Supplementary Information

Elucidating the Optical, Electronic, and Photoelectrochemical Properties of p-Type Copper Vanadate (p-Cu₅V₂O₁₀) Photocathodes

Angang Song,^{ab} Sean P. Berglund,^a Abdelkrim Chemseddine,^a Dennis Friedrich,^a Fatwa F. Abdi^a and Roel van de Krol^{ab*}

a. Institute for Solar Fuels, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Hahn-Meitner-Platz 1, 14109 Berlin, Germany.

b. Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, 10623 Berlin, Germany.

*E-mail: roel.vandekrol@helmholtz-berlin.de

Experimental methods

Photocathode Synthesis

Cu₅V₂O₁₀ photocathode thin films were prepared using a low-cost and facile spray pyrolysis process. The typical spray pyrolysis synthesis procedure for a Cu₅V₂O₁₀ photocathode is as follows. First, 20mM Cu(NO₃)₂ precursor was prepared by dissolving Cu(NO₃)₂·3H₂O (99–104%, Sigma-Aldrich) in ethanol (\geq 99.8%, Sigma-Aldrich). Next 8mM VO(AcAc)₂ precursor was prepared by dissolving VO(C₂H₇O₂)₂ (99%, Alfa Aesar) in absolute ethanol (≥99.8%, Sigma-Aldrich). The Cu solution was then added to the V solution, and the mixture was diluted to the desired concentration with additional ethanol. Before deposition was started the substrates (FTO-coated glass, 15 Ω per square, TEC-15, Pilkington), which were cleaned by three successive 15 min ultrasonic rinsing treatments in a Triton solution, acetone, and ethanol, were placed on the hot plate and heated to the preset temperature of 300 °C. The spray nozzle (Quickmist air atomizing spray) was placed 20 cm above the heating plate and driven by an overpressure of 0.6 bar of nitrogen gas. Pulsed deposition mode was used, with one spray cycle consisting of 5 s spray time followed by a delay of 55 s to allow complete evaporation of the solvent and pyrolysis of any remaining organics. After deposition, a post annealing treatment for the $Cu_5V_2O_{10}$ photocathode thin films was carried on in muffle furnace at 550 °C for 4 hours in air using a ramp of 5 °C /min. The annealing conditions were chosen to obtain maximum crystallization of the film without degradation of the FTO substrate.

Material Characterization

X-ray diffraction (XRD) measurements were performed using a Bruker D8 diffractometer in the 20 range from 10° to 90° with Cu K_a radiation of 0.15406 nm wavelength. The acceleration was operated at a voltage of 40 kV and a current of 40 mA. The step size of the measurements was 0.02° with an integration time of 3.5 seconds per step. The morphology of the films was analyzed using a LEO GEMINI 1530 field emission scanning electron microscope (FESEM), operated at an acceleration voltage of 7 kV. Energy-dispersive X-ray analysis (EDX) was also conducted on the same FESEM using a silicon drift detector (Thermo Fisher Scientific) at an acceleration voltage of 20 kV. The surface structure was investigated by an atomic force microscope (AFM, Park System, XE-100) operated in tapping mode using an etched Si tip (10 nm tip radius) with force constant of 40 N/m. All scans were performed on a scale of $5 \mu m \times 5 \mu m$ with the lateral resolved height information on a square array of 256 × 256 pixels. UV-vis absorption spectra were measured inside an integrating sphere using a PerkinElmer Lambda 950 spectrometer. The short-range structure and vibration modes were analyzed by Raman spectroscopy (Dilor Micro LabRam, Horiba) with a laser excitation wavelength of 635 nm and a power of 0.6 mW at the objective (spot size: ~1 um in diameter). Ultraviolet photoelectron spectroscopy (UPS) was conducted using a He I source (E = 21.21 eV) with the same hemispherical analyser (Specs Phoibos 100) in an ultrahigh vacuum system (He partial pressure ~10⁻⁸ mbar). X-ray photoemission spectroscopy spectra were acquired using an instrument developed in house with a SPECS detector. All spectra were measured using a pass energy and step size of 10 and 0.05 eV, respectively. C1s at 284.8 eV were used as a standard for calibration when analyzing the data (see Fig. S17c).

