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The Electronic Structure and Performance Bottlenecks of CuFeO₂ Photocathodes

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ABSTRACT

The path to realizing low cost, stable, and earth-abundant photoelectrodes can be enabled through a detailed understanding of the optoelectronic properties of these materials, by combining theory and experimental techniques. Of the limited set of oxide photocathode materials currently available, CuFeO_2 has emerged as a promising candidate warranting detailed attention. In this work, highly compact thin films of rhombohedral (3R) CuFeO_2 were prepared via reactive co-sputtering. Despite its 1.43 eV indirect bandgap, a cathodic photocurrent of 0.85 mA/cm^2 was obtained at 0.4 V vs. RHE in the presence of sacrificial electron acceptor. This unexpected performance was related with inefficient bulk charge separation due to the ultrafast ($< 1 \text{ ps}$) self-trapping of photogenerated free carriers. The electronic structure of 3R- CuFeO_2 was elucidated through a combination of optical and X-ray spectroscopic techniques and further complemented by first principles computational methods, including the many-body approach for computing the O K-edge X-ray absorption spectrum. Through resonant inelastic X-ray scattering (RIXS) spectroscopy, the visible absorption edges of CuFeO_2 were found to correspond to $\text{Cu} \rightarrow \text{Fe}$ metal-to-metal charge transfer, which exhibits a high propensity toward self-trapping. Findings of the present work enable us to understand the performance bottlenecks of CuFeO_2 photocathodes and suggest feasible strategies for improving material limitations.

▪ INTRODUCTION

Cu(I)-based semiconducting metal oxides, due to their native *p*-type conductivities, have garnered significant attention in recent studies of photoelectrochemical (PEC) solar fuel production.¹⁻³ The prototypical photocathode Cu₂O, with a 2 eV bandgap, demonstrates excellent hydrogen production efficiency *via* solar water splitting.⁴⁻⁶ However, because the Cu₂O/Cu redox potential lies within the electronic bandgap,⁷ Cu₂O suffers from photocorrosion in aqueous environments and thus requires multilayer protection schemes.⁸ Consequently, ternary oxides containing Cu(I) motifs have been investigated to allow for more versatile property design and optimization. Notably, the group of cuprous delafossite oxides (Cu¹⁺M³⁺O₂, M = Fe, Rh, Cr, Al, etc.) exhibit tunable optical bandgaps and suitable conduction band energetic positions, making them promising photocathode candidates.⁹⁻¹³ Among cuprous delafossites, CuFeO₂ possesses the smallest bandgap ($E_g \sim 1.5$ eV), consists of earth-abundant elements, and can be prepared by various scalable and low cost deposition methods.¹³⁻²¹ The PEC stability of CuFeO₂ is also significantly improved compared with Cu₂O, which can be explained by its conduction band edge character. According to recent first principles results, the lowest optical transition in CuFeO₂ is associated with Cu 3*d* + O 2*p* → Fe 3*d* charge transfer, thus greatly reducing the probability of Cu self-reduction.²²⁻²⁵ Nonetheless, unraveling the detailed electronic structures of ternary oxides, including CuFeO₂ and other cuprous delafossites, is difficult to achieve experimentally. Conventional optical spectroscopy alone does not suffice for resolving and assigning the origins of various elementary excitations that define the absorption characteristics of such complex semiconductors. Given that CuFeO₂ offers a promising path to efficient and low-cost PEC solar fuels production, understanding of its fundamental properties, such as electronic structure and charge transport mechanisms, would provide guiding principles for further material design and optimization.

CuFeO₂ photocathodes exhibit catalytic activities that are highly dependent on the preparation methods. When fabricated by the Pechini sol-gel process, the material provides limited photovoltage and photocurrent density in the absence of sacrificial electron acceptors.¹⁶⁻¹⁹ The poor hydrogen evolution reaction (HER) catalytic activity of CuFeO₂ is attributed to the high surface state density ($\sim 10^{14}$ cm⁻²) that causes severe Fermi level pinning at the semiconductor-liquid junction.²⁶ In comparison, CuFeO₂ photocathodes prepared by electrodeposition are capable of driving kinetically more challenging CO₂ reduction (CO₂R)

reactions, with formate and acetate reported as the main products.¹³⁻¹⁵ Nevertheless, whether such CO₂R catalytic activity stems from CuFeO₂ remains unclear because electrodeposited CuFeO₂ films often have complicated hollow morphologies and contain CuO as a secondary phase. Although the high surface area of electrodeposited CuFeO₂ benefits the PEC performance, discerning the role played by CuO in such photocathode assembly presents a challenge. In this work, we decouple the role of phase impurity from structural morphology through preparation of high quality CuFeO₂ thin films with controllable secondary phase contents *via* reactive co-sputtering. This method enables further examination of the fundamental optoelectronic properties and intrinsic PEC characteristics of the CuFeO₂ thin films.

The electronic structure of CuFeO₂ is studied by resonant inelastic X-ray scattering (RIXS) spectroscopy.²⁷ In this photon-in/photon-out technique, the incident X-ray resonantly promotes a core electron into a specific unoccupied level, which is sensitive to local chemical environment. The relaxation of intermediate core excited-states, detected in the form of X-ray emissions, provides insights into various elementary processes such as charge transfer, *d-d*, and phonon excitations.²⁸ The effectiveness of RIXS in resolving inherently complex electronic structure of ternary oxides has been previously demonstrated on BiVO₄ and γ -Cu₃V₂O₈ photoanodes.²⁹⁻³² Herein, our O K-edge RIXS experiment is supported by first principles calculations describing the distribution of each constituent element in CuFeO₂: The valence band maximum (VBM) comprises primarily Cu 3*d* states whereas the conduction band minimum (CBM) is of non-bonding Fe 3*d* character. Furthermore, RIXS measurement at the Fe L-edge verifies that the visible absorption edges of CuFeO₂ are corresponding to Cu \rightarrow Fe metal-to-metal charge transfer. The low bulk charge separation efficiency in CuFeO₂, as well as the observation of long-lived excited state by transient absorption spectroscopy, implies ultrafast electron self-trapping being responsible for the low PEC performance. We also demonstrate that, while the presence of CuO enhances the CO₂R photocurrent density, phase pure CuFeO₂ is an intrinsically poor catalyst for both HER and CO₂R. These results provide fundamental insights into the performance bottlenecks of CuFeO₂ photocathodes, inform strategies for improving PEC performance, and highlight the significance of interactions between different metals in multinary metal oxides.

▪ EXPERIMENTAL SECTION

Preparation of CuFeO₂ Thin Films. Thin film samples of rhombohedral (3R) CuFeO₂ were deposited on 50 × 50 mm² fluorine-doped tin oxide (FTO) coated glass (TCO10-10, Solaronix) or 25 × 75 mm² quartz (CGQ-0640-01, Chemglass) substrates by magnetron co-sputtering in a LAB Line sputtering system (Kurt J. Lesker). Two radio frequency power supplies were separately controlled to manipulate the sputtering powers on circular (2" diameter) Cu and Fe targets. In order to optimize the Cu/Fe ratio in the samples, the power on the Cu target was fixed at 32 W, while the Fe sputtering power was varied between 120 – 160 W. The working atmosphere consisted of 9 mTorr of inert Ar and 1 mTorr of O₂, and the substrate temperature was kept at 200 °C during the deposition process. The as-deposited samples underwent 6 h post-annealing at 600 °C in a 1" diameter quartz glass tube furnace under a flowing (180 sccm) Ar atmosphere.

