

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

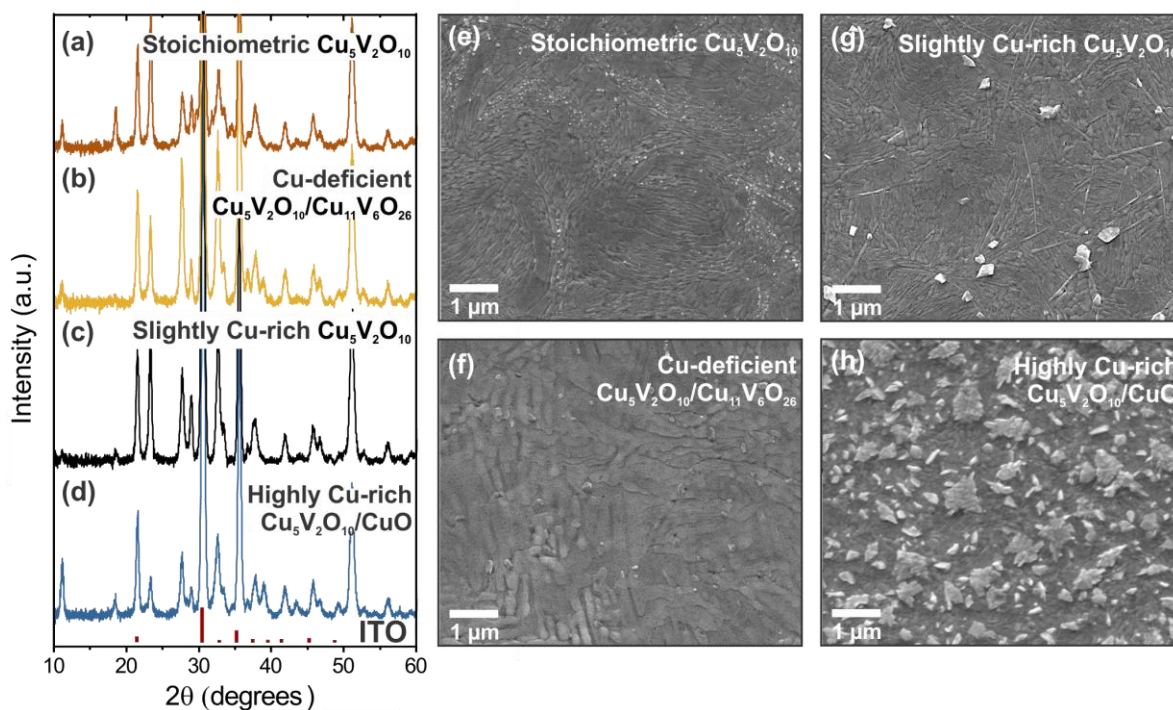


Figure S1. (a-d) X-ray diffraction pattern and (e-h) SEM images of copper vanadate thin films on ITO coated glass substrates for different Cu concentrations, namely stoichiometric $\text{Cu}_5\text{V}_2\text{O}_{10}$, Cu-deficient $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{Cu}_{11}\text{V}_6\text{O}_{26}$, 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.

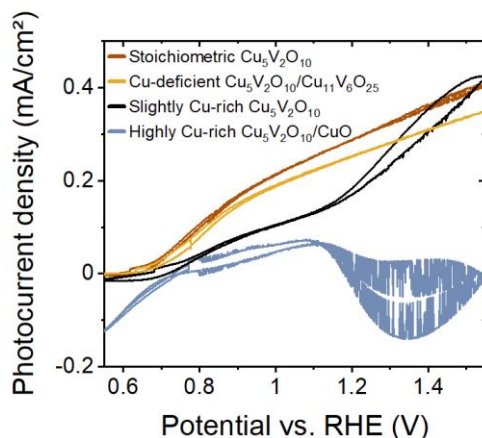


Figure S2. Photocurrent of stoichiometric $\text{Cu}_5\text{V}_2\text{O}_{10}$, Cu-deficient $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{Cu}_{11}\text{V}_6\text{O}_{26}$, slightly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}$, and highly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{CuO}$. The JV-characteristics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

