Electronic supplementary information

Template-directed growth of Ag nanostructures: Soft templates versus hard templates

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Experimental

Chemicals

$HAuCl_4 \cdot 3H_2O$ (99%), $NaBH_4$ (98%), trisodium citrate (99%), ascorbic acid (99%) and $AgNO_3$ (99%) were purchased from Sigma-Aldrich. Cetyltrimethylammonium bromide (CTAB, 98%) were obtained from Alfa Aesar. H_2O_2 solution (30 wt% in water), cetyltrimethylammonium chloride (CTAC, 97%), NaOH (96%), $NH_3 \cdot H_2O$ solution (25 wt% in water) and HCl solution (37 wt% in water) were purchased from Aladdin Reagent. Deionized water with a resistivity of 18.2 MΩ cm produced by a Direct-Q 5 ultraviolet water purification system was used in all experiments.

Synthesis of the Au NBPs

The Au NBP samples were prepared through a seed-mediated method. Firstly, the $HAuCl_4$ (0.125 mL, 0.01 M), trisodium citrate (0.25 mL, 0.01 M) and water (9.625 mL) were mixed at room temperature. Next, a freshly prepared, ice-cold $NaBH_4$ solution (0.15 mL, 0.01 M) was

injected quickly under vigorous stirring for 2 min. The resultant seed solution was kept at room temperature for 2 h before use. For the growth solution, CTAB (40 mL, 0.1 M), $HAuCl_4$ (2 mL, 0.01 M), $AgNO_3$ (0.4 mL, 0.01 M), HCl (0.8 mL, 1 M) and ascorbic acid (0.32 mL, 0.1 M) were mixed together, followed by the injection of seed solution (0.4 mL) with gentle inversion mixing for 10 s. The reaction solution was left undisturbed overnight at room temperature. The longitudinal dipolar plasmon wavelength of the obtained Au NBP sample was 794 nm. The purification of the as-prepared Au NBPs was conducted using a depletion-induced separation method. The number percentage of the purified Au NBPs was found from TEM imaging to be 99%.

Synthesis of the Au CNFs and ONFs

In a standard synthesis of Au CNFs, the purified Au NBPs (10 mL, the longitudinal dipolar plasmon peak extinction value is ~1 when measured with a 0.5-cm cuvette) were collected by centrifugation at 7000 rpm for 10 min. The precipitate was redispersed into a CTAC solution (10 mL, 0.08 M), followed by the addition of $AgNO_3$ (250 μL, 0.01 M) and ascorbic acid (125 μL, 0.1 M) under gentle shaking. The mixture solution was placed in an air-bath shaker (65 °C, 100 revolutions per minute) and kept for 4.5 h. The resultant sample was centrifuged twice at 6000 rpm for 10 min. The precipitate was redispersed into a CTAB solution (4 mL, 0.05 M), followed by the addition of ascorbic acid (1 mL, 0.1 M) and aqueous NaOH (1 mL, 0.2 M) under gentle shaking. Afterwards, aqueous $HAuCl_4$ (1.3 mL, 0.1 mM) was titrated into the solution using a syringe pump at a rate of 20 μL/min at room temperature. The reaction was left for another 20 min once the titration was completed. The product was centrifuged twice at 6000 rpm for 10 min and then redispersed into 4 mL of water, followed by the addition of CTAB (0.08 mL, 0.1 M), H_2O_2 (4 mL, 6 wt%) and $NH_3 \cdot H_2O$ (0.2 mL, 28 wt%). The resultant sample was left at room temperature for 1.5 h and then centrifuged at 4000 rpm for 10 min. The precipitate was redispersed into water (6 mL) for further characterization. For the synthesis of Au ONFs, the procedure was the same as that for the synthesis of Au CNFs except that aqueous NaOH (1 mL, 0.2 M) was replaced with HCl (1 mL, 0.1 M). For the synthesis of the multiple Au CNFs and ONFs, the procedure for the synthsis of Au CNFs and ONFs was repeated according to the final shapes.