Sample Characterization. The transition metal compositions of the prepared CuFeO₂ thin films were quantified by inductively coupled plasma mass spectroscopy (7900 ICP-MS, Agilent) following digestion of films with concentrated HNO₃. The crystalline structures were analyzed by an X-ray diffractometer (SmartLab, Rigaku) using Cu-K_α radiation at 0.5° grazing angle. Raman spectra were recorded using a confocal Raman microscope (LabRam HR, Horiba Jobin Yvon) with a 532 nm laser source; the excitation laser power at the sample surface was adjusted to be in the 1–2 mW range, and the spectral positions were calibrated by the characteristic Si phonon peak at 520.7 cm⁻¹. Film morphology and thickness were inspected using a scanning electron microscope (Quanta FEG 250, FEI). X-ray photoelectron spectroscopy (XPS) data were acquired by a Kratos Axis Ultra spectrometer, using an Al-K_α source (hν = 1486.69 eV) operated at 225 W and a hemispherical electron energy analyzer. XPS binding energies were calibrated using adventitious alkyl carbon signals by shifting the C 1s peak to 284.8 eV. Optical transmission and specular reflection spectra were measured at 8° incident angle, using a UV-Vis spectrometer equipped with an integrating sphere (SolidSpec-3700, Shimadzu) over the range from 300 – 1600 nm. Absorption coefficients and dielectric functions were obtained *via* spectroscopic ellipsometry, using a M-2000DI ellipsometer (J. A. Woollam, Co.) with incident angle varying between 45 – 75° with 5° increments. Photothermal deflection spectroscopy was collected on a home-built system, in which monochromatic light from a laser

stimulated light source (EQ-77, Enertiq) was modulated with an optical shutter and used for exciting the sample (immersed in perfluorohexane). The grazing probe beam was provided by a stabilized HeNe laser, and its position was detected with a position sensitive detector, amplified and filtered with a current pre-amplifier, and then recorded with a lock-in amplifier.

Photoelectrochemical Measurements. The PEC measurements were conducted using an AM 1.5 solar simulator (16S-300-002, Solar Light) in a three-electrode configuration. A Pt wire served as the counter electrode, while a Ag/AgCl electrode immersed in 3M KCl solution was used as the reference electrode. The pH 6.8 buffer solution consisted of 0.1 M KHCO₃ (Sigma-Aldrich) saturated with gaseous CO₂, with the option of adding 0.1 M Na₂S₂O₈ (Sigma-Aldrich) as a sacrificial electron scavenger. Current-voltage characteristics were recorded with a potentiostat (SP-300, Bio-Logic), and the reported potentials were converted to the reversible hydrogen electrode (RHE) scale using the following relation:

$$E_{RHE} = E_{Ag/AgCl} + 0.210 \text{ V} + (0.0591 \text{ V} \times pH) \quad (1)$$

The incident photon-to-current efficiency (IPCE) was measured with the presence of 0.1 M Na₂S₂O₈ at 0.40 V vs. RHE external bias. A 150 W Xe arc lamp (M6255, Newport) combined with a holographic grating monochromator (CS-130, Oriel Instruments) was used to illuminate the front-side of the CuFeO₂ photocathode, while differences in photocurrent and dark current responses at individual wavelength were acquired by a Gamry Reference 600 potentiostat. The reference incident spectrum was measured by recording the photocurrent response from a calibrated Si photodiode at 10 nm intervals between 330 and 850 nm. The IPCE data was then converted to APCE (absorbed photon-to-current efficiency) by dividing with (1 – Transmission – Reflection).

Transient Absorption Spectroscopy. Optical pump-optical probe transient absorption spectroscopy was performed using a 100 fs, 1 kHz, Ti:Sapphire regenerative amplifier (Coherent Libra). A portion of the laser output was coupled to an optical parametric amplifier (Coherent OPerA Solo) for generating the 350 nm pump beam with a diameter of 0.3 mm and pulse energy of 0.8 μJ at the sample. The supercontinuum probes in the visible and near infrared regions were generated using a CaF₂ and a sapphire crystal, respectively. The incident angle of the probe beam was approximately 8° with respect to the sample surface normal. An Ultrafast Systems transient absorption system, equipped with two sets of fiber-coupled grating spectrometers plus Si CMOS detector arrays, was used for data collection. The two detectors were used for simultaneous

collection of the differential transmission (dT) and the differential reflection (dR) signal. The differential absorption (dA) signal was calculated using the following equation:³³

$$dA = -\ln\left(\frac{\%T + \%R}{\%T \cdot 10^{dT} + \%R \cdot 10^{dR}}\right) \quad (2)$$

in which %T and %R are the ground-state transmission and reflectivity at 8° incident angle, respectively.

X-ray Spectroscopies. X-ray absorption (XAS), X-ray emission (XES), and resonant inelastic X-ray scattering (RIXS) measurements were performed at Beamline 8.0.1 of the Advanced Light Source, Lawrence Berkeley National Laboratory.³⁴ XAS spectra were recorded simultaneously in total electron yield (TEY) and total fluorescence yield (TFY) modes and normalized to the incoming photon flux, monitored by drain current measured from an upstream gold mesh. The incident energy resolution was set to be 100, 200, and 250 meV for O K-edge, Fe L-edge, and Cu L-edge, respectively. TiO₂, Fe₂O₃, Cu, and CuO standards were used for XAS energy calibration. Emitted X-ray photons were energetically dispersed by a slit-less variable line-spacing spectrograph mounted at 90° to the incident photon beam direction and recorded by a CCD detector (DO-936BN, Andor). The XES energy resolution was 250, 440, and 640 meV for O K-edge, Fe L-edge, and Cu L-edge, respectively. RIXS experiments were performed with the same setup by varying incident X-ray photon energies for resonant excitation across different elemental edges.

First Principles Calculations. Spin polarized density functional theory (DFT) calculations were performed with Quantum ESPRESSO.^{35,36} We use the generalized gradient approximation³⁷ (GGA) plus Hubbard U (DFT+U) approach to properly describe the magnetic properties of CuFeO₂.^{38,39} In order to account for the random spin orientation of the room-temperature paramagnetic phase of 3R-CuFeO₂, we used an antiferromagnetic (AFM) ordering with alternating in-plane spin orientation and zero total magnetization in a 2x2x1 supercell (48 atoms). We note that this AFM ordering differed from the low-temperature ground state phase,⁴⁰ and yielded a structure with lower symmetry (C2/m). Therefore, structural relaxations were performed with lattice constants fixed to their experimental values (a=b=3.0349 Å, c=17.1656 Å for the primitive unit cell) until forces were smaller than 10⁻³ Ry/a.u.. Our calculations of AFM 3R-CuFeO₂ use a kinetic-energy cut-off of 30 Ry, charge density cut-off of 300 Ry, 3x3x1 Γ centered k-point grids and ultrasoft pseudo-potentials with 11, 16 and 6 explicit valence electrons

for Cu ($3d^{10}4s^1$), Fe ($3s^23p^63d^64s^2$) and O ($2s^22p^4$), respectively.⁴¹ Projected density of states (PDOS) were computed using a denser $5 \times 5 \times 3$ Γ centered k-point grid. Band structure was computed along symmetry lines.⁴²

Many-body XAS spectra were simulated using the determinant formalism implemented in the ShirleyXAS and MBXASPY software codes.^{43,44} Our calculations used a $2 \times 2 \times 1$ supercell structure of the AFM ordering, or equivalently, a $4 \times 4 \times 1$ supercell structure of the primitive cell (192 atoms). The supercell dimensions $a=b=12.1396$ Å, $c=17.1656$ Å are sufficiently large to neglect effects from the core-hole impurity to neighboring periodic images. We use a temperature smearing of 0.3 eV, a $1 \times 1 \times 1$ Γ centered k-point grid and the same DFT parameters used for bulk calculations. The $1s$ core-excited O atom is simulated by a pseudo-potential with electronic configuration $1s^12s^22p^4$. Figure S13 shows several convergence studies performed for the XAS spectra on the k-point grid and supercell size (in all cases, the spectrum is averaged over spin-up and spin-down and in three dimensions). These DFT parameters result in excellent agreement with near-edge experimental measurements, as shown below in the results section.

