

Supporting Information

ZnO/CuO Heterojunction Branched Nanowires for Photoelectrochemical Hydrogen Generation

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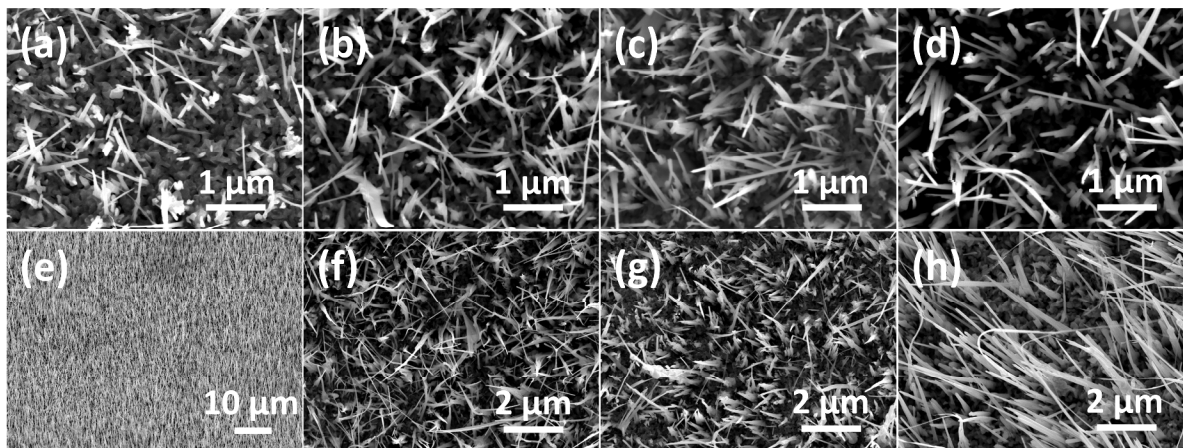


Figure S1. Top-view SEM images of CuO NW arrays grown at 400°C on Cu foil for different annealing times; (a) 2h, (b) 3h, (c) 4h, and (d) 5h. (e) Low-magnification tilted-view SEM image of 5h-400°C-CuO NWs on Cu foil. Top-view SEM images of CuO NW arrays grown for 4h on Cu foil at different annealing temperatures; (f) 400°C, (g) 450°C, and (h) 500°C.

