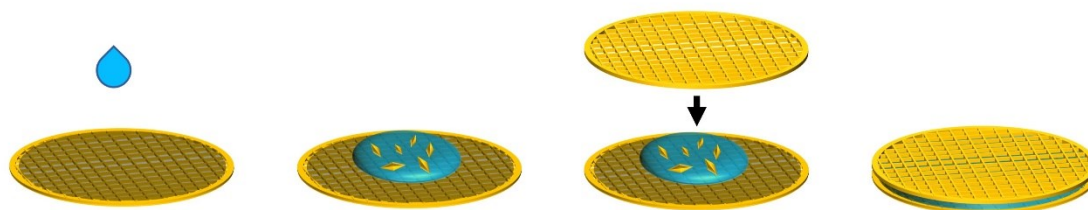
coalescence corresponding to Figure 3a.

Movie S4: *In-situ* TEM movie (accelerated 10 times) shows the crystallization process of Ag shell corresponding to Figure 4.

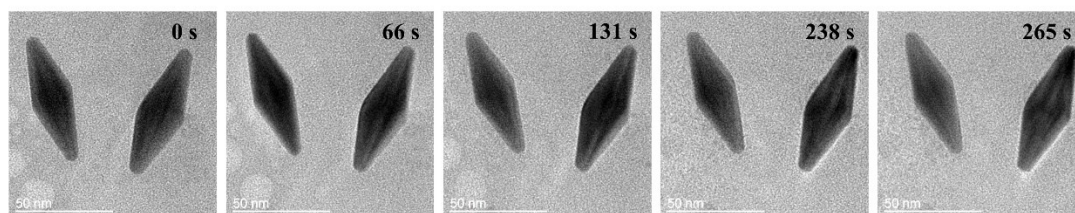
### 3. Supporting Figures



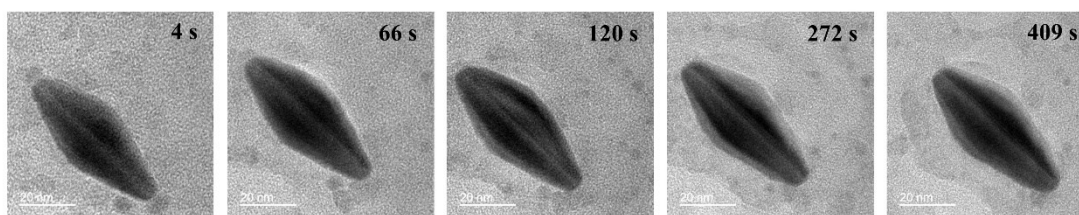
**Figure S1.** The structure of Au nanobipyramid (NBP). (a) High-resolution TEM image of a NBP. (b) The magnification of its equatorial part. (c) The power spectrum of the image. (d) 3D structure of Au NBP. (e) 2D projection of Au NBP along the electron beam. (f) The cross-section perpendicular to the growth axis of the penta-fold twinned structure. Each section was labeled as T1, T2, T3, T4, and T5, respectively, with the twinning planes pointed by the arrows



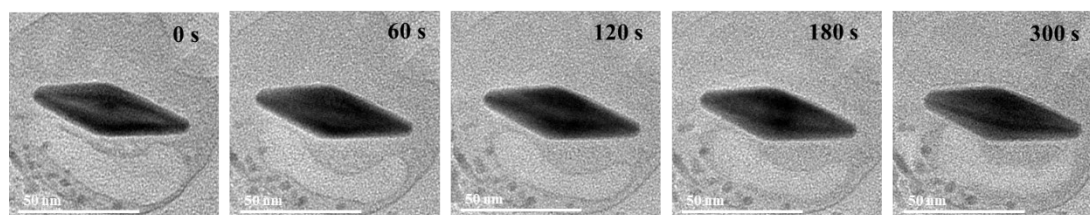
**Figure S2.** Preparation of a carbon film based liquid cell.



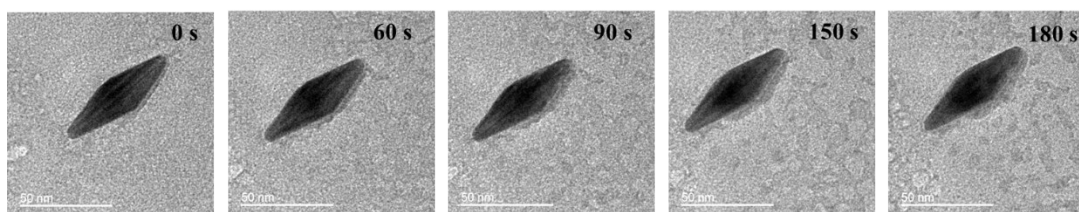
**Figure S3.** Time-lapse TEM images show Au NBPs in silver precursor solution without ascorbic acid.



