SUPPORTING INFORMATION

"Optical, Electronic, and Photoelectrochemical Properties of the *p*-type $Cu_{3-x}VO_4$ Semiconductor"

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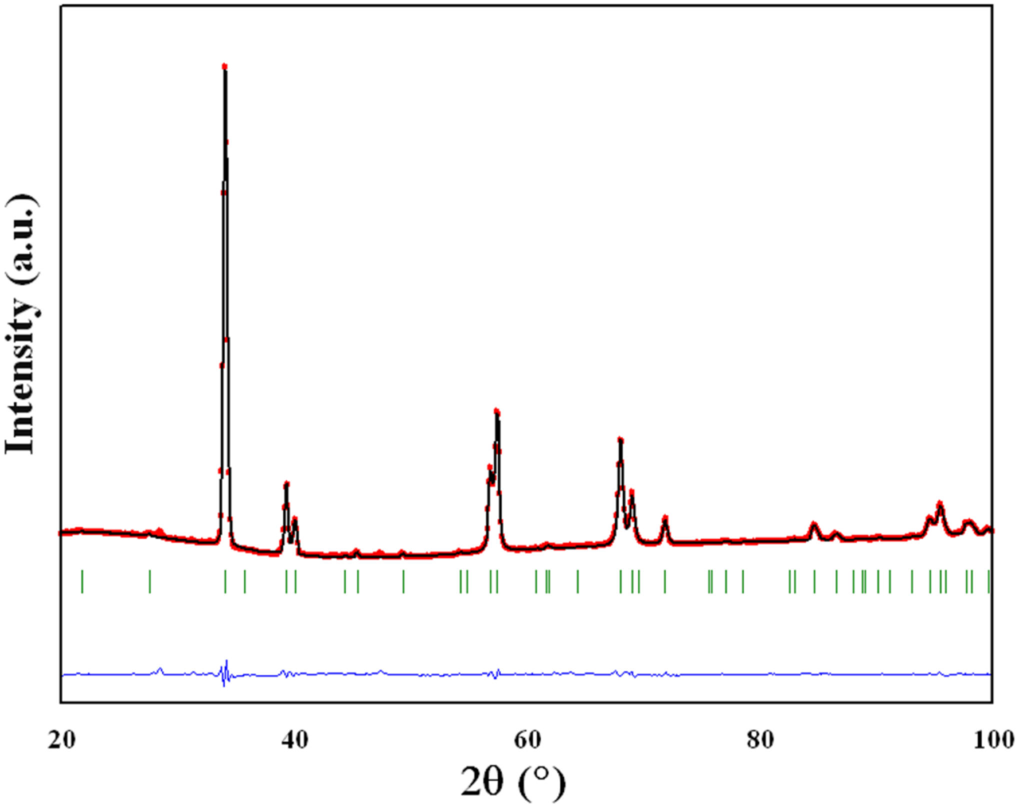

Figure S1. Whole-pattern fitting of the powder X-ray diffraction pattern of freshly prepared Cu_3VO_4. The observed profile is indicated by circles and the calculated profile by the solid line. Bragg peak positions are indicated by vertical tics, and the difference is shown at the bottom.

