Structure and Stability of Au-supported Layered Cobalt Oxide Nanoislands in Ambient Conditions

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ABSTRACT: Cobalt oxide is a promising earth-abundant electrocatalyst for water splitting, however the structural complexity of oxides coupled with the difficulty of characterizing it in its operating environment mean that fundamental understanding of its catalytic properties remains poor. In this study, we go beyond vacuum studies and investigate the morphological evolution of a $\text{CoO}_x/\text{Au(111)}$ model system from intermediate to high pressures of H_2O vapor, by means of Scanning Tunneling Microscopy (STM) and Near-Ambient Pressure (NAP)- and vacuum X-ray Photoelectron Spectroscopy (XPS). At elevated H_2O pressure, we describe the formation of a well-defined Co(OH)_2 nanoisland morphology with cobalt in the 2+ oxidation state. In contrast, the presence of O_2 , in air and liquid water, results in only partially hydroxylated Co^{3+} phases comprising sheets of CoO(OH)_x trilayer, corresponding to a single sheet of cobalt(III) oxyhydroxide. We conclude that the oxyhydroxide structure, known to be the catalytically active phase for the oxygen evolution reaction (OER) is stabilized by aerobic conditions, which inhibits further transformation into the catalytically inactive cobalt (II) hydroxide.

Introduction

First-row transition metal oxides (Fe, Ni, Co) show great promise as earth-abundant electrocatalysts for the oxygen evolution reaction (OER) - one of the half-reactions in electrochemical water splitting. Improving the efficiency of OER electrocatalysts is a key bottleneck to the development of commercially viable electrochemical water splitting, so there has been intense activity in understanding the structure and electrocatalytic properties of these oxides¹⁻³. However, it is becoming clear that it is critical to study these catalysts in a realistic operating environment in order to fully understand them and reveal their working principles in detail. Specifically, for cobalt and iron oxides, evidence is growing that the active phases for electrocatalysis are in fact the oxyhydroxide phases, and not the bulk crystalline oxides⁴.

In the recent years, significant efforts have therefore been devoted to application and development of surface science techniques towards feasible *in situ* studies of catalysts under realistic operating conditions, mainly exploiting spectroscopic techniques until now⁵⁻⁸. For example, several oxide films, including Cu_2O , MgO , Si_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$ and Fe_3O_4 , have been investigated with Near-Ambient Pressure XPS (NAP-XPS)⁹⁻¹³, revealing adsorption of molecular H_2O and high levels of hydroxylation up to a monolayer coverage of OH on the oxide surface. In parallel, the use of Scanning Tunneling Microscopy (STM) is emerging, including demonstrations of *ex-situ* studies of oxide sur-

faces after immersion into water bath^{14,15} and image acquisition of oxides in liquid environment by means of electrochemical STM^{15,16}. These techniques have successfully been applied to a range of thin oxide film systems supported on noble metals that are interesting for fundamental studies of model catalysts or as novel catalysts in their own right¹⁷⁻²⁰.

To study the fundamental properties of cobalt oxide nanocatalysts and understand reported activity enhancement effects in combination with gold^{21,22}, we have provided a detailed structural and spectroscopic analysis of a model system comprising crystalline CoO_x nanoislands dispersed on Au(111) single crystals, that allows for high-resolution STM studies under vacuum conditions. Common to the stable morphologies is that they exist in layered structures with alternating O- and Co sheets parallel to the substrate, terminated by the (111) facet of the rock salt structure. Although these structures are stabilized by charge transfer from the gold, they are structurally and chemically very similar to the oxyhydroxide electrocatalyst, exhibiting the same layered structure and so are studied as a model system. In the present context, we focus on the atomically thin Co-O film, referred to as a bilayer. Throughout the text, we will also refer to the UHV prepared O-Co-O($\text{H}_{0.33}$) trilayer for comparison, which is stabilized by H on 1/3 of the surface O basal plane atoms²³. The system has previously been extensively characterized by means of STM, X-ray Photoelectron spectroscopy (XPS/XAS) and Density Functional Theory (DFT), as well

as investigated for its fundamental interaction with low pressures of H_2O and O_2 in the vacuum regime²³⁻²⁷. The trilayer structure is a single sheet of cobalt(III) oxyhydroxide - considered the active phase for the OER. Starting with the well-defined bilayer CoO structure, we recently demonstrated the OER activity of the Co oxide/Au in an electrochemical setup under anaerobic conditions and provided a post-reaction analysis of the surface morphology by STM²⁸. These studies clearly pointed to a stabilizing role of the Au that supports the formation of the active cobalt(III) oxyhydroxide phase in the alkaline electrolyte.

