**Electrochemical Interfaces** 

# Potential-Specific Structure at the Hematite– Electrolyte Interface

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The atomic-scale structure of the interface between a transition metal oxide and aqueous electrolyte regulates the interfacial chemical reactions fundamental to (photo)electrochemical energy conversion and electrode degradation. Measurements that probe oxide-electrolyte interfaces in situ provide important details of ion and solvent arrangements, but atomically precise structural models do not exist for common oxide-electrolyte interfaces far from equilibrium. Using a novel cell, the structure of the hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) (1102)-electrolyte interface is measured under controlled electrochemical bias using synchrotron crystal truncation rod X-ray scattering. At increasingly cathodic potentials, charge-compensating protonation of surface oxygen groups increases the coverage of specifically bound water while adjacent water layers displace outwardly and became disordered. Returning to open circuit potential leaves the surface in a persistent metastable state. Therefore, the flux of current and ions across the interface is regulated by multiple electrolyte layers whose specific structure and polarization change in response to the applied potential. The study reveals the complex environment underlying the simplified electrical double layer models used to interpret electrochemical measurements and emphasizes the importance of conditionspecific structural characterization for properly understanding catalytic processes at functional transition metal oxide-electrolyte interfaces.

# 1. Introduction

Chemical processes at transition metal oxide (TMO) interfaces with aqueous electrolyte are controlled by the structure that emerges from the chemical and physical interaction of nearsurface atoms with adjacent water molecules and solute ions. In this nanometer-thin domain, the outermost few atomic

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layers of the surface relax or reconstruct, terminal oxo groups are protonated, and a few layers of overlying water molecules self-organize via hydrogen bonding.<sup>[1]</sup> The unique chemistry in this local environment regulates charge and mass transfer across the interface; adsorption and dissolution processes are well known to depend on the organization of water and solute at the interface.<sup>[2]</sup> Predicting the molecular mechanisms of chemical reactions at functional TMO–electrolyte interfaces therefore requires accurate models of the interfacial environment under reaction conditions.

Because of the challenges in selectively probing interfacial structure between a solid and bulk solution at high resolution in situ, present understanding of TMO– electrolyte interfaces is mostly limited to molecular simulations and measurements at near-equilibrium conditions.<sup>[2c,3]</sup> How the interfacial structure changes at conditions far from equilibrium, i.e., under chemical or electrochemical flux, is poorly understood for electrode materials with structurally and chemically complex

surfaces. Measurements of the structure of water near single crystal<sup>[4]</sup> and liquid<sup>[5]</sup> metal electrodes and ionic liquids near atomically flat nonmetal electrodes<sup>[6]</sup> demonstrate the utility of in situ synchrotron X-ray methods to probe interfaces under electrochemical bias. However, few detailed structural measurements of electrically biased TMO–aqueous electrolyte interfaces exist<sup>[7]</sup> despite the importance of these interfaces to energy technology, catalysis, and geochemistry.

The structures of atomically well-defined crystal surfaces and their interfaces can be measured with sub-Å precision using synchrotron X-ray techniques such as crystal truncation rod (CTR) scattering.<sup>[1a]</sup> CTRs are measured as streaks of X-ray scattering between Bragg reflections in the surface normal direction, and this scattered intensity encodes subtle changes in the atomicscale structure of an interface relative to the underlying material. Models of interfacial atomic configurations are typically fitted to measured CTRs using kinematical X-ray scattering theory,<sup>[8]</sup> yielding the occupancy, disorder parameter, and position of each set of symmetry-equivalent interfacial atoms. The penetrating power of hard X-rays enables measurements of surface and interface structures in realistic functional environments.

This study examines the changing atomic arrangement of the hematite–electrolyte interface as it is driven increasingly

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far from equilibrium by cathodic electrochemical potential. Hematite is a key functional TMO archetype, as it is both naturally abundant and a photoactive n-type semiconductor with a bandgap of about 2 eV. The (1102) ("*r*-cut") is a prominent low-index surface in natural and engineered iron oxides.<sup>[9]</sup> This termination exposes fast electron transport pathways in the hematite crystal structure<sup>[10]</sup> and is therefore more active toward interfacial (photo)redox reactions than the more widely studied (0001) termination of hematite.<sup>[11]</sup> Under open-circuit conditions, the *r*-cut surface is terminated by a complex topology of hydroxyls and surface aquo groups which frequently exchange with bulk water.<sup>[12]</sup> Cathodic potentials driving excess electrons to this surface can induce reductive dissolution (RD),<sup>[13]</sup> which proceeds according to Equation (1) with an equilibrium potential at room temperature defined in Equation (2).

