

# Atomic-Scale Study of Ambient-Pressure Redox-Induced Changes for an Oxide-Supported Submonolayer Catalyst: $VO_x/\alpha$ -TiO<sub>2</sub>(110)

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Supporting Information

**ABSTRACT:** The activity of supported catalysts is strongly linked to the structure of the surface species. However, direct in situ structural measurements of submonolayer catalysts are lacking. Using in situ X-ray standing wave analysis combined with ex situ X-ray photoelectron spectroscopy and atomic force microscopy, we observed reversible redoxinduced surface cation dynamics for three-fourths of a monolayer of vanadia grown by atomic-layer deposition on an  $\alpha$ -TiO<sub>2</sub>(110) surface. On the basis of first-principles density functional theory calculations, we propose vanadia submonolayer structures that agree with and suggest explanations for the observed redox-induced structural changes. Under oxidation conditions, the correlated submonolayer structure is a 2D trimer-decorated polymeric chain along the rutile  $\begin{bmatrix} -1 & 1 & 0 \end{bmatrix}$  direction; under reducing conditions, the more stable polymeric chain remains unreduced, whereas the less stable decorating trimers become reduced and uncorrelated with the support lattice. These results show that a large fraction of V sites retains redox activity at submonolayer V coverages.



SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

he activity and selectivity of a catalyst is strongly linked to its structure.<sup>1-3</sup> In particular, in heterogeneous catalysis, the structure provides a framework for the arrangement and strategic placement of key catalytic sites, hosting them in a prescribed configuration to exhibit desired catalytic functions.<sup>4</sup> Under reaction conditions, such catalytic structures undergo dynamic processes,<sup>5-10</sup> becoming active participants in the overall catalytic process.<sup>4</sup> Therefore, it is important to understand fully the atomic-scale structures of catalysts under reaction conditions and the catalytic reaction mechanisms for tuning their catalytic properties.

Supported vanadium oxide is of great interest as an active catalyst for selective oxidation reactions.<sup>11,12</sup> It is welldocumented that submonolayer (sub-ML) vanadia is significantly more catalytically active than crystalline V2O5 nanoparticles or multilayer films.<sup>13-15</sup> Numerous experimental and theoretical studies have found that the supported catalyst exists in isolated monomeric form at low coverage and in polymeric island form at higher coverage.<sup>11,16-23</sup> The nature of the vanadia catalyst support modifies both the catalyst dispersion and the properties of V-O-S linkages between the support (S) and vanadia (V) species.<sup>12</sup> These linkages and the presence of accessible V5+ species are often related to the high activity of sub-ML films. Interestingly, the structure of sub-ML supported catalysts not only determines their activity but also undergoes

dynamic changes in the course of the reaction.<sup>8</sup> In situ probes of such structural changes are indispensable to understand and tune catalytic activity. In this regard, the X-ray standing-wave (XSW) technique is capable of sub-ML structural characterization with atomic-scale sensitivity.8 Our previous XSW and Xray photoelectron spectroscopy (XPS) work<sup>9</sup> for a 2 ML VO<sub>x</sub> film on  $\alpha$ -TiO<sub>2</sub>(110) showed a reversible coherent-incoherent transformation between a well-ordered VO<sub>2</sub> film and disordered V5+ oxide as the oxidation state cycles between V<sup>4+</sup> and V<sup>5+</sup>. Thus, observations of structural transformations and coherence of supported catalyst accompanying changes of the oxidation state  $V^{5+}$  to  $V^{4+}$  or  $V^{3+}$  under redox cycling provides information on the structure of active sites and reversibility of the reaction.

Herein we study a sub-ML of vanadia grown on the  $\alpha$ -TiO<sub>2</sub> rutile (110) surface using XSW and XPS and directly observe a reversible redox-induced atomic-scale structural and chemicalstate modification of the catalyst, which differs significantly from the 2 ML case. Furthermore, on the basis of density functional theory (DFT) calculations, we propose polymeric chain structures of the supported vanadia sub-MLs with the

Received: August 8, 2012 Accepted: September 14, 2012 same coverage for the correlated part of the reduced structures. The oxidized structures are proposed to have additional nonpolymeric correlated vanadia attached to the chains. We provide a comparison of the calculated structures with experimental measurements and explanations of the observed cation dynamics during redox reaction.

