Supporting Information

Photoelectrochemical Investigation and Electronic Structure of a *p*-type $CuNbO_3$ Photocathode

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Incident Photon-to-Current Efficiency (IPCE) Calculations: All photoelectrochemical measurements (i.e., cyclic voltammetry and chronoamperometry) were carried out in a custom-fabricated Teflon cell using the $CuNbO_3$ film as the working electrode, a Pt counter electrode, and a standard calomel electrode (sat. KCl) as the reference electrode. A 0.5 M Na_2SO_4 aqueous solution was used as the electrolyte. Argon was bubbled through the electrolyte solution for 30 min before each measurement and then used to purge the cell continuously throughout each measurement. The pH of the electrolyte was adjusted using a dilute NaOH solution to pH = 6.31. All photoelectrochemical measurements were carried out using PARSTAT 2263 potentiostat-galvanostat instrument and the data recorded and plotted using the PowerSuite software. The experimental setup is as shown in Figure S2. For incident-photon-to-current measurements, the arc-lamp source was fitted with four different 50nm bandpass filters, which centered on wavelengths of 352 nm, 451 nm, 522 nm, 603 nm. A Si photodiode was used to measure the photon flux of monochromatic light that irradiated the electrode surface. The incident-photon-to-current conversion efficiency for monochromatic light is defined as follows:

$$\text{IPCE (\%)} = \frac{1239.8 \text{ x photocurrent density } [\frac{\text{mA}}{\text{cm}^2}]}{\text{wavelength } (\lambda) \text{ [nm] x photon flux}[\text{mW/cm}^2]} \text{ x } 100$$

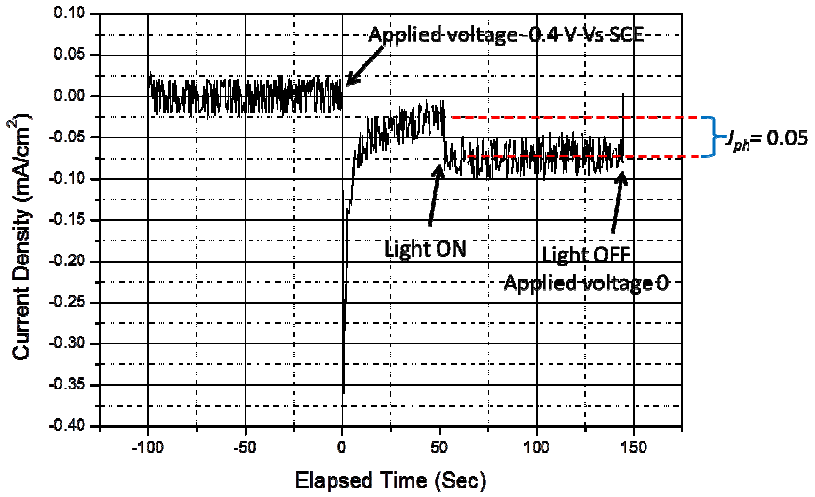

Figure S1. IPCE experiments were carried out in a 3-electrode system using a 400W Xe arc-lamp (photon flux = 10.83 mW/cm^2) and bandpass filters (e.g., 451.48 nm). The $CuNbO_3$ film on FTO glass was the working electrode, together with a Pt counter electrode and a standard calomel electrode as the reference electrode. A 0.5 M Na_2SO_4 (pH =6) solution was used as the electrolyte, and Ar gas was bubbled through the solution as a purge gas throughout the experiment.

In an example calculation, the following values were measured and used in the above equation:

Wavelength = 451.48 nm

Photon Flux = 10.83 mW/cm^2

Photocurrent Density = 0.05 mA/cm^2

An IPCE = 1.2678% is calculated.

Similarly, IPCE values were calculated for all other wavelengths, including 352 nm, 522 nm and 603 nm, and which are plotted in Figure 1b.

The following values of photon-flux and saturated photocurrent (with the dark current subtracted) were used for the calculations

Wavelength (λ) nm	Photon Flux (mW/cm^2)	Saturated Photocurrent (mA/cm^2)
351.95	8.29	0.125
451.48	10.83	0.05
522.49	13.50	0.025
602.75	13.75	0.01

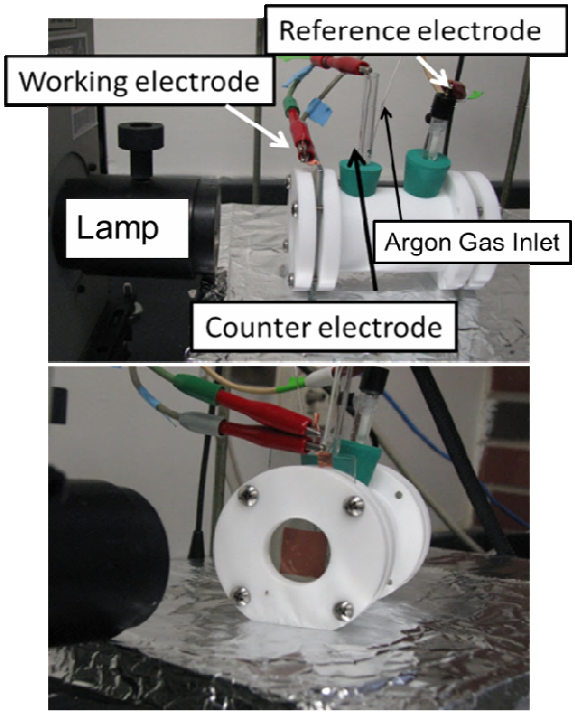

Figure S2. The experimental photoelectrochemical measurement setup.