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$$Fe_2O_{3(s)} + 6H^+ + 2e^- \rightarrow 2Fe_{(aq)}^{2+} + 3H_2O$$
 (1)

 $E_0$  (V vs Ag/AgCl<sub>(sat'd)</sub>) = 0.531 - 0.1773 pH - 0.0591 log([Fe<sup>2+</sup><sub>(aq)</sub>)]) (2)

This process is of broad natural and technological relevance; the source of electrons could be a photoexcitation event near the hematite surface,<sup>[14]</sup> a photoexcited organic reductant or dye,<sup>[15]</sup> adsorbed  $Fe^{2+}_{(aq)}$ ,<sup>[16]</sup> dissimilatory iron-reducing bacteria,<sup>[17]</sup> or external applied bias. Electrochemically biasing the hematite surface in solution is a simple means to control and monitor the flux of charge and ions (e.g., dissolved  $Fe^{2+}$ ) across the interface while enabling the simultaneous probing of the interface using in situ techniques.

Using CTR scattering, we measured the structure of the interface between a freshly polished *r*-cut hematite crystal and aqueous electrolyte ( $5 \times 10^{-3}$  M Na<sub>2</sub>SO<sub>4</sub>, pH 7.4) under steady-state current flow at applied cathodic potentials surrounding the nominal onset of RD. CTR analysis yielded 3D atomic-scale maps of this interface which are unique at each potential, revealing systematic changes in the coordination and speciation of surface oxygen groups and the organization of interfacial water within the Stern layer. Irreversible changes to the interface hydrogen bonding network due to excess protonation of the hematite surface under cathodic bias.

### 2. Results and Discussion

CTRs were measured in electrolyte under five conditions (Figure 1 and Figures S6 and S7, Supporting Information), with potentials all reported relative to Ag/AgCl(sat'd). First, the pristine surface was measured at the open circuit potential (OCP) of +0.23 V (Figure S5, Supporting Information); this condition is referred to as OCP1. Biases of -0.2 V and -0.7 V were subsequently applied, which surround the equilibrium bulk RD potential of  $\approx$ -0.4 V under our experimental conditions (Figure S2, Supporting Information). After the bias was removed, the OCP stabilized at +0.21 V (condition OCP2). A final limited CTR measurement was performed after injecting fresh solution into the cell (OCP = +0.29 V, condition OCP3, not shown in Figure 1). Under no measured condition was a monotonic

increase in cathodic current observed, which would have indicated runaway RD and substantial surface alteration (see the Supporting Information).

The atomic topologies of the hematite surface at various applied potentials have generally common features, consistent with a lack of substantial dissolution. Interface structures corresponding to the best fits to the CTRs are shown in **Figure 2**, and fit parameters are given in Tables S1 and S2 in the Supporting Information. The outermost oxygen atoms of the hematite crystal, labeled <sup>1</sup>O, are bonded to one iron atom each and form ridges which zigzag along the *b* direction of the orthorhombic surface cell. The oxygen atoms labeled <sup>2</sup>O are each bonded to two iron atoms and sit in valleys between the <sup>1</sup>O ridges. These layers are almost certainly protonated based on bond valence analysis,<sup>[12]</sup> as discussed below, although X-ray scattering methods cannot directly detect protons. Our model must also include two oxygen layers (<sup>2W</sup>O and <sup>1W</sup>O) corresponding to ordered water above the surface to achieve good CTR fits.

For the OCP1 structure, the <sup>1</sup>O fractional occupancy is 0.65, indicating that a typical terminal oxygen site is vacant about one-third of the time; meanwhile, the fractional occupancy of the <sup>1</sup>WO site is about one-third (0.28). Assuming that the <sup>1</sup>O species is a doubly protonated terminal aquo group, it appears that water molecules exchange between surface-bound <sup>1</sup>O sites and liquid <sup>1</sup>WO sites, as predicted through first-principles molecular dynamics simulations of hematite (1102)<sup>[12]</sup> and other iron (oxyhydr)oxide surfaces.<sup>[18]</sup> A second ordered water layer <sup>2</sup>WO sits approximately above <sup>1</sup>WO, forming an overall ridge-like water structure. The best-fit disorder parameters of layers <sup>1</sup>O, <sup>1</sup>WO, and <sup>2</sup>WO are fairly small, but much larger disorder parameters lie within the uncertainty of the fit (see Table S2, Supporting Information).

