Electronic Supplementary Material (ESI) for Nanoscale.

SUPPLEMENTARY INFORMATION

Enhanced photolysis stability of Cu_2O grown on Cu nanowires with nanoscale twin boundaries

Chun-Lung Huang, Wei-Lun Weng, Yan-Syun Huang and Chien-Neng Liao *

Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC

*To whom correspondence should be addressed. Email: cnliao@mx.nthu.edu.tw

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 0.2 mm-thick Al foil (99.9995%, Strem Chemicals) by a two-step anodization process. 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 $HClO_4$ (70%, Sigma-Aldrich) and C_2H_5OH (99.5%, Echo Chemical) for 10 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 ℃ 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.% H_3PO_4 (70%, J.T. Baker Chemicals) and 1.8 wt.% $K_2Cr_2O_7$ (99.5%, ProChem Inc.) at 60 ℃ 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^{TM} 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 $NiCl_2$ (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.% H_3PO_4 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.

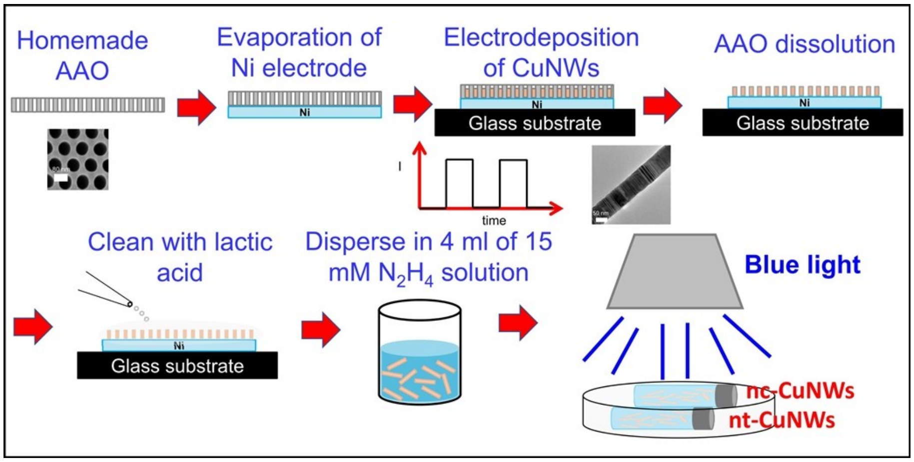
A standard three-electrode cell is setup with the AAO membrane at working electrode, a graphite bar at counter electrode and a saturated calomel electrode (SCE) at reference electrode, respectively. The electrolyte is 0.7 M $CuSO_4$ (99.5%, Showa Kako) solution with the pH value adjusted to 3 ~ 4. The 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/cm^2 in density, while the nt-CuNWs at 0 °C by applying a pulse current of 0.4 A/cm^2 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.

TEM analysis of CuNWs

Both nc-CuNWs and nt-CuNWs were collected and keeped in anhydrous ethanol. Samples for TEM were prepared by dropping the CuNWs suspension onto a Mo-grid specimen holder that was coated with a carbon film, and dried under ambient condition for 20 min. These CuNWs were examined by high-resolution TEM (HRTEM, JEM-3000F, JEOL) after exposed to air ambient at room temperature for different durations.

Light exposure testing of CuNWs in an aqueous solution

The fabrication process of nc-CuNWs and nt-CuNWs in aqueous solution for light exposure testing is shown below. After dissolving the AAO template, we dipped several drops of lactic acid to clean CuNW surface for 10 s. Then, the CuNWs were dispersed in DI water using ultrasonic device. Next, both types of CuNWs of 3.89 mg were individually kept in a glass vial containing 4 ml of 15 mM N_2H_4 solution and shun with blue light (λ= 455 – 465 nm) for different duration up to 192 h. The tested vials with CuNWs suspension were not agitated during the storage and light exposure. They were agitated only when photo pictures were taken at different exposure stages.


Homemade AAO
50 nm
Evaporation of Ni electrode
Ni
Electrodeposition of CuNWs
Ni
Glass substrate
AAO dissolution
Ni
Glass substrate
I
time
50 nm
Clean with lactic acid
Ni
Glass substrate
Disperse in 4 ml of 15 mM N_2H_4 solution
Blue light
nc-CuNWs
nt-CuNWs