In this paper, we investigate the structure and composition of the $\text{CoO}_x/\text{Au(111)}$ model system under the real operating environment of an OER electrocatalyst (i.e. ambient pressures with both water and oxygen present). The results show that the model system is robust against these conditions and remains in all cases in its characteristic layered morphology.

We observe that under high pressures of water vapor (~ 10 mbar) a complete transformation to the catalytically inactive cobalt(II) hydroxide structure occurs via water dissociation and incorporation of OH above and below the cobalt layer. However, we reveal that this hydroxide is easily transformed back into the trilayer (oxyhydroxide) structure by low-temperature annealing in an oxygen atmosphere. Surprisingly, under direct immersion of the nanoislands within a water droplet under ambient conditions (in air), the transformation to cobalt (II) hydroxide does not occur and instead the bilayer islands transform to the cobalt (III) - containing trilayer structure. This is direct confirmation that the oxyhydroxide structure is favored over hydroxide under the liquid operating conditions of cobalt oxide electrocatalysts.

Methods

The experiments were performed using an ultrahigh vacuum (UHV) chamber system comprising isolated loadlock, preparation and analysis chambers separated by valves for sample transfer. The preparation chamber was equipped with an Oxford Applied Research e-beam evaporator (model EGCO4) and a gas inlet system for synthesis and exposures. The analysis chamber contained an ion source for Ar^+ sputtering, an Aarhus-type STM²⁹ as well as an XR50 X-ray source from SPECS GmbH in combination with a SPECS Phoibos analyzer for X-ray photoelectron spectroscopy (XPS). The base pressure of both preparation and analysis chamber is 1×10^{-10} mbar. Au(111) single crystals (Mateck) were mounted on Ta sample plates and equipped with thermocouple wires connected at the edge of the sample for temperature readout. Clean Au(111) samples were obtained by repeated sputter and annealing cycles (1.5 keV Ar^+ / 800 K, 15 min). The synthesis of bilayer CoO was carried out by Co evaporation in 1×10^{-6} mbar O_2

and post annealing treatments according to previously described procedures^{23, 26}.

H_2O and O_2 exposures in the UHV regime (below 1×10^{-6} mbar) were carried out by backfilling the preparation chamber through a leak valve. An intermediate pressure was reached using a movable doser tube brought close to the sample surface (less than 1 mm distance) to generate a high local pressure estimated to $\sim 1 \times 10^{-4}$ mbar (an order of magnitude larger than the maximum reachable chamber pressure of 1×10^{-5} mbar). High-pressure exposures in the mbar regime were carried out by removing the sample into the loadlock and backfilling it with water vapor. Samples exposed to air were transferred to the load lock and remained in the manipulator while opening the load lock door to the laboratory air. To immerse samples into liquid water (milliQ water), crystals were transferred out of the UHV chamber in a wobble stick and covered by a droplet which was subsequently removed and the sample dried by an N_2 flow.

A second vacuum chamber system was used to perform Near-Ambient Pressure (NAP)-XPS. This system was equipped with similar instrumentation for sample cleaning and preparation, a differentially pumped SPECS Phoibos 150 NAP analyzer with a 1D Delay Line Detector (DLD) and a Specs FOCUS 500 monochromated Al $K\alpha$ X-Ray source. The system contains a SPECS "DeviSim" NAP cell which can be docked onto the analyzer and allows the study of samples in $\sim$ mbar gas pressure whilst the X-Ray gun and rest of the analysis chamber are retained in ultrahigh vacuum (base pressure of $\sim 5 \times 10^{-10}$ mbar)

All XPS measurements used Al K-alpha X-ray radiation (1486.6 eV) and the spectra were calibrated against the Au $4f_{7/2}$ peak at 84 eV. Linear backgrounds were used for background subtraction in the Co 2p region, whereas a polynomial was used for O 1s spectra (for a detailed discussion of baseline selection, please see the Supporting Information). O 1s spectra were deconvoluted by fitting the spectra with pseudo-Voigt line profiles (product of Gaussian and Lorentzian with a (30:70) mixing, using CASAXPS).

Results

We have compared the morphology and composition of the cobalt oxide nanoislands under four regimes of H_2O pressure: "UHV regime" (defined as $< 1 \times 10^{-6}$ mbar), "Intermediate pressure" ($\sim 1 \times 10^{-4}$ mbar), high pressure (10 mbar) and immersion (sample was immersed in liquid water). Unless otherwise stated, all experiments were performed at room temperature (295K).