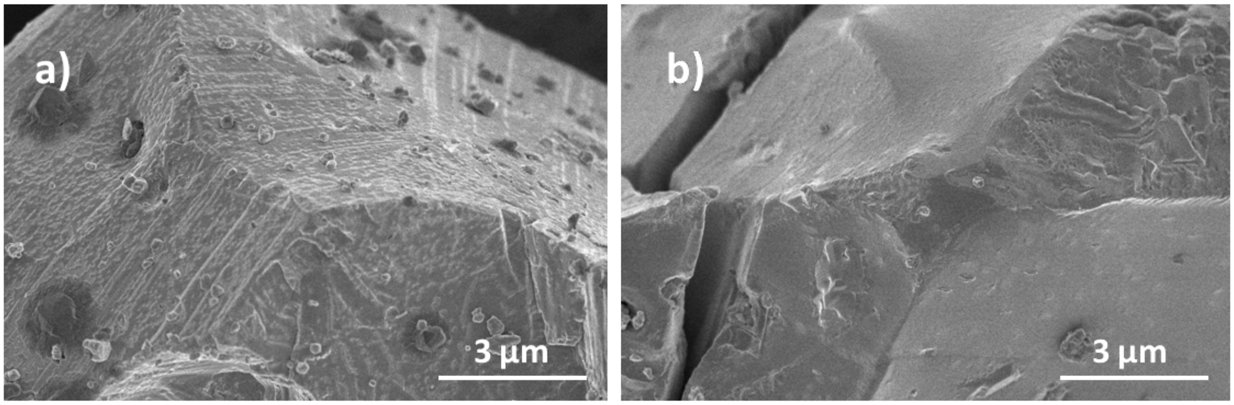

Figure S2. Scanning electron microscopy images of the surfaces of Cu_3VO_4 after the initial synthesis (a), and after annealing it at 400 ^{o}C under vacuum (b).

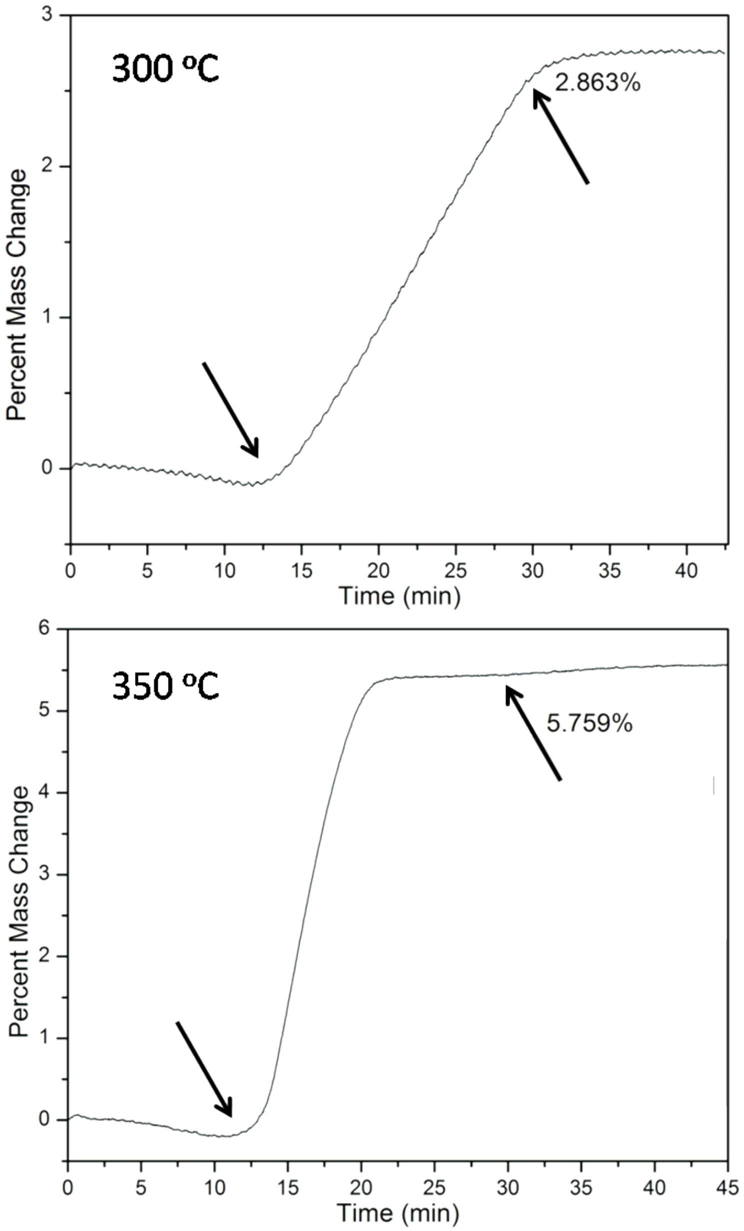

Figure S3. Thermogravimetric plots of mass change versus time at temperatures (in air) of 300 °C (upper) and 350 °C (lower). The arrows label the beginning and end points of the heating cycle, which lasted ~15 minutes for each one. At 300 °C, the weight change was still continuing at the time of stoppage of the 15 min heating cycle.