Supplementary Figures

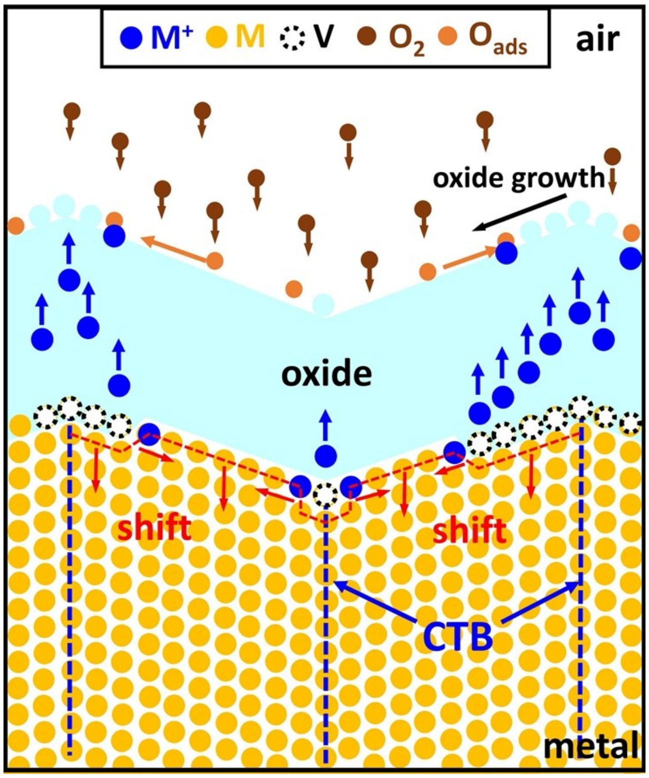


Figure S1. A schematic illustration of how a void-free oxide layer forms on twin-induced faceted planes of the nt-CuNWs. Vacancies are orderly absorbed at Cu/Cu_2O interface, leading to Kirkendall shift and void-free feature. A Cu_2O layer is epitaxially grown on the nt-CuNWs owing to very slow out-diffusion of Cu cations and low nucleation site density on oxide surface.

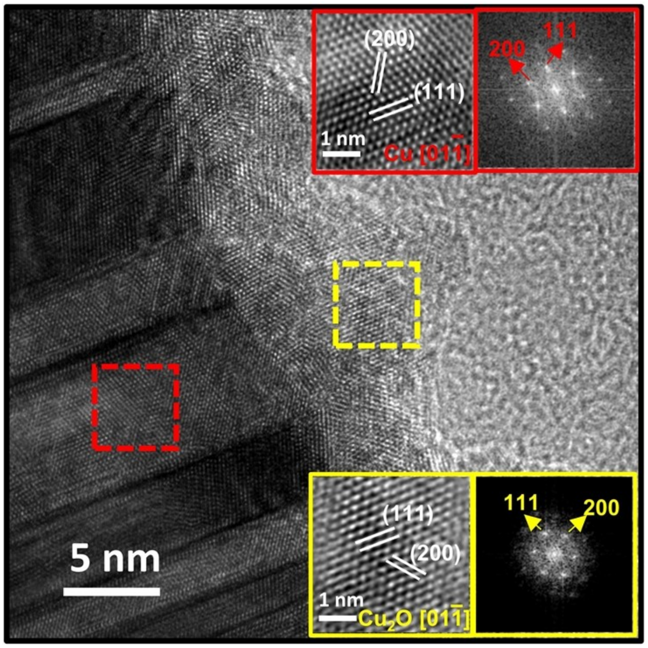


Figure S2. HRTEM image of nt-CuNWs. The insets are atomic images and electron diffraction patterns of Cu (red box) and Cu_2O (yellow box) obtained by fast Fourier transform (FFT) technique.

