Electronic Supplementary Information for

## Halide-Free Synthesis of Gold Nanoplates and Monitoring the Shape Evolution Process through A Marker Experiment

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**Materials**. Silver nitrate (AgNO<sub>3</sub>), polyvinyl pyrrolidone (PVP,  $M_w \sim 40000 \text{ g/mol}$ ), trisodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>), chloroauric acid (HAuCl<sub>4</sub>), sodium borohydride (NaBH<sub>4</sub>) and L-ascorbic acid (AA) were purchased from Sigma Aldrich. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 *wt.*%) was purchased from sinopharm. Sodium Oleate (NaOL) was purchased from TCI (China). Milli-Q water is under the condition of 18.2MΩ·cm at 25 °C.

## Synthesis of triangular silver nanoplates.

First, 100 mL anqueous solution containing AgNO<sub>3</sub> (50 mM, 200  $\mu$ L), PVP (17.5 mM, 0.8 mL), trisodium citrate (75 mM, 2 mL) and hydrogen peroxide (30 *wt*. % , 240  $\mu$ L) was prepared under vigorous stirring at room temperature in air, followed by rapidly injecting 1 mL of NaBH<sub>4</sub> solution (100 mM,). After the color changed to dark blue, the mixed solution was centrifuged at 11000 rpm for 15 min and washed with TSC solution (4.5 mM) to collect silver nanoplates. After that, the silver nanoplates were re-dispersed in 1 mL (4.5 mM) TSC solution.

## Synthesis of Au/Ag nanorings.

0.5 mL of the as-prepared triangular silver nanoplates were quickly injected to a solution

containing 30 mL of deionizer water, 2 mL of PVP ( $M_w \sim 40000 \text{ g/mol}$ , 3.5 mM), 80µL of trisodium citrate (75 mM,) and 0.2 mL of AA (3 mM) in a water bath at 60 °C. Immediately after the addition of Ag nanoplates, 500 µL of HAuCl<sub>4</sub> (1 mM) was dropwise added into the mixed solution under rapid stirring to initial the galvanic replacement. The zero-valance silver was replaced by the gold atoms and turned into ions diffused in the solution. During the reaction, the color changed from blue to colorless indicating the scarification of silver nanoplates. After that, the solution was immediately centrifuged at 11000 rpm for 15 min to collect the Au/Ag nanorings by carefully removing the supernatant.

## Synthesis of gold nanoplates.

The pre-prepared gold nanorings were suspended in 5 mL deionized water. 250  $\mu$ L of PVP (M<sub>w</sub> ~ 40000 g/mol, 3.5 mM), 10  $\mu$ L of sodium oleate (50 mM), 20 $\mu$ L for inner growth and 40 uL for outer growth of HAuCl<sub>4</sub> (15 mM) and 5  $\mu$ L of H<sub>2</sub>O<sub>2</sub> (30 wt. %) was sequently added into the solution. After 40 min, the color of the solution changed from colorless to light blue-green, indicating the formation of gold nanoplates. The mixed solution was centrifuged at 6000 rpm for 5 min and washed with water to collect the products.

**Characterization.** Transmission electron microscopy (TEM) were collected TECNAI G2 F20 (FEI, USA), operating at 200 KV. The UV-Vis spectra were obtained by using the LAMBDA 750 spectrograph in a range of 300-1050 nm from PERKINELMER, USA.

Element	Concentration (ppb)	RTD %
Au	119.179	5
Ag	3.040	5

 Table S1 Concentration of the component of gold nanoplate measured by ICP.



Fig. S1 TEM image of silver nanoplates.



Fig. S2 TEM image of gold nanorings.



Figure S3. SEM image showing the high-yield of Au nanoplates.



Figure S4. The EDS measurement of the sample. The Ag content has been determined as 7.47%.



Fig. S5 TEM image of flower-like gold nanoplate obtained from hexagonal gold nanoring.

The red dashes line out the different growth regions.