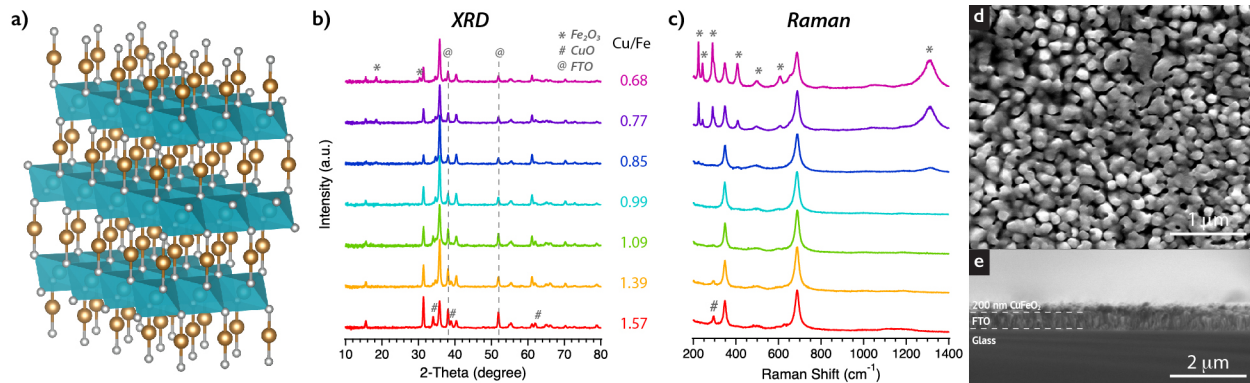


Figure 1 (a) Crystal structure of rhombohedral 3R-CuFeO₂. The Cu, Fe, and O atoms are labeled in brown, cyan, and gray, respectively. (b) In-plane X-ray diffraction patterns and (c) Raman spectra of CuFeO₂ thin films with various Cu/Fe stoichiometric ratios. (d) Plane view and (e) cross-sectional view SEM images of a 200 nm thick 3R-CuFeO₂ thin film prepared by reactive sputtering on a FTO-coated glass substrate.

RESULTS AND DISCUSSIONS

CuFeO₂ can exist in rhombohedral (3R) or hexagonal (2H) polytypes, and most PEC applications have been developed on 3R-CuFeO₂, the crystal structure of which is shown in Figure 1(a). Each Fe³⁺ is coordinated by six O²⁻ in slightly distorted FeO₆ octahedra. Edge-sharing FeO₆ layers stack along the c -axis alternatively with Cu⁺ layers. The linear O-Cu-O units in CuFeO₂ resemble Cu₂O, a prototypical p -type oxide semiconductor.^{4,6} In this study, CuFeO₂

thin films with varying Cu/Fe elemental ratios were deposited on FTO substrates by reactive co-sputtering. Following 6 h post-deposition annealing at 600 °C in Ar atmosphere, X-ray diffraction (XRD) patterns of the prepared samples matched that of 3R-CuFeO₂ found in the ICDD database (Figure 1b and Figure S1). Raman microspectroscopy (Figure 1c) also revealed the signatures of E_g and A_{1g} phonon modes of 3R-CuFeO₂ at 348 and 688 cm⁻¹, respectively.⁴⁵ A secondary α-Fe₂O₃ phase was detected in Raman spectra when Cu/Fe ratios (quantified by ICP-MS) were smaller than 0.85. This result is consistent with the previously reported phase segregation phenomenon in Fe-rich CuFeO₂ thin films prepared by sol-gel process.⁴⁶ When Cu/Fe ratios were greater than 1.09, a secondary CuO phase was characterized by the XRD peaks at 34.0, 38.9, and 62.0°, as well as the Raman shift at 296 cm⁻¹. Within the composition window of Cu/Fe ratios between 0.85 and 1.09, no evidence for secondary phases was observed. These phase pure 3R-CuFeO₂ thin films enable the study of fundamental optoelectronic properties and intrinsic PEC characteristics.

As shown in the SEM images (Figure 1d-e), our sputtered CuFeO₂ formed a uniform coverage with nanoporous morphology, which could be attributed to the rough surface of FTO substrates. When deposited on a quartz substrate with the same sputtering procedure, the resulting CuFeO₂ layer was more continuous and the intensity of the (012) diffraction peak increased (Figure S1). It should be noted that the desired 3R-CuFeO₂ phase on FTO glass was only obtained at 600 °C annealing temperature (Figure S2). The transformation from as-grown films to 3R-CuFeO₂ was not achieved at 550 °C or lower temperatures. At above 650 °C, Fe₂O₃ peaks can be observed in the Raman spectra even for stoichiometric films, suggesting the decomposition of CuFeO₂ at higher temperatures. In comparison, on quartz substrates, annealing to 650 °C was required to achieve conversion to the delafossite phase, and no decomposition was observed at 700 °C (Figure S2).

The transmission and reflectivity spectra measured from a phase-pure 3R-CuFeO₂ sample on FTO glass are shown in Figure S3, and the clear absorption onset at 880 nm matched the previously reported bandgap values.^{13,16} To mitigate light scattering and reflection from the rough FTO layer, spectroscopic ellipsometry was performed instead on a CuFeO₂ sample deposited on quartz (fitting results in Figure S4) to extract the refractive index (n), extinction coefficient (k), and absorption coefficient (α). As shown in Figure 2a, 3R-CuFeO₂ exhibits significant absorption in the visible wavelengths, with α ~ 1 × 10⁵ cm⁻¹ at 600 nm. Tauc analysis

indicated that the indirect and direct allowed bandgaps are 1.43 and 3.20 eV, respectively. For many cuprous delafossites, a strong and narrow absorption peak can be found between 3.7 – 4.5 eV.^{23,47} This feature has been assigned to the first excitonic peak of the direct allowed $\text{Cu } 3d + \text{O } 2p \rightarrow \text{Cu } 4s$ transition, enabled by the linear O-Cu-O structure. Thus, in the current study the sharp absorption feature at 280 nm (~ 4.4 eV) is referred as the $\text{Cu } 3d + \text{O } 2p \rightarrow \text{Cu } 4s$ exciton peak. Although Tauc analysis is generally not valid for excitonic transitions, the bandgap assignment of CuFeO_2 was not affected because the exciton peak is located far from both the direct and indirect bandgaps. Three broader absorption features at 340, 450, and 660 nm can also be distinguished in Figure 2a, and the optical excitation pathways associated with these features will be investigated by RIXS and discussed later in this work. Photothermal deflection spectroscopy (PDS), which detects the heat dissipated from the sample through non-radiative recombination,⁴⁸ also revealed a sharp absorption onset at 880 nm (Figure 2b). The extended absorption character at ~ 900 nm can be related to defect-related tail states, and we relate the broad absorption peak at ~ 1250 nm (0.99 eV) to absorption from on-site Fe $d-d$ excitations, which is further confirmed by Fe L-edge RIXS, as discussed below.