Polished rutile  $\alpha$ -TiO<sub>2</sub>(110) single-crystal substrates were cleaned and oxygen-annealed to obtain atomically flat surfaces. The substrates were then exposed to a single atomic layer deposition (ALD) growth cycle to grow sub-ML VO<sub>X</sub>. The AFM analysis after each redox-processing step, namely, asdeposited (AD), oxidized (Ox), and reduced (Re) (Figure S3, Supporting Information), showed a consistent surface morphology that had atomically flat terraces separated by atomic steps. Figure 1 shows the XP spectra from the surface at



**Figure 1.** XP spectra of the as-deposited (AD), oxidized (Ox), and reduced (Re) 3/4 ML VO<sub>X</sub>/ $\alpha$ -TiO<sub>2</sub> (110) surfaces with a 45° electron emission angle. The V  $2p_{3/2}$  peak fitting indicates that V is totally converted to the V<sup>5+</sup> oxidation state for the AD and Ox surfaces, but split 25% V<sup>3+</sup>/75% V<sup>5+</sup> for the Re surface. Reoxidation (Ox2) returned all vanadium cations back to V<sup>5+</sup> (not shown). Also shown are the O 1s and chemically shifted OH peaks for the AD, Ox, and Re surfaces. The measured chemical shifts for the 3+, 4+, and 5+ V peaks (see vertical dashed lines) are improved in reliability by referencing the respective binding energy differences (BEDs) relative to the O 1s peak.

the AD, Ox, and Re states. We used the data processing and assignment methods described elsewhere for fitting the XPS peaks.<sup>10,24,25</sup> As seen in Figure 1 for the AD and Ox states, the V  $2p_{3/2}$  binding energy (BE) is 517.2 eV and the binding energy difference (BED) between the O 1s and V  $2p_{3/2}$  is 12.8 eV. This indicates that V is V<sup>5+</sup> for the AD and Ox states. However, in the Re state, the V  $2p_{3/2}$  peak becomes broader, indicating the coexistence of multiple chemical states. Detailed analysis in Figure 1 shows that V in the Re state is 25% V<sup>3+</sup> (BED: 14.6 eV) and 75% V<sup>5+</sup>. Similar coexistence of V<sup>3+</sup> and V<sup>5+</sup> has been previously reported for V on silica and alumina.<sup>26,27</sup> Furthermore, XPS of the reoxidized (Ox2) surface (not shown) is identical to the Ox, indicating reversibility of vanadia in this redox reaction.

Survey XP spectra (Figure S2, Supporting Information) covering an extended BE range from 250 to 550 eV were also collected and analyzed to show that the Ox treatment removed C contamination from the ALD process and that there was no measurable V loss from the surface by desorption or diffusion. (See the SI for more details.) Note that the XPS and XSW (discussed below) observations of redox reversibility are also evidence against any V diffusion into the TiO<sub>2</sub> subsurface.

In situ XSW analysis was used to measure the V atomicdensity map relative to the rutile substrate lattice of each sample state. When scanning in angle through a selected substrate H = hkl Bragg reflection, we observed an XSWinduced modulation of the V K $\beta$  fluorescence yield that was analyzed to determine the Fourier amplitude ( $f_H$ ) and phase ( $P_H$ ) for the V atomic density. Reviews of the XSW method can be found elsewhere.<sup>28–30</sup> As previously demonstrated for bulk impurities and surface adatoms, a Fourier summation with these measured amplitudes and phases can be used to generate a model-independent 3D map,  $\rho(r)$ , for the XRF selected atomic species.<sup>31–33</sup>

$$\rho(\mathbf{r}) = 1 + 2 \sum_{\substack{\mathbf{H}=-\mathbf{H}\\\mathbf{H}\neq 0}} f_H \cos[2\pi (P_H - \mathbf{H} \cdot \mathbf{r})]$$
(1)

Because of the Fourier summation process the XSW map has the 3D periodicity of the substrate tetragonal primitive unit cell. The rutile  $\alpha$ -TiO<sub>2</sub>(110) surface unit cell used for the generation of the 3D map is shown in Figure 2. Possible surface V sites are also depicted.<sup>34,35</sup>

The XSW data and analysis for the different *hkl* reflections (Figure S5, Supporting Information, and Table 1) show differences that indicate different structures for each step of the redox reaction (AD, Ox, and Re). The V coherent fraction for the AD surface of  $f_{110} = 0.18(7)$  is much smaller compared with that of the Ox and Re surfaces, indicating that the V spatial distribution is mostly uncorrelated to the  $\alpha$ -TiO<sub>2</sub> substrate lattice after the ALD growth and becomes more correlated after the oxidation and reduction processing steps. This may be due to the ALD process being performed at a lower temperature than the Ox and Re steps.