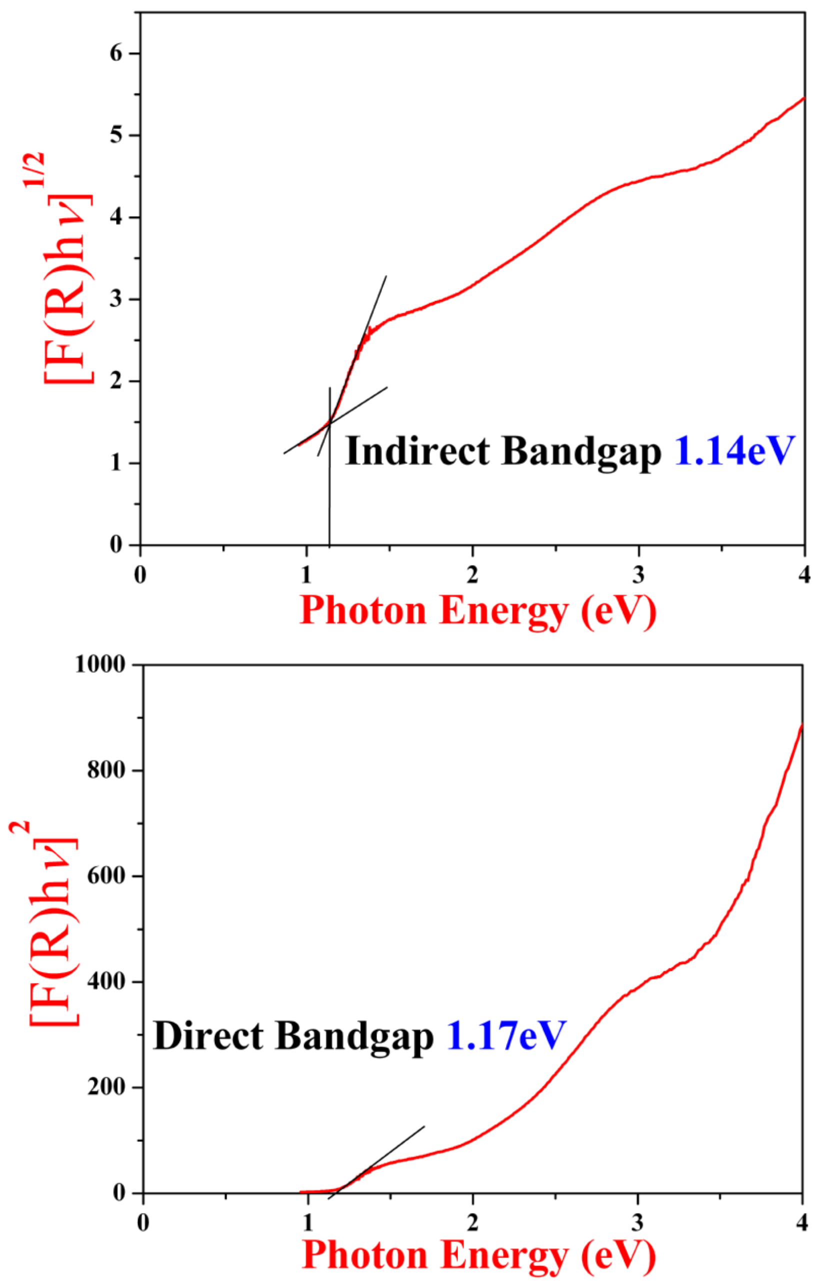

Figure S4. Tauc plots of $[F(R)hv]^n$ versus $[hv]$ ($n = 2$ and ½ for direct (lower) and indirect (upper) bandgap transitions) for a polycrystalline freshly-prepared sample of Cu_3VO_4.

