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**Understanding the Mechanism of Catalytic Selectivity During Electrochemical CO<sub>2</sub> Reduction Using Nonlinear Soft X-Ray Spectroscopy**

**Lawrence Baker  
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# Understanding the Mechanism of Catalytic Selectivity During Electrochemical CO<sub>2</sub> Reduction Using Nonlinear Soft X-Ray Spectroscopy - Air Force Office of Scientific Research Young Investigator Award (FA9550-15-1-0204)

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## 1 Executive Summary

The environmental consequences of continued fossil fuel consumption, as well as the economic uncertainty of hydrocarbon sources are strong motivations for developing catalysts capable of reducing CO<sub>2</sub> to a high-energy-density fuel or other value-added products. Selectively converting CO<sub>2</sub> to fuels requires control of electron motion at a catalyst surface. Detailed understanding of electron dynamics at surfaces of heterogeneous catalysts can inform relevant design parameters for next generation materials with high efficiency for CO<sub>2</sub> reduction to valuable products. Unfortunately, there is a shortage of spectroscopic probes capable of following these charge transfer processes with element specificity, ultrafast time resolution, and surface sensitivity.

To enable the study of surface electron dynamics, we have recently designed and constructed an ultrafast soft X-ray and extreme ultraviolet (XUV) light source based on high harmonic generation (HHG). Using this light source, we have shown that XUV reflection-absorption (RA) spectroscopy combines the benefits of X-ray absorption, such as element and oxidation state specificity, with surface sensitivity and ultrafast time resolution, having a probe depth of only a few nm and an instrument response less than 100 fs. Additionally, by operating in a grazing angle reflectivity, XUV RA spectroscopy is independent of the sample thickness. This provides a major advantage over traditional transmission experiments where the sample thickness is limited to  $\sim 100$  nm. Since catalytic properties of metal oxides change with thickness, it is imperative to study the electron dynamics of actual functional materials that show highest catalytic activity and selectivity toward CO<sub>2</sub> reduction.

Using these unique capabilities, we have measured electron dynamics in two closely related materials,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and CuFeO<sub>2</sub> to reveal the origin of their different catalytic properties. We show that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> suffers from carrier self-trapping (i.e. small polaron formation) at the surface which limits its efficiency as a photocatalyst. Specifically, we show that the lattice expansion during small polaron formation occurs on the identical time scale as surface trapping, strongly suggesting that lattice distortion represents the probable driving force for sub-ps electron localization to the surface of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. On the contrary, CuFeO<sub>2</sub> is an active and selective catalyst for CO<sub>2</sub> reduction. We find that the higher photocurrent in this material compared to Fe<sub>2</sub>O<sub>3</sub> is correlated with ultrafast hole thermalization from O 2p to Cu 3d states which leads to spatial charge separation in this layered crystal lattice, which cannot occur in Fe<sub>2</sub>O<sub>3</sub>. While the electron dynamics between the two materials are nearly identical, the hole in CuFeO<sub>2</sub> delocalizes across a strongly hybridized Cu-O valence band. This ultrafast spatial charge separation, which is unique to the layered delafossite crystal structure, provides an important design parameter for controlling catalyst performance for CO<sub>2</sub> reduction based on the material's underlying photophysics.

## 2 Developing XUV Reflection-Absorption Spectroscopy (XUV-RA)

To enable the study of electron dynamics in relevant catalytic materials, we have constructed an ultrafast grazing angle soft X-ray and extreme ultraviolet (XUV) light source based on high harmonic generation (HHG).<sup>2</sup> A diagram of the table-top spectrometer is shown in Figure 1.

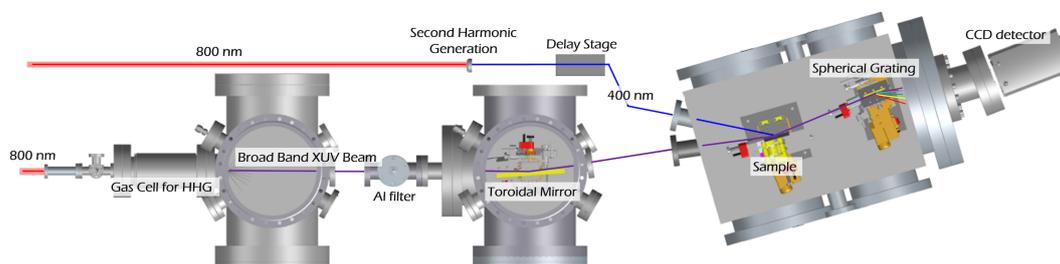


Figure 1: Overview of the XUV-RA spectrometer. Semi-infinite gas cell (40 cm) is used for HHG. Residual driving field is removed with an Al filter. Toroidal mirror is used to focus the XUV radiation onto the sample after which it is spectrally dispersed onto a CCD camera by a spherical grating. The 400 nm pump beam is generated by frequency doubling the 800 nm fundamental.