CTRs measured at -0.2 V and -0.7 V show subtle changes versus the OCP1 condition. Changes in the rod intensities are most clearly apparent in the low-L regions of the 00L and 10L rods as well as near (0 0 4.8) and (2 0 4.9). CTR analysis reveals significant changes in the terminal oxygen and water layer structure, as shown in Figure 2 and Figure 3 and detailed in Table S3 in the Supporting Information. The <sup>1</sup>O layer occupancy increases to 1.00 with applied bias, but the <sup>1</sup>O position in the surface normal direction becomes more disordered with increasing bias. The <sup>1W</sup>O layer occupancy also rises significantly. At -0.2 V, the water oxygen layers become disordered (see Table S2, Supporting Information) and move away from the surface; the  ${}^{1W}O - {}^{1}O$  interlayer spacing increases by 0.6 Å, and the  ${}^{2W}O - {}^{1W}O$  spacing increases by 0.4 Å. At -0.7 V, the water layers retreat slightly toward the surface and become more ordered relative to the -0.2 V structure. In both cathodically biased cases, the <sup>1W</sup>O and <sup>2W</sup>O atoms move to positions above the valleys between <sup>1</sup>O ridges; however, large values of the lateral disorder parameter  $u_{x,y}$  suggest that near-surface water molecules are only very weakly correlated to the hematite surface (Table S2, Supporting Information).

The bias-induced changes to the interface structure were only partially reversible after the cathodic bias was turned off. At OCP2, the <sup>1</sup>O occupancy dropped slightly, but in contrast to the OCP1 condition, the <sup>1W</sup>O atoms localized above the "valleys" between <sup>1</sup>O atoms. Flushing fresh solution through the cell (the OCP3 condition) resulted in some recovery toward the



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**Figure 1.** Measured CTR structure factor magnitudes |F| (points) and best fits (lines) for the *r*-cut hematite surface at four conditions: prior to cathodic bias (OCP1, cyan circles and dotted lines); at -0.2 V versus Ag/AgCl(sat'd) (green squares and dotted-dashed lines); at -0.7 V versus Ag/AgCl(sat'd) (magenta triangles and dashed lines); and after removing cathodic bias (OCP2, red diamonds and solid lines). CTRs are offset by factors of 2 for clarity.

OCP1 condition, as indicated by a rise in the low-L intensity of the 10L rod (Figure S7, Supporting Information); however, this corresponds to only a slight drop in the  $^{1W}$ O position.

The nanoscale morphology of the *r*-cut hematite surface was also modified in response to cathodic bias. Interface roughening manifests as a monotonic drop in the CTR midzone intensities; this was observed between the OCP1 and -0.2 V conditions (see Figure S7, Supporting Information). The nanoscale roughness of the interface, quantified as the  $\beta$  roughness parameter<sup>[8]</sup> in the CTR fit, increased between OCP1 ( $\beta$  = 0.05) and -0.2 V ( $\beta$  = 0.21) but did not change substantially through the remaining

CTR experiments. Nanoscale lateral disordering is clearly shown in atomic force microscopy (AFM) images taken before and after benchtop cathodic aging (**Figure 4**). Power spectral density (PSD) analysis of AFM images confirmed that disordering occurred after benchtop cathodic aging (Figure 4c). The initial condition shows a PSD peak at about 30  $\mu$ m<sup>-1</sup> corresponding to the 33 nm step edge spacing; after cathodic aging, the frequency distribution was much broader, signifying lateral disorder.

Beyond the initial roughening at the onset of cathodic bias, RD did not significantly modify the interfacial structure. Steady-state cathodic current (Figure S3, Supporting ADVANCED SCIENCE NEWS\_\_\_\_\_ www.advancedsciencenews.com





**Figure 2.** Atomic models of the hematite–water interface derived from CTR fits. Each column corresponds to the specified electrochemical condition. Models are viewed along the b (top row) and a (bottom row) axes of the orthorhombic r-cut hematite surface cell. Larger red balls represent oxygen atoms; smaller brown balls represent iron atoms. Fractional occupancies are represented by the colored portion of each ball.