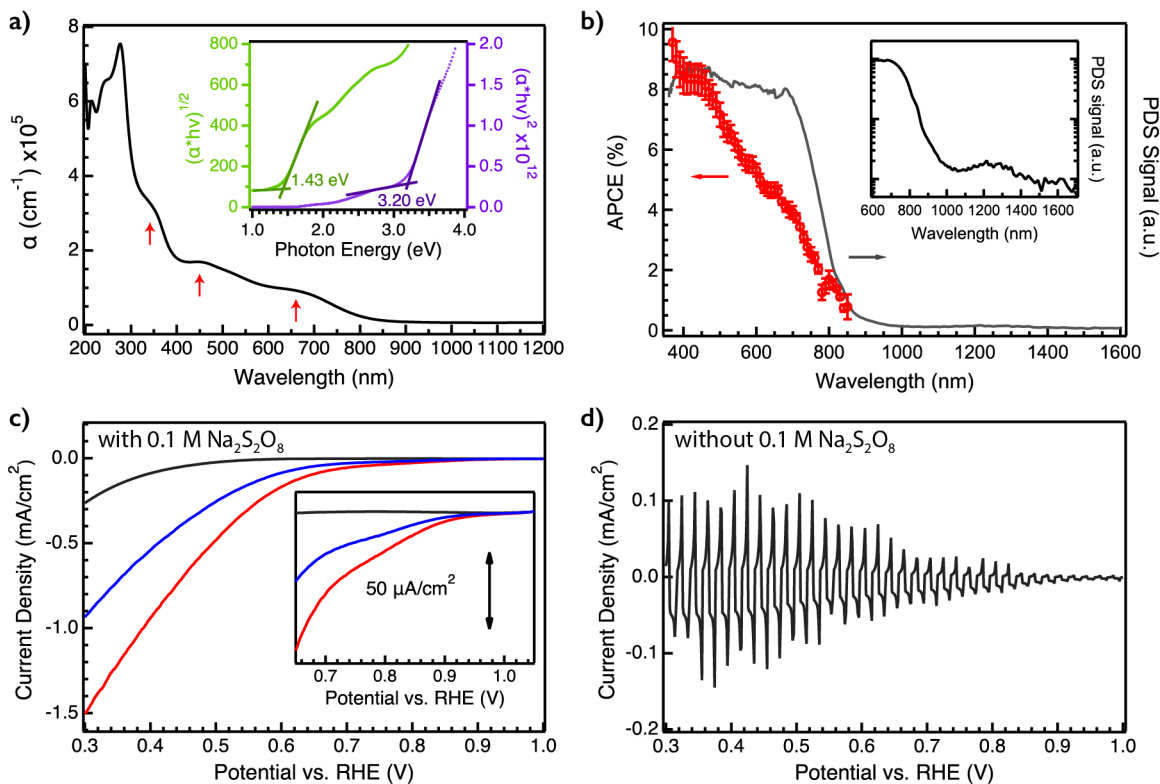


Figure 2 (a) Absorption coefficients of 3R-CuFeO₂ as a function of wavelength. Inset: Tauc plots for indirect (green) and direct (purple) allowed transitions. (b) APCE (red) and PDS (gray) profiles of CuFeO₂. APCE was measured at 0.4 V vs. RHE with 0.1 M Na₂S₂O₈ as sacrificial electron scavenger. Inset: PDS signal plotted in log scale in order to highlight the mid-bandgap absorption feature. (c) Linear sweep voltammetry (LSV) measurement of a CuFeO₂ photocathode under dark condition (black), front-side (red) and back-side (blue) illumination in the presence of 0.1 M Na₂S₂O₈. Scan rate was 50 mV/sec in cathodic direction. (d) LSV measurement of a CuFeO₂ photocathode under chopped front-side illumination at 20 mV/sec scan rate without the addition of Na₂S₂O₈.

PEC performances of the sputtered CuFeO₂ thin films were tested in pH 6.8 buffer (0.1 M KHCO₃ solution constantly saturated with CO₂ gas), using a simulated AM1.5 solar spectrum at 100 mW/cm² intensity. When 0.1 M Na₂S₂O₈ was added as the sacrificial electron acceptor, the phase-pure CuFeO₂ photocathode with ~ 1:1 Cu/Fe ratio showed a cathodic photocurrent onset at 0.92 V vs. RHE, and the photocurrent density increased sharply at 0.6 V vs. RHE, eventually reaching 0.85 mA/cm² at 0.4 V vs. RHE (Figure 2c). These characteristics are similar to those measured from phase-pure CuFeO₂ electrodes prepared by the sol-gel process¹⁶ or electrodeposition,¹³ in 1 M NaOH with O₂ gas as sacrificial electron acceptor. If no sacrificial reagent was present in the electrolyte, only ~ 50 μA/cm² photocurrent density was obtained from the same photocathode (Figure 2d), suggesting that CuFeO₂ has very limited surface catalytic activity for either HER or CO₂R.

Figure S5 compares the PEC performances of CuFeO₂ thin films with different Cu/Fe ratios. When Na₂S₂O₈ was present, no systematic change in photocurrent amplitude was observed. In the absence of sacrificial reagent, CuFeO₂ photocathodes with higher Cu/Fe ratios (*i.e.* with CuO secondary phase) exhibited three times higher photocurrent densities. On these Cu-rich CuFeO₂ photocathodes, an additional reduction (oxidation) half-wave was observed at ~ 0.6 V (~ 0.8 V) vs. RHE in the cyclic voltammetry scan, which can be attributed to the Cu²⁺ redox process from the CuO secondary phase. Therefore, the higher photocurrents obtained from these photocathodes were not indicative of intrinsically improved catalytic activity, but rather CuO (or its *in situ* reduced form) acting as the catalyst atop the CuFeO₂ light absorber. This observation partly explains the CO₂R catalytic activity difference between CuFeO₂ photocathodes prepared by sol-gel or electrodeposition methods, where CuO phase segregation is typical. Although beyond the scope of the present work, further understanding of the interplay between CuFeO₂ and CuO would help facilitate the development of efficient PEC CO₂R systems.

Even with sacrificial electron acceptor, photocurrents generated from CuFeO₂ photocathodes were more than 1 order of magnitude lower than the theoretical limit; considering the absorption characteristics of CuFeO₂ (200 nm thickness) and the photon flux of the AM 1.5 solar spectrum, a maximum photocurrent of 24.2 mA/cm² is expected (Figure S6). The onset of the absorbed photon-to-current efficiency (APCE), measured at 0.4 V vs. RHE in the presence of Na₂S₂O₈, occurred at 850 nm, which is similar to the optical absorption onset determined by PDS (Figure 2b). However, while the PDS signal quickly reached a plateau at 700 nm, the APCE profile increased more gradually and barely surpassed 10% at 400 nm. This suggests that a large percentage of photogenerated charge carriers undergo bulk recombination instead of being collected at the semiconductor-liquid junction. Moreover, the observation of lower photocurrent when illuminated from the backside of the photoelectrode (Figure 2c) also points to the minority carrier (electron) diffusion length being a primary performance-limiting factor.