Note that our  $f_H$  and  $P_H$  measured values for the Re state match reasonably with the previous reported (110) and (101) back-reflection XSW results<sup>36</sup> for V<sup>3+</sup> cations. This previous UHV case, which vapor-deposited V, used XSW-induced XPS to find V<sup>3+</sup> and V<sup>0</sup> on the surface in different geometries.

Inserting the Table 1 XSW measured  $f_H$  and  $P_H$  values into eq 1 generates the model-independent 3D V atomic density maps that are shown in Figure 2b,c for the Ox and Re surfaces. These 3D maps are referenced to the same  $TiO_2$  (110) unit cell that is outlined with black lines in Figure 2a. There are two symmetry inequivalent Ti sites denoted by the solid and open circles in Figure 2b,c. These are the atop (AT) and bridge (BR) respective sites.<sup>34,37</sup> As can be seen, our measurement has the maxima in the V density laterally aligned with these two Ti sites with a slight outward vertical offset in the [110] direction. Numerical analysis of the model-independent maps in Figure 2 gives a BR to AT site occupation ratio of 4:3 for the oxidized and 1:1 for the reduced surface. (Supporting Information) This analysis also shows that in the Ox state the V heights above the TiO plane are 3.69 and 3.60 Å for BR and AT sites, respectively, whereas in the Re state, both sites have the same height, 3.56 Å.

To quantify the structural parameters associated with these two adsorption sites, we performed a least-squares global fit of each condition to the measured set of  $f_H$  and  $P_H$  values. The *H*th Fourier component for the V atomic distribution is then described as

$$F_{H} = f_{H} \exp(2\pi i P_{H})$$
  
=  $c_{AT} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_{AT}) + c_{BR} \exp(2\pi i \mathbf{H} \cdot \mathbf{r}_{BR})$  (2)



**Figure 2.** (a) Ball-and-stick model showing the  $\alpha$ -TiO<sub>2</sub> (110) surface termination with oxygen atoms in red, Ti in gray, and possible adsorbed cation sites in white (atop (AT), bridge (BR), and tetradentate (TD)). The nonprimitive unit cell, outlined with heavy black lines, referred to as the (110) surface unit cell, is used as the reference to locate vanadium cation positions in XSW 3D atomic density maps shown in panels b and c for the oxidized (Ox) and reduced (Re) surfaces, respectively. As a point of reference, open and filled circles denote the two Ti symmetry inequivalent sites in the ideal bulk-like structure with (110) Ti planes at heights of 0, 3.25, and 6.50 Å. Because of the Fourier summation process, XSW maps have the 3D periodicity of the substrate unit cell. To locate the V adsorption sites, compare the top layer in panels b and c to the model in panel a.

Table 1. Summary of the XSW Experimental Results from the Oxidized (Ox) and Reduced (Re) Surface Treatments of the 0.74 ML  $VO_X/\alpha$ -TiO<sub>2</sub> (110) Surface<sup>*a*</sup>

	oxidized surface						reduced surface					
hkl	$f_{\rm meas}$	$f_{\rm calc}$	$f_{\rm DFT}$	$P_{\rm meas}$	$P_{\rm calc}$	P <sub>DFT</sub>	$f_{\rm meas}$	$f_{\rm calc}$	$f_{\rm DFT}$	$P_{\rm meas}$	$P_{\rm calc}$	$P_{DFT}$
110	0.45(3)	0.47	0.51	0.07(1)	0.09	0.09	0.35(8)	0.27	0.31	0.09(4)	0.09	0.03
101	0.43(7)	0.49	0.40	0.16(3)	0.04	0.05	0.28(4)	0.27	0.18	0.08(3)	0.05	0.02
200	0.8(1)	0.47	0.22	0.09(3)	0.09	0.07	0.18(7)	0.27	0.08	0.01(8)	0.01	-0.09
111	0.3(2)	0.17	0.22	-0.26(7)	-0.28	-0.20	0.1(1)	0.00	0.04			
211	0.7(2)	0.45	0.27	0.19(3)	0.13	0.12	0.3(1)	0.27	0.15	0.12(6)	0.14	0.04

