Supporting information

Oleic Acid-Assisted Synthesis of Tunable High-Aspect-Ratio Multiply-Twinned Gold Nanorods for Bioimaging

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Experimental

Materials. Gold (III) chloride trihydrate ($HAuCl_4.3H_2O$, ≥99.9% trace metals basis), D-(−)-isoascorbic acid (AA, 98%), Oleic acid (OA, technical grade, 90%) and sodium borohydride ($NaBH_4$, powder, ≥98.0%) were purchased from Sigma Aldrich. Cetyltrimethylammonium bromide (CTAB, 99%+) was received from Acros organics. 37% Hydrochloric acid (Merck Millipore) and sodium hydroxide (pellets AnalaR NORMAPUR® ACS) were purchased from VWR.

Preparation of Au seed particles. 10 mL aqueous solution was prepared by mixing 5 mL of 0.5 mM $HAuCl_4.3H_2O$ and 5 mL of 0.2 M CTAB. The solution was stirred at 1200 rpm for 2 min at 30°C. A 1.6 mL of freshly prepared 3.75 mM $NaBH_4$ solution was rapidly injected to stirred solution under vigrous stirring. The colour of the solution immediately turned to brown, indicating the formation of Au seed particles. After stirring at 1200 rpm for 2 min, the seed solution was aged for 30 min at 30°C prior to use.

Synthesis of multiply twinned Au NRs. To prepare growth solution for the fabrication of multiply twinned Au NRs, first, 1.2 g of CTAB and 30 μL of OA were added to 15 mL of warm deionized water (80°C), and the turbid solution was stirred at 1000 rpm at 100°C. After 30 min, the solution became transparent indicating the complete dissolution of CTAB and OA in water. The solution was cooled down to 30°C. A 15 mL of 0.5 mM $HAuCl_4.3H_2O$ was added to the reaction mixture and left for stirring at 1000 rpm for 5 min. A yellow solution turned to colorless after adding 135 μL of 128 mM AA and stirred at 1000 rpm for 1 min. A 96 μL portion from the seed solution was transferred to the growth solution and the solution turned to purple within 2 min. The growth solution was left for 12 hr at 30°C. After the reaction, we discarded upper pink colour solution without disturbance. The deionized water was added to disperse the precipiated product of Au NRs at the bottom of vial. The solution of Au NRs (brown color) was centrifuged twice to remove the excess surfactant and

stored in 1 mL deionized water. The experimental conditions for synthesizing multiply twinned Au NRs of different aspect ratio are described in Table S1. Au nanotriangles and nanoplates were synthesized under similar conditions except for changing the amount of CTAB (2.4 g) and OA (175 μL).

Characterization technique. A Hitachi S-5500 scanning transmission electron microscope (STEM) operating in bright field (BF) mode at an accelerating voltage of 30 kV was used to acquire BF STEM images. High-resolution (HR) TEM images and electron diffraction patterns were collected from a JEOL 2100F operating at 200 kV. UV–vis spectra were acquired with a UV-2401PC (Shimadzu) spectrophotometer. X-ray photoelectron spectroscopy (XPS) analyses were performed using a Kratos Axis Ultra DLD spectrometer (Kratos Analytical, UK), equipped with a monochromatized aluminum X-ray source (Al, hυ = 1486.6 eV) operating at 10 mA and 12 kV (150 W). Survey spectra were collected over the range of 0-1100 eV binding energy with analyzer pass energy of 160 eV, and high resolution spectra of C 1s, O 1s, N 1s, and Mn 2p were obtained with an analyzer pass energy of 20 eV. XPS data were processed with Casa XPS software (Casa Software Ltd., UK).

Table S1. Experimental conditions for growing Au NRs of different aspect ratio. Here, l, w, AR refer to length, width and aspect ratio of NRs.

Sample	15 mL of deionized water		1 mM $HAuCl_4$ (mL)	128 mM AA (μL)	12. 1 M HCl (μL)	1 M NaOH (μL)	Seed (μL)	Dimension of NRs (average)		
	CTAB (g)	OA (μL)						l (nm)	w (nm)	AR
Fig. 1a	1.2	30	15	135			96	226±32	18±3	13±3
Fig. 3a	1.2	30	15	135	20		96	242±36	25±2	10±2
Fig. S4	1.2	30	15	135	50		96	285±34	26±3	11±4
Fig. 3g	1.2	30	15	135	75		96	441±56	19±4	23±4
Fig. 3h	1.2	30	15	135	100		96	543±72	22±4	25±5
Fig. 3b	1.2	30	15	135		1000	96	189±19	16±3	12±2
Fig. 3c	1.2	30	15	135		750	96	215±23	17±2	13±3
Fig. 3d	1.2	30	15	135		500	96	278±21	19±5	15±4
Fig. 3e	1.2	30	15	135		250	96	289±31	16±2	18±5
Fig. 3f	1.2	30	15	135		100	96	298±39	16±4	19±4
Fig. 4a	1.2	30	15	30			96	271±17	15±4	19±3
Fig. 4b	1.2	30	15	60			96	241±23	14±2	17±4
Fig. 4c	1.2	30	15	100			96	225±35	18±2	12±3
Fig. 4d	1.2	30	15	200			96	203±27	19±5	11±3