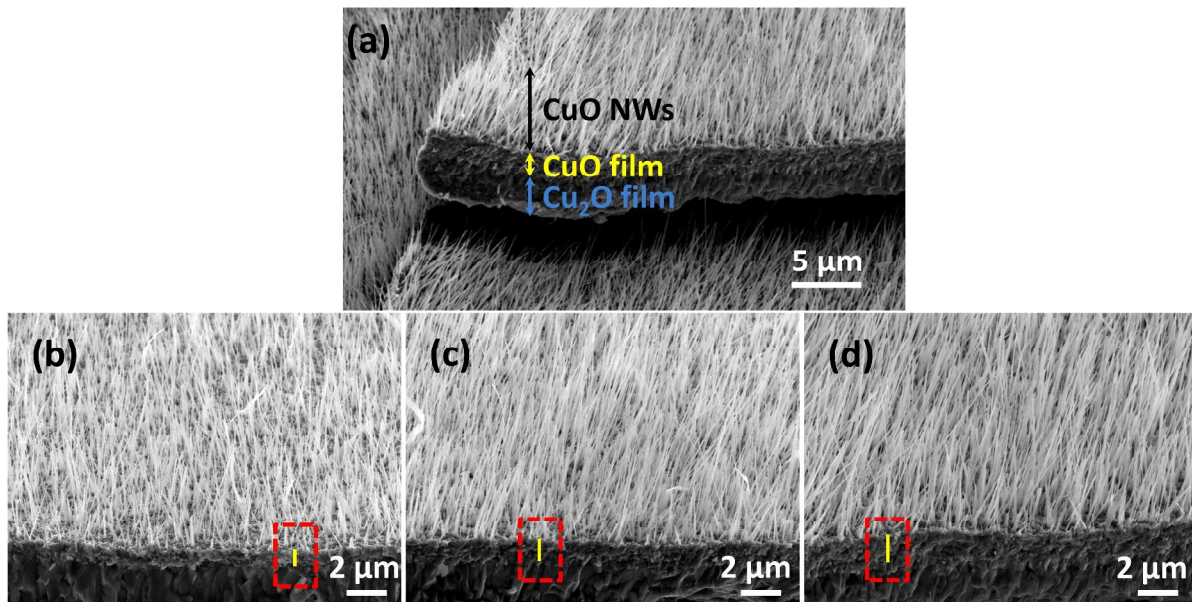


Figure S2. (a) SEM image of 5h-400°C-CuO NWs on Cu foil showing formation of three different copper oxide layers on the Cu substrate. SEM images of CuO NWs grown at 400°C on Cu foil for different annealing times ((b) 2h, (c) 3h, and (d) 5h). For longer annealing time, the CuO film thickness increases.

