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Journal

The Journal of Physical Chemistry B, 122(2)

ISSN

1520-6106

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Publication Date

2018-01-18

DOI

10.1021/acs.jpcc.7b10732

Peer reviewed

Water Adsorption and Dissociation on Polycrystalline Copper Oxides: Effects of Environmental Contamination and Experimental Protocol

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ABSTRACT

We use ambient pressure X-ray photoelectron spectroscopy (APXPS) to study chemical changes, including hydroxylation and water adsorption, at copper oxide surfaces from ultra-high vacuum to ambient relative humidities of ~5%. Polycrystalline CuO and Cu₂O surfaces were prepared by selective oxidation of metallic copper foils. For both oxides, hydroxylation occurs readily, even at high vacuum conditions. Hydroxylation on both oxides plateaus near ~0.01% relative humidity (RH) at a coverage of ~1 monolayer. In contrast to previous studies, neither oxide shows significant accumulation of molecular water; rather, both surfaces show a high affinity for adventitious carbon contaminants. Results of isobaric and isothermic experiments are compared, and the strengths and potential drawbacks of each method are discussed. We also provide critical evaluations of the effects of the hot filament of the ion pressure gauge on the reactivity of gas-phase species, the peak fitting procedure on the quantitative analysis of spectra, and rigorous accounting of carbon contamination on data analysis and interpretation. This work underscores the importance of considering experimental design and data analysis protocols during APXPS experiments with water vapor in order to minimize misinterpretations arising from these factors.

1 Introduction

The interaction between water and metal oxide surfaces is an important process in a wide range of environmental and atmospheric systems, industrial heterogeneous catalysis, and corrosion. One of the most intriguing questions is the influence of hydroxylation and molecular water adsorption on the reaction of metal oxide surfaces with other trace gases. The chemical effects of ambient water are of particular interest for the performance of filtration materials for protection against chemical warfare agents and other toxic gases.¹⁻³ Metals, metal salts, and/or metal oxides are components of commonly utilized filtration materials for absorption and degradation of various toxic organic compounds.⁴ Changes in the chemical environment of metal-containing surfaces by exposure to common atmospheric components (e.g. water) may affect the adsorption and eventual decomposition mechanisms of toxic molecules in filtration materials. The effects of relative humidity on filter performance are not well understood, and water will certainly be present during filter storage (from the ambient environment) and use (from respiration).

Ambient pressure X-ray photoelectron spectroscopy (APXPS) is an excellent method to investigate the reaction of water vapor with metal oxides and the influence of hydroxylation and water adsorption of the metal oxide surface on the reaction with trace gases. The particular strength of APXPS is that lattice oxygen, hydroxyl groups, and adsorbed molecular water can, in most cases, be easily distinguished from each other in O 1s spectra due to differences in their chemical shifts. While APXPS experiments at 1 atm were recently demonstrated,^{5,6} they are still far from routine due to the strong scattering of electrons at atmospheric pressures and/or the need for the use of specially designed and fabricated isolated gas-filled experimental cells which use ultrathin membranes; such constraints greatly hamper, at the time of this writing, the study of a broad range of samples. Fortunately, the need for specialized equipment to approach 1 atm is not a requirement

in measurements that are solely concerned with the influence of water vapor and trace gases on the surface chemistry of the material under investigation. The saturation water vapor pressure at room temperature is about 20 Torr, and the partial pressures of the trace gases in the environment (e.g., CO_x, NO_x, SO_x, O₃) is much lower, with the CO₂ pressure as the highest with about 0.4 Torr. These are conditions that can now be achieved fairly routinely in APXPS experiments.