Time-resolved microwave conductivity (TRMC) measurements were conducted using a wavelength tunable optical parametric oscillator (OPO) coupled to a Q-switched Nd:YAG laser at wavelengths of 410, 450, 500, and 550 nm as the excitation source with a 3 ns pulse (full-width at half maximum) and a X-band (8400–8700 MHz) microwave probe. The sample was place in a cavity to enhance the sensitivity. The sensitivity factor *K* of the cavity was determined in an iterative fashion by numerically solving Maxwell's equations to determine the frequency response of the cavity and comparing the calculated frequency response to the measured one. Based on the value of *K*, the carrier mobility values could then be calculated.¹ During TRMC measurements the Cu₅V₂O₁₀ samples were exposed to air. The effective charge carrier diffusion lengths were calculated using the following relationship,

$$L_D = \sqrt{\left(\frac{\mu \, k \, T}{q}\right) \tau} \tag{1}$$

where μ is mobility (m² V⁻¹ s⁻¹), *k* is the Boltzmann constant, *T* is the temperature (K), *q* is the electronic charge (C), and τ is the charge carrier lifetime (s).

[1] T. J. Savenije, A. J. Ferguson, N. Kopidakis and G. Rumbles, J. Phys. Chem. C, 2013, 117, 24085-24103.

Photoelectrochemical and Electrochemical Characterization

Photoelectrochemical measurements were performed in three-electrode configuration under the control of a potentiostat (EG&G Princeton Applied Research 273A). Samples were connected as the working electrode while a Pt wire was used as the counter electrode, and an Ag/AgCl electrode (saturated KCl) was used as the reference electrode. A WACOM super solar simulator (Model WXS-50S-5H, class AAA) that was calibrated to closely resemble the AM1.5 global spectrum at 100 mW/cm², was used as the illumination source. All of the measured potentials were converted to the reversible hydrogen electrode (RHE) scale using the Nernstian relation:

$$V_{RHE} = V_{Ag/AgCl} + 0.0591(V) \times pH + 0.197(V)$$
⁽²⁾

Incident photon-to-current conversion efficiency (IPCE) and absorbed photon-to-current efficiency (APCE) measurements were performed with a 300 W xenon lamp (Oriel) connected to a grating monochromator (Acton Spectra Pro 2155). IPCE and APCE were calculated from the following formulas:

$$IPCE \ \% = \frac{J_{pho}(\lambda)}{P(W)} \times \frac{1240}{\lambda(nm)} \times 100$$
(3)

$$APCE \% = \frac{IPCE \%}{A} \tag{4}$$

Where J_{pho} is the average photocurrent (mA/cm²), *P* is power density of the light incident on the entire photocathode (mW/cm²), λ is the wavelength (nm), and *A* is the absorptance of the entire Cu₅V₂O₁₀ photocathode. Fig. S18 shows the power spectra for back illumination IPCE measurements. The IPCE measurements were done at 0.8 V vs. RHE with Ar bubbling or with H₂O₂. The predicted AM1.5 photocurrent density ($J_{AM1.5}$) of the photocathodes was estimated by multiplying the IPCE values by the AM1.5 solar photon flux and the electronic charge and subsequently integrating this for wavelengths below 700 nm according to the following relationship,

$$J_{AM1.5} = \int_{300 nm}^{700 nm} (IPCE(\lambda) \times \Phi_{AM1.5}(\lambda) \times q) d_{\lambda}$$
(5)

where $J_{AM1.5}$ is the total solar photocurrent in (A m⁻²), λ is the light wavelength (m), $\Phi_{AM1.5}(\lambda)$ is the photon flux of AM1.5 sunlight (photons per m² per s), and q is the electronic charge (1.602 × 10⁻¹⁹ C).

Electrical impedance spectroscopy (EIS) and Mott-Schottky measurements were performed with a VersaSTAT 3 Potentiostat (AMETEK Co., Ltd.). EIS was performed in the dark near the flat band potential (Fig. S19). Mott–Schottky plots were created based on the following relationship,

$$\frac{1}{c^2} = \frac{2}{q \,\varepsilon_{\rm r} \,\varepsilon_0 \,N_A} \left(-\varphi + \varphi_{fb} - \frac{k \,T}{q} \right) \tag{6}$$

where *C* is the capacitance (F/m²), ε_r is the relative permittivity or dielectric constant, ε_0 is the permittivity of free space, N_A is the acceptor density (m⁻³), φ is the applied potential (V vs reference), and φ_{fb} is the flat band potential (V vs reference). The space charge width (W) was estimated using the following expression.

$$W = \sqrt{\frac{2 \varepsilon_{\rm r} \varepsilon_0}{q N_A} \left(-\varphi + \varphi_{fb} - \frac{k T}{q}\right)} \tag{7}$$

The band positions can be calculated by extrapolating the Mott-Schottky plot to the x-axis (where $1/C^2 = 0$), which gives the flatband potential (in V vs. RHE). This potential corresponds to the Fermi level under flatband conditions. The valence band edge is positioned at a 0.1 - 0.2 eV more negative energy (i.e., more positive potential), with the exact difference given by

$$E_F - E_V = -kT ln\left(\frac{N_A}{N_V}\right) \tag{8}$$

where N_V is the effective density of states in the valence band (typically $10^{19} - 10^{20}$ cm⁻³).