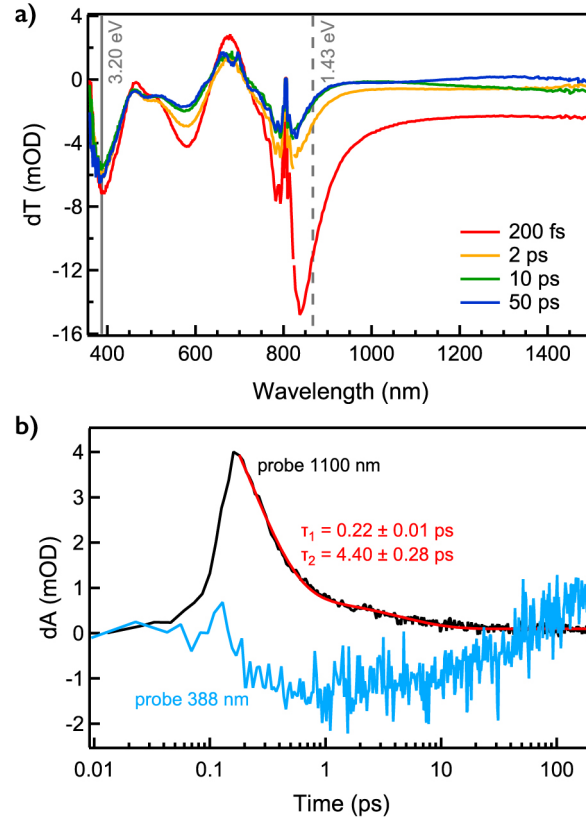


Figure 3 (a) Differential transmission (dT) spectra of CuFeO₂ (200 nm on quartz) at various pump-probe delays. Excitation wavelength: 350 nm, power: 0.8 μ J/pulse, beam diameter \sim 0.3 mm. (b) Time dependence of differential absorption (dA) signal at 1100 nm (black) or 388 nm (blue) probe wavelengths. The red line indicates the bi-exponential decay fitting result to the 1100 nm dA data.

The bulk carrier transport limitation of CuFeO₂ is not only evidenced through PEC measurements, but also complemented by time-resolved optical spectroscopy. Figure 3a represents the differential transmission (dT) spectra at various time delays following an optical excitation. As previously studied in the case of BiVO₄ photoanodes,³³ the derivative-like features near the optical transitions originate from shifting and broadening of oscillators, while the broad negative background in the near infrared range ($>$ 1000 nm) is related to the free carrier absorption. The actual differential absorption (dA) signal was reconstructed by collecting both differential transmission and differential reflectivity simultaneously, and the free carrier lifetime in CuFeO₂ was found to be extremely short. As shown in Figure 3b, a bi-exponential decay model gave an excellent fit to the dA signal measured at 1100 nm, with decay time constants being 0.22 ± 0.01 and 4.40 ± 0.28 ps, respectively. It should be noted that time-resolved microwave conductivity measurement, which probes conducting charge carriers (as opposed to

free carriers), yields a much longer (200 ns) lifetime.²⁶ Comparison of these results suggests the photogenerated free carriers may quickly self-trap and form small polarons by distorting the surrounding lattice. Thus, it is likely that polaronic transport serves as the dominating conduction mechanism in CuFeO₂, as in a range of other transition metal oxides.^{49–52} Indeed, inspection of dT spectra (Figure 3a) reveals that the feature near 388 nm, associated with the direct bandgap (3.20 eV), persisted to much longer times than the rapidly relaxing spectral response in the near infrared. Moreover, the reconstructed 388 nm dA signal exhibited a rise that correlated well with the rapid decay of the free carrier signal at 1100 nm, and then subsequently persisted for tens of picoseconds (Figure 3b), thus indicating a long-lived excited state that may be associated with the existence of electron or hole polarons. Even though the excitation energy density used in this measurement was much higher than the 1 sun intensity for PEC performance evaluation, it worth noting that higher-order phenomena, such as Auger recombination, can be ruled out as the signal intensity was linear with excitation energy (Figure S7). Previously, Prévot *et al.* reported a surface hydroxide layer of CuFeO₂ promotes charge recombination and reduces photovoltage.²⁶ Our findings suggest, in addition to the detrimental surface states, that poor bulk charge transport also warrants further attention. To realize the full potential of CuFeO₂ as a photocathode, the surface states need to be effectively passivated and the charge diffusion length must be improved to be comparable with the absorption depth.

To obtain further insight into the room-temperature electronic structure of 3R-CuFeO₂, we performed zero-temperature spin polarized DFT+U calculations for an antiferromagnetic spin arrangement of 3R-CuFeO₂ (see Experimental Section for details). At this level of theory, electronic structure calculations are sensitive to the Hubbard U value chosen for on-site correlation. In this work, a Hubbard U value of 2 eV was chosen for Fe ions to approximate the experimental crystal field splitting, however we note that varying the U value from 1 to 3 eV has a negligible qualitative impact on the calculated PDOS (Figure S8). Because Cu¹⁺ has a closed *d* shell configuration, a Hubbard U value correction has a negligible effect on the computed spectrum.⁵³ The band structure shown in Figure 4a confirms the indirect bandgap of CuFeO₂: the VBM and the CBM are located at the *M*₂ and the *A* point of the Brillouin zone, respectively. The calculated 0.444 eV bandgap severely underestimated the experimental value by 70 %. The disagreement on bandgap is not uncommon at this level of theory, and is largely explained by strong on-site correlation effects arising from the frontier Fe 3*d* orbitals. According to the band

structure, the electron and hole effective masses were found to be $1.828m_0$ and $1.348m_0$, respectively, although effective masses are expected to display small variations with the level of theory. PDOS for Cu, Fe, and O are shown in Figure 4b, and the results are in good agreement with previous DFT+U calculations for CuFeO_2 .^{23,53,54} The VBM is dominated by Cu $3d$ states (Figure S9), with some degree of hybridization with O $2p$. The occupied O $2p$ and Fe $3d$ states were found to be 4.5 and 7 eV away from the VBM, respectively. The CBM was found to consist of mainly Fe $3d$ states, with a ~ 1.1 eV splitting due to the octahedral O coordination around Fe ions. Unoccupied Cu $4s$ and $4p$ states are located at ~ 2.5 eV above the CBM.

