Built-In Potential in Fe$_2$O$_3$-Cr$_2$O$_3$ Superlattices for Improved Photoexcited Carrier Separation


Hematite, α-Fe$_2$O$_3$, is an attractive photocatalyst to split water as a source of H$_2$ fuel because it is nontoxic, Earth abundant, stable in aqueous environments and possesses a bandgap in the visible wavelength range (∼2.1 eV). Efforts have been undertaken to engineer the bandgap and electronic structure of Fe$_2$O$_3$ for more efficient light harvesting through doping or structural alterations.

Recently, attention has turned to improving photoexcited electron–hole separation in hematite. Fast electron–hole recombination, facilitated in part by slow carrier transport kinetics, has long been identified as a major obstacle in the utilization of hematite photocatalysts. One route to improve excited carrier transport properties is provided by rationally designed nanostructures that reduce the path length that carriers must travel to reach the hematite surface, while simultaneously increasing the available surface area for photochemical reaction. Taking this approach, Kay et al. developed Si-doped Fe$_2$O$_3$ mesostructured thin films that substantially improved photon-to-current efficiencies relative to planar Fe$_2$O$_3$ photoanodes. Although improving photocurrents, the high surface areas of these mesostructures also accelerate surface electron–hole recombination, with important consequences for surface catalysis.

A more direct method to reduce photogenerated carrier recombination employs heterojunctions to spatially separate excited electrons and holes. Lin and co-workers separated the carrier generation (Fe$_2$O$_3$) and carrier transport (metallic TiSi$_2$ or Al:ZnO) functions in core–shell nanowire structures to realize improved photocurrents. Although they demonstrated a reduction in the photocurrent onset potential in an n-Fe$_2$O$_3$/p-Mg:Fe$_2$O$_3$ homojunction. The built-in field provides a driving force to separate photoexcited electrons to one side of the junction and holes to the other. Additionally, the potential drop generated by the electric field can be used to shift the band edges of Fe$_2$O$_3$, reducing the external applied potential necessary for water reduction. Steier et al. found that diffusion-doped n-Fe$_2$O$_3$ reduced the thickness of the surface space charge layer; the resulting steeper band bending is more efficient at separating excited electrons and holes.

An alternative approach to obtain built-in electric fields is to exploit the band alignment characteristics of epitaxial Fe$_2$O$_3$/Cr$_2$O$_3$ heterojunctions. The Fe$_2$O$_3$-Cr$_2$O$_3$ system exhibits noncommutative band offsets that differ by ∼0.4 eV depending on the order of deposition. This noncommutative property was hypothesized to arise from subtle differences in interface structure resulting from the deposition sequence. An early attempt to harness the band alignment properties of Fe$_2$O$_3$-Cr$_2$O$_3$ for photocatalysis was hampered by the apparent photocactivity of Cr$_2$O$_3$ at the incident wavelength of interest (3.2 eV).

Recent work by our group has confirmed that epitaxial thin films of Cr$_2$O$_3$ deposited on Al$_2$O$_3$(0001) by molecular beam epitaxy exhibit a surface termination which differs from that of Fe$_2$O$_3$ films under similar deposition conditions: Cr$_2$O$_3$ exhibits a full bilayer of Cr cations on the surface, while Fe$_2$O$_3$ terminates with half a bilayer of Fe cations on the surface. With this insight, the noncommutative band offset properties of Fe$_2$O$_3$-Cr$_2$O$_3$ can be exploited in a superlattice (SL) structure to build up an intrinsic potential that is sufficient to spatially separate electrons and holes, as originally suggested. We demonstrate precise, sublayer control over the Fe$_2$O$_3$-Cr$_2$O$_3$ interface structure and show direct evidence that Fe$_2$O$_3$-Cr$_2$O$_3$ superlattice layers generate an intrinsic built-in potential that drives holes to the surface and electrons into the bulk. This potential leads to improved e–h pair separation, reflected by an increased photocurrent in photoconductivity (PC) measurements.