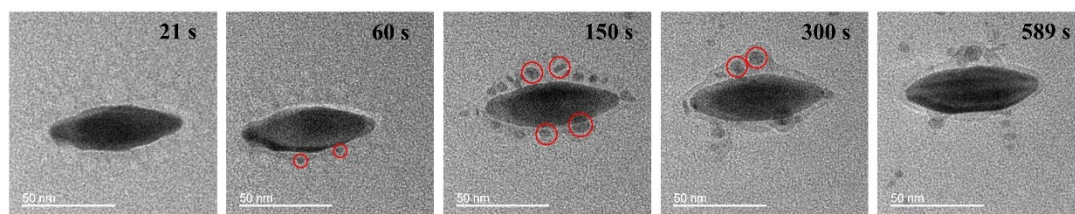
**Figure S4.** Time-lapse TEM images show Ag growth on a Au NBP with 0.01 mM ascorbic acid



**Figure S5.** Time-lapse TEM images show Ag growth on a Au NBP with 0.005 mM ascorbic acid

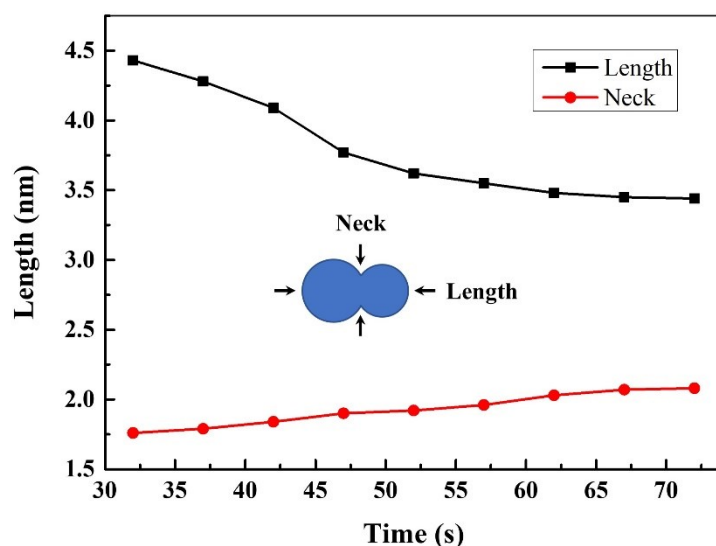


**Figure S6.** Time-lapse TEM images show Ag growth on a Au NBP with 0.02 mM ascorbic acid

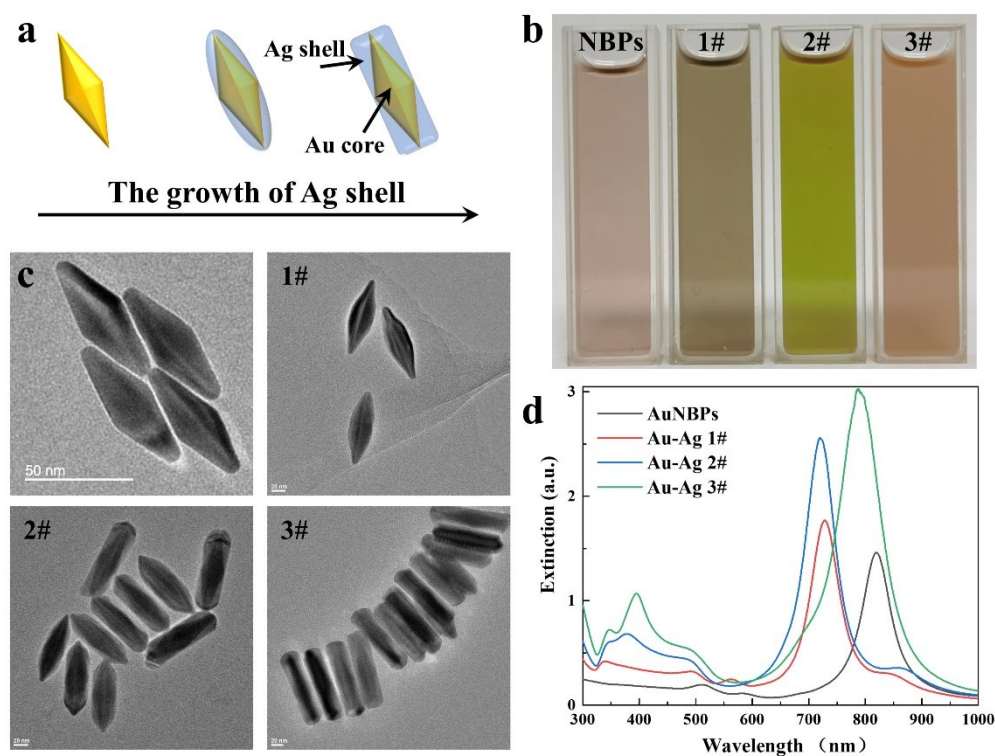


**Figure S7.** Time-lapse TEM images show Ag growth on a Au NBP with 0.01 mM ascorbic acid and 0.01 mM PVP.





**Figure S8.** The evolution of neck and length of two Ag nanoparticles as a function of time.



**Figure S9.** Au NBP-supported Ag nanostructures. (a) Schematic illustrating Ag overgrowth on the Au NBPs. (b) Digital photograph of the colloidal solutions of the Au NBP and Au NBP-Ag nanostructure samples with increasing Ag content. (c) TEM images of the Au NBP and Au NBP-Ag nanostructure samples. (d) UV-visible spectra of the Au NBP and Au NBP-Ag nanostructure samples. These as-prepared Au NBPs-Ag nanostructure could be employed as a sensitive colorful chromogenic substrate for multiple bio-targets.