Synthesis of the Au NBP/CNF/ONF@Ag nanorods and multiple CNF/ONF@Ag nanorods

In a standard synthesis, the obtained Au NBP/CNF/ONFs and multiple CNF/ONFs (2 mL, the longitudinal dipolar plasmon peak extinction value is ~0.83 when measured with a 0.5-cm cuvette) were collected by centrifugation at 7000 rpm for 10 min. The precipitate was redispersed into a CTAC solution (2 mL, 0.08 M), followed by the addition of $AgNO_3$ (0.01 M) and ascorbic acid (0.1 M) under gentle shaking. The volume of the $AgNO_3$ solution was varied from 10 μL to 600 μL. The volume of the ascorbic acid solution was the same as that of the $AgNO_3$ solution for each overgrowth experiment. The mixture solution was placed in an air-bath shaker (65 °C, 100 revolutions per minute) and kept for 4.5 h. The resultant sample was centrifuged twice at 6000 rpm for 10 min. The precipitate was redispersed into a CTAB solution (4 mL, 0.05 M) for further use. For the synthesis of t-ONF@Ag nanorods, the procedure was the same as that for the synthesis of Au ONF@Ag nanorods except that aqueous $AgNO_3$ (0.2 mM) was titrated into the solution using a syringe pump at a rate of 20 μL/min.

Instrumentation

Extinction spectra were measured on a Shimadzu UV-3600 Plus ultraviolet/visible/near-infrared spectrophotometer with plastic cuvettes of 0.5-cm optical path length. TEM imaging was carried out on a FEI Tecnai 12 microscope operated at 120 kV. HRTEM imaging, HAADF-STEM characterization and elemental mapping were performed on a FEI Tecnai F20 microscope operated at 200 kV and equipped with an Oxford energy-dispersive X-ray (EDX) analysis system.

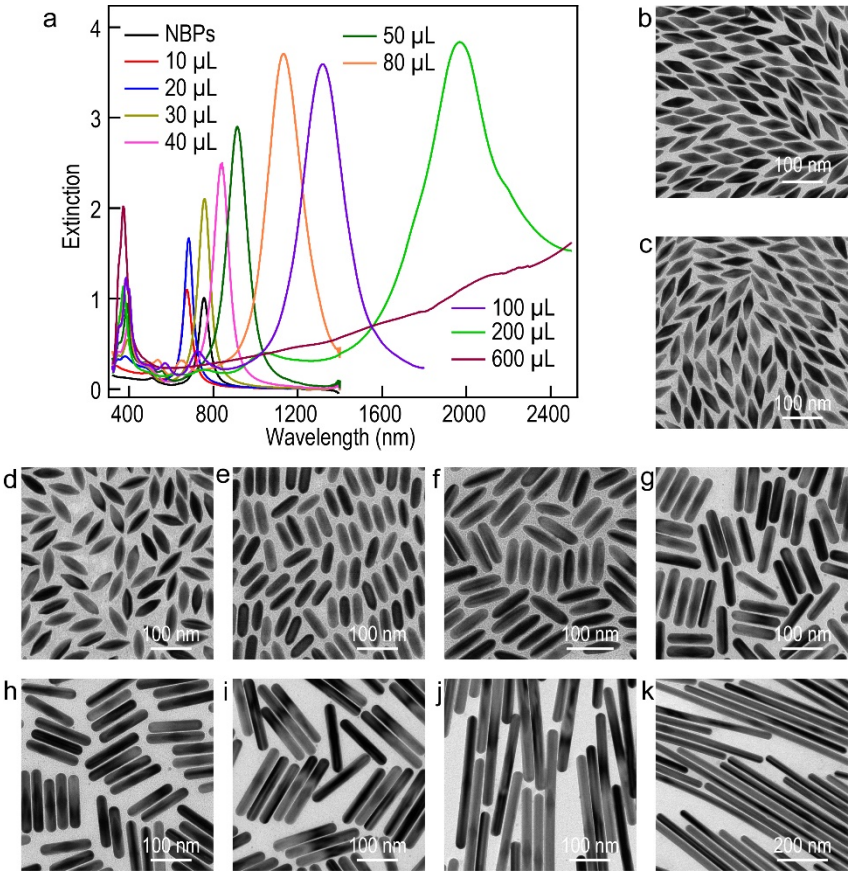

Fig. S1 Overgrowth of Ag on the Au NBPs. (a) Extinction spectra of the Au NBPs and NBP@Ag nanostructures with varied amounts of $AgNO_3$. (b–k) TEM images of the Au NBPs and NBP@Ag nanostructures produced with 10, 20, 30, 40, 50, 80, 100, 200, and 600 µL of $AgNO_3$, respectively.