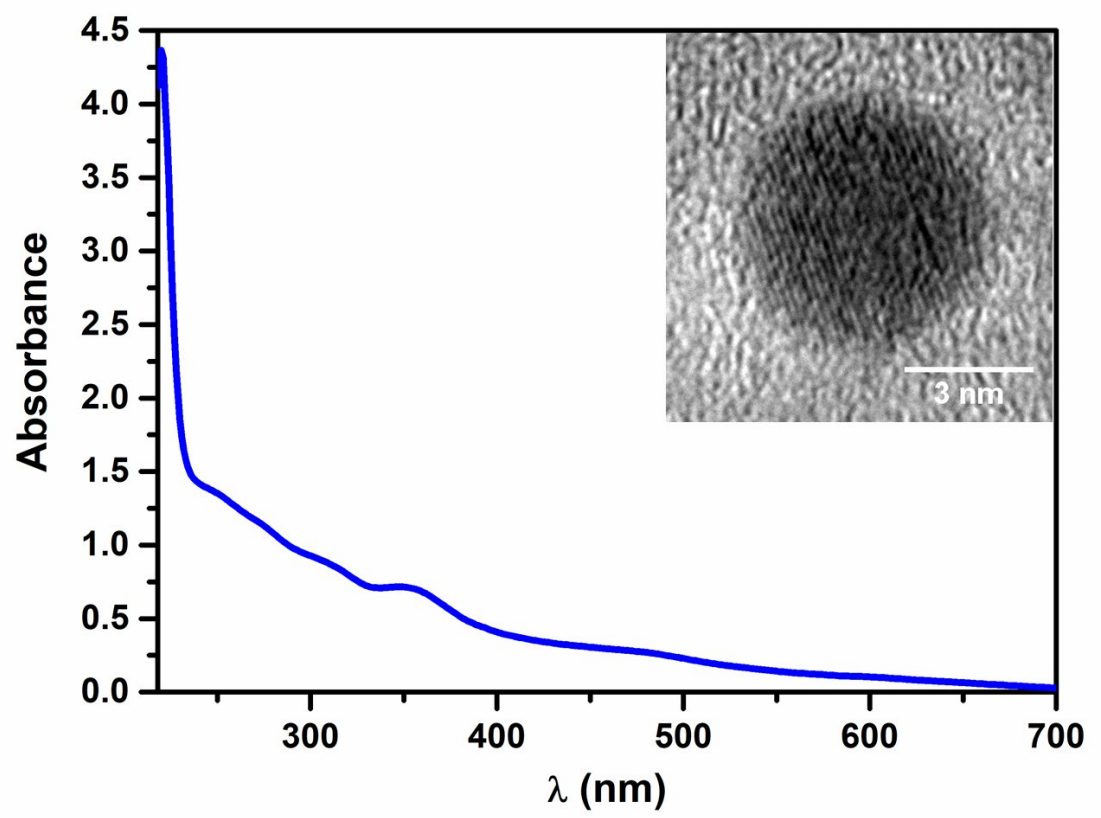

Figure S1. UV-vis spectrum of CTAB coated Au seed particles (inset HRTEM image reveals the single crystalline nature of the seed particle).