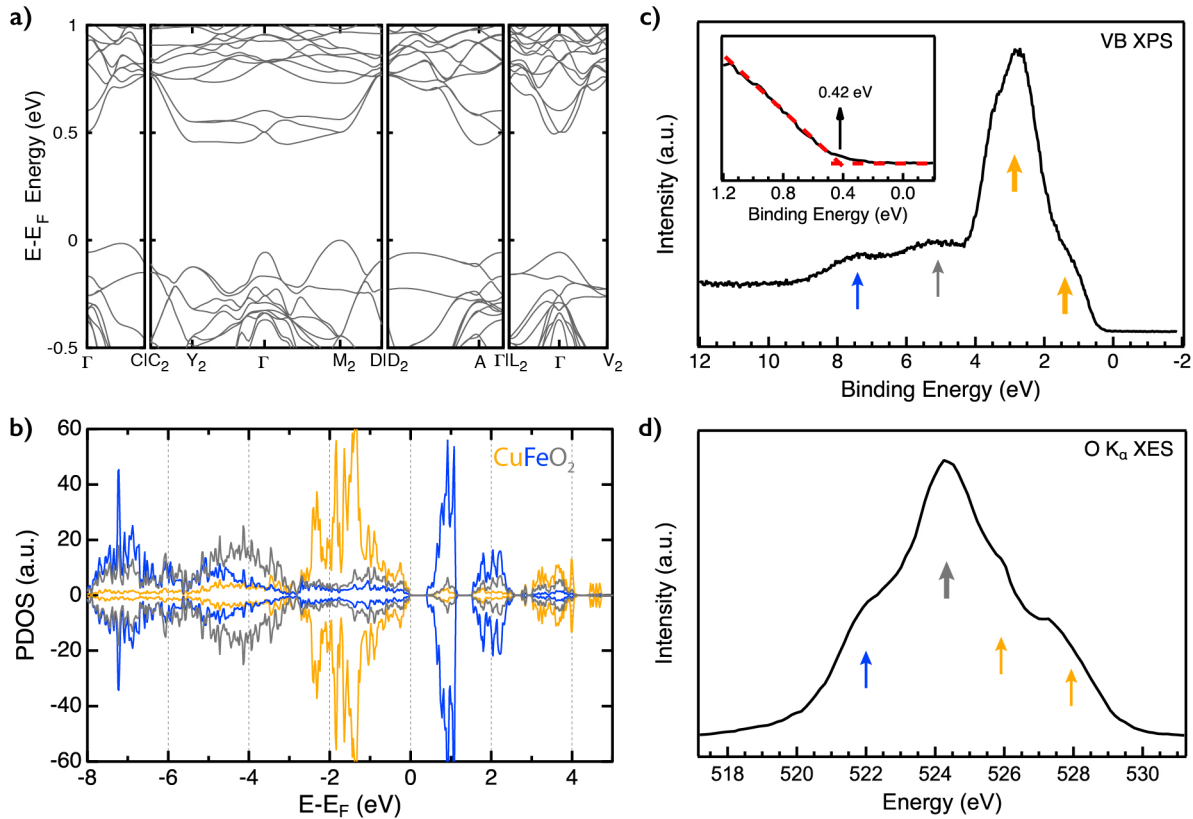


Figure 4 (a) Band structure calculation for 3R- CuFeO_2 using DFT+U with $U = 2$ eV for Fe. The room temperature paramagnetic phase of 3R- CuFeO_2 was simulated using an antiferromagnetic spin ordering. (b) PDOS calculations for 3R- CuFeO_2 using DFT+U. Colors denote Cu (yellow), Fe (blue) and O (gray) orbital contribution. The Fermi level is set at the highest occupied state. (c) Experimental valence band XPS spectrum of CuFeO_2 . Inset: the enlarged valence band onset region. (d) Experimental O K_α nonresonant XES spectrum. Arrows indicate the contributions from Cu (yellow), Fe (blue), and O (gray) PDOS.

The computed PDOS provides guidance for the analysis of a combination of soft X-ray spectroscopies that probe the valence and conduction bands. Starting with probes of the valence band, XPS revealed that the Fermi level at the surface is located 0.42 eV above VBM, which is

consistent with the *p*-type conductivity of CuFeO₂ (Figure 4c). At least four peaks were resolved and matched well with the calculated PDOS distribution in Figure 4b. The peaks related to Cu 3*d* states were of higher amplitudes, because with the Al-K_α radiation ($h\nu = 1486.69$ eV) used in the XPS measurement the photoionization cross section for Cu 3*d* electrons is ~ 50 and ~ 5.5 times larger than that for the O 2*p* and Fe 3*d* electrons, respectively.⁵⁵ In comparison, non-resonant O K_α X-ray emission spectroscopy (XES) also revealed four peaks, but with the main peak (524.5 eV) located ~ 5 eV below the emission onset (Figure 4d). Because XES detects the radiative recombination between a core-hole and a valence electron, it carries higher element specificity toward O PDOS in the valence band, with the PDOS of Cu and Fe still visible as the weak shoulders flanking the main emission peak.

X-ray absorption spectroscopy (XAS) acquired in total fluorescence yield (TFY) mode is more bulk-sensitive and was used to probe the unoccupied levels in the conduction band. At the Cu L₃-edge, CuFeO₂ exhibited a broad absorption peak at 934 eV (Figure S10). These results, in conjunction with the Cu 2*p* XPS emission shown in Figure S11, supports the Cu oxidation state in CuFeO₂ to be +1.^{56,57} At the Fe L-edge XAS, CuFeO₂ exhibited a doublet with 1.60 eV separation (Figure S10), similar to Fe₂O₃, which is related to *d*-orbital manifold (*t*_{2*g*} and *e*_g) in the octahedral ligand field.⁵⁸ In the O K-edge XAS (Figure S10), three absorption peaks (530.6, 532.1, and 533.7 eV) were resolved in the pre-edge region, originating from hybridization between oxygen and metals. The energy positions and separation (~ 1.3 eV) between the first two absorption peaks of CuFeO₂ resemble the doublet peaks measured from a Fe₂O₃ reference and are related to the Fe 3*d* states.⁵⁹ When compared with the conduction band PDOS (Figure 4b), the third pre-edge absorption peak at 533.7 eV can be reasonably assigned to hybridized Cu 4*s*/4*p* states.

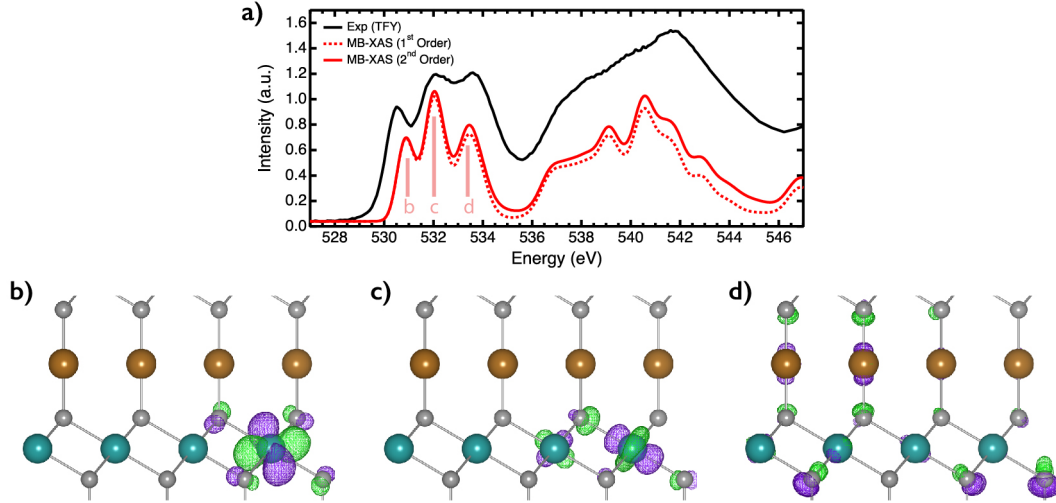


Figure 5 (a) Experimental versus theoretical XAS spectrum of 3R-CuFeO₂. The computed spectrum, obtained with the determinant formalism, is averaged over spin-up and spin-down AFM configurations and in three dimensions. Note that the energy axis is shifted for the calculated spectrum in order to give a better comparison to the experimental data. (b-d) Probability densities of the final state wavefunctions for the three pre-edge peaks at O K-edge. Wavefunction orbitals for spin-up and spin-down are equivalent, therefore only the spin-up case is shown in the figure. The Cu, Fe, and O atoms are labeled in brown, cyan, and gray, respectively.

