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Supporting Information

Facile synthesis of Ag@Au core-sheath nanowires for improved stability against oxidation†

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Experimental Section

Chemicals and Materials. *L*-ascorbic acid (>99.0%), sodium hydroxide (NaOH, >98%), poly(vinyl pyrrolidone) (PVP, MW ≈ 1,300,000 and 55,000), gold(III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, >99.9%), iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, >98%), and hydrogen peroxide solution (H_2O_2, 30% w/w in H_2O) were all obtained from Sigma-Aldrich (St. Louis, MO). Oxygen (O_2, ultra high purity) was purchased from Nexair (Memphis, TN). All chemicals were used as received. Deionized water with a resistivity of 18.2 MΩ·cm at room temperature was used throughout the experiments.

Synthesis of Ag Nanowires. The silver nanowires were synthesized by following a recently reported protocol with slight modifications.[1] In a typical synthesis, two solutions of $AgNO_3$ (100 mM) and NaBr (250 mM) in ethylene glycol (EG) were prepared. At the same time, 250 mg PVP (MW ≈ 1,300,000) was dissolved in 20 mL of EG in a 50 mL flask and heated in an oil bath at 170 °C for 60 min under magnetic stirring (320 rpm). After 60 min, 120 μL of the NaBr solution in EG was added into the flask. After another 5 min, 15 mL of the $AgNO_3$ solution in EG was added using a syringe pump at an injection rate of 1.5 mL/min. The synthesis was quenched by immersing the flask in an ice water bath 35 min after the introduction of $AgNO_3$ solution. The solid products were crashed out with acetone, washed twice with water, and finally re-dispersed in 30 mL of water. The suspension was centrifuged at a speed of 800 rpm for 15 min to remove Ag nanoparticles larger than 100 nm in size. The supernatant containing Ag nanowires was collected while the precipitate (containing nanoparticles and some nanowires) was discarded. The washing procedure was repeated three additional times. Finally, the Ag nanowires were collected by centrifugation at 3,000 rpm for 10 min and re-suspended in 5 mL of water.

Preparation of $Au(OH)_4^-$ solution. We prepared an aqueous $Au(OH)_4^-$ solution by mixing aqueous solutions of $HAuCl_4$ and NaOH. Specifically, 0.1 mL of aqueous $HAuCl_4$ (20 mM), 2 mL of aqueous NaOH (200 mM), and 17.9 mL water were added into a 20 mL vial, and the mixture was incubated at room temperature (22 °C) on an orbital shaker for 1 h. This solution contained $Au(OH)_4^-$ at a concentration of 0.1 mM, together with NaOH at 20 mM.

Synthesis of Ag@Au core-sheath nanowires. In a typical synthesis, 1 mL of aqueous PVP (MW ≈ 55,000, 40 mg/mL) and 2 mL water were mixed in a 20 mL glass vial. The mixture was then heated to 60 °C under magnetic stirring at a speed of 400 rpm. After 2 min, 500 μL of aqueous AA (100 mM) and 500 μL of aqueous NaOH (200 mM) were added sequentially, followed by 70 μL of the aqueous suspension of Ag nanowires. The aqueous solution of $Au(OH)_4^-$ (0.1 mM) and NaOH (20 mM) was then titrated using a syringe pump at an injection rate of 0.02 mL/min. After a certain amount of the $Au(OH)_4^-$ solution had been added, the solid products were collected by centrifugation at 3,500 rpm for 10 min, washed twice with water, and finally re-dispersed in 0.5 mL of water. During the synthesis, it was critical to introduce the Au^{3+} precursor solution through a syringe pump with an injection rate of 0.02 mL/min. The slow injection rate, together with the low concentration of Au^{3+} precursor (0.1 mM), ensured that the concentration of Au atoms in the reaction solution was kept below supersaturation. As a result, self-nucleation of Au^0 did not occur during the Au coating process.