Information) was primarily due to other processes in the electrochemical cell. Cyclic voltammograms (Figure S4, Supporting Information) did not show features associated with RD except possibly when the crystal was freshly polished and mounted. Based on poor correlation between morphological features and dissolution sites (Figure 4b), we posit that a limited quantity of labile iron dissolved from randomly distributed surface defect sites.<sup>[13,15b,19]</sup> Because these sites are dilute and probably



**Figure 3.** Time-averaged atom density in the surface normal direction. The density is calculated from atomic positions, occupancies, and disorder parameters derived from CTR fits, and it is plotted relative to the <sup>2</sup>O plane position. Density is normalized such that the integrated area of each peak gives the fractional O occupancy. Gray dotted lines track the <sup>1</sup>WO and <sup>2</sup>WO positions. Plots are offset in increments of 2 for clarity.

not coherently periodic with the hematite lattice or interface structure, they would not be detectable by CTR measurements. Thus, the observed changes in surface oxygen group occupation and overlying water structure pertain more to the effects of the accumulation of negative charge density at the hematite surface than to modification of surface topology by RD.

The movement of water oxygen atoms away from the surface under cathodic bias is likely due to electrostatic dipole flipping of water molecules. At a flat, positively charged surface, water molecules are oriented with their electronegative oxygen atoms pointing toward the surface; however, when surface charge becomes negative, water molecules flip such that the hydrogen end points toward the surface.<sup>[2c,4]</sup> Complex rearrangements of water molecules, including disordering with increasing cathodic bias, have been observed at TMO-electrolyte interfaces.<sup>[7a,b]</sup> As shown in Figure 3, the shift in water positions is most extreme between the OCP1 and -0.2 V conditions as water molecules flip; the larger electric field at -0.7 V induces stronger ordering of the water layers and pulls them closer to the surface. The broad water feature at OCP2 indicates a state of intermediate order as water molecules reorganize when the field is turned off.

Between OCP1 and the conditions under cathodic bias, the occupancy of the <sup>1</sup>O site (which is likely doubly protonated, see below) rises from 0.65 to 1.00. Although the terminal aquo groups exhibit some structural flexibility as shown by a larger surface normal disorder parameter under cathodic bias, the increase in <sup>1</sup>O occupancy to unity suggests that the water exchange observed at open circuit conditions<sup>[12]</sup> is significantly slowed or stopped as terminal aquo groups are more attractively bound at the <sup>1</sup>O site. This is initially counter intuitive to the expectation of accumulating electron density at surface Fe sites. Applied cathodic potential at the hematite–electrolyte interface should populate the Fe 3d orbitals at the bottom of the conduction band.<sup>[20]</sup> Disregarding any other effects, if <sup>2</sup>Fe was being





**Figure 4.** AFM images and analysis of the *r*-cut hematite surface before and after cathodic aging. a) Image of the freshly polished *r*-cut hematite crystal surface. b) Image of the surface after cathodic aging as described in the text. The scale bar to the right of (a,b) shows the height range in the surface normal direction for both images, which each have a rootmean-square (RMS) roughness of about 1 Å. c) 2D power spectral density (PSD) of images a) (black line) and b) (red line).

partially reduced, then the  ${}^{2}Fe-{}^{1}OH_{2}$  bond would weaken as electron density accumulated, increasing the water exchange frequency.<sup>[21]</sup> In this scenario, the time-averaged  ${}^{1}O$  occupancy would remain partial or possibly even decrease, but since this

is not observed, we must consider other compensation mechanisms for the increasing negative charge at the surface.