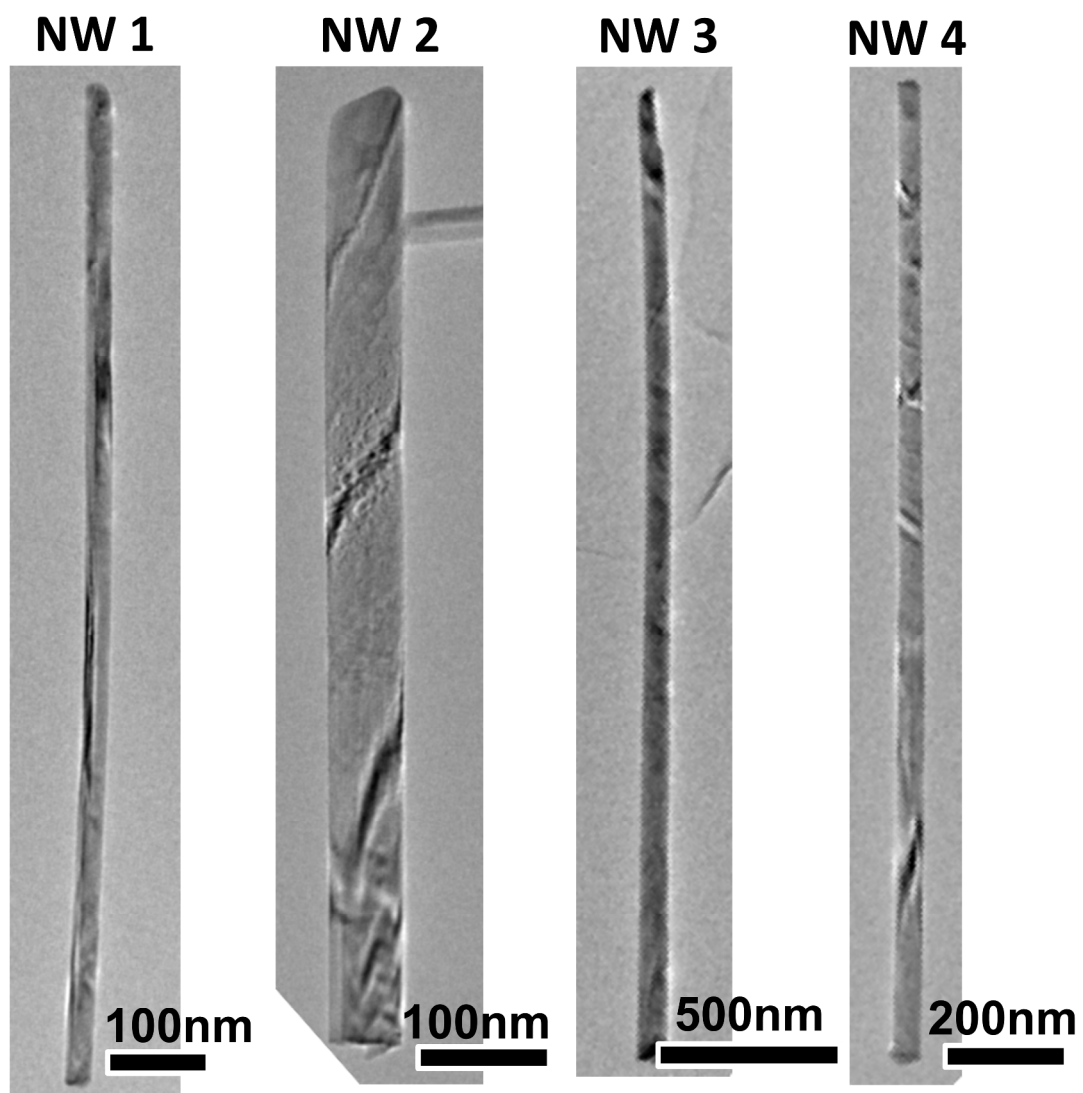


Figure S3. Low-magnification TEM images of 4h-400°C-CuO NWs showing different sizes for NWs.

