

Supporting Information

Nanoscale Heterogeneities and Composition-Reactivity Relationships in Copper Vanadate Photoanodes

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Table S1. Average transition metal composition Cu/(Cu+V) of different $\text{Cu}_5\text{V}_2\text{O}_{10}$ films on ITO and SiN_x determined by coupled plasma mass spectroscopy (ICP-MS). The films were deposited simultaneously on both substrates.

Composition	ITO	SiN_x
Stoichiometric	0.717 ± 0.003	0.723 ± 0.003
Cu-deficient	0.713 ± 0.002	0.710 ± 0.003
Slightly Cu-rich	0.738 ± 0.004	0.731 ± 0.005
Highly Cu-rich	0.798 ± 0.003	0.787 ± 0.012

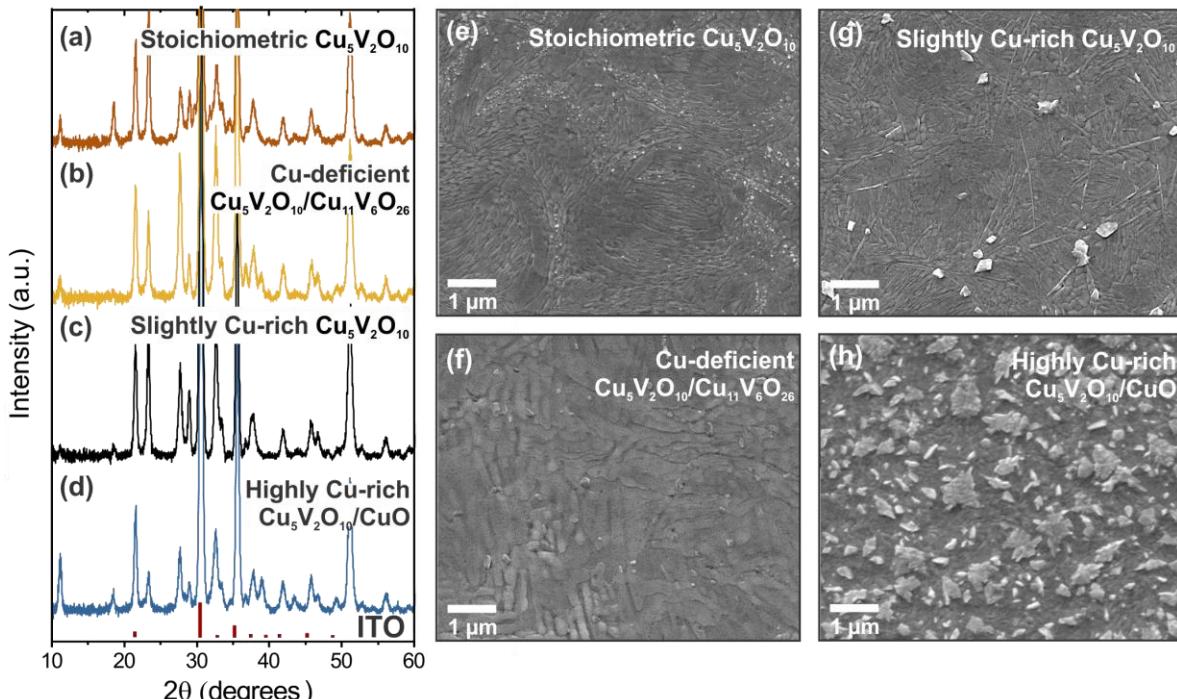


Figure S1. (a-d) X-ray diffraction pattern and (e-h) SEM images of copper vanadate thin films on ITO coated glass substrates for different Cu concentrations, namely stoichiometric $\text{Cu}_5\text{V}_2\text{O}_{10}$, Cu-deficient $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{Cu}_{11}\text{V}_6\text{O}_{26}$, slightly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}$, and highly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{CuO}$. The diffraction peaks at 21° , 30° , 35° , and 51° correspond to the ITO substrate.

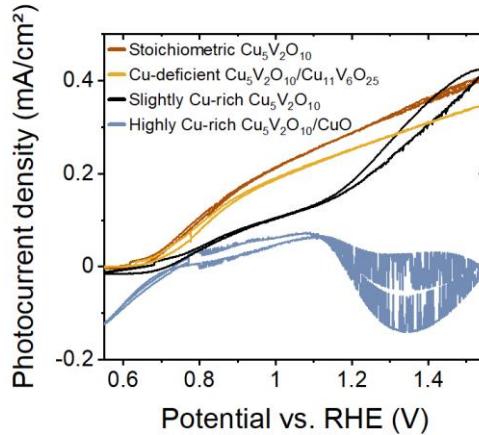


Figure S2. Photocurrent of stoichiometric $\text{Cu}_5\text{V}_2\text{O}_{10}$, Cu-deficient $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{Cu}_{11}\text{V}_6\text{O}_{26}$, slightly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}$, and highly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{CuO}$. The JV-characteristics were recorded in sulfite 0.1 M sodium borate (NaB_i , pH 9.4) with 0.1 M sodium.

