## **SUPPORTING INFORMATION**

## Enhancing Electrocatalytic Semihydrogenation of Alkynes via

## Weakening Alkene Adsorption over Electron-depleted Cu Nanowires

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**Figure S1.** (a) TEM image and (b) width distribution of the Cu NWs with an average diameter of  $24.2 \pm 3.0$  nm; (c, d) HRTEM and the corresponding FFT of one Cu NW.



**Figure S2.** (a) TEM image, (b) HRTEM, and (c) size distribution of the Ag NPs with an average diameter of 13.6 nm.



Figure S3. TEM images of (a) Cu<sub>99.3</sub>NW@Ag<sub>0.7</sub>NPs, (b) Cu<sub>96</sub>NW@Ag<sub>4</sub>NPs and (c) Cu<sub>90</sub>NW@Ag<sub>10</sub>NPs hybrids.



**Figure S4.** HAADF-STEM images and the corresponding EDX elemental mappings of Cu (red) and Ag (green) of the CuNW@AgNPs hybrids with three different Cu/Ag ratios: (a) Cu<sub>99.3</sub>NW@Ag<sub>0.7</sub>NPs, (b) Cu<sub>96</sub>NW@Ag<sub>4</sub>NPs and (c) Cu<sub>90</sub>NW@Ag<sub>10</sub>NPs hybrids.



**Figure S5.** XRD pattern of  $Cu_{90}NW@Ag_{10}NPs$  hybrids, with the boxed region enlarged in the inset, showing the diffraction peak from the Ag(111) planes.



Figure S6. XPS Cu 2p spectra of (a) Cu NWs, (b) Cu<sub>99.3</sub>NW@Ag<sub>0.7</sub>NPs, (c) Cu<sub>96</sub>NW@Ag<sub>4</sub>NPs, and (d) Cu<sub>90</sub>NW@Ag<sub>10</sub>NPs hybrids.



Figure S7. XPS Ag 3d spectra of (a) Ag NPs, (b) Cu<sub>99.3</sub>NW@Ag<sub>0.7</sub>NPs, (c) Cu<sub>96</sub>NW@Ag<sub>4</sub>NPs, and (d) Cu<sub>90</sub>NW@Ag<sub>10</sub>NPs hybrids.



**Figure S8.** Standard curves used to quantify (a) alkynes (EYA), (b) alkenes (VYA), and (c) alkanes (4-ethylaniline).



Figure S9. LSV curves of  $Cu_{96}NW@Ag_4NPs$  in 1.0 M KOH solution [dioxane/H<sub>2</sub>O, 2/5 (v/v)] at a scan rate of 5 mV s<sup>-1</sup> with and without 0.4 mmol of EYA.



**Figure S10.** Time-dependent conversions (Con.) of EYA and selectivity (Sel.) for VYA over Cu NWs at -0.75 V.



**Figure S11.** Time-dependent conversions (Con.) of EYA and selectivity (Sel.) for VYA over Ag NPs at -0.75 V.



**Figure S12.** Potential-dependent conversions (Con.) of EYA and selectivity (Sel.) for VYA over Cu NWs within 4 h.



**Figure S13.** Potential-dependent conversions (Con.) of EYA and selectivity (Sel.) for VYA over Ag NPs within 4 h.



**Figure S14.** LSV curves of Cu NWs, Cu<sub>99.3</sub>NW@Ag<sub>0.7</sub>NPs, Cu<sub>96</sub>NW@Ag<sub>4</sub>NPs, and Cu<sub>90</sub>NW@Ag<sub>10</sub>NPs in 1.0 M KOH solution [dioxane/H<sub>2</sub>O, 2/5 (v/v)] at a scan rate of 5 mV s<sup>-1</sup> (a) with and (b) without 0.4 mmol of EYA.



Figure S15. (a) TEM and (b) HAADF-STEM image (c) XPS Cu 2p spectra of Cu<sub>96</sub>NW@Ag<sub>4</sub>NPs hybrids after 4h's electrolysis at -0.75 V vs. RHE, (d) comparison between XPS Cu 2p spectra of Cu<sub>96</sub>NW@Ag<sub>4</sub>NPs hybrids before and after reaction and XPS Cu 2p spectra of Cu NWs.



Figure S16. Raman spectra of 4-Ethynylaniline (EYA) powders.



Figure S17. In situ potential-dependent Raman spectra measured on Cu NWs.



**Figure S18.** Theoretical calculation models of catalysts: (a) CuNW@AgNPs hybrids and (b) Cu NWs. Cu and Ag atoms are shown as blue and white spheres, respectively.



**Figure S19.** Transformation of adsorption configurations in H<sub>2</sub>O decomposition on CuNW@AgNPs hybrids surface.



**Figure S20.** Transformation of adsorption configurations in H<sub>2</sub>O decomposition on Cu NWs surface.



**Figure S21.** (a) TEM image and (b) HAADF-STEM image of CuNW@AgNPs-GRR bimetallic catalysts fabricated by the galvanic replacement reaction (GRR) method with an atomic ratio: Cu/Ag = 96.4/3.6.

Note: CuNW@AgNPs-GRR hybrids were synthesized using the following method. The as-prepared Cu NWs were evenly dispersed in 10 mL of oleylamine through sonication. Simultaneously, 20 mg of AgNO<sub>3</sub> were dissolved in 10 mL of oleylamine at 30°C through sonication. The two solutions were then mixed to initiate a galvanic replacement reaction (GRR) at 60°C for 2 hours. Afterward, the solution was cooled to room temperature, and the catalysts were washed three times with an ethanol/hexane mixture (1:1 volume ratio). The CuNW@AgNPs-GRR hybrids were collected by centrifugation at 9500 rpm for 5 minutes and dried in a vacuum oven at room temperature for 4 hours.



**Figure S22.** Potential-dependent conversion (Con.) of EYA and selectivity (Sel.) for VYA over CuNW@AgNPs-GRR bimetallic catalysts.