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 ($HAuCl_4 \cdot 3H_2O$, ≥99.9%), hydrogen tetrabromoaurate(III) hydrate ($HAuBr_4 \cdot xH_2O$), ascorbic acid (AA, ≥99.0%), sodium borohydride ($NaBH_4$, 98%), hexadecyltrimethylammonium bromide (CTAB, ≥99%), hexadecyltrimethylammonium chloride (CTAC, ≥98.0%), sodium bromide (NaBr, ≥99.99%), and silver nitrate ($AgNO_3$, 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.[1] In detail, a fresh aqueous $NaBH_4$ solution (10 mM, 0.6 mL) was rapidly added to a thoroughly mixed 10 mL aqueous solution containing $HAuCl_4$ (0.25 mM) and CTAB (100 mM) using a pipette. It could be observed that a brown solution immediately formed upon the introduction of $NaBH_4$. 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 ^{o}C) for 3 h to ensure complete decomposition of $NaBH_4$ 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 $HAuBr_4$ (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 μL, 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 ^{o}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 $HAuCl_4$ (0.5 mM, 2.0 mL) to replace the $HAuBr_4$ (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 μL 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 ^{o}C for 10 min. Then, an aqueous solution of $AgNO_3$ (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 ^{o}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:

1. 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

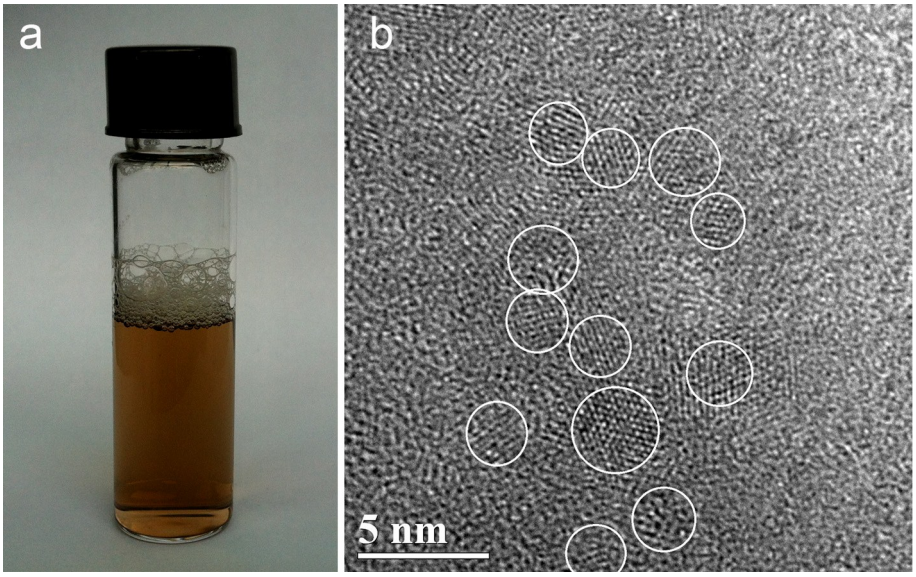

Fig. S1 (a) Photograph of the solution and (b) HRTEM image of the Au nanoclusters that were used as initial seeds for the growth of truncated Au RBPs.

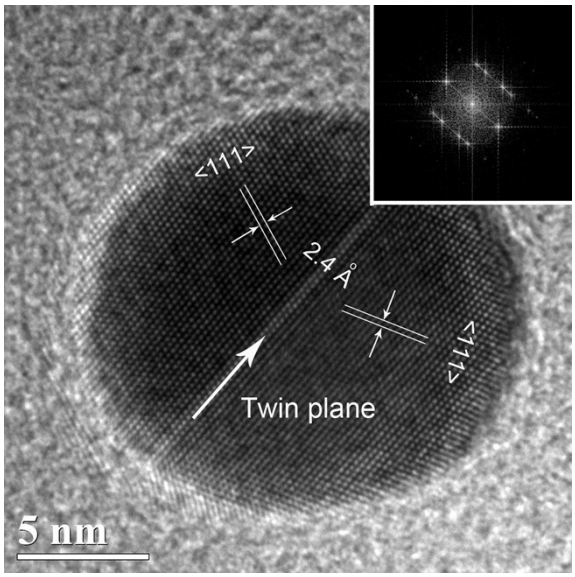

Fig. S2 HRTEM image of a typical singly twinned Au nanocrystal that was obtained at early stage of the synthesis of truncated Au RBPs. The inset shows the corresponding FT pattern of this nanocrystal.

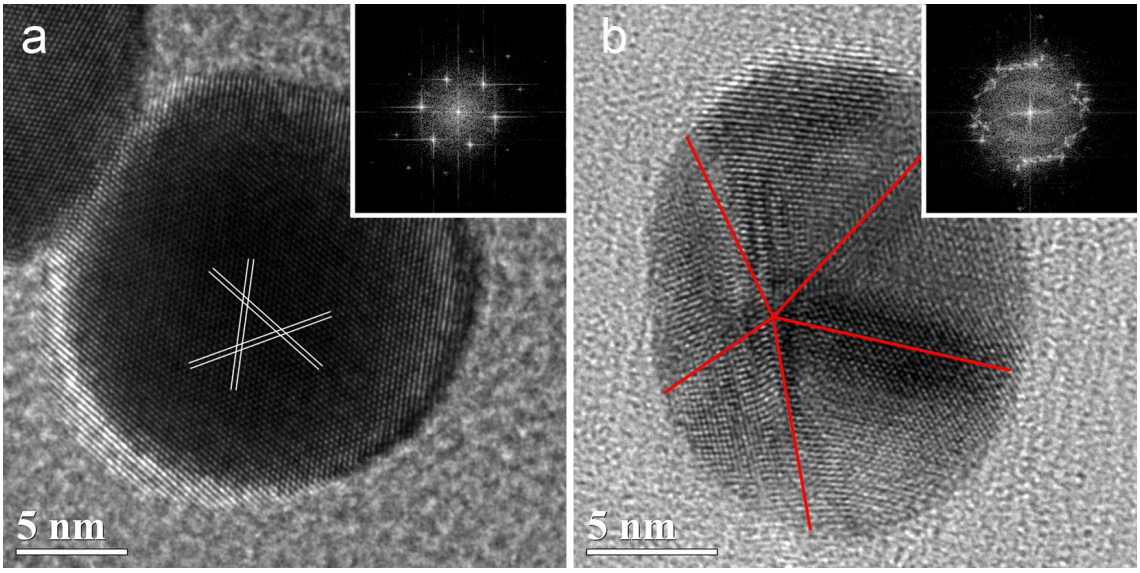

Fig. S3 HRTEM images of the typical (a) single-crystal and (b) multiply twinned Au nanocrystals that were selected from the samples in Fig. 3a and 3d, respectively. The insets show the corresponding FT patterns for the (a) single-crystal and (b) multiply twinned Au nanocrystals, respectively. The as-marked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