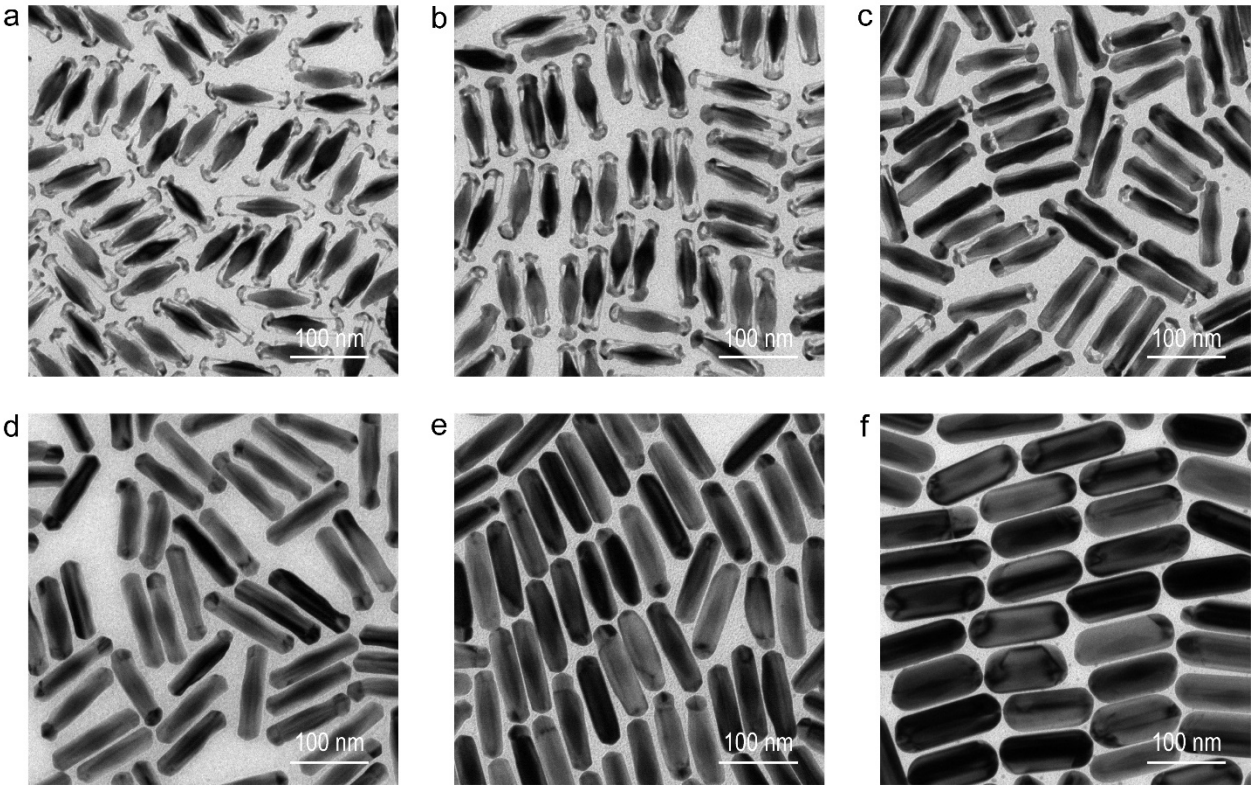

Fig. S2 Overgrowth of Ag on the Au NBPs in the presence of Au CNFs. (a–f) TEM images of the CNF@Ag nanostructures produced with 10, 20, 30, 50, 80, and 200 μL of $AgNO_3$, respectively.