Etching of Ag@Au core-sheath nanowires with O_2. To a 1.5 mL centrifuge tube, 0.5 mL of water was added, followed by 0.5 mL of the as-prepared suspension of Ag@Au core-sheath nanowires. After mixing, O_2 gas was bubbled through the solution for 1 h. Finally, the remaining solid was collected for further characterization.

Etching of Ag@Au core-sheath nanowires with H_2O_2. To a 1.5 mL centrifuge tube, 0.5 mL of the as-obtained suspension of Ag@Au core-sheath nanowires was added, followed by 0.5 mL of 5% aqueous H_2O_2. The initial concentration of H_2O_2 in the final reaction mixture was 2.5% (*i.e.*, 0.85 M). The suspension was vortexed for 5 s to ensure thorough mixing and then kept at room temperature for 1 h. Afterwards, the mixture was centrifuged at 3,500 rpm for 10 min to separate the solid products. After removing the supernatant, the remaining Ag@Au core-sheath nanowires were collected and re-dispersed in 0.5 mL of water for further characterization.

Etching of Ag@Au core-sheath nanowires with aqueous $Fe(NO_3)_3$. The procedure was the same as what was used for H_2O_2 etching except that the H_2O_2 was replaced with 0.5 mL of aqueous $Fe(NO_3)_3$ (2 mM). The initial concentration of $Fe(NO_3)_3$ in the final reaction mixture was 1 mM.

Instrumentation and characterization. UV-vis spectra were collected on a Cary 60 spectrometer (Agilent Technologies), and the metal contents were quantified using inductively coupled plasma mass spectrometry (ICP-MS, NexION 300Q, Perkin Elmer). TEM images were collected on a Hitachi HT7700 microscope operated at 120 kV by drop casting samples onto carbon-coated Cu TEM grids. High-resolution TEM imaging, high-angle annular dark-field (HAADF) imaging, and energy-disperse X-ray spectroscopy (EDS) analysis were all performed on an aberration-corrected JEOL JEM 2200FS STEM/TEM microscope operated at 200 kV, equipped with a CEOS probe detector (Heidelberg, Germany) and a Bruker-AXS silicon drift detector (SDD).

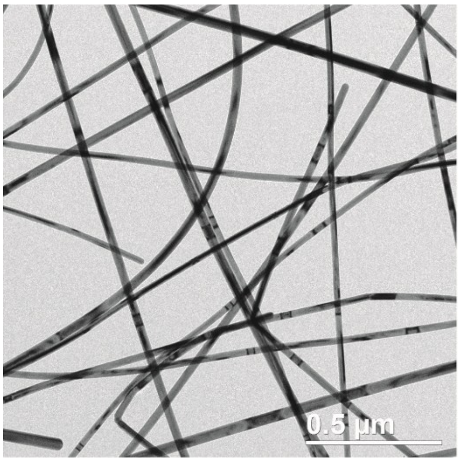

Fig. S1 TEM image of the pristine Ag nanowires before Au deposition.

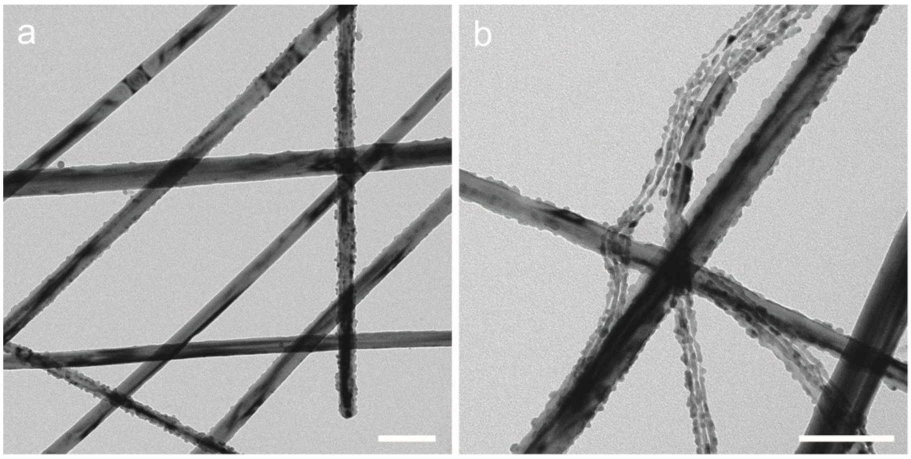

Fig. S2 TEM images of the Ag@Au core-sheath nanowires synthesized at room temperature (a) before and (b) after H_2O_2 etching. The scale bars are 100 nm.