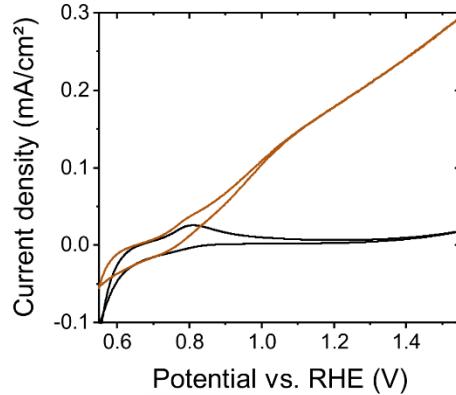


Figure S3. Cyclic voltammetry of highly Cu-deficient $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{Cu}_{11}\text{V}_6\text{O}_{26}$ on ITO glass with $\text{Cu}/(\text{Cu}+\text{V})$ ratio of 0.688. The JV-characteristics were recorded in sulfite 0.1 M sodium borate (NaB_i , pH 9.4) with 0.1 M sodium in the dark and under AM 1.5 simulated solar irradiation at 1 sun intensity (100 mW cm^{-2}).

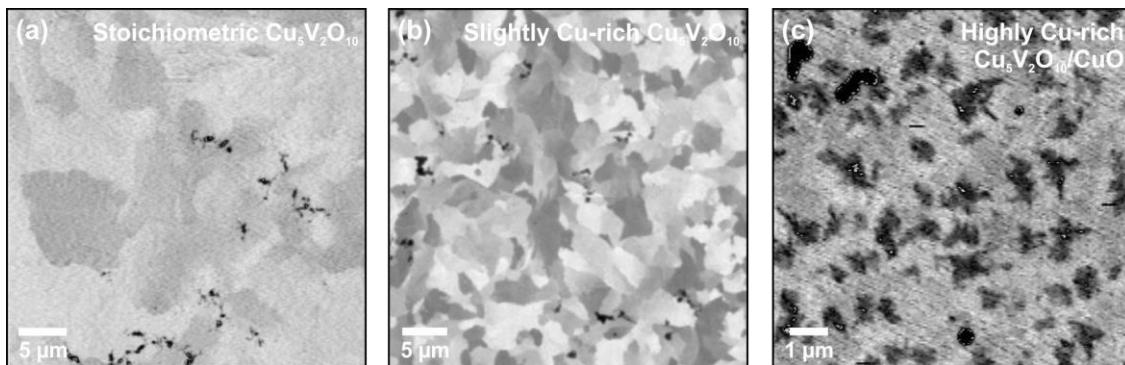


Figure S4. Large scale X-ray absorption maps at the Cu L-edge (932 eV) of stoichiometric $\text{Cu}_5\text{V}_2\text{O}_{10}$ (a), slightly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}$ (b), and highly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{CuO}$ (c) photoelectrodes.

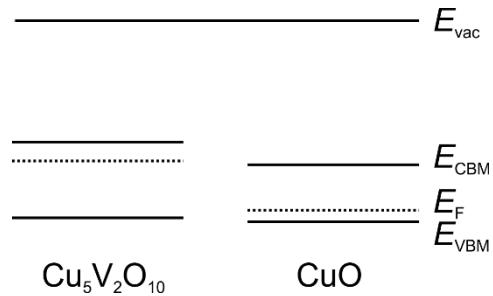


Figure S5. Scheme of the band energy diagram for $\text{Cu}_5\text{V}_2\text{O}_{10}$ and CuO relative to vacuum.

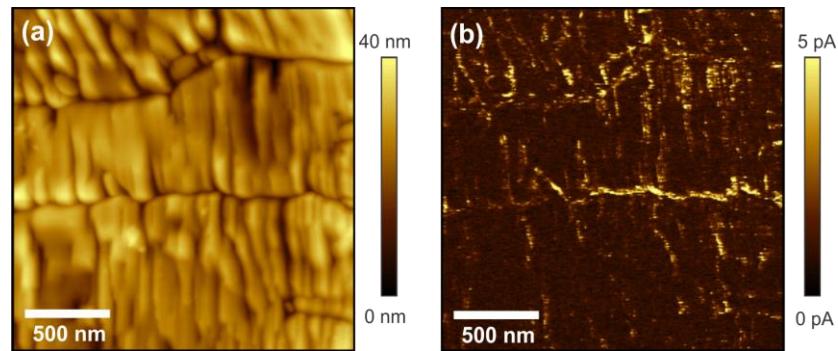


Figure S6. Topography (a) and photocurrent (b) maps of stoichiometric $\text{Cu}_5\text{V}_2\text{O}_{10}$ photoanodes.