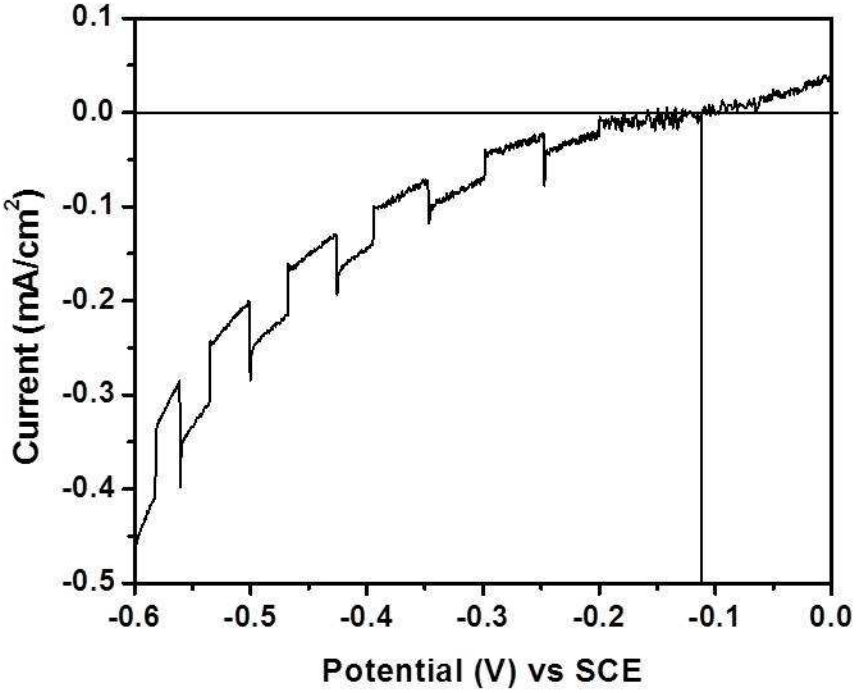

Figure S3. The current-potential curve for a freshly prepared $CuNbO_3$ film without the oxidation treatment in air. The cyclic-voltammetry experiment was carried out in an aqueous 0.5M Na_2SO_4 solution at pH = 6.31 under chopped visible light irradiation. The onset potential begins at approximately -0.11 V vs SCE.

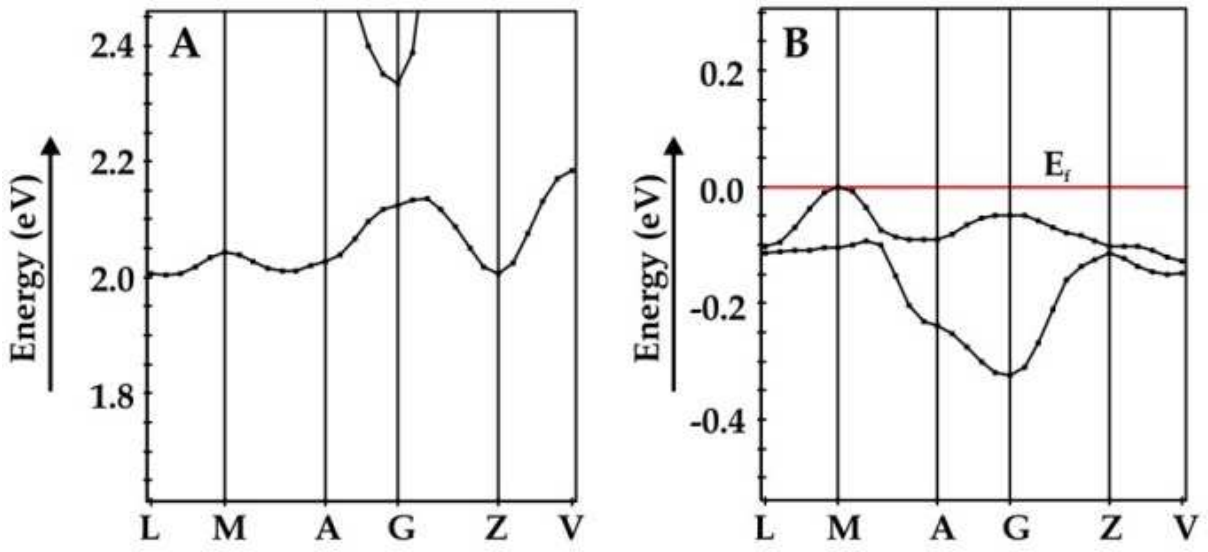

Figure S5. Plots of the band-structure diagram for a very narrow energy range that includes only (A) the lowest unoccupied crystal orbital in the conduction band, and (B) the two highest occupied crystal orbitals of the valence band, with the Fermi level labeled.