Figure 2 presents the spectral profile produced by HHG in Ne gas using an 800 nm beam with 2 mJ pulse energy and 35 fs pulse width. To produce an XUV probe spectrum containing both even and odd harmonics, a 400 nm symmetry breaking field of low pulse energy (45  $\mu$ J) is overlapped with the 800 nm driving field in the gas cell. This allows for generation of a continuous XUV spectrum to use as an analog to white light in optical spectroscopy. Reflected XUV harmonics from Si and Fe<sub>2</sub>O<sub>3</sub> are shown in Figure 2A and 2B, respectively.

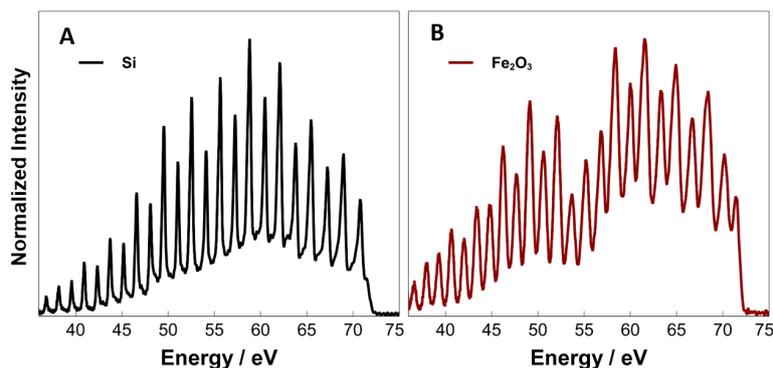


Figure 2: XUV harmonic spectrum generated in Ne gas as measured after reflectance from a Si mirror (A) and from a Fe<sub>2</sub>O<sub>3</sub> sample (B).

As shown in Figure 3 XUV-RA spectra are very different from those measured in transmission for the same material.<sup>2:1</sup> Therefore, it is necessary to understand the origin of the difference in XUV-RA lineshapes compared to transmission experiments to obtain the same chemically rich information available in a traditional absorption experiment. We have developed a semi-empirical method to simulate XUV-RA spectra from their known transmission analogues.

This simulation method reveals the physical origin of the distinct lineshapes measured by XUV-RA spectroscopy. In contrast to transmission experiments which are dominated by the imaginary part of the refractive index ( $k$ ), reflection experiments additionally probe the real part of the refractive index,  $n$ . To simulate a reflection-absorption spectrum, we begin by 1) simulating a ground-state absorption spectrum using charge transfer multiplet code, 2) derive from it the imaginary part of the refractive index using classical electromagnetic theory, 3) obtain the real part of the refractive index via the Kramers-Kronig transformation, and 4) use the Fresnel coefficient corrected for non-resonant surface scattering (Debye-Waller factor) to derive the RA spectrum.

To demonstrate the element specificity as well as the accuracy of the simulation method, we have collected and simulated RA spectra of several first row transition metal oxides, including TiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and NiO as shown in Figure 4 A, B, C, and D, respectively. As shown, the resonance position of the M<sub>2,3</sub>-edge transitions (3p  $\rightarrow$  3d) increases with atomic number. This is because the binding energy of the 3p orbital scales with effective nuclear charge from left to the right across the periodic table. In contrast to the 3p core orbitals, the binding energy of 3d valence orbitals is less influenced by nuclear charge due to screening by core electrons. As