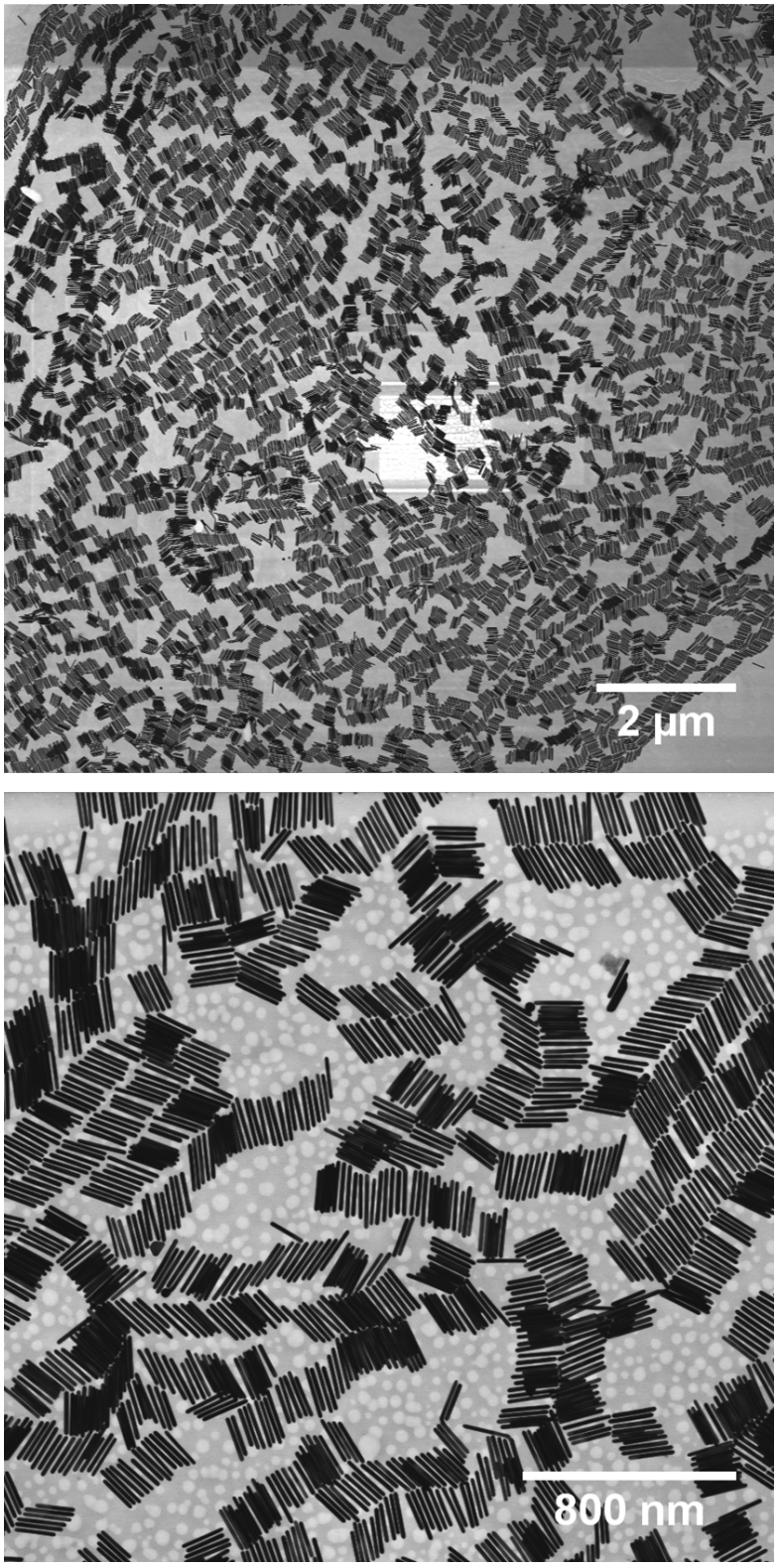

Figure S2. Large area BF STEM images of Au NRs of AR ~ 13 obtained by a five times scale synthesis of growth conditions specified in Fig. 1a (CTAB: 6 g, OA: 150 µL, $HAuCl_4$: 90 µL, AA: 810 µL and seed: 480 µL).

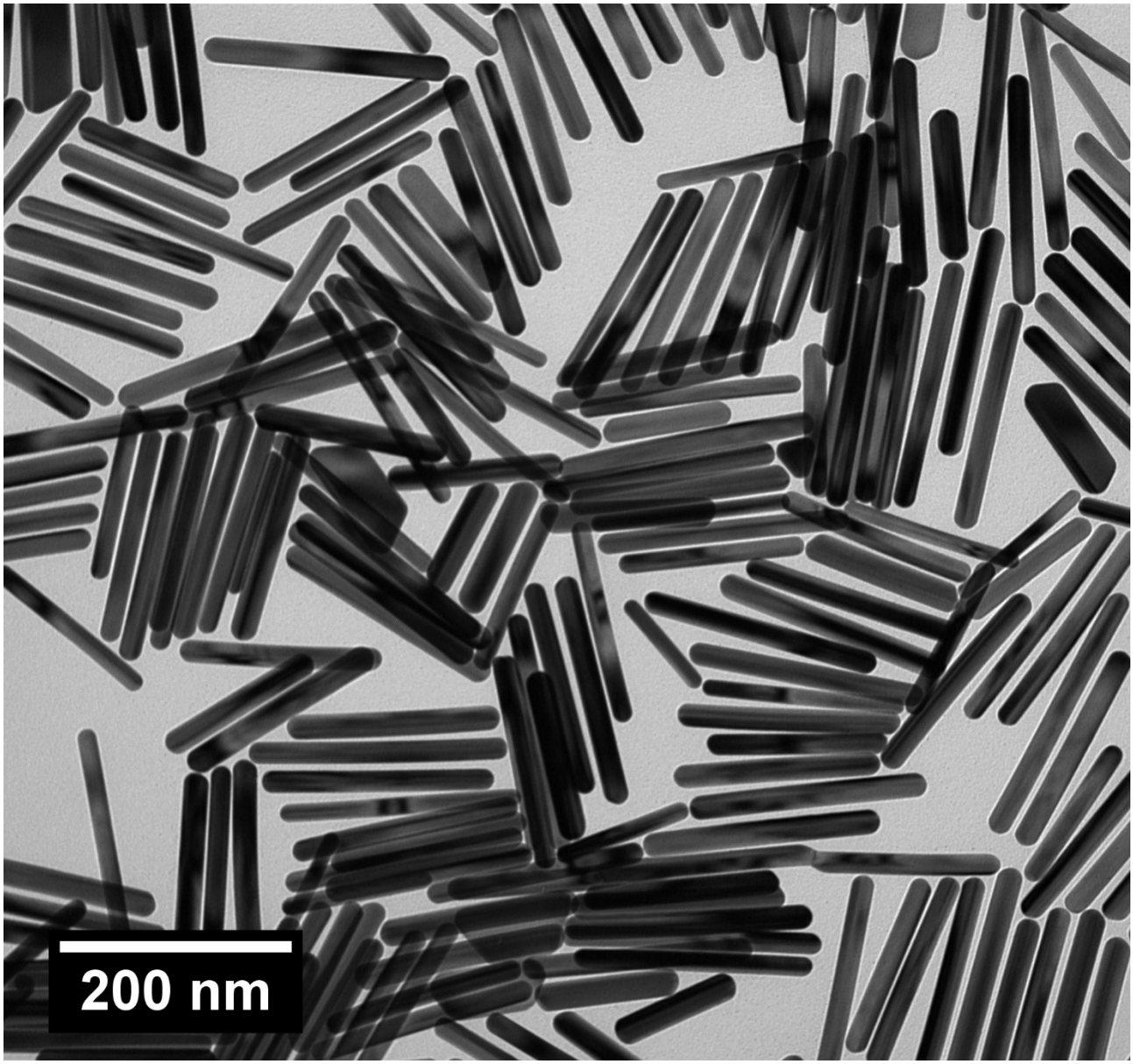

Figure S3. TEM image of ~6 month aged Au NRs (~13).