Intermediate- and high pressure of H_2O

We first address the effect of elevating the pressure to an intermediate value of $\sim 1 \times 10^{-4}$ mbar water vapor. Figure 1a-

Figure 1. Exposure of bilayer to H₂O at intermediate (b-c)- and high (d-e) pressure. (f) XPS O 1s peak area percentages (blue: OH, white: lattice O) and total normalized area (red trace). Corresponds to the samples shown in (a)-(e). (g) Sketch of the proposed OH-Co-OH hydroxide phase. Red: Oxygen, blue: Cobalt and white: Hydrogen. STM parameters in (a-c): -1.16 V/ -0.35 nA, -1.25 V/ -0.18 nA and -1.23 V/ -0.23 nA and (d-e): 1.47 V/ 0.17 nA and 0.41 V/ 0.38 nA.

c shows the pristine bilayer sample in STM as synthesized as well as after 5 min and 60 min exposure time. Figure 1d-e shows bilayer sample after 10 mbar exposure. In the pristine state the CoO islands are characterized by hexagonally shaped islands exposing a flat (111) basal plane oriented in parallel with the Au substrate (see CoO/Au(111) in Figure 1f). After 5 min exposure (Figure 1b), we observe the onset of a transformation process due to hydroxylation initiated by the appearance of areas of greater apparent height (3.7 ± 0.2 Å vs. 1.8 ± 0.2 Å bilayer island height at the chosen imaging conditions) located at the island edges. This process progresses further with exposure time until the bright patches almost completely cover the basal plane (Figure 1c).

By monitoring the O 1s peak in XPS, we observe evidence of an increased amount of hydroxyl (OH) species indicated by an evolving peak located at 531.1 eV at a separation from the main lattice oxygen component of 1.7 eV (see Figure 1g and 2a) ³⁰. The amount of OH present on the sample scales with exposure time, but saturates after 60 min. Furthermore, the total O 1s area - normalized to the Co 2p signal (red trace in Figure 1g) increases significantly to ~ 1.45 relative to the fresh bilayer.

Increasing the H₂O vapor pressure further to 10 mbar causes further hydroxylation, beyond the saturation point at intermediate pressure. In the XPS O 1s core level spectrum, we now observe one single component at 531.2 eV corresponding exclusively to OH, indicating that all lattice oxygen is hydroxylated (Figure 2a). At the same time, the total O 1s peak area increases further to 1.76 relative to pristine bilayer. STM overview images of the sample in this

state (Figure 1d) reveal homogeneous, flat islands on the Au(111) surface remaining in the hexagonal shape in an essentially unchanged coverage compared to the corresponding bilayer islands before the exposure. High-resolution images (Figure 1e) show a disordered surface structure at the atomic level with island edges now displaying significant deviation from the perfect straight state on pristine bilayer.

This behavior of the system at intermediate and high H₂O pressure deviates from the previously described hydroxylation process in the UHV regime. The STM images revealing the onset of the process in the intermediate pressure regime (Figure 1b) show that our previous finding of edge mediated water dissociation as a crucial step in the hydroxylation process ²⁵ is still valid at the elevated pressure. However, in the UHV regime the total O 1s area as function of water exposure stayed constant apart from a slight increase originating from OH adsorption at island edges only ²⁵.

We propose the structural model depicted in Figure 1f for this new phase, comprising a layered OH-Co-OH “trilayer hydroxide” (formally Co(OH)₂). The oxygen content in this structure is in agreement with the measured increase in O 1s area of 1.76 by taking into account the photoelectron intensity attenuation of lower layer oxygen. The attenuation was previously determined experimentally in the case of the similar O-Co-(OH)_{0.33} trilayer (~ 1.8 relative to bilayer ²⁷). We propose that the emerging structure at intermediate pressure (Figure 1a-c) is the same, however

Figure 2. XPS and O 1s (a) and Co 2p (b) regions of bilayer exposed to increasing pressure of H₂O, as well as air and liquid water. The dotted line indicates the beginning of trilayer formation (OH-Co-OH/O-Co-OH_x) which is not observed at low H₂O pressure (light blue). SS: Shakeup satellites. (c) O 1s areas normalized to the background intensity.

not reaching the full transition into pure OH-Co-OH islands due to kinetic effects.

XPS measurements were also performed to probe changes in the chemical state of oxygen species and Co in the transition from Co-O bilayer to OH-Co-OH hydroxide (Figure 2a and b). For comparison, we also added the spectra from a sample exposed to 2000 L H₂O (L, Langmuir = 1.33×10^{-6} mbar · s) at a lower water pressure of 1×10^{-6} mbar. In the Co 2p core level spectrum, we observe gradual changes associated with the hydroxylation towards a strong shakeup satellite (SS) and a significant main peak position shift of approximately 2 eV to a higher binding energy of 781.1 eV. Comparing to existing X-ray photoelectron spectroscopy studies in the literature of cobalt oxide and (oxy)hydroxides, these features bear the characteristics of the Co(OH)₂ bulk phase^{34, 32} with the cobalt in a Co²⁺ oxidation state. However, we note that only the Co 2p spectrum after 10 mbar H₂O corresponding to the fully converted OH-Co-OH hydroxide exactly matches the reference spectrum of Co(OH)₂ bulk phase.