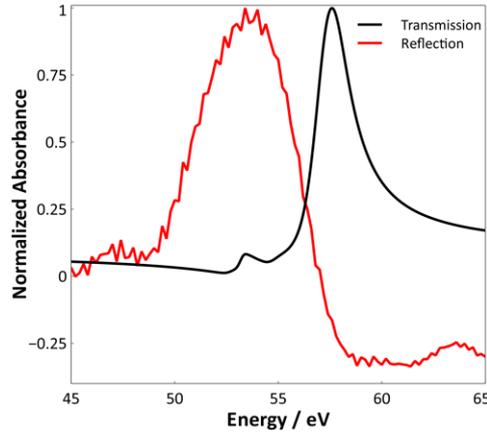


Figure 3: Normalized static spectrum of  $\text{Fe}_2\text{O}_3$  as measured by Reflection-Absorption (red) and transmission (black) experiments.

a result, the  $3p \rightarrow 3d$  transition energy increases with atomic number along the series  $\text{TiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{NiO}$ , giving rise to the element specificity of core-hole spectroscopy, which is preserved in the XUV-RA measurements shown here.

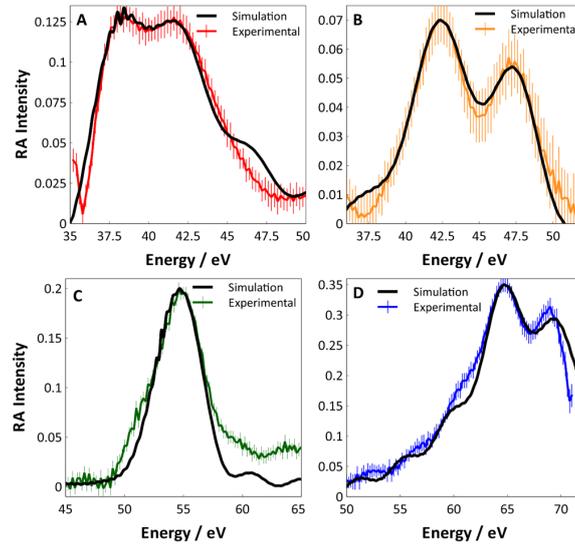


Figure 4: Simulated (black) and experimental (color) static XUV-RA spectra of (A)  $\text{TiO}_2$ , (B)  $\text{Cr}_2\text{O}_3$ , (C) polycrystalline  $\text{Fe}_2\text{O}_3$  and (D)  $\text{NiO}$ . The error bars on the experimental spectra are the standard deviation associated with each data point.

The predicted probe depth of a grazing angle reflectance measurement based on the attenuation length of the transmitted XUV field is only a few nm for the metal oxides shown here. To experimentally validate this predicted probe depth, we have collected ground state RA spectra of  $\text{TiO}_2$  thin films at various thicknesses. The resonant intensity at the Ti  $M_{2,3}$ -edge has been plotted as a function of the  $\text{TiO}_2$  film thickness (see purple squares in Figure 5). The XUV-RA intensity at the Ti  $M_{2,3}$ -edge increases with  $\text{TiO}_2$  film thickness as long as the thickness is less than the probe depth of the measurement. However, when the film thickness exceeds the measured probe depth, no further signal enhancement is observed.

XPS measurements have also been collected for each film thickness. From XPS it is possible to determine the atomic fraction of Ti and Si by taking a ratio of the Ti 3d and the Si 2p XPS lines and correcting for the atomic sensitivity factors. Plotting this fraction as a function of film thickness and fitting to an exponential rise reveals the probe depth of this XPS measurement, where the Ti atomic fraction approaches 100% as the  $\text{TiO}_2$  film thickness exceeds the XPS probe depth. This probe depth is found to be 2.8 nm as shown by the best fit to the green circles in Figure 5. This value closely matches the known surface sensitivity for XPS based on tabulated values for the inelastic mean free path of the Ti 3p and Si 2p photoelectrons. Comparing the XUV-RA intensity with the Ti atomic fraction determined by XPS shows that the XUV-RA probe depth for these samples is similar within error to the probe depth of XPS which is considered one of the primary tools

for surface sensitive electronic structure characterization.

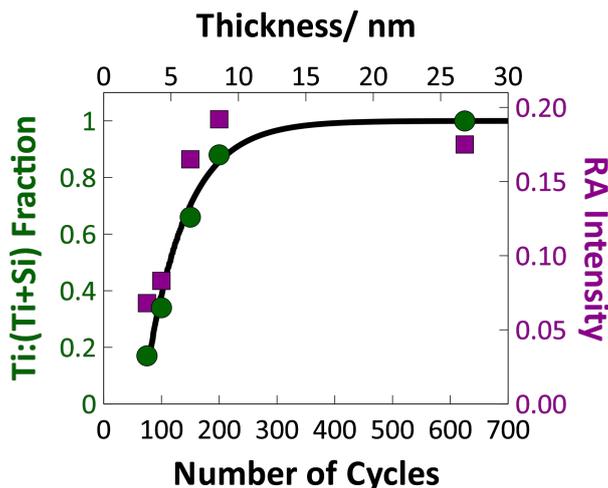


Figure 5: The experimentally determined probe depth for XUV-RA spectroscopy and XPS. Fitting an exponential rise to the XPS data points yields a probe depth of 2.8 nm (shown by the black line).