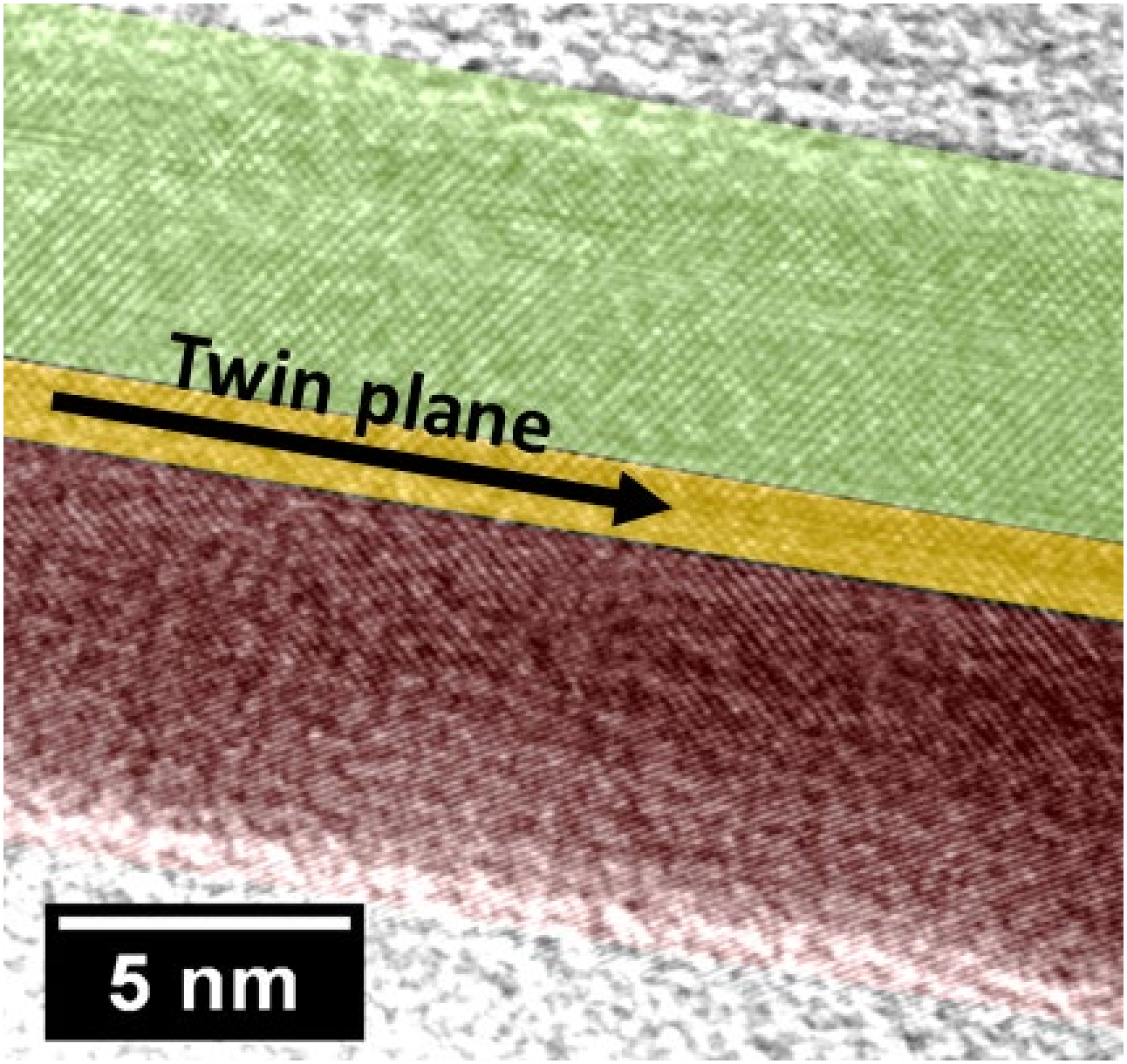

Figure S4. Enlarged HRTEM image of Au NRs obtained in the presence of low amount of OA (30 μL) as shown Fig. 1c. The black arrow indicates the presence of twin plane in Au NR.

Table S2. Elemental composition (at %) of CTAB and OA functionalized Au NRs determined by a wide scan XPS spectra.