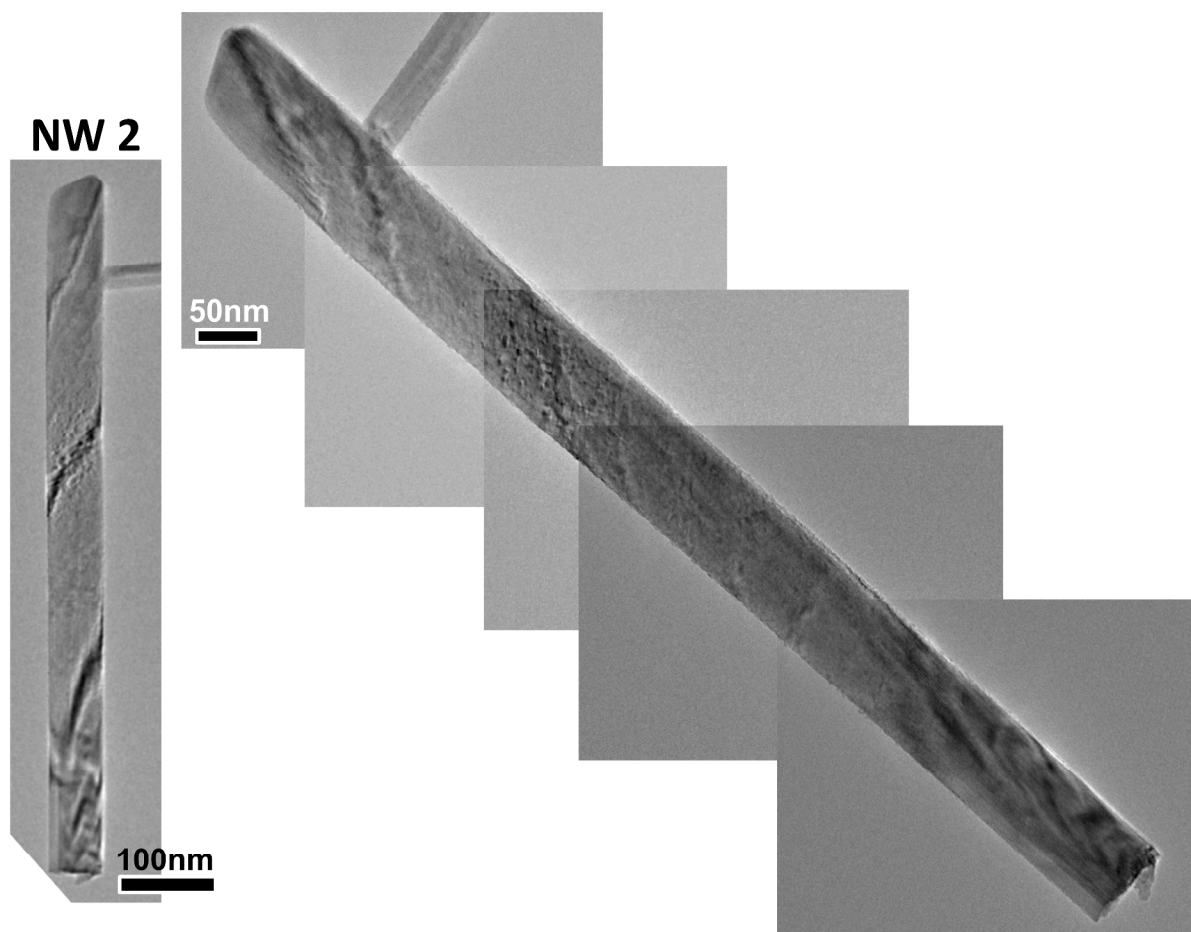


Figure S4. Partly-magnified TEM image of a single CuO NW (NW 2 in Figure S3 which is also shown here as reference) consisting of five separate high-magnification images closely showing different parts of CuO NW from the bottom to the top of NW.

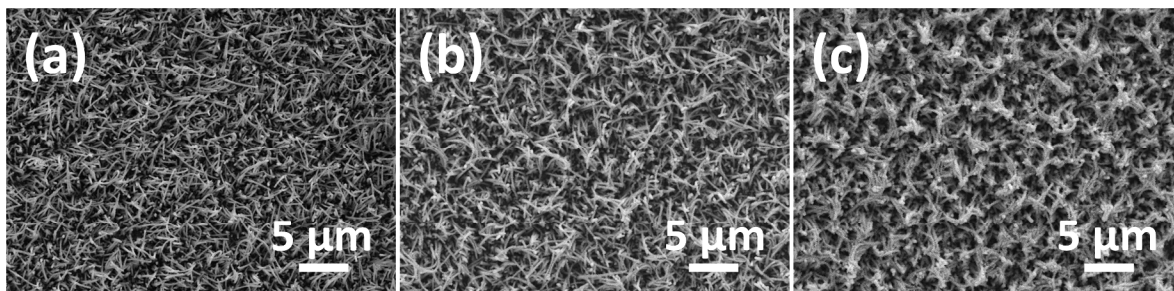


Figure S5. Top-view SEM images of ZnO/CuO b-NWs on Cu foil with 3h-400°C-CuO NW cores, and different ZnO NW branches ((a) 5m-ZnO, (b) 10m-ZnO, (c) 15m-ZnO).