The effect of surface termination on subsequent interface formation in the corundum structure adopted by hematite and eskolaite is shown schematically in **Figure 1a**. In the [0001] direction, the corundum structure consists of oxygen layers separated by buckled or bilayers (BLs) of cations. If the equilibrium surface termination is a full cation BL, as in Cr$_2$O$_3$, then subsequent deposition of Fe$_2$O$_3$ will result in an interface in which an oxygen layer separates a full BL of Fe from a full BL of Cr; we will refer to this interface structure as “abrupt.” In contrast, if the equilibrium surface termination is a half BL, as in Fe$_2$O$_3$, the interface will consist of a BL that is half Fe and half Cr; we will refer to this structure as “mixed.” In a previous
Jaffe et al. used density functional theory (DFT) to model the two interface structures and found that the valence band offset (VBO) differed between the two: the VBO calculated for the mixed interface (referred to as “split-metal” in ref. [15]) was 0.6 eV, while the calculated VBO for the abrupt interface (referred to as “oxygen-divided” in ref. [15]) was 0.4 eV.

Experimental confirmation that the noncommutative band offset property of the Fe$_2$O$_3$-Cr$_2$O$_3$ system is a consequence of the interface structure is given in Figure 1b. The natural half-BL termination of Fe$_2$O$_3$ (0001) is expected to lead to a mixed interface when a thin layer (6 BL) of Cr$_2$O$_3$ is deposited on top, and indeed the magnitude of the VBO for this heterojunction is 0.79 eV. In contrast, the full BL termination of Cr$_2$O$_3$ (0001) is expected to lead to the formation of an abrupt interface when 6 BLs of Fe$_2$O$_3$ are subsequently deposited. As predicted by DFT, the magnitude of the VBO for this structure is 0.35 eV, lower. To further explore the role of interface structure in determining the VBO, heterojunctions were synthesized in which a half BL was deposited on the half-BL-terminated Fe$_2$O$_3$ surface, immediately followed by Cr$_2$O$_3$ deposition, to render the interface more “abrupt”-like. A reduction in VBO from 0.79 to 0.65 eV is observed. Likewise, a “mixed”-like interface was formed on the full-BL-terminated Cr$_2$O$_3$ surface by depositing one BL of (Fe$_{0.5}$Cr$_{0.5}$)$_2$O$_3$, followed by 5 BLs of Fe$_2$O$_3$. The VBO is increased from 0.35 to 0.54 eV. These results, qualitatively consistent with the predictions from DFT, confirm the primary role that interface structure plays in determining the electronic structure, and thus the VBO, of the Fe$_2$O$_3$-Cr$_2$O$_3$ interface. Fortuitously, the largest difference in noncommutative band offset results when the naturally occurring Fe$_2$O$_3$ and Cr$_2$O$_3$ terminations are employed.

The noncommutative band offset properties of the Fe$_2$O$_3$-Cr$_2$O$_3$ system can be exploited to generate an intrinsic, built-in potential in multiple-heterostructure or SL (defined as alternating layers of one to a few BL thickness) thin film structures, as originally suggested by Chambers et al. The large difference in the absolute value of the VBO, ≈ 0.4 eV, makes it possible to build up a significant potential within just a few Fe$_2$O$_3$-Cr$_2$O$_3$ periods (Figure 1c). Built-in potentials are typically inferred from careful line broadening analysis of component core level peaks of X-ray photoelectron spectroscopy (XPS) data. Because the Fe 2p and Cr 2p XPS core level peaks both exhibit broad, complex lineshapes due to multiplet splitting, BLs of (Fe$_{0.5}$Ti$_{0.5}$)$_2$O$_3$ were included in the SL structure. The Ti 2p core level peak is narrow, corresponding to Ti$^{4+}$, when doped in Fe$_2$O$_3$, and thus Ti can serve as a probe of
the intrinsic potential present in the SL structure. The positions of (Fe$_{0.9}$Ti$_{0.1}$)$_2$O$_3$ BLs are illustrated schematically by arrows in Figure 1c and by shading in Figure 2a. The presence of a built-in potential will shift the Ti 2p peak originating from Ti top to lower binding energy (BE) relative to the Ti 2p peak originating from the Ti buried layer. This shift can be observed as a broadening of the resultant Ti 2p core level peak.