### 3 Surface Electron Dynamics of Catalytic Materials Probed by XUV-RA Spectroscopy

$\text{CuFeO}_2$  and  $\text{Fe}_2\text{O}_3$  are closely related earth-abundant photocatalysts with band gaps ideally suited for solar light harvesting. However, photo-electrochemical properties differ significantly between these two materials:  $\text{Fe}_2\text{O}_3$  is a water oxidation catalyst, which suffers from poor conversion, while  $\text{CuFeO}_2$  is photocathode with activity for both  $\text{H}_2$  evolution and  $\text{CO}_2$  reduction. We have recently demonstrated that  $\text{CuFeO}_2$  shows selectivity for  $\text{CO}_2$  conversion to the  $\text{C}_2$  product, acetate, under photoelectrochemical conditions.<sup>5</sup>

Using XUV-RA spectroscopy, we have investigated the ultrafast electron and hole dynamics in the photocatalytic metal oxides,  $\text{Fe}_2\text{O}_3$  and  $\text{CuFeO}_2$ .<sup>3</sup>

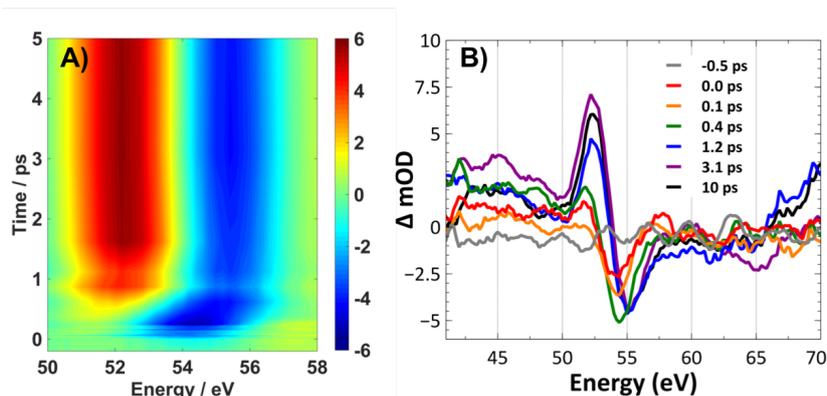


Figure 6: (A) The experimental contour plot for  $\text{Fe}_2\text{O}_3$  up to 5 ps post-excitation. (B)  $\text{Fe}_2\text{O}_3$  after photoexcitation at 400 nm depicting the spectral evolution up to 10 ps post-excitation.

Figure 6A shows the XUV spectral evolution of  $\text{Fe}_2\text{O}_3$  for time delays up to 5 ps following photoexcitation with a 400 nm pump pulse. Select transient spectra are shown in Figure 6B. The transient spectra of photoexcited  $\text{Fe}_2\text{O}_3$  are characterized at early times by a ground state bleach centered at 54 eV formed within the 85 fs instrument response function of the XUV spectrometer. This bleach subsequently undergoes a hypsochromic shift to 55.5 eV, and is accompanied by the growth of an excited state absorption feature centered at 52 eV. The hypsochromic shift of the ground state bleach and the rise of excited state absorption both evolve with a single correlated time constant of 640 fs. The observed bleach corresponds to the loss of  $\text{Fe}^{3+}$  while the excited state absorption at slightly lower energy is an indication of the formation of  $\text{Fe}^{2+}$ . The fast hypsochromic shift of the ground state bleach feature is the result of lattice expansion during electron self-trapping, and we have assigned these kinetics to surface electron trapping and small polaron formation at the catalyst surface.<sup>4</sup> Additionally,

we show that the observed small polaron formation rate is independent of surface defects by performing detailed kinetic analyses on poly- as well as single crystalline  $\text{Fe}_2\text{O}_3$  substrates, as shown in Figure 7.