To support our assignments of the XAS spectrum and provide deeper fundamental insights into the optoelectronic properties of CuFeO₂, first principles many-body XAS calculations were performed on the AFM configuration with the determinant formalism to simulate the room temperature 3R-CuFeO₂.^{43,44} The calculated O K-edge XAS spectrum for the AFM configuration agrees well with the experimental data (Figure 5a), supporting the accuracy of the DFT modeling of the conduction band PDOS in the paramagnetic phase. The position and relative magnitude of the three pre-edge absorption peaks are clearly reproduced at this level of theory. First and second order excitation are shown to emphasize that many-body effects can lead to peak intensity increases at higher energies above the absorption onset. Alternative, XAS spectra computed for ferromagnetic (FM) and nonmagnetic (NM) ordering of 3R-CuFeO₂ are shown in Figure S14. The AFM state corresponds to the lowest total-energy structure; the FM and NM configurations are 53.9 and 1464.2 meV per formula unit above the AFM configuration, respectively. While the computed XAS spectra for the FM and NM configurations display similarities with the experimental results, these magnetic orderings correspond to metastable states and are therefore disregarded. This approach further enables plotting of the probability densities of the final state wavefunctions associated to the three pre-edge oscillators, as shown in Figures 5b-d. The orbital projections suggested that the CBM of CuFeO₂ consists of Fe 3*d* non-

bonding states, while the higher-energy Fe states exhibit a certain degree of Fe-O anti-bonding character. The highest pre-edge peak is mainly associated with anti-bonding Cu *sp* hybrid orbitals, but also involves Fe-O anti-bonding interactions. With this information on the conduction band PDOS distribution, we then performed RIXS at the O K-edge in order to investigate the nature of various band-to-band transitions in CuFeO₂.

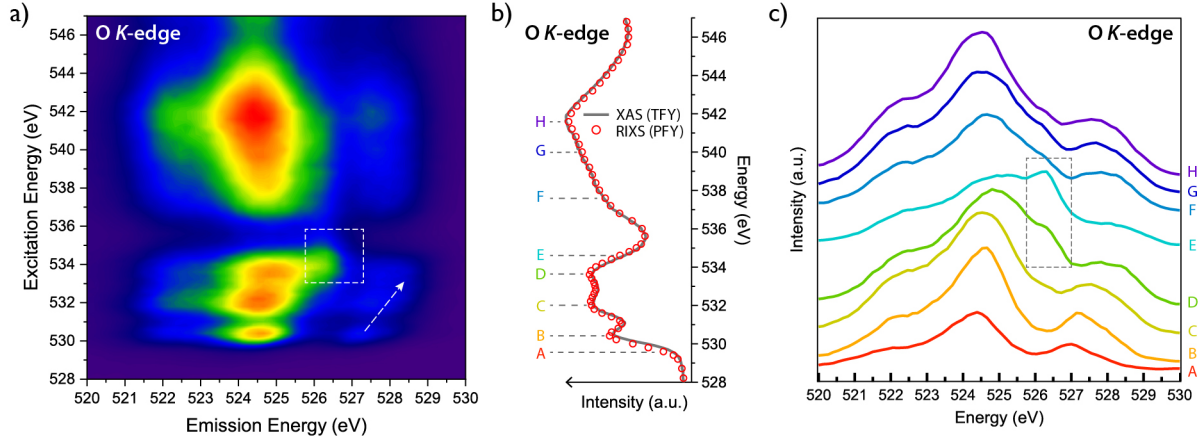


Figure 6 (a) RIXS mapping results at O K-edge. (b) XAS spectrum of CuFeO₂ at O K-edge (black line) and integrated O K_α XES intensity as a function of excitation energy (red circles). (c) Selected XES spectra with excitation energies labeled in accordance with panel (b).

Figure 6a gives a two-dimensional plot of the O K-edge emission spectra as a function of X-ray excitation energy. For each excitation energy, the integrated X-ray emission intensity gave a measure of X-ray absorption strength in the form partial fluorescence yield (PFY). It can be seen in Figure 6b that the reconstructed PFY-XAS spectrum matches well with the scanning TFY result. Eight representative O K-edge resonant XES spectra are plotted and compared in Figure 6c. A blue-shifting of XES onset can be observed when the excitation moves from CBM to higher photon energies, indicating the VBM and CBM are not aligned in *k*-space and the optical bandgap is an indirect transition.⁶⁰ When the X-ray excitation resonantly excites a core electron into the unoccupied Fe *3d* levels near the CBM (530.6 and 532.1 eV), the corresponding X-ray emission carries more weight from the occupied Fe *3d* levels near the bottom of the valence band (522 eV). A narrow emission peak at 526.4 eV was only observed with excitation energy between 533 – 535 eV, corresponding to excitation into the Cu *4s/4p* states. This result confirms the VBM consists of occupied Cu *3d* states, as also supported by XPS, non-resonant O K_α XES, and first principles calculation.

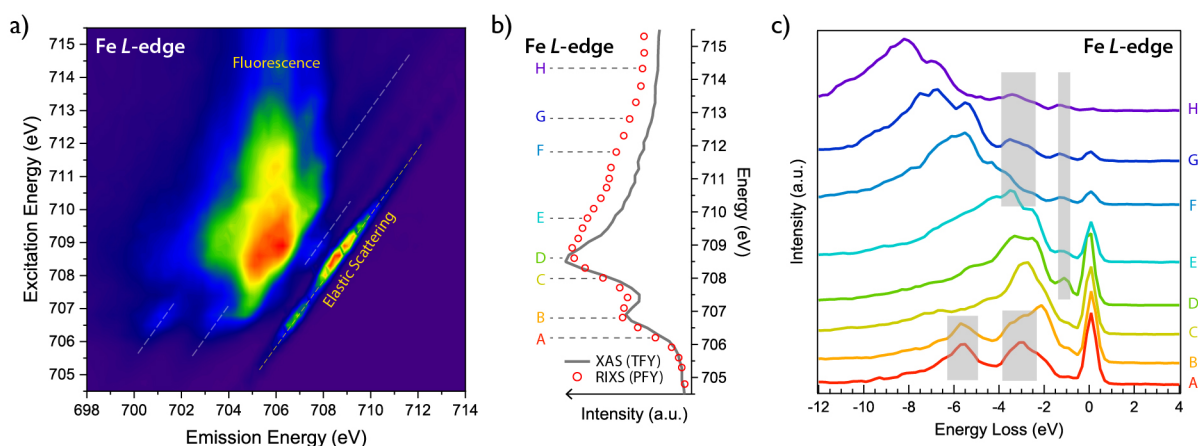


Figure 7 (a) RIXS mapping results at Fe L-edge. Dashed lines indicate the inelastic scattering peaks. (b) XAS spectrum of CuFeO_2 at Fe L-edge (black line) and integrated $\text{Fe L}\alpha$ XES intensity as a function of excitation energy (red circles). (c) Selected XES spectra with excitation energies labeled in accordance with panel (b). The energy loss x-scale is defined relative to the excitation energy.