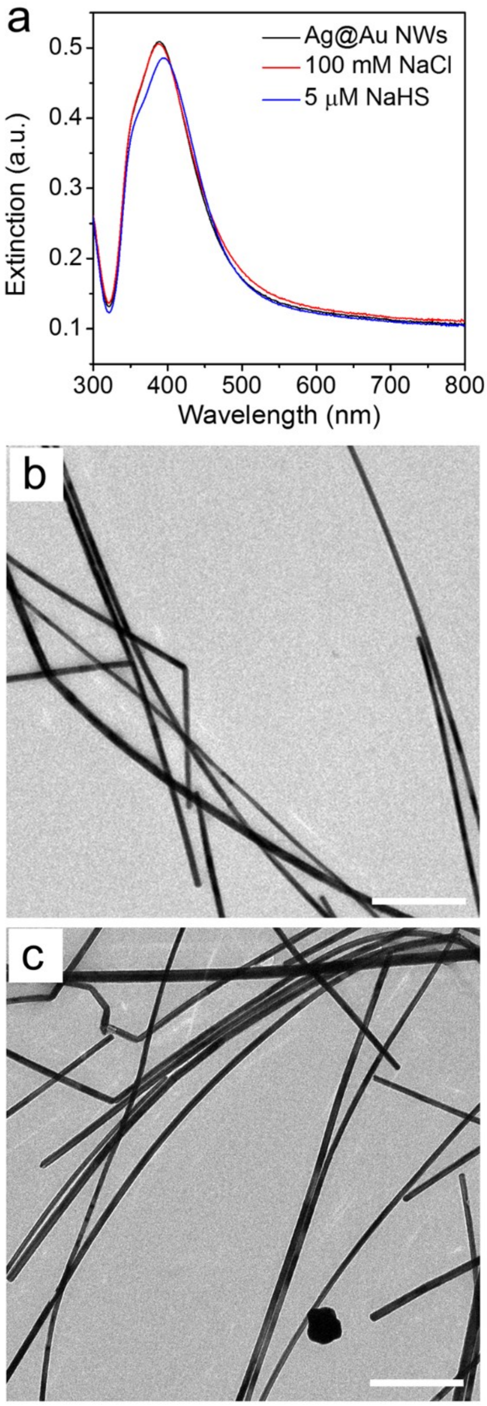

Fig. S3 (a) UV-vis spectra of the Ag@Au core-sheath nanowires before and after incubation with two different aqueous solutions: 100 mM NaCl and 5 μM NaHS for 2 h, respectively. (b) TEM image of the Ag@Au core-sheath nanowires after incubation with 100 mM NaCl aqueous solution. (c) TEM image of the Ag@Au core-sheath nanowires after incubation with 5 μM NaHS aqueous solution. The scale bars are 500 nm.

Table 1 Gold contents in Ag@Au core-sheath nanowires prepared by adding different volumes of $Au(OH)_4^-$ solution (0.5, 1.0, 1.5 and 2.0 mL) as determined by ICP-MS.

Volume of 0.1 mM $Au(OH)_4^-$ solution added (mL)	% Au in Ag@Au core-sheath nanowires
0.5	5.1
1.0	6.6
1.5	7.6
2.0	10.8

Reference

1. R. R. Silva, M. Yang, S.-I. Choi, M. Chi, M. Luo, C. Zhang, Z.-Y. Li, P. H. C. Camargo, S. J. L. Ribeiro and Y. Xia, *ACS Nano*, 2016, **10**, 7892.