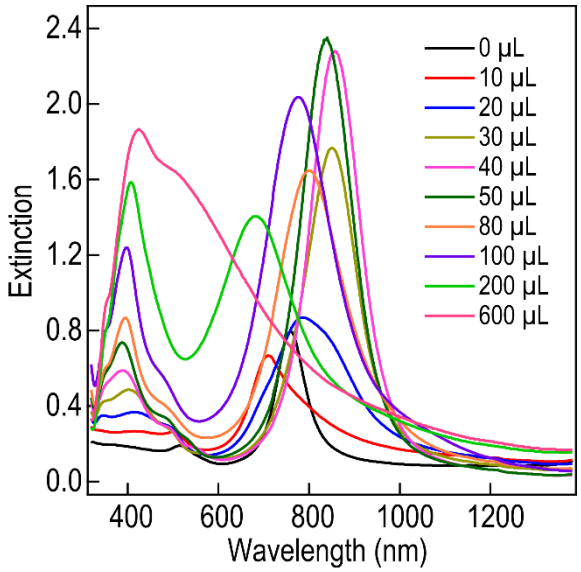

Fig. S3 Extinction spectra of the CNF@Ag nanostructures produced with varied amounts of $AgNO_3$.

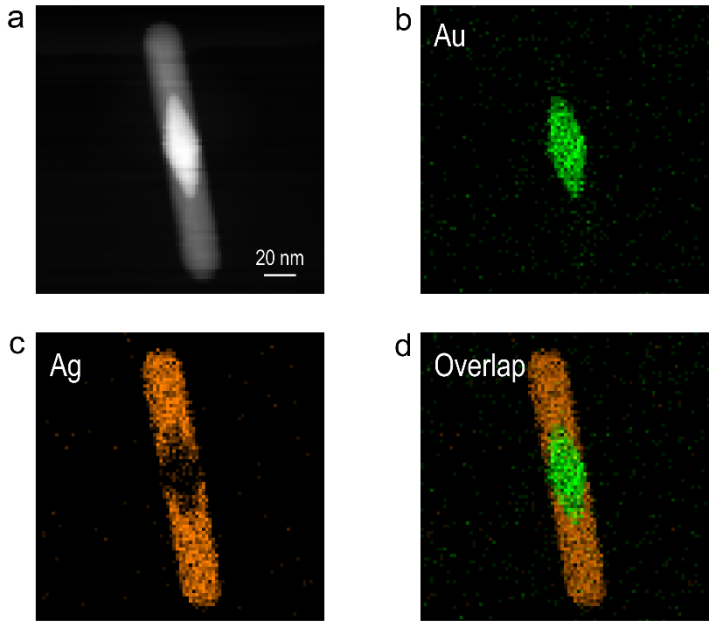

Fig. S4 (a–d) HAADF-STEM and elemental mapping images of a single 100-μL NBP@Ag nanorod. The elemental mapping images have the same size scale as the HAADF-STEM image.