 ${}^{a}f_{meas}$  and  $P_{meas}$  are the experimentally measured coherent fractions and coherent positions, respectively.  $f_{calc}$  and  $P_{calc}$  are calculated from the best-fit model described by eq 2.  $f_{DFT}$  and  $P_{DFT}$  are calculated based on the DFT structures in Figure 3. The *P* values are referenced to an origin that coincides with a bulk Ti atom at the AT site.

Table 2. XSW Determined Best Fit Model Parameters from Equation 2 for the V Occupation Fractions,  $c_{X}$ , and Heights,  $z_{X}$ , above the Bulk TiO (110) Plane<sup>*a*</sup>

surface	$c_{ m BR}$	$c_{\rm AT}$	$\Sigma c$	$z_{ m BR}~({ m \AA})$	$z_{ m AT}$ (Å)	${z_{ m BR}}^{ m DFT}$ (Å)	$z_{ m AT}{}^{ m DFT}$ (Å)
Ox	0.30(7)	0.19(5)	0.49(9)	3.65(9)	3.35(6)	3.8	3.3
Re	0.14(3)	0.14(3)	0.28(4)	3.38(9)	3.38(9)	3.3	3.5
<sup>a</sup> V correlated fra	$f(\Sigma_{c} = c_{m} + $	$(\dots)$ is also listed A	verage V heights a	DFT and 7. DFT	for structures in Fig	rure 3 obtained from	DFT are given fo

"V correlated fraction ( $\Sigma c = c_{BR} + c_{AT}$ ) is also listed. Average V heights  $z_{BR}^{DFT}$  and  $z_{AT}^{DFT}$  for structures in Figure 3 obtained from DFT are given for comparison. For reference, Ti in bulk  $\alpha$ -TiO<sub>2</sub> has  $z_{BR} = z_{AT} = 3.25$  Å.

where  $c_X$  denotes the V occupation fraction at the AT and BR sites with positions  $r_{AT} = (0,0,z_{AT})$  and  $r_{BR} = (1/2,1/2,z_{BR})$ locating the V heights,  $z_X$ , above the TiO plane. As shown in Table 2, the best-fit determined results for V BR and AT occupation ratios and heights are consistent with the modelindependent analysis. As an additional consistency check, we also calculated and listed in Table 1 the  $f_{cal}$  and  $P_{cal}$  that would have been observed if V occupied sites as dictated by this bestfit model. These calculated values are also in good agreement with the measurement. From Table 2, we see that V atoms have an ordered fraction (or correlated fraction) of 49% ( $c_{AT} + c_{BR} =$ 0.49) in the oxidized state. The remaining (51%) V atoms, which are measured to be in an uncorrelated distribution relative to the substrate lattice, could be VO<sub>X</sub> nanoparticles or V in surface defect sites or loosely bound  $VO_X$ . Reduction causes one-half of the BR-site V cations to become uncorrelated with the substrate lattice, whereas the fraction of V occupying AT sites is slightly reduced. The fact that only part of the vanadium population is structurally modified by reduction indicates that these atoms are initially in a different structure than the rest of the submonolayer. These uncorrelated V atoms contribute only to a constant background in the 3D density map, implying that they move to uncorrelated positions on the surface upon reduction. The second oxidization reverses the process. Therefore, the V cations are directly shown to have redox reaction reversibility in both their chemical states and surface bonding sites.

On the basis of DFT calculations, we propose structures for the coherent parts of the oxidized and reduced sub-ML vanadium oxide shown in Figure 3. The structures are



Figure 3. DFT-optimized coherent vanadium oxide sub-ML structures on rutile (110) under (a) oxidized and (b) reduced conditions. Oxygen atoms are in red and vanadium atoms are in blue. The symmetry inequivalent sites the V atoms belong to, BR and AT as defined in Figure 2a, are indicated.