Element	at%
C	88.1
N	1.6
O	5.4
Br	0.5
Au	4.4

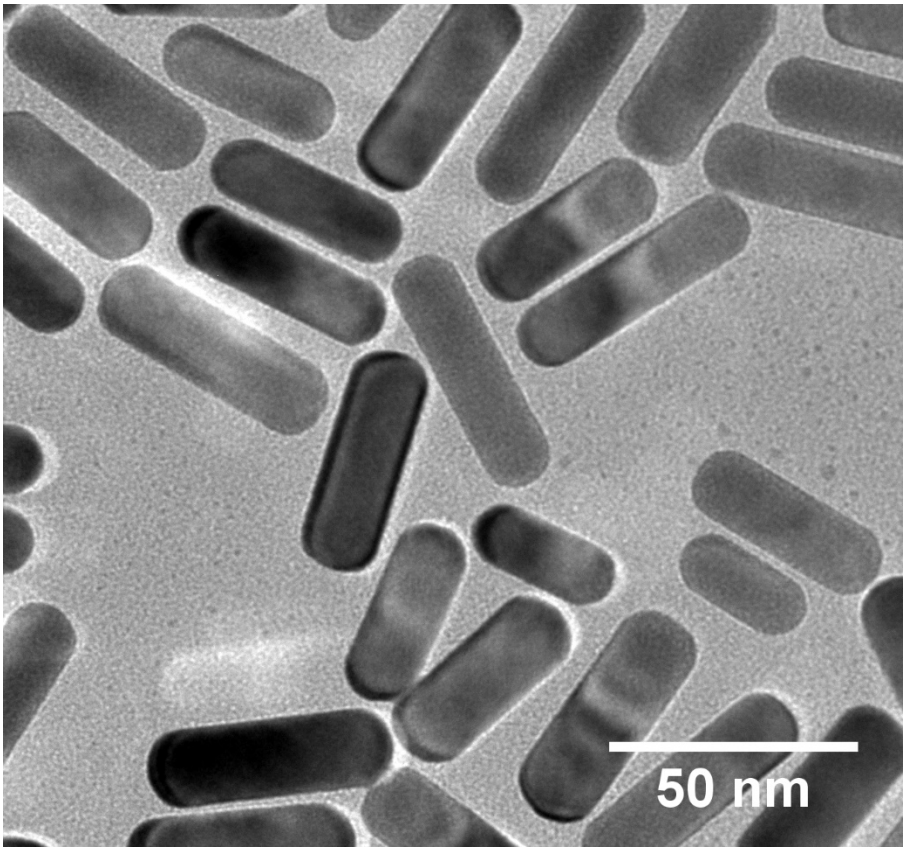

Figure S5. TEM image of low aspect ratio Au NRs (length= 48±5 nm, width=16±4 nm and AR~3) synthesized by adding 750 µL of 4 mM $AgNO_3$ to the growth solution (in the absence of OA).

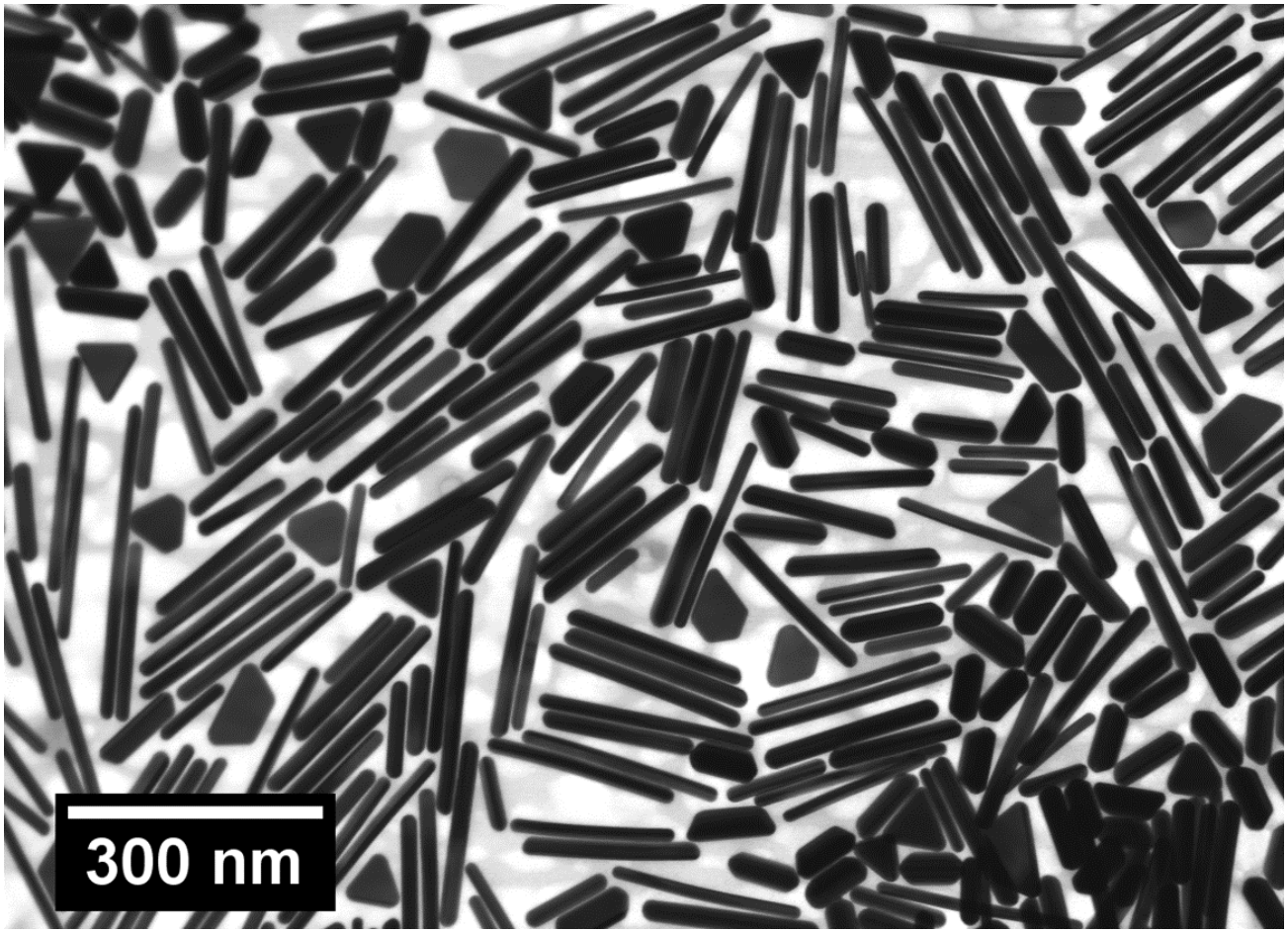

Figure S6. BF STEM image of Au NRs obtained in the presence of excess OA (175 μL).