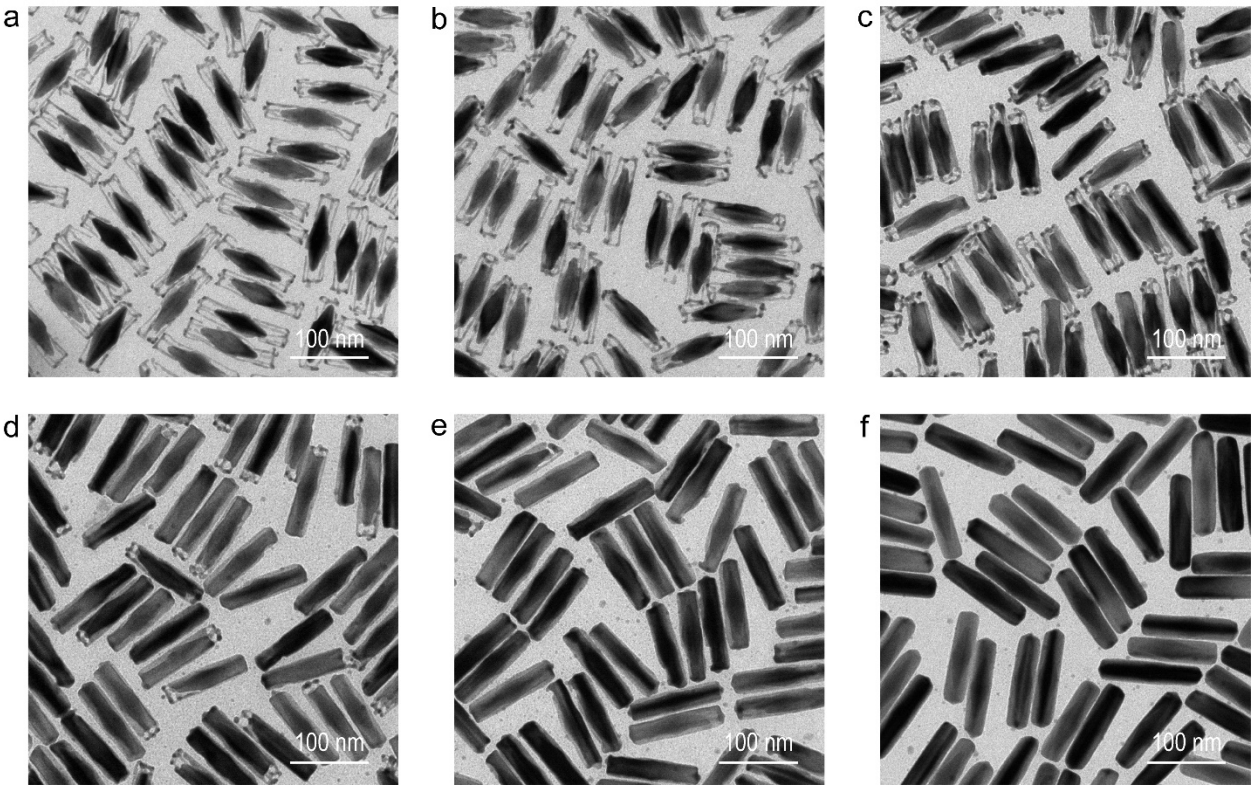

Fig. S5 Overgrowth of Ag on the Au NBPs in the presence of Au ONFs. (a–f) TEM images of the ONF@Ag nanostructures produced with 10, 20, 30, 40, 50, and 80 μL of $AgNO_3$, respectively.

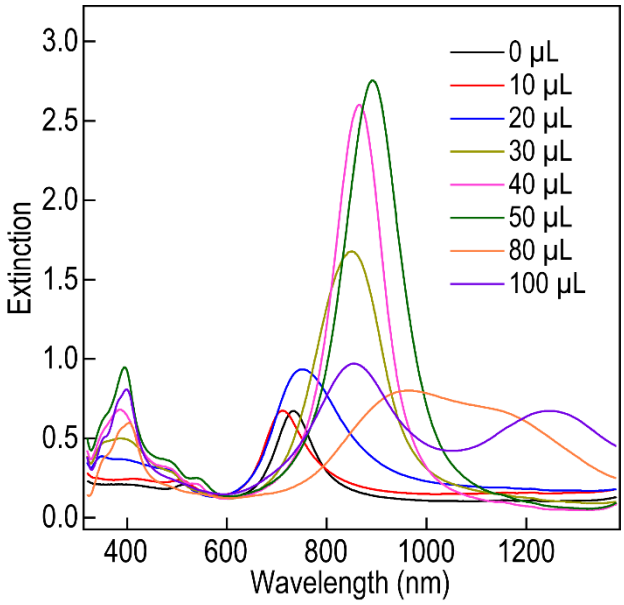

Fig. S6 Extinction spectra of the ONF@Ag nanostructures produced with varied amounts of $AgNO_3$.