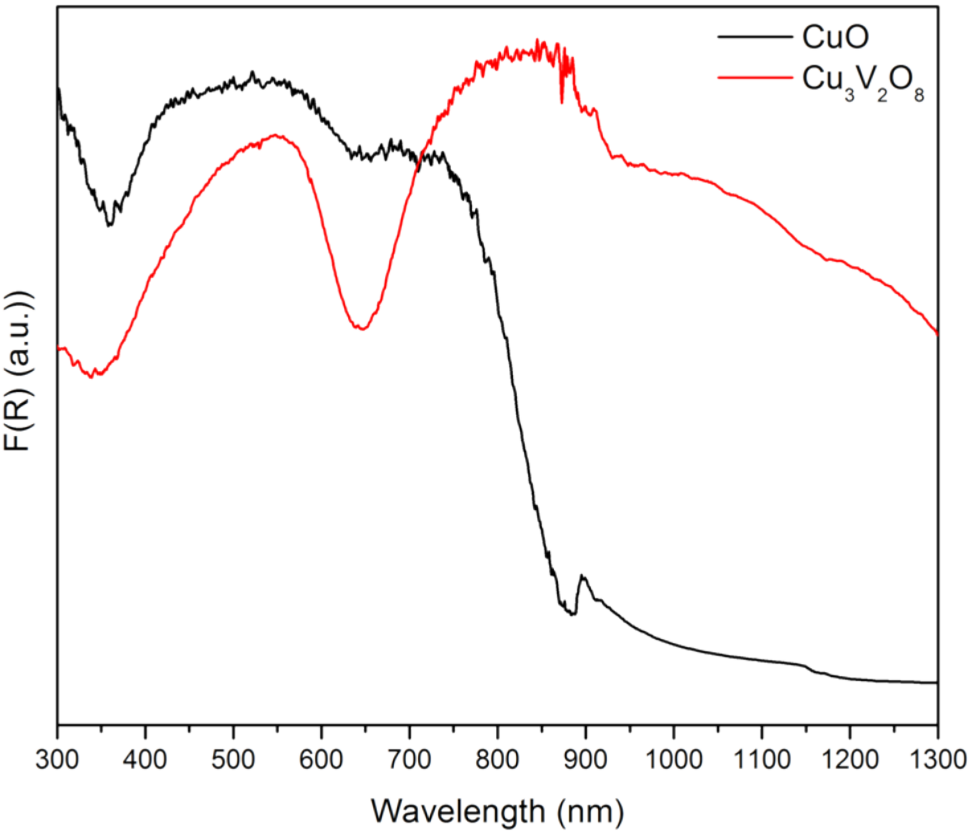

Figure S5. UV-Vis diffuse reflectance spectra of CuO (black line) and $Cu_3V_2O_8$ (red line; a mixture of related polymorphs crystallizing in the P-*1* and P*2/c* space groups), plotted as the Kubelka-Munk function (F(R)) versus wavelength (nm).

