Supporting Information

for

## Facile synthesis of high-purity single-twinned Au nanocrystals through manipulating reaction kinetics

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## **Experimental Section**

**Chemicals and materials**. Gold(III) chloride trihydrate (HAuCl<sub>4</sub>·3H<sub>2</sub>O,  $\geq$ 99.9%), hydrogen tetrabromoaurate(III) hydrate (HAuBr<sub>4</sub>·xH<sub>2</sub>O), ascorbic acid (AA,  $\geq$ 99.0%), sodium borohydride (NaBH<sub>4</sub>, 98%), hexadecyltrimethylammonium bromide (CTAB,  $\geq$ 99%), hexadecyltrimethylammonium chloride (CTAC,  $\geq$ 98.0%), sodium bromide (NaBr,  $\geq$ 99.99%), and silver nitrate (AgNO<sub>3</sub>, 99.9999%) were all obtained from Sigma–Aldrich and used as received. Deionized (DI) water with a resistivity of 18.2 MΩ·cm was used throughout the experiment.

**Preparation of the initial Au nanoclusters.** The initial Au nanoclusters were prepared according to a reported method with slight modification.<sup>1</sup> In detail, a fresh aqueous NaBH<sub>4</sub> solution (10 mM, 0.6 mL) was rapidly added to a thoroughly mixed 10 mL aqueous solution containing HAuCl<sub>4</sub> (0.25 mM) and CTAB (100 mM) using a pipette. It could be observed that a brown solution immediately formed upon the introduction of NaBH<sub>4</sub>. The mixture was placed on an orbital shaker at a speed of 300 rpm for 2 min and

then kept undisturbed at room temperature (25  $^{\circ}$ C) for 3 h to ensure complete decomposition of NaBH<sub>4</sub> remaining in the reaction solution.

Standard procedure for the synthesis of truncated Au RBPs. Aqueous solutions of CTAC (200 mM, 1.0 mL), AA (10 mM, 0.2 mL), and HAuBr<sub>4</sub> (0.5 mM, 2.0 mL) were mixed with 1.0 mL of water in a 20 mL glass vial. Then, an appropriate volume (1-20  $\mu$ L, see the main text for different amounts of Au nanoclusters and the corresponding size of truncated Au RBPs) of the aqueous initial Au nanoclusters were rapidly added using a pipette. The reaction was allowed to proceed undisturbedly at room temperature (25 °C) for 10 min after the solution was slightly shaken by hand for 5 seconds. The final product was collected by centrifugation at 14000 rpm for 10 min and washed with water twice prior to characterization.

Control the Br/Au ratios for tuning the shape and crystallinity of AuNCs. For the sample with Br/Au ratio of 4:1, the above standard procedure for the synthesis of truncated Au RBPs was employed. For the sample without Br, the standard procedure was employed except for the use of HAuCl<sub>4</sub> (0.5 mM, 2.0 mL) to replace the HAuBr<sub>4</sub> (0.5 mM, 2.0 mL) as a precursor. For other samples with Br/Au ratios of 20:1, 50:1 and 100:1, the standard procedure was also employed except for the addition of 32, 92 and 192  $\mu$ L of 500 mM NaBr, respectively.

**Synthesis of single-twinned Au@Ag NCs using truncated Au RBPs as seeds.** Aqueous solutions of CTAC (20 mM, 3.0 mL), AA (10 mM, 0.2 mL), and the 20 nm truncated Au RBP seeds (0.8 mL) were mixed in a 20 mL glass vial and pre-heated at 60 °C for 10 min. Then, an aqueous solution of AgNO<sub>3</sub> (1.0 mM, 1.0 mL) was added using a syringe pump at an injection rate of 1.0 mL/h. The reaction was allowed to proceed at 60 °C for another 1 h after the injection had been completed. The final products of Au@Ag bimetallic NCs were collected by centrifugation at 10000 rpm for 10 min and washed with water once prior to characterization.

**Instrumentation.** Transmission electron microscopy (TEM) images were taken using a JEM-1400 microscope (JEOL, Japan) operated at 120 kV. The samples were prepared by dropping aqueous suspensions of the nanoparticles onto carbon-coated copper grids and dried under ambient conditions. High-resolution TEM (HRTEM) images were captured

by field-emission JEM-2100F (Japan) and Tecnai G2 F20 (USA) microscopes that were operating at 200 kV. Scanning electron microscopy (SEM) images were taken using a Hitachi S-4800 microscope (Japan) operated at 30 kV. An Eppendorf (5430, Germany) centrifuge was used for the centrifugation and washing of all samples.

## **Reference:**

 Y. Zheng, Y. Ma, J. Zeng, X. Zhong, M. Jin, Z.-Y. Li and Y. Xia, *Chem. Asian J.*, 2013, 8, 792-799.

## Additional Figures



*Fig. S1* (a) Photograph of the solution and (b) HRTEM image of the Au nanoclusters that were used as initial seeds for the growth of truncated Au RBPs.



*Fig. S2* HRTEM image of a typical singly twinned Au nanocrystal that was obtained at early stage of the synthesis of truncated Au RBPs. The inset shows the corresponding FT pattern of this nanocrystal.



*Fig. S3* HRTEM images of the typical (a) single-crystal and (b) multiply twinned Au nanocrystals that were selected from the samples in Fig. 3a and 3d, respectively. The insets show the corresponding FT patterns for the (a) single-crystal and (b) multiply twinned Au nanocrystals, respectively. The as-marked white lines in (a) show the directions of the crystal lattice, and the red lines in (b) show the twin planes in the nanocrystal.