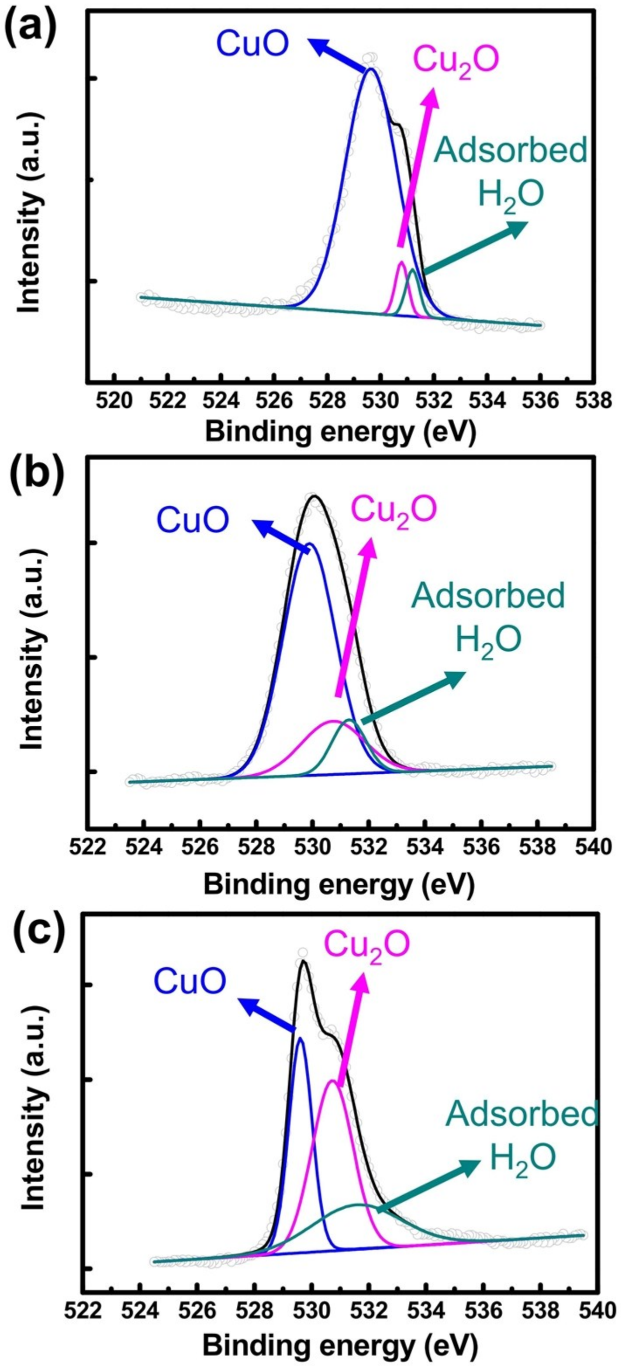


Figure S3. XPS O 1s spectra of the nt-CuNWs kept (a) in the air for less than 1 day; (b) in dry O_2 for 1 day; (c) in saturated water vapor for 1 day.

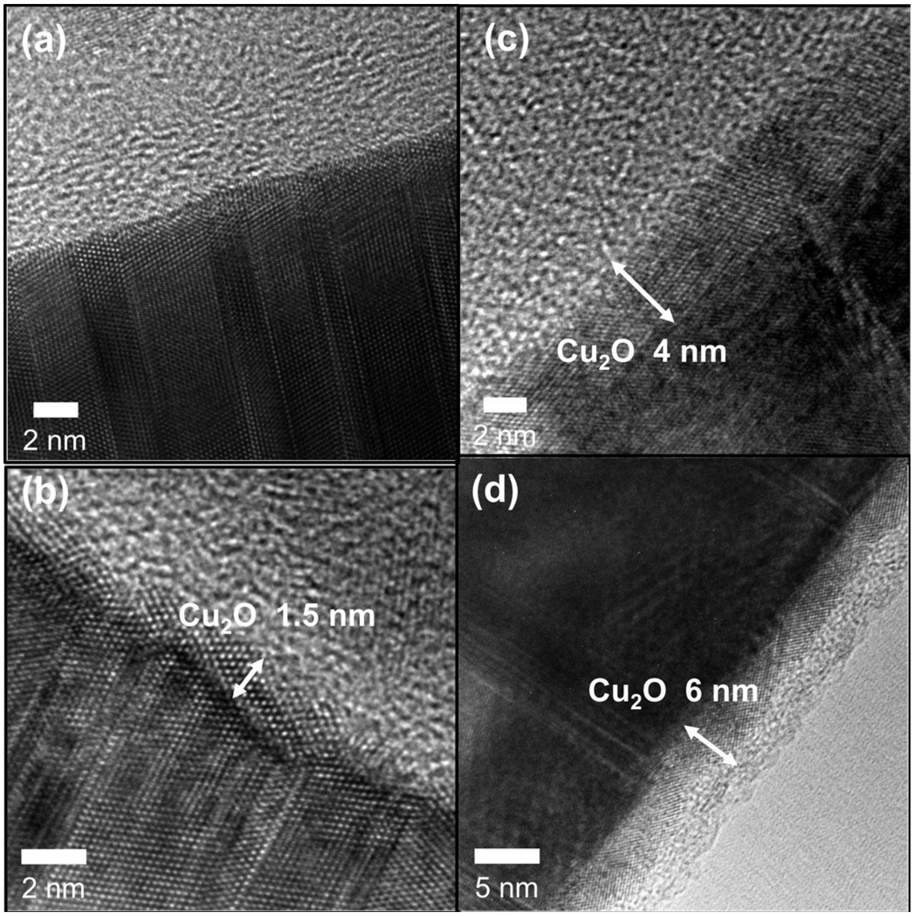


Figure S4. HRTEM images of nt-CuNWs oxidized in air at different temperature and duration. (a) Fresh nt-CuNWs; (b) nt-CuNWs treated at 65 °C for 14 h; (c) nt-CuNWs treated at 90 °C for 7 h; (d) nt-CuNWs treated at 150 °C for 1 h.