"polymeric", with all V atoms bound to neighboring V through bridging oxygen (V-O-V). Most vanadium atoms have a terminal vanadyl bond as well as three V-O single bonds, very similar to the bonding features of the V atoms in other supported V<sub>2</sub>O<sub>5</sub> sub-ML structures.<sup>11</sup> The oxidized structure shown in Figure 3a, referred to as a 2D trimer-decorated polymeric chain, is composed of two parts: a chain (highlighted in red) that is continuous along the  $\begin{bmatrix} -1 & 1 & 0 \end{bmatrix}$  direction and a trimeric cluster that is attached to the chain through bridging oxygens (highlighted in green). It has a V occupation ratio at AT and BR sites  $(c_{AT}/c_{BR})$  of 3:4 and a theoretical total correlated coverage of 0.44 ML. The average heights of AT and BR vanadium are 3.3 and 3.8 Å, respectively, relative to the calculated bulk TiO<sub>2</sub> plane. These are all in good agreement with the best-fit parameters shown in Table 2 as well as with the coherent fractions and coherent positions measured experimentally and calculated using the best-fit model. (See Table 1.) The stoichiometry of the structure is  $V_7O_{17}$ , corresponding to an average of +4.85 formal charge on vanadium. The small deviation of the charge from the +5 charge deduced from the XPS measurement is within the accuracy of the XPS measurement and peak fitting.

In our proposed model of the reduced structure, the decorating trimers in the oxidized structure are reduced. The reduced V atoms have a larger spread in their positions relative to the support lattice, resulting in a smaller total correlated fraction compared with the fully oxidized structure. Therefore, the correlated structure of the reduced sample, as shown in Figure 3b, is just the fraction that remains unreduced and still correlated to appear in the XSW density map: the continuous chain. It has  $c_{AT}/c_{BR}$  ratio of 1:1 and the theoretical correlated coverage of 0.25 ML. The average heights of AT and BR vanadium are 3.5 and 3.3 Å. These results again agree well with the measured and best-fit model parameters (Tables 1 and 2). The chain structure that is initially part of the oxidized sub-ML "survived" reduction because it is more stable than the rest of the sub-ML. This chain structure is the most energetically stable among all of the stoichiometric structures we have investigated (Supporting Information). In contrast, the trimeric part of the oxidized structure is more easily reduced to V3+ cations and becomes uncorrelated and produces a constant background in the XSW map. We have calculated that removing a vanadyl oxygen from the end of the trimeric cluster is more favorable (by at least 0.2 eV) than removing it from the four possible sites of the decorated chain. We also find that removing an O from V belonging to the undecorated part in a decorated chain structure is 0.98 eV more costly than removing the vanadyl O at the end of the decorating trimer. Similarly, chain-like structures were also found to be more stable than isolated trimers for the case of WO<sub>3</sub> supported on the rutile  $TiO_2$  (110) surface in first-principles molecular dynamics simulations.<sup>7</sup> However, we would like to note that the decorating polymeric cluster does not have to be uniquely trimeric. Other noncontinuous decorating clusters are still likely to be less stable than the bare chain and disordered upon reduction. Our results suggest that the reducibility of the supported vanadia species is structure-dependent: the fraction of the structure that forms a stable chain is less reactive than the fraction in trimeric geometry.

In conclusion, for 3/4 ML ALD-grown VO<sub>X</sub> catalyst on  $\alpha$ -TiO<sub>2</sub>(110) support, we demonstrated atomic-scale analysis for the redox-driven cation dynamics under ambient flowing H<sub>2</sub> and O<sub>2</sub> gas conditions. XPS shows that O<sub>2</sub> oxidizes all V to the 5+ state and that H<sub>2</sub> reduces part of the V<sup>5+</sup> cations. In situ XSW analysis of the oxidized (Ox) surface shows that 0.36 ML of the vanadium atoms occupy bridge (BR) or atop (AT) sites on rutile (110) surface and the remaining V ions are uncorrelated to the substrate lattice. XSW also shows that reduction causes 0.16 ML of the correlated V structure to become uncorrelated, and this process is reversible. By comparing V coherent fractions and coherent positions obtained from experiment to those calculated from structures optimized using DFT, we predicted surface oxygen configurations, which are inaccessible to the XSW measurements.