Superlattice structures corresponding to 2.5 periods of (Fe$_2$O$_3$)$_3$-(Cr$_2$O$_3$)$_3$ were fabricated as epitaxial thin film stacks on a thick (12 nm) Cr$_2$O$_3$ buffer layer, as illustrated schematically in Figure 2a. For SL(A), the interface structure was not modified during deposition; thus, the interfaces possess their natural VBO values of ≈0.8 eV (Cr$_2$O$_3$ on Fe$_2$O$_3$, mixed interface) and ≈0.4 eV (Fe$_2$O$_3$ on Cr$_2$O$_3$, abrupt interface). From Figure 1c, an intrinsic potential of ≈0.8 eV is predicted for the SL(A) structure. The deposition of SL(B), in contrast, included modification of both the Fe$_2$O$_3$/Cr$_2$O$_3$ and Cr$_2$O$_3$/Fe$_2$O$_3$ interfaces as described above, which is expected to reduce the overall difference in VBOs from the two interfaces. From the VBO values in Figure 1b (≈0.7 eV for Cr$_2$O$_3$ on Fe$_2$O$_3$, abrupt-like interface, and ≈0.5 eV for Fe$_2$O$_3$ on Cr$_2$O$_3$, mixed-like interface), the intrinsic potential for SL(B) is expected to be ≈0.2 eV.

The Ti 2p core level spectra for SL(A) and SL(B) are compared in Figure 2b to a reference spectrum of Ti taken from the first Ti:Fe$_2$O$_3$ layer in SL(A). When the photoelectrons are collected at normal takeoff angle, resulting in the greatest sensitivity to the bulk of the superlattice, both SL(A) and SL(B) exhibit broadening on the high BE side compared to the reference spectrum. As expected, the broadening for SL(A) is greater than that for SL(B), implying a greater built-in potential in SL(A). Further corroborating the presence of a built-in potential as the source of the peak broadening, Ti 2p data collected at a highly surface-sensitive (≈4 BL) glancing photoelectron takeoff angle exhibit narrow peak widths comparable to the reference spectrum for both SL(A) and SL(B).

The magnitude of the built-in potential can be determined by careful deconvolution of the Ti 2p peak into two components. First, the narrow Ti 2p reference spectrum was fit with two Voigt peaks to adequately model the slight asymmetry present on the high BE side. The fit was then utilized to deconvolve
the SL spectra. After appropriate weighting of the reference fit based on the expected attenuation of the Ti\textsubscript{top} and Ti\textsubscript{buried} layers, the separation of the two peaks was varied, and the resulting summed peak was normalized to the experimental spectrum and shifted to align the spectra on the low BE side. Figure 2c,d plots the best fit for SL(A) and SL(B), respectively. For SL(A), an intrinsic potential of 0.8 ± 0.1 eV is found, which matches well with the prediction of 0.8 eV from the heterojunction VBOs. For SL(B), however, the built-in potential determined from the Ti 2p peak is 0.6 ± 0.1 eV, which is larger than the estimated value of 0.2 eV. This is likely due to partial but imperfect realization of the nonequilibrium interface structures during film growth. Intermixing of these thermodynamically less stable interfaces may occur in the time required to deposit the full SL stack.