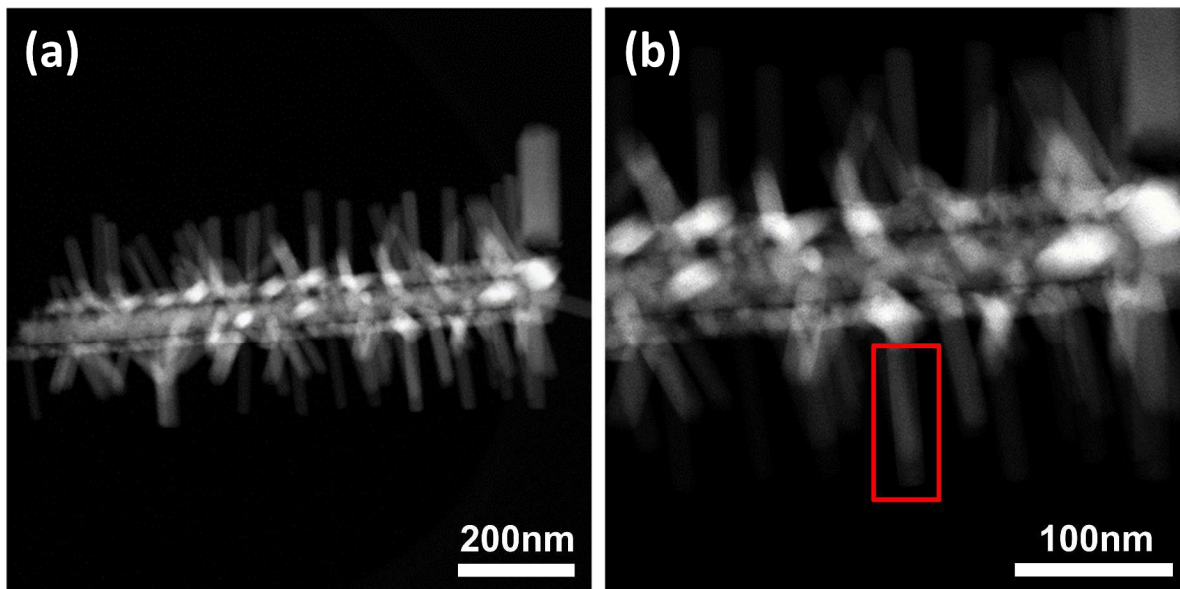


Figure S6. (a)-(b) Low-magnification annular dark field STEM images of a single ZnO/CuO b-NW (the same b-NW shown in Figure 4a in the main text). The labeled ZnO NW in (b) is the same ZnO NW shown in Figure 4b in the main text.

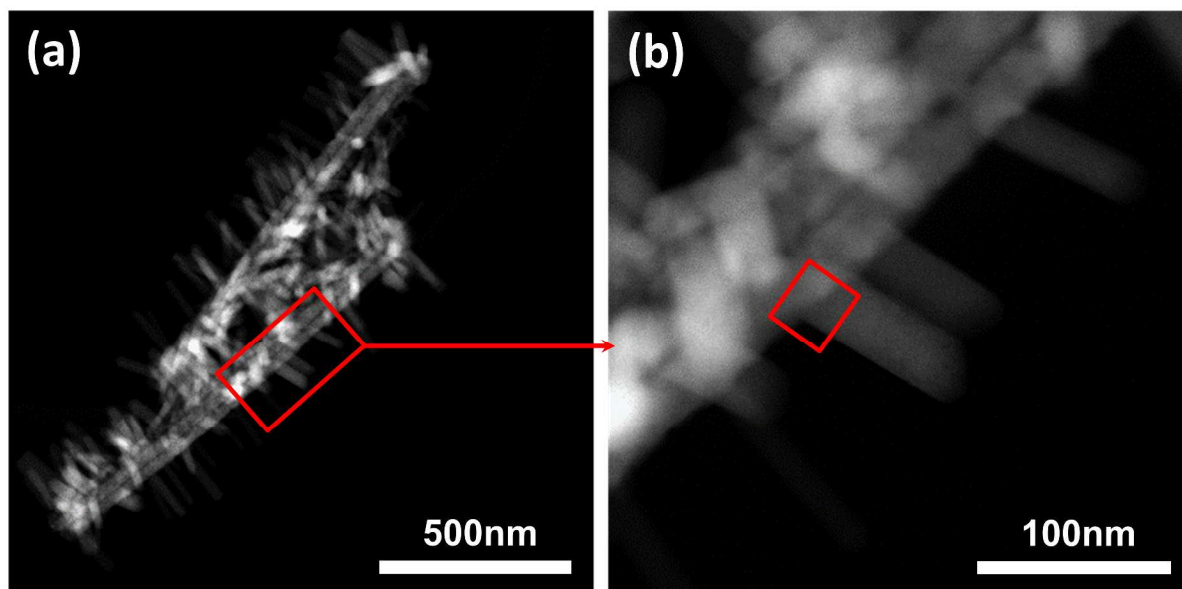


Figure S7. (a) Low-magnification annular dark field STEM image of two single b(10m-ZnO/4h-400°C-CuO) NWs connecting to each other. (b) Enlarged image of labeled part in (a). The labeled part in (b) is the part that was used to show the interface in Figure 4f in the main text.