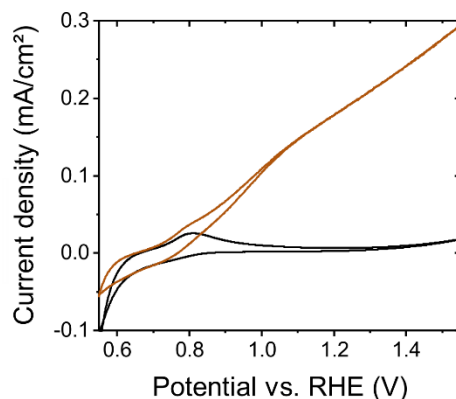


Figure S3. Cyclic voltammetry of highly Cu-deficient $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{Cu}_{11}\text{V}_6\text{O}_{26}$ on ITO glass with Cu/(Cu+V) ratio of 0.688. The JV-characteristics were recorded in sulfite 0.1 M sodium borate (NaB_i , pH 9.4) with 0.1 M sodium in the dark and under AM 1.5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

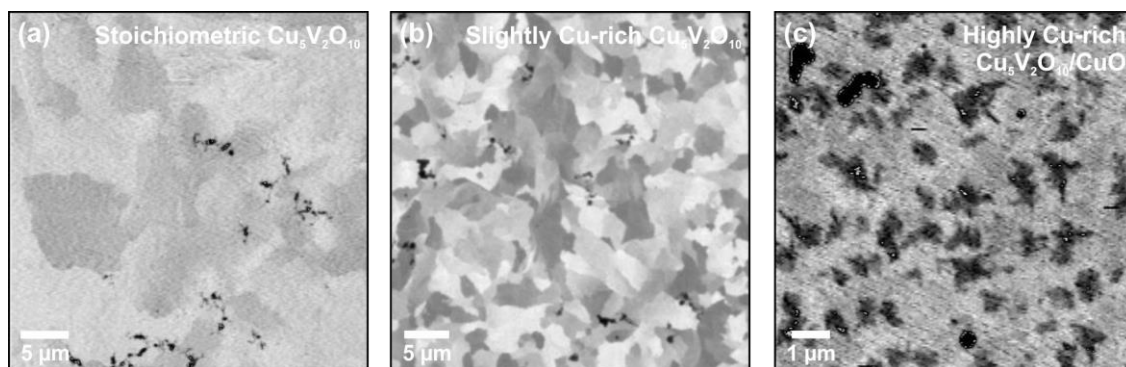


Figure S4. Large scale X-ray absorption maps at the Cu L-edge (932 eV) of stoichiometric $\text{Cu}_5\text{V}_2\text{O}_{10}$ (a), slightly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}$ (b), and highly Cu-rich $\text{Cu}_5\text{V}_2\text{O}_{10}/\text{CuO}$ (c) photoelectrodes.

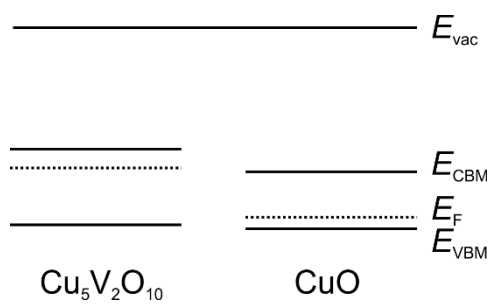


Figure S5. Scheme of the band energy diagram for $\text{Cu}_5\text{V}_2\text{O}_{10}$ and CuO relative to vacuum.

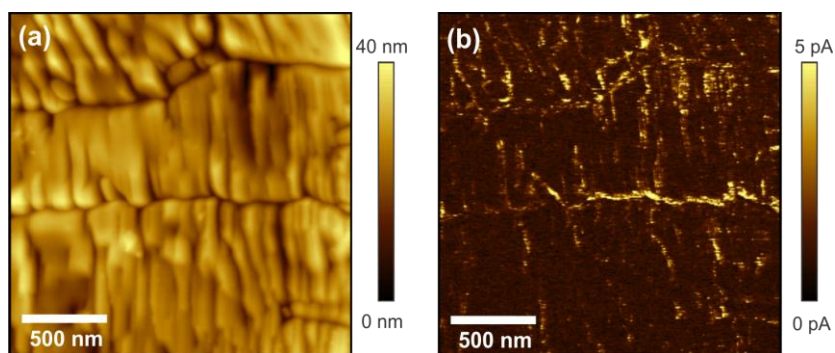


Figure S6. Topography (a) and photocurrent (b) maps of stoichiometric $\text{Cu}_5\text{V}_2\text{O}_{10}$ photoanodes.