To visualize the superlattice structure that gives rise to the built-in potential, both atom probe tomography (APT) and scanning transmission electron microscopy (STEM) were employed. Figure 3 presents the 3D APT reconstruction of a superlattice with the SL(A) structure (Figure 2a), which is sandwiched between epitaxial Cr\textsubscript{2}O\textsubscript{3} buffer and capping layers. In the reconstruction, the three Fe\textsubscript{2}O\textsubscript{3} layers are well resolved. The 1D concentration profile in Figure 3, generated from the reconstruction data, reveals sharp interfaces for all layers. The Fe data indicate that the interface widths are 0.5 nm or less, which approaches the resolution limit of the technique itself for thin-film specimens.\textsuperscript{[21]} Since each bilayer in the corundum structure is ≈0.23 nm thick, this confirms nearly atomically abrupt interfaces between the SL layers. In the Cr data, the interfaces are less distinct, and some diffusion of Cr into the first Fe\textsubscript{2}O\textsubscript{3} layer is possible. The Ti signal is weak, as expected given the low doping concentration (≈10%) in the Fe\textsubscript{2}O\textsubscript{3} layers, but the signal is consistent with Ti remaining in the layers in which it was initially deposited. Although small concentrations of Ti are also documented in the 1D concentration profile for the middle Fe\textsubscript{2}O\textsubscript{3} layer, close inspection of the isotopic abundances in this region suggests that this is primarily the consequence of an isobaric overlap of \textsuperscript{48}Ti\textsuperscript{16}O\textsuperscript{2+} with \textsuperscript{16}O\textsuperscript{2+}, and is not indicative of Ti diffusion.

Scanning transmission electron microscopy and electron energy loss spectroscopy (STEM-EELS) provide valuable complementary structural and chemical information about the film structure. Figure 4a shows a high-angle annular dark field (STEM-HAADF) image of the film, overlaid with detailed insets of the film-substrate interface and the superlattice. The overall film structure is well-resolved and exhibits some undulation, which propagates to the surface of the Cr\textsubscript{2}O\textsubscript{3} capping layer as surface roughness; this is expected given the fairly large lattice mismatch between Al\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3}.

STEM-EELS measurements provide an atomic-scale probe of interface abruptness and local cation valence changes. Figure 4c shows a radial difference filtered STEM-HAADF image of the superlattice from which an EELS line scan was collected. The resulting background-subtracted integrated signals of the Fe L\textsubscript{2,3}, Cr L\textsubscript{2,3}, and Ti L\textsubscript{2,3} edges, normalized to the Cr\textsubscript{2}O\textsubscript{3} buffer layer, are shown in Figure 4d. These profiles indicate the presence of all the superlattice components; however, there is some intermixing on the order of 0.5 nm, which is particularly visible at the buffer and capping layer interfaces. Because the electron probe size and beam broadening limit the effective resolution of this measurement to a few unit cells, this profile likely represents the upper bound of interfacial mixing in the sample.

Any associated changes in valence throughout the SL can be explored using the core-loss fine structure of the Ti L\textsubscript{2,3}, O K, Cr L\textsubscript{2,3}, and Fe L\textsubscript{2,3} edges. As shown in the Supporting Information, Ti L\textsubscript{2,3} edge spectra extracted from the numbered integration windows in Figure 4c exhibit characteristic crystal-field...
splitting indicative of a Ti $^{4+}$ charge state, while the O K line shape agrees very well with the expected structure for Fe $^{3+}$ and Cr $^{3+}$.\cite{22,23} To quantify possible Cr valence changes, we have explored systematic shifts in the separation between the O K–Cr L$_3$ edge, which does not depend on background subtraction and can serve as an alternative to white-line ratios.\cite{24} As shown in Figure 4e, the O K–Cr L$_3$ separation for the low concentration of Cr confined in the first, thicker Fe$_2$O$_3$ SL layer differs from that for Cr$_2$O$_3$ collected in the thick Cr$_2$O$_3$ buffer layer or subsequent Fe$_2$O$_3$ layers, although the charge state remains within the range of values found for Cr $^{3+}$.$^{[24]}$ This behavior may be the result of intermixing with the Fe layer. Turning to the Fe edge, we observe a more uniform trend in the Fe L$_{2,3}$ white-line ratios across the SL; these ratios, shown in Figure 4f, are in good agreement with literature values for the Fe $^{3+}$ state.\cite{25}