The O 1s core level spectra evidence the increasing level of hydroxylated oxygen species (OH) relative to the main lattice oxygen. Furthermore, the total oxygen content determined by the normalized O 1s areas (Figure 2c) indicate oxygen uptake by dissociative adsorption and lattice incorporation of OH from H₂O that results in OH-Co-OH hydroxide from intermediate pressure and upwards (indicated in Figure 2a-b by the dotted line). Another difference between samples hydroxylated in the UHV regime and at intermediate pressure is the magnitude of energy separation between the OH peak and main oxygen lattice components that changes from 2.0 eV in UHV to 1.7 eV upon formation of OH-Co-OH hydroxide at elevated pressure. We ascribe this difference to a change in chemical environment of the OH species the OH-Co-OH hydroxide compared to the hydroxylated bilayer at low H₂O pressure (formally Co-OH_{-0.5}²⁵). The change in measured core level binding energies in XPS can be rationalized by, e.g., charge

transfer mechanisms with the substrate; for instance, previous density functional theory (DFT) calculations showed that Co-O bilayers and O-Co-(OH)_{0.33} trilayers, respectively, are stabilized charge transfer to the substrate with opposite sign²⁴.

Since our measurements of the OH-Co-OH phase formed at high H₂O pressure were conducted *ex situ* by transfer back into the UHV chamber for STM and XPS evaluation, we also performed Near-Ambient Pressure (NAP)-XPS on Co-O bilayer/Au(111) samples at high pressures of H₂O to establish that the phase *in situ* is in fact the same. Monitoring the progression of hydroxylation by the ratio between the O 1s lattice oxygen and OH components (Figure 3a-b), the results show that 9 mbar H₂O pressure is necessary in order to form the full hydroxide, reached at, i.e. just below our *ex situ* exposure pressure (10 mbar). After pumping out the H₂O gas from the NAP-cell, the full hydroxide persisted and maintained an oxygen content of 1.7 relative to fresh bilayer verifying the islands are the OH-Co-OH hydroxide phase, as expected from the ex-situ measurements. The accompanying Au 4f and C 1s scans for these measurements are shown in the Supporting Information.

We also addressed the thermal stability of the OH-Co-OH phase in a temperature programmed NAP-XPS experiment with the sample held in O₂ atmosphere, ramping the temperature from 300 K in steps while repeatedly recording the O 1s spectrum (Figure 4a). The temperature dependent evolution revealed that the phase is only stable in 3 mbar O₂ up to 420 K. Above this temperature, we observe a loss of OH simultaneously with the reappearance of non-hydroxylated lattice oxygen (O_{lattice}). At 470 K, the O 1s spectrum corresponds to a 50 % hydroxylated phase, and the Co 2p spectrum at this point shows a shift from Co²⁺ to a Co³⁺ oxidation state (Figure 4b). The spectrum is very similar to that of the as-prepared O-Co-OH_{0.33} trilayer - however we cannot rule out the presence of multilayer structures which contain cobalt (III) species²³. In comparison, annealing the hydroxide in UHV reduced the sample

and a metallic cobalt peak emerged in the Co 2p spectrum (not shown).

Figure 3. NAP-XPS measurements on a bilayer exposed to different pressures of water vapor. a) O 1s core levels showing progressive hydroxylation as water vapor pressure increases. b) hydroxylation percentage as a function of water vapor pressure, determined from the ratio of the O_{lattice} to the OH peaks in the O 1s spectrum.

Air and liquid water

STM images of bilayer samples exposed to air and after immersion in a droplet of liquid water respectively are shown in Figure 5a-b. In both cases, the islands retain their characteristic hexagonal shape, reflecting that no or very little Co redistribution or dissolution takes place. The basal planes appear disordered and no atomic resolution was obtained. However, overview images confirm the stability of the flat morphology comprising one atomic layer of cobalt.