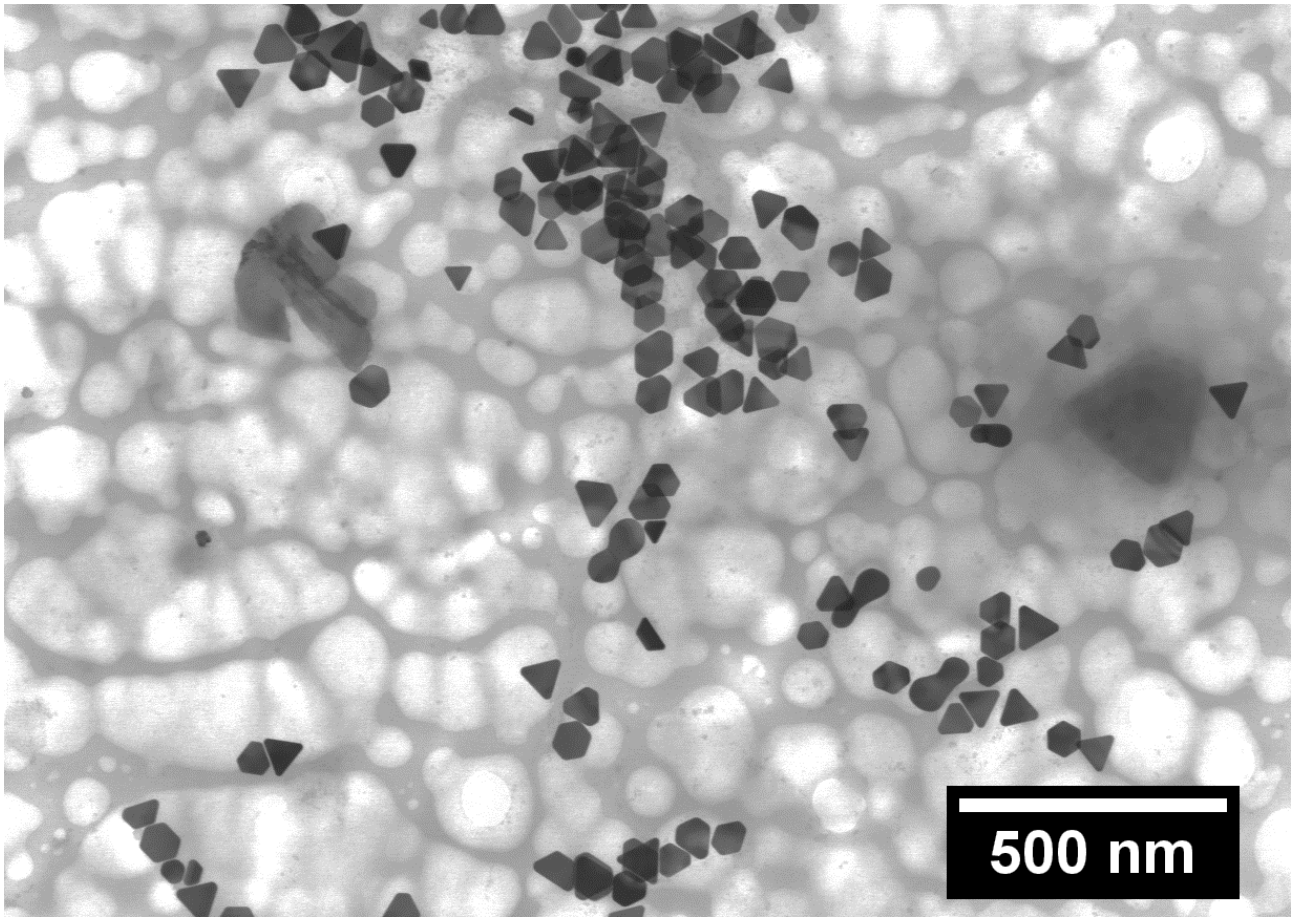

Figure S7. BF STEM image showing the fabrication of Au nanotriangles and nanoplate formation in the presence of excess OA (175 μL) and CTAB (2.4 g).