Surface proton density is correlated with the trapping of excess electrons at Fe sites on hematite surfaces,<sup>[15a]</sup> so protonation is a likely charge compensation mechanism. Prior studies suggest that <sup>1</sup>O is doubly protonated, <sup>2</sup>O is singly protonated, and <sup>3</sup>O is not protonated at equilibrium at circumneutral pH and OCP.<sup>[12,22]</sup> To estimate the degree of protonation, we calculated surface  $pK_a$  values using the fitted CTR models and the method of Bickmore et al.<sup>[23]</sup> The  $pK_{a2}$  values for the addition of a second proton onto <sup>1</sup>O and <sup>2</sup>O sites (Table S5, Supporting Information) are most relevant, since at least single protonation is likely and triple protonation is unlikely on both sites.  $pK_{2}$  of <sup>1</sup>O ranges from 8.0 to 9.2, indicating that at the circumneutral conditions of our experiments, an <sup>1</sup>O atom is likely doubly protonated as a terminal aquo group but may be transiently deprotonated.  $pK_{a2}(^{2}O)$  is 3.2 under cathodic bias and ranges from 5.7 to 6.1 at OCP.  $pK_{a1}(^{3}O)$  ranges from -5.9 to -5.6, suggesting that these sites are not protonated. Because the  $pK_{a2}(^{2}O)$  values are not far below the solution pH of 7.4, the accumulation of electron density at the surface during cathodic bias could drive excess protonation of <sup>2</sup>O sites. The presence of doubly protonated <sup>2</sup>O moieties would yield additional <sup>2</sup>OH-<sup>1</sup>OH<sub>2</sub> hydrogen bonds, stabilizing aquo groups at the <sup>1</sup>O site,<sup>[1b,24]</sup> consistent with our measurements.

This interpretation complements prior electrochemical studies. The strengthening of surface hydrogen bond networks over atomically flat terraces may act as a barrier to RD, preventing the solvation and removal of Fe<sup>2+</sup> from the terraces. This could explain why potentials several tenths of a volt more cathodic than the equilibrium RD potential are required for substantial hematite RD to proceed.[25] Because surface protonation is a consequence of either cathodic bias or reduced pH, the inverse relationship between interfacial capacitance and pH observed by Shimizu and Boily<sup>[26]</sup> for the hematite (1102)-electrolyte interface is probably linked to the complex potential-dependent rearrangement of electrolyte layers we observed. Prior evidence of the slow relaxation of this interface,<sup>[26,27]</sup> attributed to screening of <sup>2</sup>O sites by terminal <sup>1</sup>OH<sub>2</sub> ligands,<sup>[27]</sup> is also consistent with transient metastable protonation of the hematite surface.

## 3. Conclusion

These collective findings point to an interfacial structure governing charge and ion transport that is dynamically responsive to the applied potential and thus different from its corresponding equilibrium model. This work constitutes the first in situ systematic study, to our knowledge, of the atomic- to nanoscale structure of an iron (oxyhydr)oxide interface poised far from equilibrium. The electrochemical cell (Figure S1, Supporting Information) provided a novel platform for accurate electrochemical measurements under bulk-like solution conditions while enabling 3D structural determination via X-ray scattering experiments. This approach could be extended to other technologically relevant interfaces between aqueous electrolyte and functional materials with well-defined crystal terminations.

Our structural characterization reveals the fine details of the ordering and polarization of the electrolyte near a topographically and chemically complex TMO surface and how it changes as it is driven far from equilibrium. When cathodic bias is applied, charge-compensating protonation of surface oxygen groups increases the coverage of specifically bound water by strengthening the hydrogen bonding network. Weakly adsorbed water molecules undergo dipole flipping and are pulled closer to the surface with increasing cathodic bias. A persistent metastable state is observed upon return to open circuit potential. These combined responses dictate the potential-specific dielectric structure and chemical environment which control the flux of current and ions across an interface. Even the most sophisticated equivalent circuit interpretations of macroscopic electrochemical measurements<sup>[26]</sup> mask these critical details. The precise structural determination of reactive TMO interfaces poised far from equilibrium constitutes a significant advance toward accurate models of catalytic and geochemical processes.

## 4. Experimental Section

Sample Preparation and Characterization: A naturally conductive (1102)-oriented cylindrical hematite crystal (3 mm diameter  $\times$  1 mm thick, Bahia, Brazil) was used for all measurements. After crystal orientation, cutting, and mechanical polishing, the crystal underwent chemical-mechanical polishing with a 20 nm colloidal silica suspension (Buehler MasterMet 2, Lake Bluff, IL, USA). After polishing, the crystal was soaked successively in NaOH (pH 10) and HNO<sub>3</sub> (pH 2) solutions and then cleaned with acetone followed by methanol or isopropanol. The surface morphology was checked using a Veeco Dimension Icon atomic force microscope operated in PeakForce Tapping mode using Bruker SCANASYST-AIR cantilever tips (2 nm nominal tip radius).