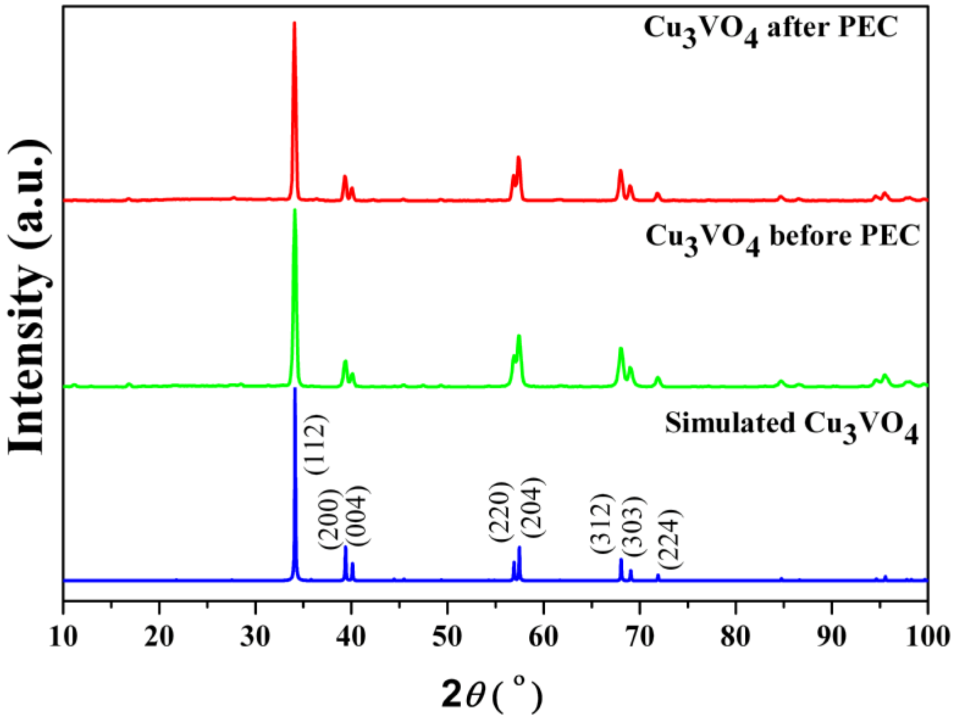

Figure S6. Powder X-ray diffraction patterns of $Cu_{3-x}VO_4$ films before and after the photoelectrochemical measurements, and compared to its calculated pattern (lower).

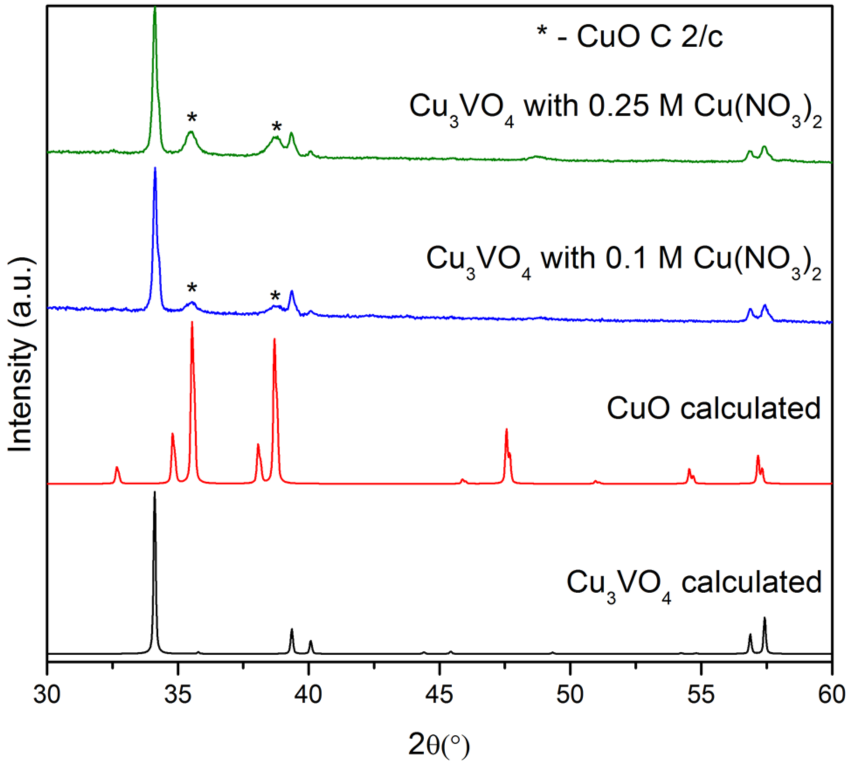

Figure S7. Powder X-ray diffraction patterns of Cu_3VO_4 after two different concentrations of $Cu(NO_3)_2$ were heated to create CuO at the surface of Cu_3VO_4 films.