After air exposure, the Co 2p spectrum (see Figure 2b) indicates a Co³⁺ oxidation state, evidenced by the narrow main component and the absence of the strong shakeup satellite (SS) at ~786 eV associated with Co⁺²³³. The total O 1s area increases to 1.90, suggesting that the structure stabilizes in a trilayer morphology that contains cobalt in a

pure 3+ oxidation state²⁶. However, the trilayer in air hydroxylates to a level that is significantly higher than for UHV prepared trilayer (see the OH/main component ratios in the O 1s spectra, Figure 2a). After immersion of bilayer into liquid water similar results are obtained, i.e., the cobalt is present in a 3+ oxidation state and the level of hydroxylation is high compared to the O-Co-(OH_{0.33}) reference, but slightly lower as compared to the air exposed sample. We therefore suggest that the resulting structure is again a trilayer, also explaining the increase in oxygen content to 1.72 relative to bilayer (Figure 2c).

Figure 4. a) TP-XPS measurements of the O 1s core level showing the removal of hydroxyls in 3 mbar of O₂ upon heating. b) Co 2p core levels for bilayer, OH-Co-OH structure and the sample after the TP-XPS measurement in a), showing the formation of O-Co-O(H_{0.33}) trilayer structures

We summarize the effects of air and liquid water on bilayer in Figure 5c, showing the proposed structural model of a hydroxylated O-Co-O(H_x) trilayer, where x is close to 1 after air exposure. In line with observations of UHV prepared O-Co-O($H_{0.33}$) trilayer where OH is located on the upper basal plane and due to the facile access to this environment compared to the buried lower oxygen layer, we sketch the location of OH species on the top oxygen layer in Figure 5c, although distribution to the lower layer is also a possibility. It is noteworthy that we consistently observed a lower hydroxylation degree after immersion in water compared with exposure to water vapor in air. Scans of the carbon 1s region acquired at the same time as the Co 2p and O 1s scans in Figure 2a and 2b demonstrate that exposure to air or water vapor causes a minimal increase in adventitious carbon contamination of the sample. Conversely, the liquid water exposure causes a significant increase in adventitious carbon on the surface (see Figure S1). As the transformation from 2+ bilayer to 3+ trilayer occurs in both air and liquid water, we conclude that adventitious carbon does not affect this transformation. However, we suggest that the presence of adventitious carbon in significant amounts in the liquid water explains the lower level of hydroxylation in these samples. Randomly physisorbed hydrocarbons, although not chemically interacting with the surface, could block the active sites for water dissociation (the island edges) and thus hinder the hydroxylation of the sample.

Figure 5. Bilayer exposed to air and liquid water. (a) air, 300 K, 30 min. (b) immersion into a droplet of liquid water, 300 K, 30 min. (c) Proposed O-Co-O H_x structure after both treatments, depicted with an OH coverage on the basal plane of 100 % ($x = 1$). Red: Oxygen, blue: Cobalt and white: Hydrogen. STM parameters in (a-b): 1.25 V/0.19 nA and -1.44 V/-0.15 nA.

Discussion

We demonstrate that the Au/CoO $_x$ model system is robust and retains its characteristic layered structure in the real operating conditions of an OER electrocatalyst (in the presence of both water and oxygen at ambient pressures).

Our results also show that the interaction with H $_2$ O of gold-supported cobalt oxide nanoparticles depends fundamentally on the presence or absence of oxygen, leading to qualitatively different hydroxylation processes and states of the final hydroxide. We reveal that in mbar pressures of water (comparable to ambient conditions) a complete transformation to a layered cobalt(II) hydroxide is possible. However, surprisingly this transformation is only possible in the absence of oxygen. With the oxygen environment present in ambient air or in a water droplet, this transformation is inhibited in favor of transformation to the trilayer oxyhydroxide structure with the cobalt in the 3+ oxidation state.

In principle, our water vapor-only experiments should mimic the partial pressure of water in air (the 10 mbar used corresponds to a relative humidity of approx. 40%, which is fairly typical of ambient conditions). It is therefore surprising that we do not observe the expected 100 % hydroxylation in either air or liquid water. However, the presence of oxygen in both environments is an obvious factor to influence the processes. O $_2$ constitutes 21 % of laboratory air, but it also has a solubility of 6.4ml/L at 20 °C in water³⁵. We therefore specifically probed the consequence of exposing bilayer to the same 10 mbar H $_2$ O in a ~ 40 mbar O $_2$ background. In agreement with the hypothesis of oxygen affecting the hydroxylation process, this treatment did not result in the OH-Co-OH hydroxide, but rather a O-Co-O($H_{0.33+x}$) trilayer (Co $^{3+}$), similar to UHV prepared O-Co-O($H_{0.33}$) trilayer samples, but hydroxylated to a higher extent ($x > 0.5$), i.e. very similar to the state after exposure to air and liquid water.

The TP-XPS experiments demonstrate the full OH-Co-OH hydroxide structure is easily converted into a cobalt (III) containing phase, most likely a O-Co-O($H_{0.33}$) trilayer, even in a relatively low pressure oxygen environment (3 mbar) with minimal heat input. This result adds further evidence that the presence of oxygen favors the oxyhydroxide trilayer structure over the full hydroxide. Furthermore, it suggests that conversion from 2+ hydroxide to 3+ oxyhydroxide is relatively facile.