We found that parameters for the oxidized structure match well with the correlated sub-ML "polymeric" structure consisting of a continuous  $V_2O_5$  chain in  $[-1\ 1\ 0]$  direction and decorating trimeric  $VO_x$  clusters attached to the chain. From a good match of the reduced structure to the polymeric chain without additional trimers we deduce that under H<sub>2</sub> flow the trimeric part becomes reduced and uncorrelated while the continuous chain remains unreduced. These results suggest that in the coverage regime reported in this work, the polymeric  $VO_x$  structures form on the support, and the fraction of the structure that cannot form continuous chains is more reactive toward a reduction reaction. These findings will help us understand redox-induced structural and chemical changes in supported sub-ML catalysts and be useful for improving catalytic activity.

# EXPERIMENTAL AND THEORETICAL METHODS

Sample Preparation. Rutile ( $\alpha$ -TiO<sub>2</sub>) single crystals were oriented, cut  $(10 \times 10 \times 1 \text{ mm}^3)$ , and polished parallel to the (110) by Crystal GmbH (Berlin, Germany) with miscut <0.1°. Rutile  $\alpha$ -TiO<sub>2</sub> has a tetragonal crystal structure (space group:  $P4_2/mnm$ ) with a room-temperature lattice constant of a = b = 4.594 Å and c = 2.959 Å.  $\alpha$ -TiO<sub>2</sub> (110) substrates were first annealed in a tube furnace with flowing  $O_2$  (~100 sccm) at 400 °C for 0.5 h, then at 1000 °C for 1 h. Prior to ALD, the substrates were immersed in ultrapure water (resistivity >10<sup>18</sup>  $\Omega$  cm<sup>-1</sup>) for 1 h at 90 °C to hydroxylate the surface. The substrates were then rinsed with 10% HCL, followed by an ultrapure water rinse, and then blown dry with nitrogen. The substrates were then loaded into the ALD reactor<sup>38</sup> and heated to 300 °C under ultra-high-purity nitrogen flow at 360 sccm at a pressure of 1 Torr for 1 h and then cleaned in situ with flowing ozone. For sub-ML vanadia growth, the substrates were exposed first to vanadyl oxytriisopropoxide (VOTP) at a partial pressure of 0.05 Torr for 2 s, followed by a nitrogen purge for 5 s. The substrates were then exposed to hydrogen peroxide at a partial pressure of 0.2 Torr for 2 s, followed by a nitrogen purge for 5 s. This process is defined as one ALD cycle. This is the AD sample. The Ox and Re surfaces were prepared by annealing at 350 °C for 1/2 h in O2 and 2% H2 in helium at 760 Torr, respectively.

*Characterization.* Ex situ atomic force microscopy (AFM) and ex situ XPS were used to examine the surface morphology and chemical states of the surface atoms after each step of the reaction process. The ALD-processed substrate was placed on a ceramic heating stage inside a beryllium dome gas reaction cell that was mounted on a four-circle diffractometer at the Advanced Photon Source (APS) for X-ray fluorescence (XRF) and in situ XSW analysis. XRF comparison with a calibrated standard sample determined the V coverage to be 0.74 ML. (One monolayer is defined as the area density of Ti atoms in the TiO (110) plane, or 10.4 atoms/nm<sup>2</sup>.)

DFT Calculation. Density functional theory with general gradient approximation (GGA) Perdew-Wang 91 (PW91)<sup>39</sup> functional as implemented in the Vienna ab initio simulation package (VASP) code<sup>40,41</sup> was used for calculations of supported sub-ML vanadia. The core electrons were described by the projector-augmented wave (PAW) method,<sup>42,43</sup> and the valence electrons were described using a plane-wave basis set with cutoff of 264 eV. Monkhorst-Pack grids<sup>44</sup> were used to sample the Brillouin zone. The geometries were optimized using conjugated gradient method in all systems until the forces on all relaxed atoms were under 0.05 eV/Å. Using these parameters, the topmost Ti height,  $d_{110}$ , was calculated to be 3.23 Å, less than 1% shorter than the experimentally measured 3.25 Å. The stoichiometric rutile surface slab consisting of 3 TiO<sub>2</sub> trilayers was used to describe the support. For supported sub-ML vanadia optimizations, the bottom TiO<sub>2</sub> trilayer was kept frozen while the rest of the atoms were allowed to relax.

# ASSOCIATED CONTENT

# **Supporting Information**

Details of the materials growth, AFM, XPS, XSW characterizations, and DFT calculations. 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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