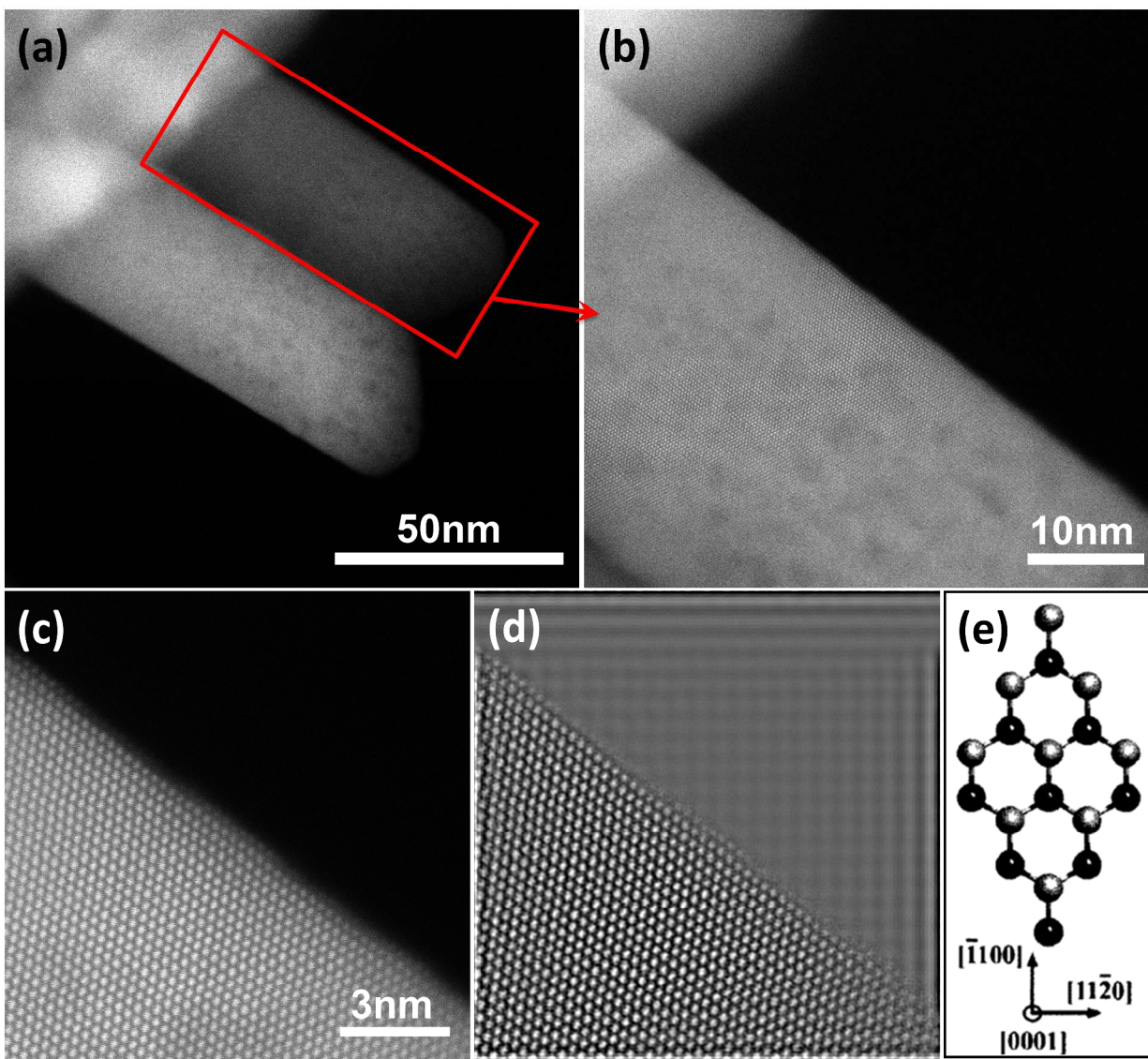


Figure S8. (a) Low-magnification annular dark field STEM image of two ZnO NW branches (enlarged image of Figure S7b). (b) Enlarged image of labeled ZnO NW in (a). (c) High-resolution image of (b). (d) The corresponding noise-filtered image of (c). (e) Crystallography of (0001) plane showing the ZnO NW growth orientation of $[110]$.

