

SUPPLEMENTARY INFORMATION

**Twin-mediated epitaxial growth of highly lattice-mismatched Cu/Ag
core-shell nanowires**

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Experimental details

Fabrication of porous anodic aluminum oxide membranes

A porous anodic aluminum membrane (AAO) with regular pore array (60 – 80 nm in diameter) were fabricated from a 0.127 mm-thick Al foil (99.9995%, Strem Chemicals) by a two-step anodization process.^{1,2} The Al foil was cleaned with acetone (95%, Echo Chemical), isopropyl alcohol (95%, Echo Chemical) and deionized water, and then electropolished in a 1:4 (volume ratio) mixture of HClO₄ (70%, Sigma-Aldrich) and C₂H₅OH (99.5%, Echo Chemical) for 20 s at a voltage of 40 V. The first anodization process was conducted in a 0.3 M oxalic acid (99.5%, Showa Kako) at 10 °C for 30 min under a constant applied voltage of 40 V. The oxide film was then removed by dipping the foil in a solution of 6 wt.% H₃PO₄ (70%, J.T. Baker Chemicals) and 1.8 wt.% K₂Cr₂O₇ (99.5%, ProChem Inc.) at 60 °C for 30 min. The second anodization process was carried out under the same electrochemical condition for 12 h to form a 40 μm-thick AAO film with regular pore array. Consequently, a 200 nm-thick Ni layer was vaporated at one side of AAO by e-gun deposition as a contact electrode for subsequent electroplating of Cu nanowires. The AAO (Ni side) was glued with epoxy resin (QuickStick™ 135, Electron Microscopy Sciences) on a glass substrate using a hot plate at the temperature of 135 °C. The backside AAO was removed by 1 M NaOH (97%, Showa Kako) followed by etching the residual Al in a solution of 0.5 M NiCl₂ (99.3%, Alfa Aesar) and 1 M HCl (37 %, Scharlau) at room temperature. Finally, the AAO template with uniform open pores was achieved by removing the barrier oxide in a 5 wt.% H₃PO₄ solution at room temperature.

Electrochemical deposition of copper nanowires (CuNWs)

Two types of CuNWs with nanocrystalline (nc) and nanotwinned (nt) features were electrodeposited into the AAO template by direct-current and pulse-current plating,

respectively.^{1,2} A standard three-electrode cell is setup with the AAO membrane at working electrode, a graphite bar at counter electrode and a saturated calomel electrode (SCE) at reference electrode, respectively. The electrolyte is 0.7 M CuSO₄ (99.5%, Showa Kako) solution with the pH value adjusted to 3 ~ 4. The plating cell is kept at a temperature-controlled tank with magnetic stirring. The nc-CuNWs were electroplated at room temperature by applying a direct current of 0.015 A/cm² in density, while the nt-CuNWs at 0 °C by applying a pulse current of 0.4 A/cm² in peak density with a duty cycle of 0.02 s (on) / 1 s (off). Finally, both types of CuNWs were retrieved after dissolving the AAO template in NaOH solution.

Synthesis of Ag-coated CuNWs

A 10 mL solution consisting of 10 mg CuNWs, 5 mg polyvinylpyrrolidone (PVP, wt ~ 10000, Sigma-Aldrich) and 1 g ascorbic acid (> 98%, Alfa Aesar) was stirred in a round bottom scintillation vial with a magnetic stirrer at 200 rpm for 15 min. Next, a 0.7 mM silver nitrate solution containing 0.0056 mM citric acid monohydrate was gradually added into the CuNW-contained suspension using titration at a rate of 1 mL/min. The reaction was complete when the color of suspension varied from reddish to dark red. The suspension was centrifuged at 4000 rpm for 20 min to obtain an aggregate of Ag-coated CuNWs. The aggregate was then rinsed by ethanol several times to remove the residual PVP around the Ag-coated CuNWs.

Characterization of Ag-coated CuNWs

The Ag-coated CuNWs were kept in an anhydrous ethanol for storage. Prior to TEM inspection, a drop of nanowire-contained suspension was dipped onto a Mo-grid specimen holder coated with a carbon film, and dried under ambient condition for 20 min. These Ag-coated CuNWs were examined by Cs-corrected field emission transmission electron microscopy (JEM-ARM200FTH, JEOL). The electrical property of Ag-coated CuNWs were measured by dipping a

drop of suspension on a test chip with pre-patterned Au pads on a $\text{Si}_3\text{N}_4/\text{SiO}_2/\text{Si}$ substrate. The electrical connection between Au pads and the Ag-coated CuNW was achieved by depositing Pt wires using focused ion beam (FIB) techniques. A semiconductor characterization system (Keithley 4200) was used to measure the I-V behavior and electrical resistivity of the Ag-coated CuNW.