*Electrochemical Measurements*: Two sets of electrochemical measurements were carried out: benchtop and in situ (during CTR measurement). All electrochemical measurements were performed using a CHI 660C potentiostat. The electrolyte ( $0.005 \text{ M} \text{ Na}_2\text{SO}_4$ , pH 7.3–7.4) was chosen for its geochemical abundance and the minimal specific adsorption of sulfate to hematite at circumneutral pH.<sup>[28]</sup> All glassware was cleaned in 0.5 M HNO<sub>3</sub> or 5 M HCl prior to use.

Benchtop cathodic aging and cyclic voltammetry were performed in a glass cell in open air using a Pt wire counter electrode and a reference electrode composed of an AgCl-coated Ag wire in a KCl-saturated gel (Pine Instruments). The electrolyte solution was prepared in air using anhydrous Na2SO4 (ACS reagent, Sigma-Aldrich) and deionized ultrafiltered water (Fisher Chemical). Prior to measurements, solution impurities were removed by holding a carbon cloth working electrode in the cell at -0.4 V versus Ag/AgCl(sat'd) for 15 min. The 10 mL cell volume was sparged with  $N_2$  for 30–60 min before measurements and during benchtop cathodic aging and cyclic voltammetry measurements. The freshly polished and cleaned r-cut hematite crystal was mounted to an Ag wire using Ag paint, which also coated the back and sides of the crystal to ensure good electrical contact. The wire and all sides of the crystal except the prepared r-cut face were then coated in transparent acrylic nail polish. After the nail polish dried, the crystal was dipped into the electrochemical cell for measurement.

For in situ CTR measurements, the electrolyte solution was prepared from anhydrous NaSO<sub>4</sub> (A.C.S. Grade, Fisher Scientific) in a glovebox (<1 ppm O<sub>2</sub>) using deionized water (18.2 MΩ). The water had been boiled while sparging with N<sub>2</sub> and moved into the glovebox while warm to prevent solution of O<sub>2</sub> or CO<sub>2</sub>. The electrolyte was loaded into syringes which were capped and sealed before leaving the glovebox, ensuring that the electrolyte remained anoxic.

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X-Ray Scattering Measurements: CTR measurements were performed in a novel electrochemical cell (Figure S1, Supporting Information). The hematite crystal, acting as the working electrode, was placed in an acrylic cup containing a Cu back electrode and Ag paint. The cup was sealed with acrylic nail polish below the horizon of the crystal surface. A 0.5 mm diameter Pt wire was used as a counter electrode, and an AgCl-coated Ag wire was used as the reference electrode. The OCP of the Ag/AgCl electrode in 0.005 M Na<sub>2</sub>SO<sub>4</sub> solution was +0.30 V versus Ag/AgCl in the KCl-saturated gel electrode; potentials from the in situ CTR measurements have been duly calibrated and are reported relative to Ag/AgCl(sat'd).

CTRs were measured at GeoSoilEnviroCARS end station 13-ID-C at the Advanced Photon Source (APS) at Argonne National Laboratory. A 20.00 keV beam was selected from the undulator output using an Si (111) monochromator, and X-ray mirrors were used to obtain a 84  $\mu$ m horizontal  $\times$  240  $\mu$ m vertical spot at the center of sample rotation. Scattered X-rays passed through a guard slit and a flight path tube to a Pilatus 100 K pixel array area detector. The 00L CTR was measured in specular mode, with the incident and reflected beam angles kept equal. All other rods were measured with a fixed incident beam angle of 3° and variable exit beam angle. All CTR measurements were performed at room temperature.

CTR intensities were background-subtracted and analyzed using the kinematical X-ray scattering approach<sup>[8]</sup> as implemented in GenX software;<sup>[29]</sup> further details are given in the Supporting Information. Fit parameters included atom positions, fractional occupancies (relative to the bulk layer occupancy of 7.3 atoms nm<sup>2</sup>), disorder parameters in the lateral ( $u_{x,y}$ ) and surface normal ( $u_z$ ) directions, and the roughness parameter  $\beta$ .<sup>[8]</sup> In order to make the *L* reciprocal lattice direction parallel to the surface normal, the *r*-cut surface was modeled as an orthorhombic surface cell with lattice parameters a = 5.038 Å, b = 5.434 Å, and c = 7.3707 Å. Since this surface cell does not have translational symmetry, a lattice offset parameter<sup>[30]</sup> of 0.14 in the *b* direction was used to ensure the proper crystal periodicity.

## **Supporting Information**

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

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## **Conflict of Interest**

The authors declare no conflict of interest.

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