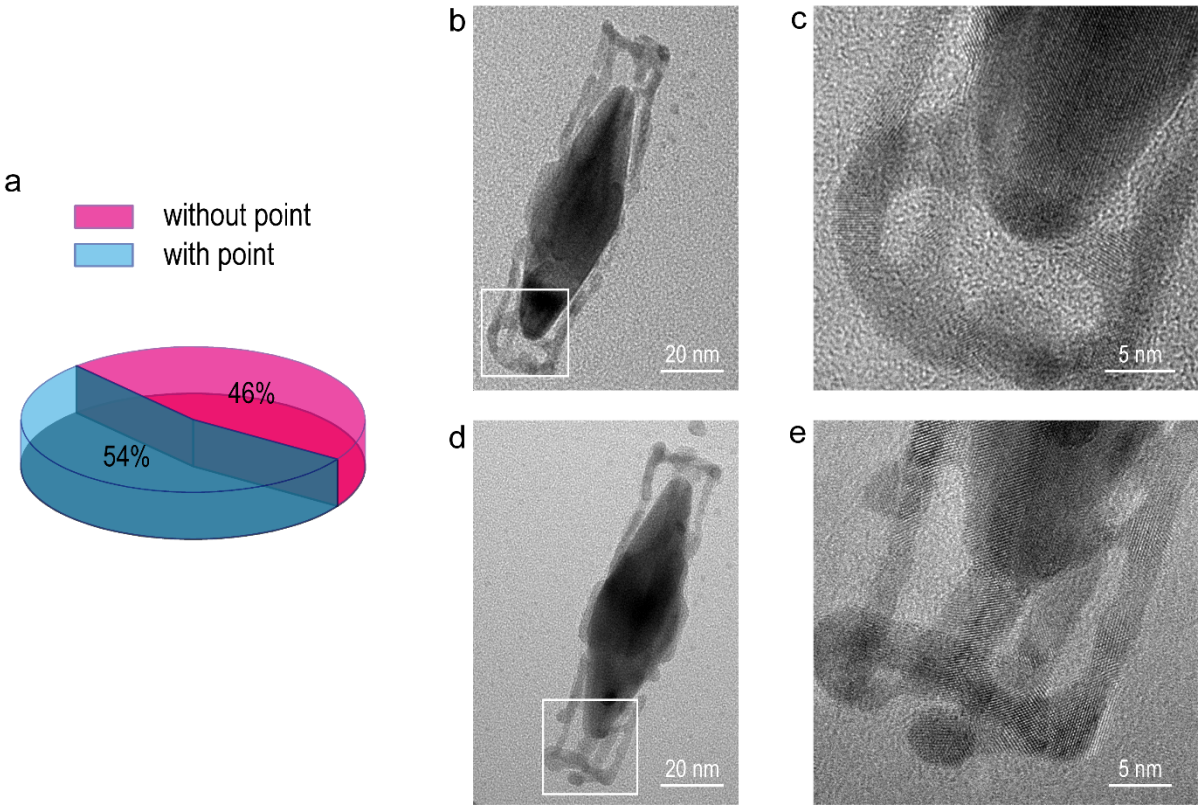

Fig. S7 Characterization of the Au ONFs. (a) The proportion between the Au ONFs with and without Au particles located at the head. (b) HRTEM image of a single Au ONF without Au particles located at the head. (c) HRTEM image recorded in the region indicated with the white box in (b). (d) HRTEM image of a single Au ONF with Au particles located at the head. (e) HRTEM image recorded in the region indicated with the white box in (d).