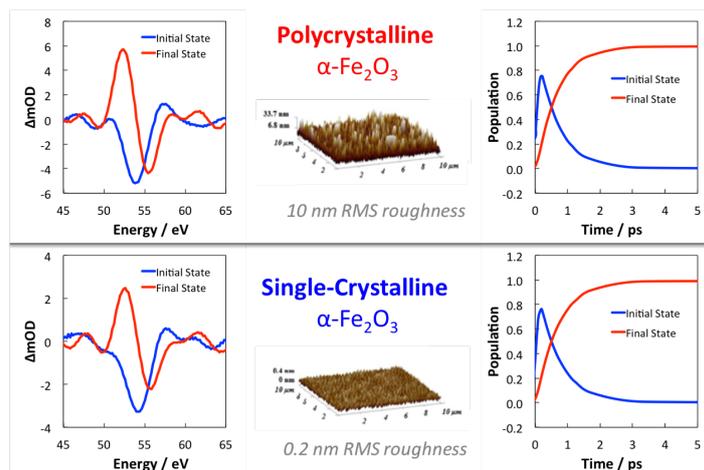


Figure 7: Comparison of transient electron dynamics for polycrystalline (top) and single crystalline (bottom)  $\text{Fe}_2\text{O}_3$ .

The measured surface roughness of the polycrystalline sample is an order of magnitude greater than for the single crystal substrate, however, We find that the spectral evolution and the small polaron formation rates are identical within error, confirming that the surface electron trapping is not mediated by surface defects. Rather, we hypothesize that the lattice expansion associated with small polaron formation represents a likely driving force for surface electron trapping in  $\text{Fe}_2\text{O}_3$ . Additional experimental and theoretical studies are underway to confirm this hypothesis and to understand the role of nuclear motion to mediate the transport properties of electrons at interfaces.

By performing spectroscopic XUV-RA measurements on the promising  $\text{CO}_2$  conversion catalyst,  $\text{CuFeO}_2$ , we demonstrate that it is possible to track electrons and holes independently in the Fe 3d, Cu 3d, and O 2p states comprising the band structure of this semiconducting metal oxide. Figure 8A shows the spectral evolution of  $\text{CuFeO}_2$  up to 100 ps post-excitation. The spectrum can be divided into three distinct regions: 1) The O  $L_1$  edge (blue) extending from 40-47 eV, 2) Fe  $M_{2,3}$  edge (red) centered at 54 eV, and 3) Cu  $M_{2,3}$  edge (green) in the high energy region above 63 eV. Nearly identical kinetics are observed at the Fe  $M_{2,3}$  edge between  $\text{CuFeO}_2$  and  $\text{Fe}_2\text{O}_3$ . Additionally, Figure 8B compares the transient spectrum at the Fe  $M_{2,3}$ -edge obtained at 1 ps for  $\text{CuFeO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and a simulated  $\text{Fe}^{2+}$  charge transfer excited state based on a ligand field multiplet calculation. The excellent match indicates that in  $\text{CuFeO}_2$ , photoexcitation results in localization of the excited electron to the Fe 3d conduction band states similar to  $\text{Fe}_2\text{O}_3$ . A weak excited state absorption feature is also observed in  $\text{Fe}_2\text{O}_3$  (Figure 6B) at  $\sim 44$  eV, corresponding to O  $L_1$ -edge absorption by the valence band hole.

In contrast to  $\text{Fe}_2\text{O}_3$ ,  $\text{CuFeO}_2$  shows the rise of strong positive absorption extending broadly at the low and high energy regions of the spectrum. This represents strong absorption by the valence band hole at the O  $L_1$  and Cu  $M_{2,3}$ -edges, respectively. Figure 8C shows that the response in these spectral ranges is correlated in time and delayed relative to the signal at the Fe  $M_{2,3}$ -edge.

This shows that following an O 2p  $\rightarrow$  Fe 3d charge transfer excitation, hole thermalization to the valence band edge is best described as electron transfer from the higher lying Cu 3d states to backfill holes in the lower lying O 2p states.