Electrical measurement of Ag-coated CuNWs

The electrical resistances were obtained from the I-V measurements of individual Cu/Ag core-shell nanowires using a four-probe method (Keithley 4200-SCS). Each resistance value was averaged from three I-V measurement results. Table S1 shows the electrical resistance and physical length of the individual nc-CuNW/Ag and nt-CuNW/Ag core-shell nanowire measured.

Table S1. Electrical resistance and physical length of the individual nc-CuNW/Ag and nt-CuNW/Ag core-shell nanowire measured at room temperature

Type	Resistance (Ω)	Length (μm)	R/L ($\times 10^7 \Omega/\text{m}$)
nt-CuNW/Ag	45.7	4.28	1.15 ± 0.23
nt-CuNW/Ag	46.3	4.46	
nt-CuNW/Ag	89.0	5.8	
nt-CuNW/Ag	93.6	10	
nc-CuNW/Ag	139.62	3.82	3.02 ± 0.64
nc-CuNW/Ag	136.22	5.72	

Supplementary Figures

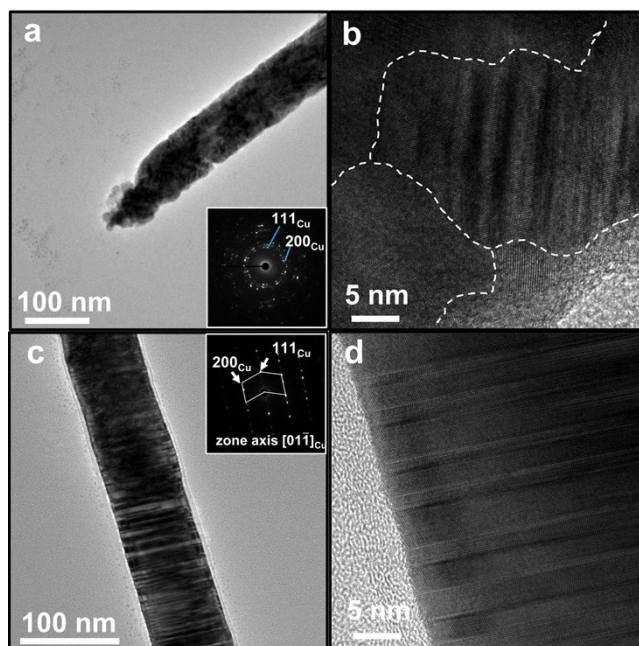


Figure S1. TEM and HRTEM images of (a,b) nc-CuNWs and (c,d) nt-CuNWs. The insets of (a) and (c) are corresponding SAED patterns.

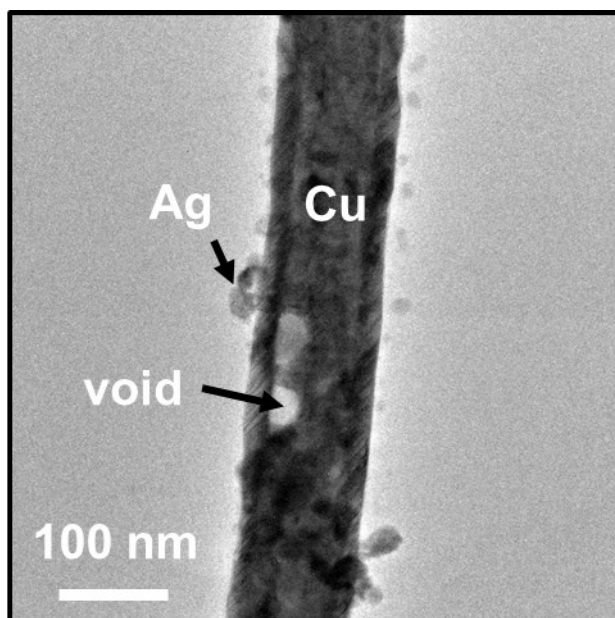


Figure S2. Galvanic replacement reaction induced Ag deposition and cavitation for nc-CuNWs.

References:

1. T.C. Chan, Y.M. Lin, H.W. Tsai, Z.M. Wang, C.N. Liao, Y.L. Chueh, *Nanoscale*, 2014, 6, 7332.
2. C.L. Huang, W.L. Weng, C.N. Liao and K. Tu, *Nat. Commun.*, 2018, 9, 340.