To elucidate the effect of (Fe$_2$O$_3$)$_n$–(Cr$_2$O$_3$)$_n$ superlattice interfaces on the competition between separation and recombination of photogenerated electron–hole pairs, PC spectra were collected on two thick (450 Å) epitaxial Fe$_2$O$_3$ films, one capped with a 54 Å thick (Fe$_{0.5}$Cr$_{0.5}$)$_2$O$_3$ alloy layer and the other capped with a 54 Å thick (Fe$_2$O$_3$)$_3$–(Cr$_2$O$_3$)$_3$ SL (interface structure the same as SL(A) in Figure 2a). A similar, uncapped epitaxial Fe$_2$O$_3$ film was shown previously to exhibit a photocurrent.\cite{3} PC spectra for both capped samples are shown in Figure 5. Below the bandgap, the samples exhibit no photoinduced current, as expected. When the incident photon energy is well above the bandgap value, the SL-capped Fe$_2$O$_3$ film exhibits strong photocurrent, while a weaker photoinduced signal is observed for the alloy-capped film.

In the inset to Figure 5, the PC signal for each film has been normalized at 2.1 eV to compare the behavior near the absorption threshold. For both the SL- and alloy-capped films, the absorption threshold is well below the Fe$_2$O$_3$ bandgap of 2.1 eV, occurring at ≈1.5 eV in both cases. Previous PC measurements of (Fe$_{1-x}$Cr$_x$)$_2$O$_3$ alloy thin films yielded a PC onset of ≈1.6 eV for (Fe$_{0.63}$Cr$_{0.37}$)$_2$O$_3$, and a somewhat higher onset (1.75–1.85 eV) for (Fe$_{1-x}$Cr$_x$)$_2$O$_3$ films with x = 0.4–0.5.\cite{3} In the SL, efficient visible-light absorption occurs at the Fe$_2$O$_3$/Cr$_2$O$_3$ interfaces, where Fe–O–Cr bonding allows occupied Cr t$_{2g}$ → unoccupied Fe t$_{2g}$ low-energy transitions\cite{3} to occur. The APT and STEM results in Figure 3 confirm some degree of mixing at the Fe$_2$O$_3$/Cr$_2$O$_3$ interfaces in the SL. Unlike a thin film alloy, however, the photo-generated electrons and holes are efficiently separated into the Fe$_2$O$_3$ and Cr$_2$O$_3$ layers of the SL, respectively, driven by the local band alignment at the Fe$_2$O$_3$/Cr$_2$O$_3$ interface and the resulting built-in potential across the SL structure. This significantly

**Figure 4.** STEM-EELS analysis of intermixing and valence. a) STEM-HAADF image of the overall film structure, overlaid with high magnification insets of the interface and superlattice. b) STEM-EDS map of the Al K, Fe K, and Cr K edges, confirming the presence of all the film layers. c) Radial-difference filtered STEM-HAADF image of the region used for EELS measurements. A line scan has been extracted and subsequent spectra have been integrated in the marked windows. d) EELS integrated signal profiles integrated from the line scan region in C. The profiles were processed using principal component analysis, then background subtracted, and normalized to the Cr$_2$O$_3$ buffer layer. e) Separation of the O K and Cr L$_3$ edges, used to estimate the effective Cr valence. The range marked corresponds to the 3$^{+}$ state from the literature\cite{24} while the error bars are the result of Gaussian fits to the edges. f) Fe L$_{2,3}$ white-line ratios calculated according to the method of van Aken et al.$^{[25]}$

**Figure 5.** PC spectra for capped Fe$_2$O$_3$ thin films. Solid lines are 20-pt boxcar average of experimental data (dots). Inset: Boxcar-averaged data are normalized at 2.1 eV. Arrow indicates approximate absorption threshold.
improved charge separation results in a substantially lower onset of measurable photocurrent in the SL-capped film than in the alloy-capped film, despite the similar nominal stoichiometry of the capping layers. Measurable photocurrent, defined in this case as above a threshold value of $5 \times 10^{-8}$ A, is observed at 1.7 eV for the SL-capped film and 2.0 eV for the alloy-capped film. The benefit of enhanced carrier lifetimes in the SL structure is retained at higher incident photon energies, where stronger PC is achieved than in the alloy-capped film.