RIXS measurement was also performed at the Fe L-edge. Following excitation of an Fe $2p$ electron into the conduction band, the resulting X-ray emission spectra also exhibit a clear dependence on the excitation energy (Figure 7). In addition to the non-resonant fluorescence peak at 705.5 eV, a few features with constant energy loss from the excitation energy were observed (dashed lines in Figure 7a). Figure 7c plots selected X-ray emission spectra with respect to the energy loss scale, and three inelastic scattering peaks were located at ~ 1.0 , ~ 3.1 , and ~ 5.6 eV, respectively. For strongly correlated materials, such as many transition metal oxides, the energy losses of this range are typically indicative of $d-d$ or charge transfer excitations.²⁸ A similar 1 eV energy loss feature has also been reported on single crystal and nanorods of $\alpha\text{-Fe}_2\text{O}_3$, which adopts the same octahedral FeO_6 local symmetry.^{61,62} One plausible origin for this 1 eV energy loss is the $d-d$ excitation of Fe^{3+} . As depicted in Figure 8a, the initial (ground) state of an octahedrally coordinated high-spin Fe^{3+} is ${}^6\text{A}_1$. Following a resonant Fe L-edge excitation, an additional electron is placed in the Fe $3d$ level while a core-hole is created at the Fe $2p$ level, leading to the $2p^5 3d^6$ intermediate state. The elastic scattering process would recreate the ground ${}^6\text{T}_1$ state by emitting an X-ray photon with the same energy as the excitation photon. However, the relaxation of intermediate state can also result in a Fe^{3+} cation with other electronic configurations, such that the final state differs from the initial state *via* a $d-d$ excitation. Given that this energy loss feature was most pronounced when the X-ray excitation aligned with the Fe e_g level absorption (708.5 eV), it is likely that the associated final state is ${}^4\text{T}_1$,

which would require 1 eV to excite a t_{2g} electron into the e_g level. We would like to note that a sub-bandgap absorption feature at 0.99 eV (1250 nm) was also observed on CuFeO₂ by photothermal deflection spectroscopy (Figure 2b), which also agrees well with the 1 eV energy-loss feature detected by the Fe L-edge RIXS. This type of on-site $d-d$ excitations only change the local electronic configuration, but does not contribute to conducting charge carriers that are required for PEC application.

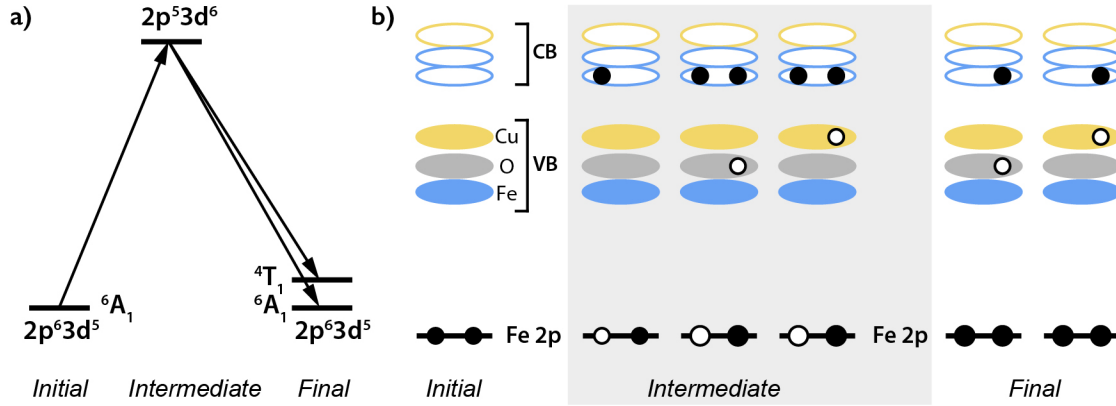


Figure 8 (a) Schematic energy level diagram of the Fe L-edge RIXS process leading to the 4T_1 $d-d$ excited state. (b) Schematic diagram of the charge transfer processes in intermediate state of the Fe L-edge RIXS.

The inelastic scattering peak at ~ 3.1 and ~ 5.6 eV energy losses are assigned as charge transfer excited states. Specifically, the ~ 5.6 eV feature corresponds to O \rightarrow Fe ligand-to-metal charge transfer while the broad feature at ~ 3.1 eV is related to Cu \rightarrow Fe metal-to-metal charge transfer. Even though electronic transitions involving core-levels are highly element-specific, the hybridization between Fe, O, and Cu enables charge transfer between different elements in the intermediate state (Figure 8b). Consequently, the resulting final states would be equivalent to the optically excited CuFeO₂ semiconductor, and the energy losses in the X-ray scattering process are equivalent to the valence-to-conduction band transition energies. According to the PDOS alignment in Figure 4b, the 5.6 eV energy loss in RIXS can be achieved by charge transfer from the O $2p$ states within the valence band to the CBM, which is of Fe $3d$ character. On the other hand, a correlation can be drawn between the 3.1 eV Fe RIXS energy loss feature and the absorption coefficient (α) spectrum obtained by spectroscopic ellipsometry (Figure S15). Under closer inspection, the broad energy loss peak between 1.5 – 3.8 eV seems to comprise several overlapping peaks that match well with the absorption edges of CuFeO₂ at 340, 450, and 660 nm (3.65, 2.76, and 1.88 eV). Because the valence band edge mainly consists of Cu $3d$ states, we can confidently suggest that Cu-to-Fe charge transfer is responsible for the visible absorption of

CuFeO₂, as well as the ~ 3.1 eV energy loss feature measured at the Fe L-edge. This finding implies that photogenerated electrons and holes separate at the atomic scale near the Fe and Cu cations, respectively, which should suppress direct electron-hole recombination because there is no direct covalent bonding between these elements. However, APCE shows that CuFeO₂ photocathodes suffers from poor bulk charge separation, especially in the visible wavelengths (Figure 2b), which may be a consequence of charge localization via small polaron formation at these sites. In addition, to reduced charge transport limitations and improve the efficiency of CuFeO₂ photocathodes, anisotropies arising from the delafossite structure should also be taken into account. In particular, given the alternating CuO₂ and FeO₆ layers in the lattice, controlled growth perpendicular to the *c*-axis, which would enable out-of-plane transport along extended Cu and Fe planes, is expected to benefit charge collection.

▪ CONCLUSIONS

In summary, we have achieved phase-pure thin films of *p*-type 3R-CuFeO₂ by reactive co-sputtering. The photoelectrochemical performance in 0.1 M Na₂S₂O₈ demonstrated an onset potential of 0.92 V vs. RHE, and 0.85 mA/cm² photocurrent density at 0.4 V vs. RHE. Optical characterization indicates indirect and direct bandgaps of 1.43 and 3.20 eV, respectively. The non-optimal PEC characteristics of CuFeO₂, largely limited by electron transport, were manifested by the 3% (10%) APCE at 750 nm (400 nm). This is further supported by the ultrafast relaxation (< 1 ps) of photogenerated free carriers, accompanied by the appearance of a longer-lived excited state, suggesting the possibility of small polaron formation. Moreover, the enhanced CO₂R photocurrent densities exhibited by Cu-rich photocathodes were originated from the secondary CuO phase, rather than an intrinsic catalytic activity of CuFeO₂. The electronic structure was elucidated through a combination of experimental X-ray spectroscopies including XAS, XES, XPS, and RIXS. This is further complemented by first principles computational methods including the many-body approach for computing O K-edge XAS spectrum. The VBM is found to be primarily of Cu *3d* character whereas the CBM consists of non-bonding Fe *3d* states. Considering the alternating CuO₂ and FeO₆ planes in the delafossite lattice, effective charge transport is likely severely limited and thus leads to significant charge recombination in these polycrystalline films. This is likely reflected in the poor fill factor observed in PEC and the larger potentials required achieving electron hole separation. In developing new ternary metal

oxides for PEC applications, most efforts have been guided by physical properties such as optical bandgap and operational stability. The results of the present work underscore the significance of interactions between different metals as well. Further optimization efforts are likely to significantly benefit from heteroepitaxial growth along the direction perpendicular to the delafossite *c*-axis.

ASSOCIATED CONTENT

Supporting Information.

XRD patterns, Raman spectra, variable angle spectroscopic ellipsometry data and fit results, J-E characteristics of CuFeO₂ thin films with different Cu/Fe ratios, theoretical cumulative photocurrent, calculated PDOS by DFT+U using different Fe U values, XAS spectra at O K-edge, Fe and Cu L-edge, XPS spectra of Cu 2*p*, Fe 2*p*, and O 1*s* levels, work function measurement result. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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