In comparison to CoO bilayer, isostructural FeO thin films and nanoislands on Pt- and Au(111) substrates exposed to H $_2$ O only hydroxylate insignificantly, even in 10 mbar H $_2$ O^{15, 36}. In air and liquid water at room temperature, the FeO film on Pt(111) is also stable and transforms into an O-Fe-OH $_x$ motif¹⁵, similarly to bilayer CoO in the present study. However, FeO preserves its moiré structure and, again, hydroxylates to a lower level. We repeated the exposure of FeO/Au(111) to H $_2$ O up to 10 mbar in our own laboratory for coverages similar to our experiments on CoO (not shown). The results are in agreement with the referenced literature and confirm a pronounced relative inertness of FeO. Furthermore, it means that the high water dissociation activity of bilayer is not only related to favorable edge sites for adsorption and dissociation, i.e. the circumstance that we study the material at coverages below 1 ML, but also directly associated with the chemical nature of cobalt, allowing facile uptake and release of both oxygen and hydroxyl groups.

Conclusions

In summary, we probed the response of cobalt oxide bilayer islands on Au(111) to H₂O vapor in four different pressure regions. The behavior of bilayer at elevated pressure differs significantly from the corresponding hydroxylation process studied previously in the UHV pressure regime. The effect of high water pressure on bilayer is the occurrence of spontaneous dissociative adsorption of H₂O, resulting in oxygen uptake, transforming it into well-defined OH-Co-OH sheets. After exposure to air or liquid water, the islands contain cobalt in the 3+ oxidation state. This finding is surprising, given that the OH-Co-OH phase generated in the 10 mbar pure H₂O environment has cobalt in the 2+ state. However, further experiments suggested that the effect can be ascribed to the high partial pressure of oxygen in air and liquid water.

These results support that the oxyhydroxide is the stable phase in the operating environment of cobalt oxide electrocatalysts, and that it is the presence of oxygen which inhibits further transformation to the catalytically inactive cobalt(II) hydroxide. Our experiments also demonstrate that the Au(111)/CoO_x system is an ideal model system to study oxygen electrocatalysis on the atomic scale as it retains the real structure of the electrocatalyst under its operating environment, but is still amenable to detailed characterization by surface science techniques.

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Supporting Information available:

C1s spectra recorded simultaneously with the Co 2p and O 1s spectra in Figure 2a-b and 3a (Figure S1 and S2); Au 4f peak recorded simultaneously with Figures 2a-b, 3a and S2 (Figure S3); representative survey scan of a typical synthesis (Figure S4); example spectrum showing effects of nearby Au peak at Co 2p and O 1s regions (Figure S5 and S6); line scans across islands shown in Figure 1a-d and 5a-b (Figure S7).

This material is available free of charge via the Internet at <http://pubs.acs.org>.