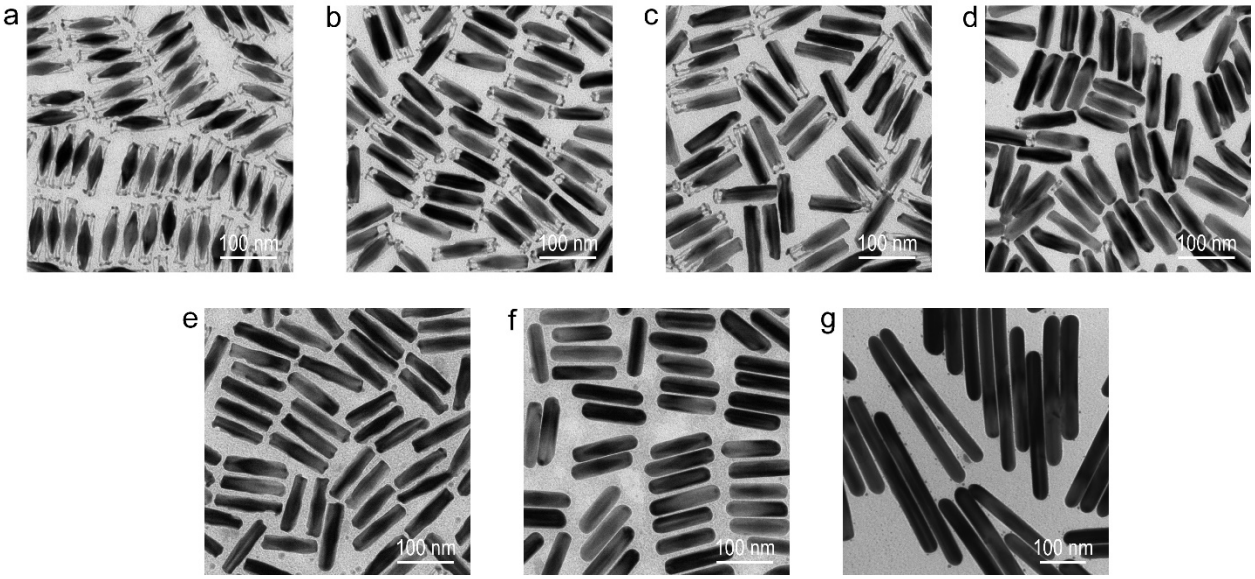

Fig. S8 Overgrowth of Ag on the Au NBPs in the presence of Au ONFs with the titration of $AgNO_3$. (a–g) TEM images of the t-ONF@Ag nanostructures produced with 10, 20, 30, 40, 50, 80, and 200 μL of $AgNO_3$, respectively.

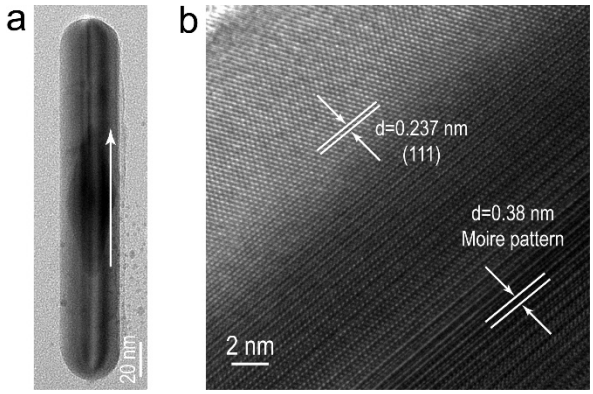

Fig. S9 Characterization of the 100-μL t-ONF@Ag nanorods. (a) TEM image. (b) HRTEM image.

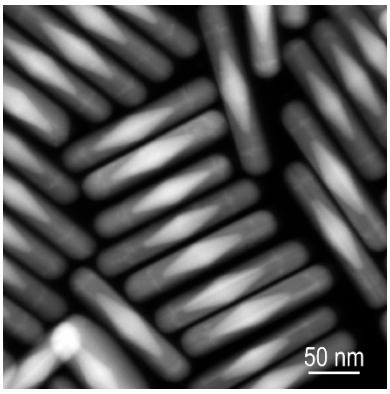

Fig. S10 HAADF-STEM image of the 100-µL t-ONF@Ag nanorods.

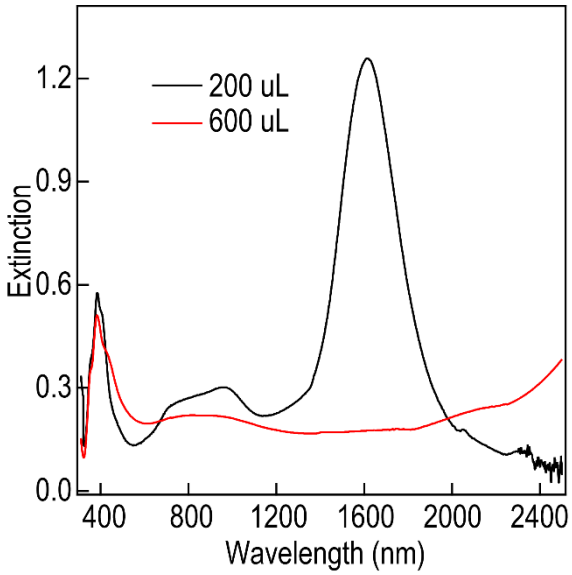

Fig. S11 Extinction spectra of the 200-µL and 600-µL t-ONF@Ag nanorods.