Field effect mobility measurement

To measure the field effect mobility of CuO NW, single CuO NW field effect transistors (FET) were fabricated using bottom gate structure with n⁺-Si gate, 600 nm SiO₂ gate oxide, and 120 nm Au for the source and drain contacts (Figures S9a). Au was used for the source and drain contacts to provide ohmic contacts with the CuO NW.¹ The radius and channel length (length between source and drain contacts) of CuO NW are 64 nm and 2.56 μm, respectively. A HP 4155 Parametric Analyzer/Probe Station was used to measure and analyze the FET device characteristics. The current-voltage characteristics of the CuO NW FET device are shown in Figures S9b and S9c indicating the p-type conductivity for the CuO NW. The field effect mobility, μ , can be estimated using²

$$\mu = g_m \frac{L^2}{C} \frac{1}{V_{ds}} \quad (1)$$

in the linear regime. $g_m = dI_{ds}/dV_{gs}$ is the transconductance in the linear regime, L is the NW channel length, and C is the back gate capacitance which for the back-gated structure can be estimated using^{2, 3}

$$C = \frac{2\pi\epsilon_0\epsilon L}{\ln(2h/r)} \quad (2)$$

with ϵ_0 as the vacuum dielectric constant, ϵ as the effective SiO₂ relative dielectric constant, h as the SiO₂ thickness, and r as the NW radius. The calculated g_m and C are 1.91×10^{-11} A/V and 1.21×10^{-16} F, respectively, resulting in a mobility of $0.0052 \text{ cm}^2/(\text{V}\cdot\text{s})$ at $V_{ds} = 2 \text{ V}$. The doping/carrier concentration density can be estimated using^{2, 4}

$$n = \frac{V_{th}C}{eL(\pi r^2)} \quad (3)$$

with V_{th} as the threshold voltage. The calculated n at $V_{ds} = 2 \text{ V}$ ($V_{th} \cong -4 \text{ V}$) is $\sim 9 \times 10^{16} \text{ cm}^{-3}$.