REFERENCES

1. Deng, X.; Tüysüz, H., Cobalt-oxide-based materials as water oxidation catalyst: Recent progress and challenges. *ACS Catal.* **2014**, *4*, 3701-3714.
2. Huang, J.; Chen, J.; Yao, T.; He, J.; Jiang, S.; Sun, Z.; Liu, Q.; Cheng, W.; Hu, F.; Jiang, Y.; et al., CoOOH Nanosheets with High Mass Activity for Water Oxidation. *Angew. Chem., Int. Ed.* **2015**, *54*, 8722-8727.
3. Liao, L.; Zhang, Q.; Su, Z.; Zhao, Z.; Wang, Y.; Li, Y.; Lu, X.; Wei, D.; Feng, G.; Yu, Q., Efficient solar water-splitting using a nanocrystalline CoO photocatalyst. *Nat. Nanotechnol.* **2014**, *9*, 69-73.
4. Burke, M. S.; Enman, L. J.; Batchellor, A. S.; Zou, S.; Boettcher, S. W., Oxygen evolution reaction electrocatalysis on transition metal oxides and (oxy) hydroxides: Activity trends and design principles. *Chem. Mater.* **2015**, *27*, 7549-7558.
5. Friebe, D.; Louie, M. W.; Bajdich, M.; Sanwald, K. E.; Cai, Y.; Wise, A. M.; Cheng, M.-J.; Sokaras, D.; Weng, T.-C.; Alonso-Mori, R., Identification of highly active Fe sites in (Ni, Fe)OOH for electrocatalytic water splitting. *J. Am. Chem. Soc.* **2015**, *137*, 1305-1313.
6. Wang, H.-Y.; Hung, S.-F.; Hsu, Y.-Y.; Zhang, L.; Miao, J.; Chan, T.-S.; Xiong, Q.; Liu, B., In situ spectroscopic identification of μ -OO bridging on spinel Co₃O₄ water oxidation electrocatalyst. *J. Phys. Chem. Lett.* **2016**, *7*, 4847-4853.
7. McAlpin, J. G.; Surendranath, Y.; Dinca, M.; Stich, T. A.; Stoian, S. A.; Casey, W. H.; Nocera, D. G.; Britt, R. D., EPR evidence for Co (IV) species produced during water oxidation at neutral pH. *J. Am. Chem. Soc.* **2010**, *132*, 6882-6883.
8. Zhang, M.; De Respinis, M.; Frei, H., Time-resolved observations of water oxidation intermediates on a cobalt oxide nanoparticle catalyst. *Nat. Chem.* **2014**, *6*, 362-367.
9. Deng, X.; Herranz, T.; Weis, C.; Bluhm, H.; Salmeron, M., Adsorption of water on Cu₂O and Al₂O₃ thin films. *J. Phys. Chem. C* **2008**, *112*, 9668-9672.
10. Newberg, J. T.; Starr, D. E.; Yamamoto, S.; Kaya, S.; Kendelewicz, T.; Mysak, E. R.; Porsgaard, S.; Salmeron, M. B.; Brown Jr, G. E.; Nilsson, A., Autocatalytic surface hydroxylation of MgO (100) terrace sites observed under ambient conditions. *J. Phys. Chem. C* **2011**, *115*, 12864-12872.
11. Verdager, A.; Weis, C.; Oncins, G.; Ketteler, G.; Bluhm, H.; Salmeron, M., Growth and structure of water on SiO₂ films on Si investigated by kelvin probe microscopy and in situ x-ray spectroscopies. *Langmuir* **2007**, *23*, 9699-9703.
12. Yamamoto, S.; Kendelewicz, T.; Newberg, J. T.; Ketteler, G.; Starr, D. E.; Mysak, E. R.; Andersson, K. J.; Ogasawara, H.; Bluhm, H.; Salmeron, M., Water adsorption on α -Fe₂O₃ (0001) at near ambient conditions. *J. Phys. Chem. C* **2010**, *114*, (5), 2256-2266.
13. Kendelewicz, T.; Kaya, S.; Newberg, J.; Bluhm, H.; Mulakaluri, N.; Moritz, W.; Scheffler, M.; Nilsson, A.; Pentcheva, R.; Brown Jr, G., X-ray photoemission and density functional theory study of the interaction of water vapor with the Fe₃O₄ (001) surface at near-ambient conditions. *Langmuir* **2013**, *117*, 2719-2733.
14. Hussain, H.; Tocci, G.; Woolcot, T.; Torrelles, X.; Pang, C.; Humphrey, D.; Yim, C.; Grinter, D.; Cabailh, G.; Bikondoa, O., Structure of a model TiO₂ photocatalytic interface. *Nat. Mater.* **2017**, *16*, 461-466.
15. Ringleb, F.; Fujimori, Y.; Wang, H.-F.; Ariga, H.; Carrasco, E.; Sterrer, M.; Freund, H.-J.; Giordano, L.; Pacchioni, G.; Goniakowski, J., Interaction of water with FeO (111)/Pt (111): environmental effects and influence of oxygen. *J. Phys. Chem. C* **2011**, *115*, 19328-19335.
16. Serrano, G.; Bonanni, B.; Di Giovannantonio, M.; Kosmala, T.; Schmid, M.; Diebold, U.; Di Carlo, A.; Cheng, J.; VandeVondele, J.; Wandelt, K., Molecular ordering at the

interface between liquid water and rutile TiO₂ (110). *Adv. Mater. Interfaces* **2015**, *2*, 1500246.

17. Liu, Y.; Yang, F.; Zhang, Y.; Xiao, J.; Yu, L.; Liu, Q.; Ning, Y.; Zhou, Z.; Chen, H.; Huang, W.; et al., Enhanced oxidation resistance of active nanostructures via dynamic size effect. *Nat. Commun.* **2017**, *8*, 14459.

18. Ning, Y.; Wei, M.; Yu, L.; Yang, F.; Chang, R.; Liu, Z.; Fu, Q.; Bao, X., Nature of interface confinement effect in oxide/metal catalysts. *J. Phys. Chem. C* **2015**, *119*, 27556-27561.

19. Zhang, K.; Li, L.; Shaikhutdinov, S.; Freund, H.-J., Carbon monoxide oxidation on metal-supported monolayer oxide films: establishing which interface is active. *Angew. Chem., Int. Ed.* **2017**, *57*, 1261-1265.