Despite similar electron dynamics in  $\text{Fe}_2\text{O}_3$  and  $\text{CuFeO}_2$ , only  $\text{CuFeO}_2$  shows cathodic photocurrent (Figure 9A). These measurements suggest that this may be largely a result of ultrafast (500 fs) hole thermalization, in which the hole transfers from O 2p to strongly hybridized Cu 3d valence band states leading to spatial charge separation within the layered  $\text{CuFeO}_2$  delafossite lattice (Figure 9B). The fast hole delocalization observed in  $\text{CuFeO}_2$  would tend to weaken the exciton binding energy, which may explain the reason that cathodic photocurrent is observed in this material but not in  $\text{Fe}_2\text{O}_3$ .

## 4 Conclusion

We have developed transient XUV Reflection-Absorption spectroscopy to elucidate surface carrier dynamics of catalytically relevant metal oxides used for the reduction of  $\text{CO}_2$  into fuels. We have demonstrated that XUV Reflection-Absorption spectroscopy combines the benefits of X-ray absorption, such as element and oxidation state specificity, with surface sensitivity and ultrafast time resolution, having a probe depth of only a few nm and an instrument response time less than 100 fs. We have highlighted a number of recent examples showing

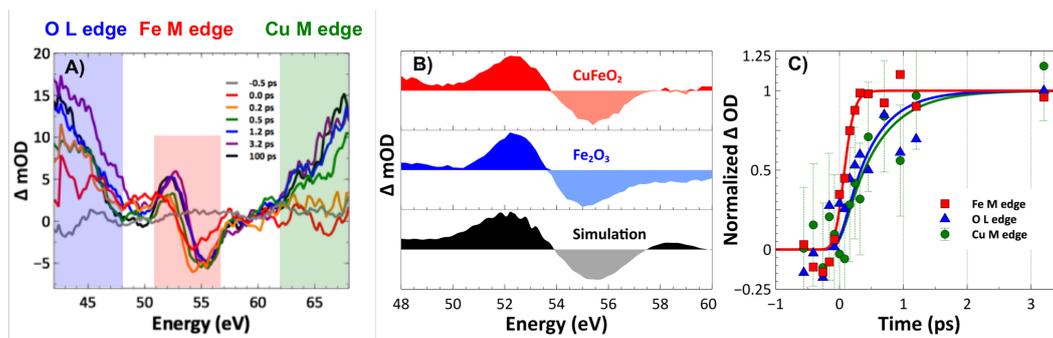


Figure 8: (A) Transient XUV-RA spectra of  $\text{CuFeO}_2$  for a series of time delays. (B) Comparison of the XUV transient spectrum at the Fe  $M_{2,3}$ -edge obtained 1 ps following photoexcitation for  $\text{CuFeO}_2$  and  $\text{Fe}_2\text{O}_3$  along with the result of a ligand field multiplet simulation depicting the expected transient spectrum. (C) Kinetic traces showing the transient response at the Fe  $M_{2,3}$ -edge, the Cu  $M_{2,3}$ -edge, and the O  $L_1$ -edge. Traces have been normalized and plotted as positive  $\Delta\text{OD}$  for clarity. Representative standard errors based on replicate measurements are shown for the Cu  $M_{2,3}$ -edge.

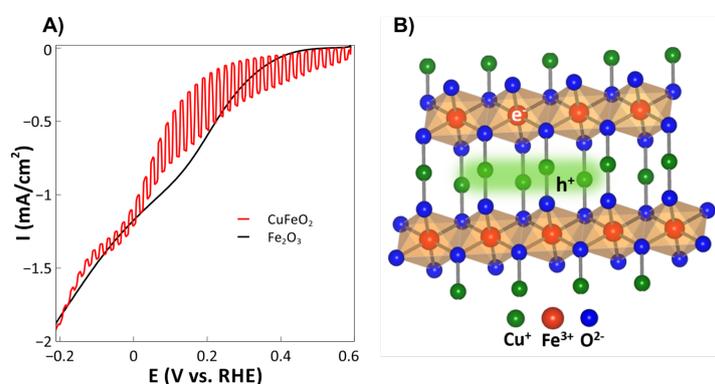


Figure 9: (A) Linear sweep voltammograms for  $\text{CuFeO}_2$  (red) and  $\text{Fe}_2\text{O}_3$  (black) under cathodic potentials from +0.6 to 0.0 V vs RHE in 0.1 M aqueous  $\text{NaHCO}_3$  during illumination with a chopped light source. (B) atomic level structure of the  $\text{CuFeO}_2$ .

the utility of XUV reflection-absorption. These include measurement of ultrafast surface electron trapping and small polaron formation in hematite as well as the ability to independently measure electron and hole dynamics in a  $\text{CO}_2$  reduction photocatalyst,  $\text{CuFeO}_2$ , by transient spectroscopy at the metal  $M_{2,3}$  and O  $L_1$ -edges, respectively. Based on our results, we anticipate that XUV Reflection-Absorption spectroscopy will continue to contribute to a detailed understanding of surface electron dynamics in relevant materials, where ultrafast time resolution and chemical state specificity are required to elucidate the mechanisms of charge transfer and energy conversion at surfaces.