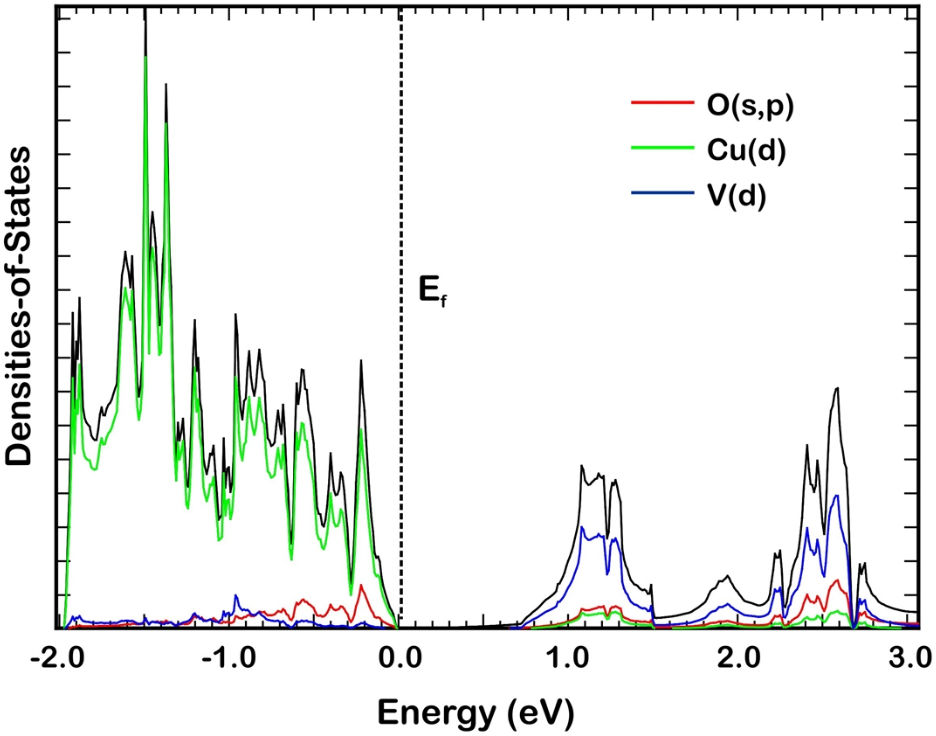

Figure S8. Calculated densities-of-states for the Cu_3VO_4 structure, with the individual atomic contributions (i.e., O, Cu, and V) overlaid on the total densities-of-states plot.

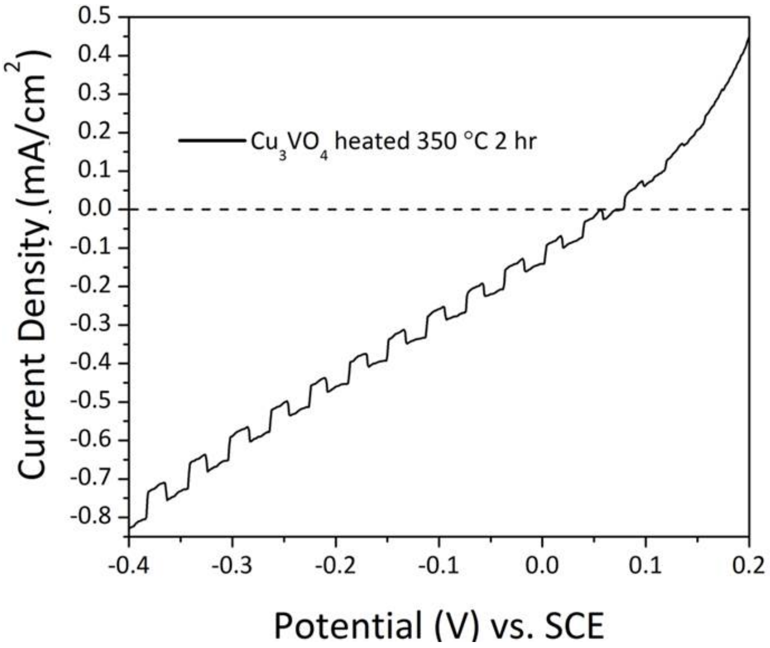

Figure S9. Current-potential curve for a polycrystalline $Cu_{3-x}VO_4$ film that had been annealed at 400 °C for 3h, following by heating in air at 350 °C for 120 min. The experimental conditions included an aqueous 0.5 M Na_2SO_4 solution (pH = 5.8) and chopped visible-light irradiation.