In summary, the different surface terminations exhibited by Fe$_2$O$_3$ and Cr$_2$O$_3$, fabricated with near-atomic precision by molecular beam epitaxy, determine the heterointerface structure and result in controllable, noncommutative band offset values. Fe$_2$O$_3$-Cr$_2$O$_3$ SLs (2.5 periods) generate built-in potentials as high as 0.8 eV, as confirmed by XPS, and the potential can be decreased by altering the atomic structure in potentials as high as 0.8 eV, as confirmed by XPS, and the potential can be decreased by altering the atomic structure at the Fe$_2$O$_3$/Cr$_2$O$_3$ interfaces. Enhanced photoconductivity is measured for a thick Fe$_2$O$_3$ epitaxial film capped with an (Fe$_2$O$_3$)$_n$(Cr$_2$O$_3$)$_n$ SL; this enhancement is attributed to efficient electron-hole separation in the SL as a result of the band alignment. The Fe–O–Cr bonds at the SL interfaces also red-shift the onset of photoconductivity to $\approx 1.5$ eV. Exploiting the band alignment and photoabsorption properties of Fe$_2$O$_3$-Cr$_2$O$_3$ SLs holds promise to increase the efficiency of hematite-based photoelectrochemical water splitting.

**Experimental Section**

**Epitaxial Film Synthesis:** Heterojunctions and superlattice structures were deposited epitaxially on Al$_2$O$_3$ (0001) substrates by molecular beam epitaxy. All films were deposited at a substrate temperature of 550 °C in 2 × 10$^{-10}$ Torr of Fe$_2$O$_3$ and Cr$_2$O$_3$ and were supplied from electron beam evaporators. Thick Cr$_2$O$_3$ buffer layers and Fe$_2$O$_3$ films for PC measurements were deposited at a growth rate of 0.24 Å s$^{-1}$ in the presence of activated oxygen from an electron cyclotron resonance microwave plasma source. Thin heterojunction and superlattice films were deposited at a growth rate of 0.075 Å s$^{-1}$ in molecular O$_2$. All films were cooled in vacuum. Films deposited for APT and STEM analysis were capped at 550 °C with 60 Å Cr$_2$O$_3$, followed by a thick protective layer of Cr metal deposited at room temperature.

**Valence Band Offset Determination:** In situ XPS measurements were made in an appended GammaData Scienta SES200 spectrometer with monochromized Al K$_\alpha$ X-rays. The energy resolution of the reported XPS data is $\approx 0.5$ eV. A low energy electron flood gun was utilized to compensate sample charging during the measurements. VB0s were determined by collecting Fe 3p, Cr 3p, and valence band data in a single scan for the experimental film and reference standards (thick epitaxial films) of Fe$_2$O$_3$ and Cr$_2$O$_3$. The Fe$_2$O$_3$ (Cr$_2$O$_3$) reference spectrum was normalized to match the Fe 3p (Cr 3p) peak area in the experimental spectrum, then shifted to align the Fe 3p (Cr 3p) core level peak with the same peak in the experimental spectrum. The position of the valence band maximum (VBM) of each reference was then calculated, and the difference (VBM$_{Fe2O3}$−VBM$_{Cr2O3}$) is reported as the VBO. Note that, for clarity, we have not employed the sign convention$^{[24]}$ of VBO$_{bulk}$−VBO$_{overlayer}$ and instead report the absolute magnitude of the VBO regardless of which layer is the overlayer. The estimated error in the VBO values is $\approx 0.05$ eV, as described in the Supporting Information. The experimental VB spectrum was then simulated by summing the shifted and attenuated reference spectra to visually confirm the VBO determination.