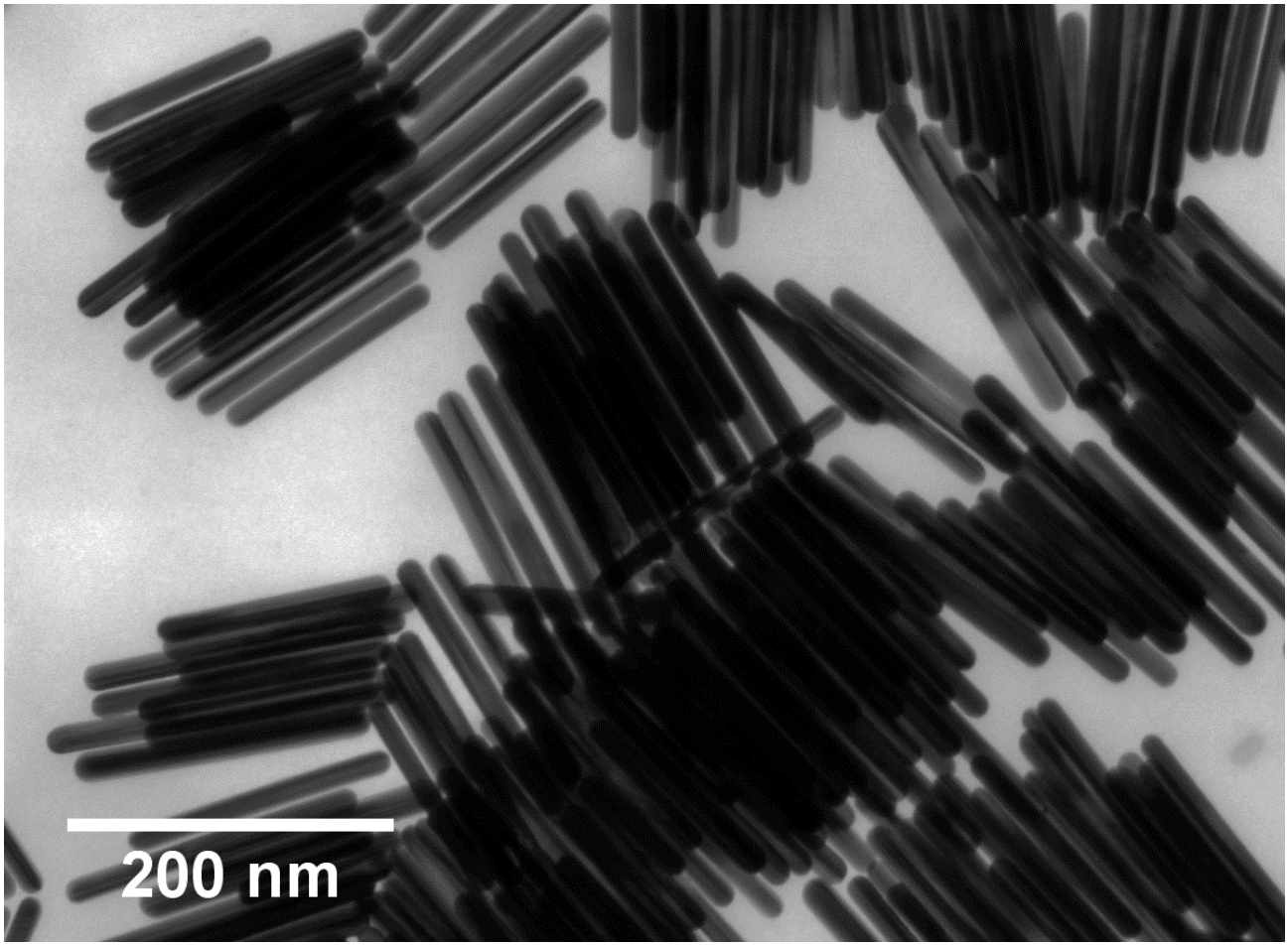

Figure S8. BF STEM image of pentatwinned Au NRs of aspect ratio ~11 synthesized in the growth solution containing 50 μL of 12.1M HCl.