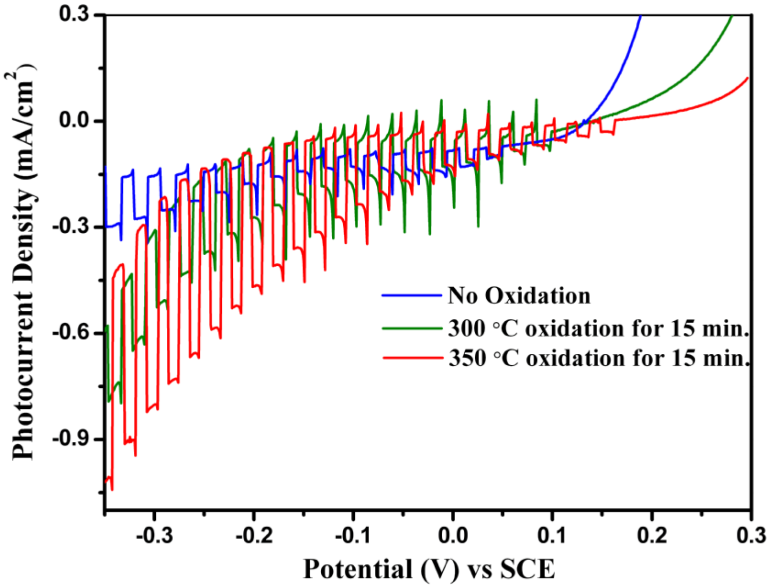

Figure S10. Current-potential curve for polycrystalline $Cu_{3-x}VO_4$ films in an aqueous 0.5 M Na_2SO_4 solution (pH = 5.8) under chopped visible-light irradiation at an irradiant power density of ~500 mW/cm^2. The films were annealed at 400 ºC for 3h, followed by heating in air for 15 min at 300 ºC or 350 ºC.

Description of Mott-Schottky Measurements and Calculations.

Mott-Schottky measurements were performed using the AC electrochemical impedance method with an AC amplitude of 10 mV at an applied frequency of 30 kHz at pH 5.8 on a PARSTAT 23263 potentiostat-galvanostat instrument. The space charge capacitance *C* may vary with the applied potential over the depletion layer as determined by the Mott-Schottky equation for a *p*-type semiconductor:

$$\frac{1}{C^2} = \left(\frac{2}{e\varepsilon_o\varepsilon_r N_A A^2}\right)\left(-V + V_{fb} - \frac{kT}{e}\right)$$

Where *e* is the electron charge, ε_r is the dielectric constant, ε_o is the permittivity of a vacuum, N_A is the acceptor density, *V* is the applied bias, V_{fb} is the flatband potential, *k* is the Boltzmann constant, *T* is room temperature, and *A* is the surface area of the film in contact with the electrolyte.

Therefore a plot of C^{-2} *versus* *V* yields a straight line with a slope than can be used to determine N_A. Slope = $(2/e\varepsilon_0\varepsilon_r N_A A^2)$; the value for ε_r was chosen as ~10, A = 0.125 m^2, $\varepsilon_0 = 8.8541 \times 10^{-12}$ Fm^{-1}, and $e = 1.602 \times 10^{-19}$ C.

Slope = -7.0×10^7 $F^{-2}V^{-1}$ and an N_A value of $1.289 \times 10^{17} cm^{-3}$ was obtained at 30 kHz.

Using the above Mott-Schottky equation, the flatband potential is determined from the intercept with the *x*-axis on the linear plot of C^{-2} *versus V*, and converted from SCE to RHE. The *x*-axis intercept was +0.40V *vs*. RHE at a pH = 5.8. Hence, V_{fb} is 0.43 V.

The energetic position of the valence band (E_{v}) is determined from the equation for a *p*-type semiconductor: $E_v = V_{fb}$ - kT ln (N_A/N_V) where Nv is the effective density of states (typically ~10^{19}) at the valence band edge. Hence, E_v is 0.54 V.

Therefore, the position of the conduction can determined when the bandgap (1.17 eV) is subtracted from the valence band. The conduction band position is therefore at approximately -0.63 V *versus* RHE at pH = 5.8.