Fig. S1. X-ray diffractograms of annealed (550 °C in air for 4 hours) $Cu_5V_2O_{10}$ films with various thicknesses. Reference patterns for $Cu_5V_2O_{10}$ as well as copper vanadates with other stoichiometry are also shown.



Fig. S2. Scanning electron micrograph (SEM) of (a) a bare FTO substrate and (b) $Cu_5V_2O_{10}$ thin film deposited on FTO at 300°C.



Fig. S3. Cross-section SEM images of $Cu_5V_2O_{10}$ film sprayed with (a) 100 mL and (b) 400 mL precursor after annealed at 550°C for 4 hours in air.



Fig. S4. Energy dispersive spectroscopy of a $Cu_5V_2O_{10}$ thin film after heating in air at 550°C for 4 hours.



Fig. S5. Top-view SEM image of 250 nm $Cu_5V_2O_{10}$ deposited on FTO after annealed at 550 °C in air for 4 hours and the corresponding EDX elemental mapping of (b) Cu, (c) V, (d) O.



Fig. S6. Atomic force microscopy (AFM) images of a bare FTO substrate used in this study.



Fig. S7. (a) Absorption spectra of annealed $Cu_5V_2O_{10}$ with various thicknesses. (b) Plot of -ln(TR) vs. film thickness at a wavelength of 450 nm, extracted from the data in (a). The slope of the curve gives an absorption coefficient (α) of (1.92 ± 0.21) × 10⁴ cm⁻¹.



Fig. S8. TRMC signal under various incident laser pulse intensities for a $Cu_5V_2O_{10}$ film synthesized by spray pyrolysis on a quartz substrate under (a) 410 nm wavelength, (b) 450 nm wavelength, (c) 500 nm wavelength and (d) 550 nm wavelength excitation.



Fig. S9. Open-circuit potential (OCP) measurements in the dark and light for a 250 nm $Cu_5V_2O_{10}$ in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.8). The illumination was from the backside.



Fig. S10. UPS cutoff spectra measured without bias for $\text{Cu}_5\text{V}_2\text{O}_{10}$ thin film.



Fig. S11. Chopped LSV scans for $Cu_5V_2O_{10}$ films at different film thicknesses (from 50 nm to 500 nm) measured with H_2O_2 as an electron scavenger under backside illumination in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.8).



Fig. S12. Chopped LSV scans for as deposited $Cu_5V_2O_{10}$ photocathodes synthesized to a thickness of ~250 nm on FTO measured with H_2O_2 as an electron scavenger under backside illumination.



Fig. S13. Fraction of the AM1.5 spectrum absorbed by an infinitely thick $Cu_5V_2O_{10}$ film (J_{Eg}) and the fraction absorbed by a 250 nm $Cu_5V_2O_{10}$ film (J_{abs}).



Fig. S14. IPCE spectra of $Cu_5V_2O_{10}$ measured with Ar bubbling at a potential of 0.8 V vs. RHE in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.8).

Fig. S15. APCE measurements for $Cu_5V_2O_{10}$ photocathodes conducted in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.8) H_2O_2 as an electron scavenger under back and frontside illumination as indicated in the figure legend.

Fig. S16. Constant potential measurement at 0.8 V vs RHE for 250 nm $Cu_5V_2O_{10}$ films in the dark and light (AM1.5 irradiation) with Ar bubbling in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.8).

Fig. S17. XPS spectra for a 250 nm $Cu_5V_2O_{10}$ showing regions for (a) Cu 2p, (b) V 2p (c) C 1s and (d) survey spectra. Measurements were performed in different sample areas that were either pristine or PEC tested at 0.8 V vs RHE for approximately 60 min in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.8) with H_2O_2 .

Fig. S18. Power density spectra of the lamp used for IPCE measurements.

Fig. S19. Electrochemical impedance spectroscopy (EIS) at 1.0 V vs. RHE for a 250 nm $Cu_5V_2O_{10}$ photocathode. The measurements were performed in 0.3 M K_2SO_4 and 0.2 M phosphate buffer (pH 6.8). Note that above 1000 Hz, the real part of the impedance is constant, whereas the imaginary part has a slope of -1. This implies that the system behaves as a resistance in series with a pure capacitance, which is a prerequisite for accurate Mott-Schottky analysis.