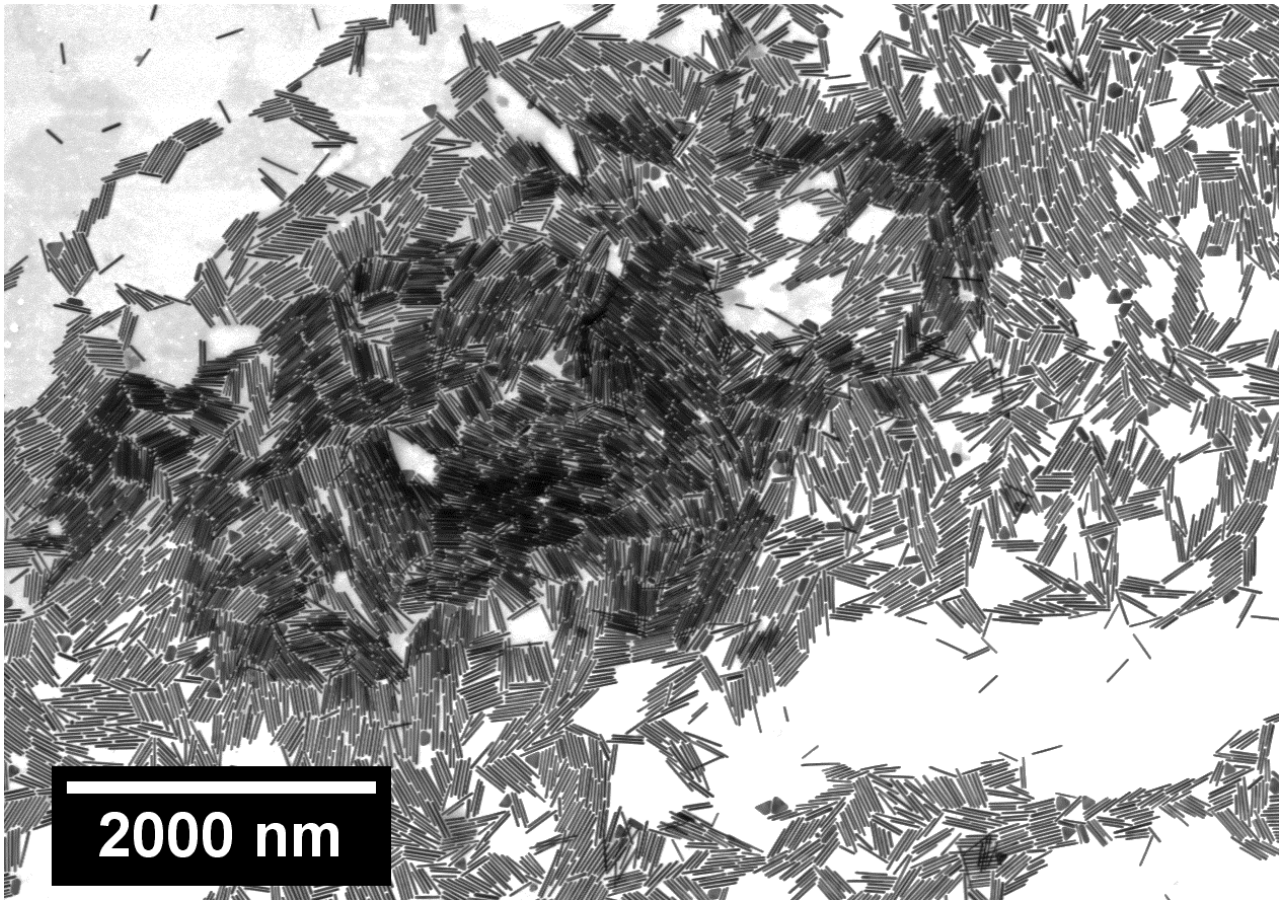

Figure S9. BF STEM image of pentatwinned Au NRs of aspect ratio ~12 synthesized in the growth solution containing 100 μL of 128 mM AA.

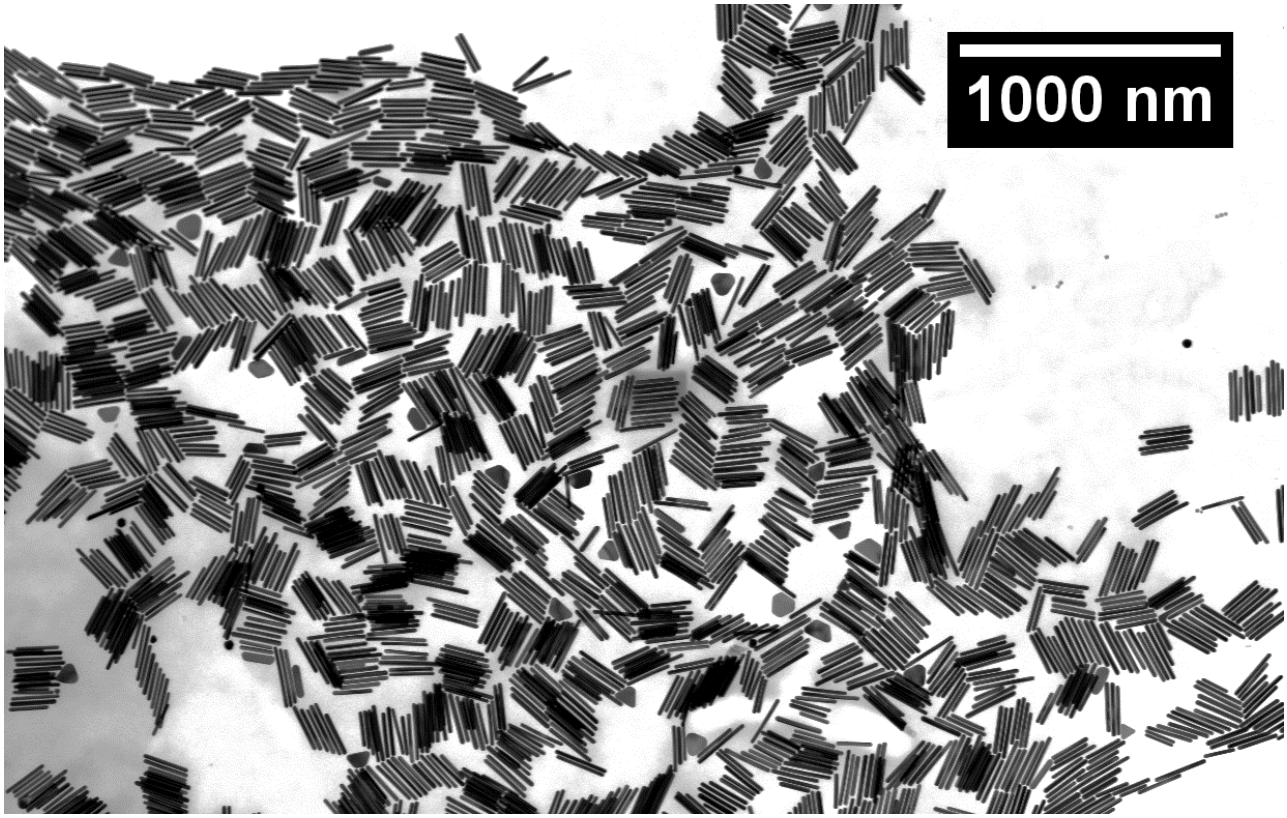

Figure S10. BF STEM image of pentatwinned Au NRs of aspect ratio ~11 synthesized in the growth solution containing 200 μL of 128 mM AA.