## Publications Acknowledging This Award

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- [2] A. Cirri, J. Husek, S. Biswas, and L. R. Baker. Achieving surface sensitivity in ultrafast XUV spectroscopy:  $M_{2,3}$ -edge reflection-absorption of transition metal oxides. *J. Phys. Chem. C*, 121(29):15861–15869, 2017.
- [3] J. Husek, A. Cirri, S. Biswas, A. Asthagiri, and L. R. Baker. Hole thermalization dynamics facilitate ultrafast spatial charge separation in  $\text{CuFeO}_2$  solar photocathodes. *J. Phys. Chem. C*, 122(21):11300–11304, 2018.
- [4] J. Husek, A. Cirri, S. Biswas, and L. R. Baker. Surface electron dynamics in hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ): Correlation between ultrafast surface electron trapping and small polaron formation. *Chem. Sci.*, 8:8170–8178, 2017.
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**Abstract**

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#### **Archival Publications (published) during reporting period:**

X. Yang, E. A. Fugate, Y. Mueanngern, L. R. Baker, "Photo-Electrochemical CO<sub>2</sub> Reduction to Acetate on Iron-Copper Oxide Catalysts," ACS Catalysis, 2017, 7, 177–180.

A. Cirri, J. Husek, S. Biswas, and L. R. Baker, "Achieving Surface Sensitivity in Ultrafast XUV Spectroscopy: M<sub>2,3</sub>-Edge Reflection-Absorption of Transition Metal Oxides," Journal of Physical Chemistry C, 2017, 121, 15861–15869.

J. Husek, A. Cirri, S. Biswas, L. R. Baker, "Surface Electron Dynamics in Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>): Correlation Between Ultrafast Surface Electron Trapping and Small Polaron Formation," Chemical Science, 2017, 8, 8170–8178.

S. Biswas, J. Husek, L. R. Baker, "Elucidating Ultrafast Electron Dynamics at Surfaces Using Extreme Ultraviolet (XUV) Reflection-Absorption Spectroscopy," Chemical Communications, 2018, 54, 4216–4230.

J. Husek, A. Cirri, S. Biswas, L. R. Baker, "Hole Thermalization Dynamics Facilitate Ultrafast Spatial Charge Separation in CuFeO<sub>2</sub> Solar Photocathodes," Journal of Physical Chemistry C, 2018, 122, 11300–11304.

DISTRIBUTION A: Distribution approved for public release.

**New discoveries, inventions, or patent disclosures:**

**Do you have any discoveries, inventions, or patent disclosures to report for this period?**

Yes

**Please describe and include any notable dates**

The following US Patent Application was filed by Ohio State University in May 2017 as a result of this project:

L. R. Baker, X. Yang, "Catalytic Materials and Methods of Making and Using Thereof," US Patent Application No. 15/602,696, (2017).

This invention is focused on production of acetate from carbon dioxide using low-cost, earth-abundant metal oxide catalysts as described in the following publication, which acknowledges support from this award:

X. Yang, E. A. Fugate, Y. Mueanngern, L. R. Baker, "Photo-Electrochemical CO<sub>2</sub> Reduction to Acetate on Iron-Copper Oxide Catalysts," ACS Catalysis, 2017, 7, 177-180.

**Do you plan to pursue a claim for personal or organizational intellectual property?**

Yes

**Changes in research objectives (if any):**

N/A

**Change in AFOSR Program Officer, if any:**

N/A

**Extensions granted or milestones slipped, if any:**

N/A

**AFOSR LRIR Number**

**LRIR Title**

**Reporting Period**

**Laboratory Task Manager**

**Program Officer**

**Research Objectives**

**Technical Summary**

**Funding Summary by Cost Category (by FY, \$K)**

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
Supplies			
Total			

**Report Document**

**Report Document - Text Analysis**

**Report Document - Text Analysis**

**Appendix Documents**

**2. Thank You**

**E-mail user**

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