20. Shaikhutdinov, S., Strong Metal-support interaction and reactivity of ultrathin oxide films. *Catal. Lett.* **2018**, *148*, 2627-2635.

21. Yeo, B. S.; Bell, A. T., Enhanced activity of gold-supported cobalt oxide for the electrochemical evolution of oxygen. *J. Am. Chem. Soc.* **2011**, *133*, 5587-5593.

22. Lu, X.; Ng, Y. H.; Zhao, C., Gold nanoparticles embedded within mesoporous cobalt oxide enhance electrochemical oxygen evolution. *ChemSusChem* **2014**, *7*, 82-86.

23. Fester, J.; Walton, A.; Li, Z.; Lauritsen, J. V., Gold-supported two-dimensional cobalt oxyhydroxide (CoOOH) and multilayer cobalt oxide islands. *Phys. Chem. Chem. Phys.* **2017**, *19*, 2425-2433.

24. Fester, J.; Bajdich, M.; Walton, A. S.; Sun, Z.; Plessow, P. N.; Vojvodic, A.; Lauritsen, J. V., Comparative analysis of cobalt oxide nanoisland stability and edge structures on three related noble metal surfaces: Au (111), Pt (111) and Ag (111). *Top. Catal.* **2016**, *60*, 503-512.

25. Fester, J.; García-Melchor, M.; Walton, A.; Bajdich, M.; Li, Z.; Lammich, L.; Vojvodic, A.; Lauritsen, J., Edge reactivity and water-assisted dissociation on cobalt oxide nanoislands. *Nat. Commun.* **2017**, *8*, 14169.

26. Walton, A. S.; Fester, J.; Bajdich, M.; Arman, M. A.; Osiecki, J.; Knudsen, J.; Vojvodic, A.; Lauritsen, J. V., Interface controlled oxidation states in layered cobalt oxide nanoislands on gold. *ACS Nano* **2015**, *9*, 2445-2453.

27. Fester, J.; Sun, Z.; Rodríguez-Fernández, J.; Walton, A.; Lauritsen, J. V., Phase transitions of cobalt oxide bilayers on Au (111) and Pt (111): the role of edge sites and substrate interactions. *J. Phys. Chem. B* **2018**, *122*, 561-571.

28. Fester, J.; Makoveev, A.; Grumelli, D.; Gutzler, R.; Sun, Z.; Rodríguez-Fernández, J.; Kern, K.; Lauritsen, J. V., The structure of the cobalt oxide/Au catalyst interface in electrochemical water splitting. *Angew. Chem., Int. Ed.* **2018**, *57*, 11893-11897.

29. Besenbacher, F.; Lægsgaard, E.; Mortensen, K.; Nielsen, U.; Stensgaard, I., Compact, high-stability, "thimble-size" scanning tunneling microscope. *Rev. Sci. Instrum.* **1988**, *59*, 1035-1038.

30. Henderson, M. A., The interaction of water with solid surfaces: fundamental aspects revisited. *Surf. Sci. Rep.* **2002**, *46*, 1-308.

31. Biesinger, M. C.; Payne, B. P.; Grosvenor, A. P.; Lau, L. W.; Gerson, A. R.; Smart, R. S. C., Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Appl. Surf. Sci.* **2011**, *257*, 2717-2730.

32. Yang, J.; Liu, H.; Martens, W. N.; Frost, R. L., Synthesis and characterization of cobalt hydroxide, cobalt oxyhydroxide, and cobalt oxide nanodiscs. *J. Phys. Chem. C* **2009**, *114*, 111-119.

33. Chuang, T.; Brundle, C.; Rice, D., Interpretation of the x-ray photoemission spectra of cobalt oxides and cobalt oxide surfaces. *Surf. Sci.* **1976**, *59*, 413-429.

34. Fester, J.; García-Melchor, M.; Walton, A. S.; Bajdich, M.; Li, Z.; Lammich, L.; Vojvodic, A.; Lauritsen, J. V., Edge reactivity and water-assisted dissociation on cobalt oxide nanoislands. *Nat. Commun.* **2017**, *8*, 14169.

35. Weiss, R., The solubility of nitrogen, oxygen and argon in water and seawater. *Deep Sea Res. Oceanogr. Abstr.* **1970**, *17*, 721-735.

36. Deng, X.; Lee, J.; Wang, C.; Matranga, C.; Aksoy, F.; Liu, Z., In Situ observation of water dissociation with lattice incorporation at FeO particle edges using scanning tunneling microscopy and X-ray photoelectron spectroscopy. *Langmuir* **2011**, *27*, 2146-2149.