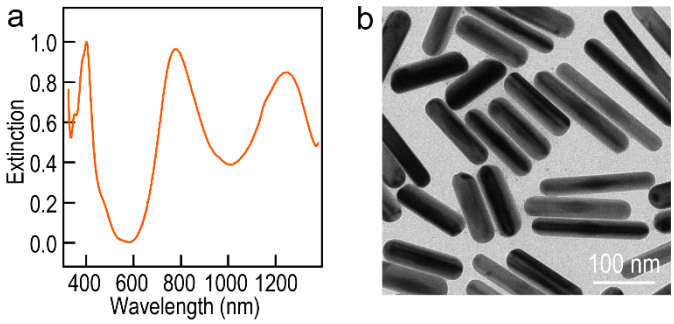

Fig. S12. Characterization of the t-CNF@Ag nanorods. (a) Extinction spectrum of the 100-µL t-CNF@Ag nanorods. (b) TEM images of the t-CNF@Ag nanorods produced with 100 µL of $AgNO_3$.

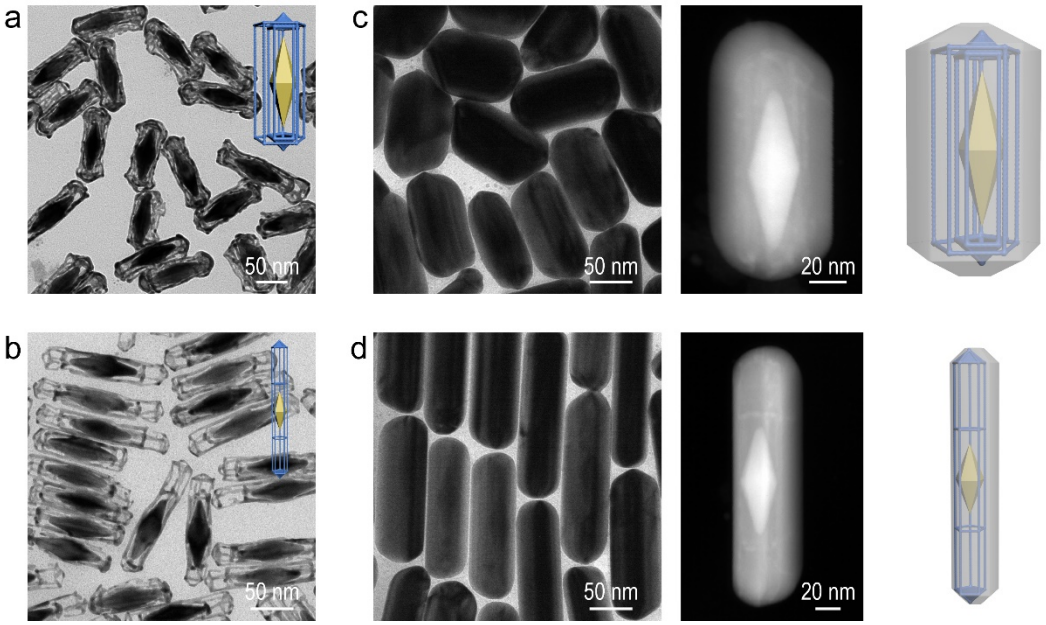

Fig. S13 Characterization of various templates and corresponding Ag nanorods. (a, b) TEM images of closed-open nanoframes (CONFs) and open-closed nanoframes (OCNFs), respectively. (c, d) TEM, HAADF-STEM and model images of CONF@Ag nanorods and OCNF@Ag nanorods, respectively.