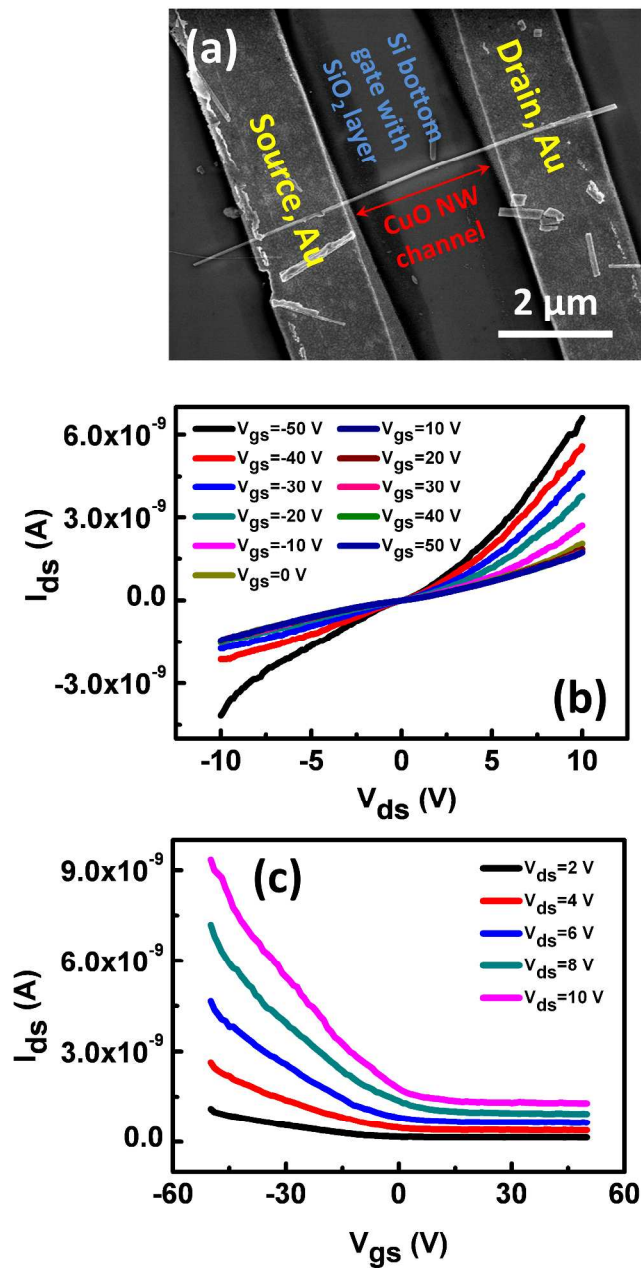


Figure S9. Field-effect characteristics of single 4h-450°C-CuO NW field effect transistor (FET). (a) SEM image of single CuO NW FET, (b) I_{ds} - V_{ds} curves at various gate voltages, and (c) I_{ds} - V_{gs} curves at different drain voltages. The CuO NW was grown on Cu foil.

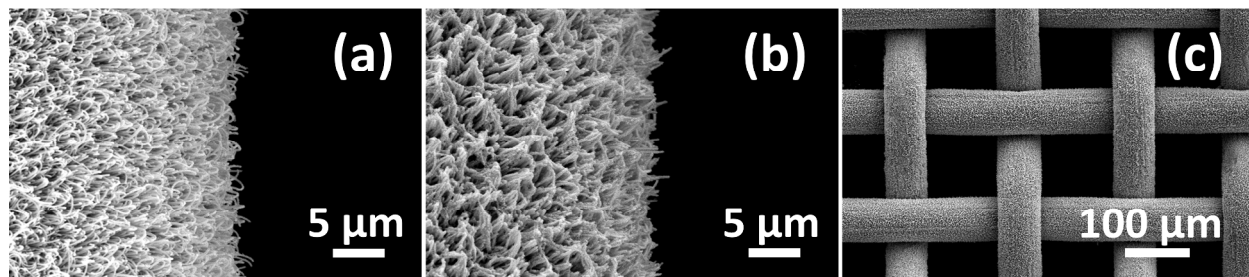


Figure S10. Low-magnification SEM images of ZnO/CuO b-NWs on Cu mesh with 4h-400°C-CuO NW cores and different ZnO NW branches ((a) 5m-ZnO and (b)-(c) 10m-ZnO). Images in (a) and (b) are from the curvature of b-NW-coated Cu wire in the Cu mesh.

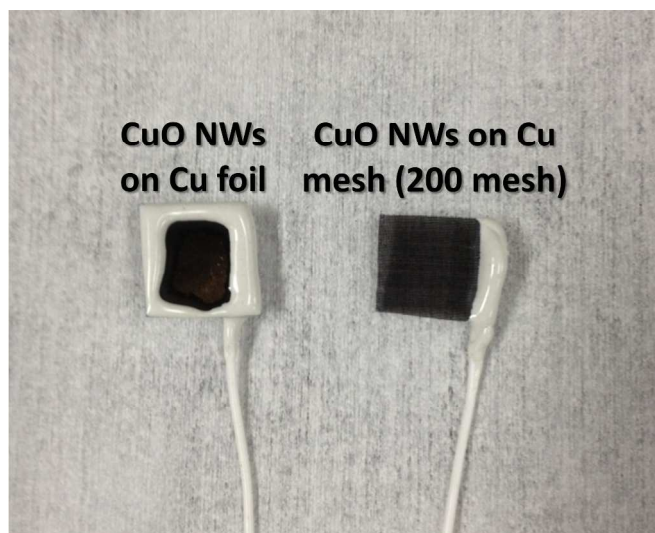


Figure S11. Optical image of CuO NW samples on Cu foil and mesh after preparing for PEC tests. The edges and backside of foil sample are sealed by epoxy while for mesh sample, only one edge is sealed by epoxy. The number of meshes in the Cu mesh substrate is 200.

References

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