APT: APT specimens were prepared using standard focused ion beam lift out methods$^{[26]}$. Annular milling was performed with 30 kV Ga$^+$ and final cleanup was done with 2 kV Ga$^+$ to minimize ion beam damage, achieving a final tip diameter of $\approx 100$ nm at the superlattice.

APT experiments were performed with a Cameca LEAP 4000X HR in laser pulsing mode ($\lambda = 355$ nm) with a laser energy of 25 pJ pulse$^{-1}$. The manufacturer estimated laser spot size is $\approx 3$ μm (4φ of the beam intensity). The specimen was cooled to 40 K in the ultrahigh vacuum analysis chamber (1.4 × 10$^{-11}$ Torr) and data were collected at a low energy-controlled constant detection rate of 0.004 detected ions/pulse.

Data reconstructions and analyses were performed with the Cameca Interactive Visualization and Analysis Software package v3.6.8. The tip radius evolution used for the reconstruction was based on scanning electron microscopy observations of the tip geometry. Fine tuning of the reconstruction was aided by STEM measurements of the superlattice layer thicknesses. The final reconstruction was cropped to the central $\approx 10$ nm of the field of view to minimize aberrations associated with the presence of layers with disparate evaporation fields. The primary Ti signal ($^{48}$Ti$^{16}$O$_2^+$) was convoluted with the prominent $^{16}$O$_2^+$ peak in the mass spectrum. An average contribution of the peak at 32 Da to TiO within the 1D concentration profile was estimated with the natural isotopic abundance of Ti while analyzing the mass spectrum for the entire superlattice.

**STEM:** Samples were prepared for STEM using a standard lift out method on an FEI Helios Dual-Beam Focused Ion Beam operating at 30 keV and were subsequently polished at 5 and 2 keV at $5^\circ$ incidence angle to clean remaining surface damage. The samples were then plasma cleaned for 2–5 min prior to imaging. STEM-HAADF images were collected on a JEOL ARM-200CF microscope operating at 80 and 200 keV with a 27.5 mrad convergence angle and 62–68 mrad collection angle. The image in Figure 4c has been processed using a radial difference filter (HREM Software) to improve signal-to-noise. STEM-EDS maps were acquired at 200 keV with a 100 μs dwell time with an averaging filter in the JEOL Analyzer Station software. STEM-EELS maps were collected at 80 keV using a 5 mm entrance aperture and a 0.25 eV ch$^{-1}$ dispersion, with a 2 s pixel dwell time and a sampling of 115 pixels. The data were first corrected for energy drift using the zero loss peak, but no Fourier deconvolution was used since the sample is quite thin (0.3–0.4 inelastic mean free paths (t/$\lambda$)). The data were then filtered using principal component analysis to remove noise and a power-law background was subtracted prior to each edge; because of the overlap of the O K edge continuum and Cr L$_{3,2}$ edge, the background subtraction for this integrated signal was done just prior to the O K edge prepeak. The separation between the O K edge prepeak and the Cr L$_3$ edge was measured by fitting Gaussian peaks to each edge, while the Fe L$_{3,2}$ white-line peak area ratio was calculated by subtracting a double arc tangent background, according to the method described by Van Aken et al.$^{[25]}$

**Photoconductivity:** Interdigitated gold electrodes with 72 µm spacing were evaporated onto the film surface. Contact was made to the gold pads with indium wires. Spectral photoconductivity data were collected at room temperature in air as a function of incident photon wavelength using a monochromator equipped with a xenon-halogen lamp. Samples were excited using chopped (42 Hz) illumination, and photocurrents detected with a Stanford Research SR830 lock-in amplifier. Reported photocurrents have been corrected for lamp intensity, but not for electrode geometry.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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