APXPS has been used over the past decade to study water interaction with a wide range of metal oxides, both on single crystals and epitaxial films, such as SiO₂/Si(111),⁷ rutile TiO₂(110),⁸ LaFeO₃/SrTiO₃(001),⁹ LaCoO₃(001),¹⁰ FeO/Au(111),¹¹ α-Fe₂O₃(0001),¹² α-Fe₂O₃ on Au(111),¹³ Fe₃O₄(001),¹⁴ Al₂O₃/NiAl(110),¹⁵ Sm-doped CeO₂(100),¹⁶ and MgO(100),^{17,18} as well as polycrystalline samples, e.g. La-based perovskites,¹⁹ anatase TiO₂,²⁰ GeO₂/Ge(100),²¹ Cu₂O,²²⁻²⁴ and Al₂O₃.²² These studies have shown that the onset and extent of surface hydroxylation depends both on the orientation of the crystal face as well as the number of surface defects; polycrystalline surfaces show in general a lower onset for hydroxylation than single crystalline samples. An intriguing finding is that most single-crystalline metal oxide surfaces show a common onset humidity of 0.01% for terrace (i.e., non-defect) hydroxylation. While the precise mechanism for this behavior is not yet understood, theoretical studies indicate that dissociation of an isolated water molecule is kinetically hindered, while dissociation of a water molecule that forms a complex with other adsorbed water molecules, as well as lattice oxygen, is more facile.^{25,26} According to this picture, a relative humidity (RH) of 0.01% is the critical onset value for the formation of these complexes; below this RH, the time-averaged number of water molecules at the metal oxide surface is not large enough to lead to complex nucleation. Since the hydroxyl-water bond is stronger than the water-water bond, adsorption of water molecules proceeds as soon as hydroxyl

groups have formed on the surface, which has been observed in APXPS measurements demonstrating that water adsorption goes hand-in-hand with hydroxylation.

While studies of water dissociation and adsorption on metal oxide surfaces are becoming more common and currently can be considered “routine” in the APXPS community, standard experimental protocols can vary considerably depending on the research group and the class of materials studied. Isobaric and isothermic experiments are both standard practice, but the relative humidity range accessible depends on the sample preparation requirements and thus the type of sample holders that can be utilized. In isobaric experiments, the relative humidity is controlled by changing the sample temperature. For example, relative humidity values approaching 100% can only be attained currently by using a sample stage that can be cooled to below the temperature of the surrounding surfaces during measurements, which often leads to enhanced adsorption of carbonaceous contaminants on the sample. In general, isobaric studies from low to high RH are the cleanest experiments, since the sample is initially kept at elevated temperatures (typically several hundred °C) where it remains clean. The sample is then cooled down in the presence of mTorr to Torr of water vapor, in which molecular H₂O represents by far the majority gas phase species and thus is favored as an adsorbate over other contaminants with lower partial pressures. Isobaric studies have the drawback that the gas phase and the sample surface temperatures are not the same, which can lead to slight uncertainties in the calculation of the RH.¹² However, isobaric water uptake experiments on MgO(100) over a pressure range of three orders of magnitude have shown distinct differences in the onset temperature for terrace hydroxylation and water uptake which, when converted to RH, coincided with each other (within the error bars), showing that the temperature effect in isobar experiments is most likely negligible.¹⁷ In isotherm experiments from low to high water partial pressure (and thus RH), the partial pressure of water in the low RH regime

is comparable to that of background contaminants which often leads to increased adsorption of carbonaceous species in these experiments.

The presence of carbon contaminants in APXPS experiments with water vapor can have unintended effects which will manifest in the measured data. Surface carbon contamination cannot be assumed to be only a spectator, as is often done with UHV XPS measurements. (This assumption is so common that the aliphatic adventitious carbon is often used for binding energy calibration.) Oxidized carbonaceous species are often inherently hydrophilic, and thus it is reasonable to expect the identity of the surface carbon contamination could influence the interaction of gas-phase water with metal oxide surfaces. In any case, the possible effects of surface carbon on surface wetting and reactivity certainly cannot be assessed if C 1s spectra are not collected and carefully analyzed.

For the correct interpretation of O 1s spectra, which contain most information on the reaction of water with the surface, it is imperative to identify oxidized surface carbon species, which will obviously contribute features to the O 1s spectra. A powerful strength of XPS is the ability to quantitatively analyze the spectra by comparing peak areas of different species, provided that relative sensitivity factors are determined when quantifying across different core levels. Jribi et al. demonstrate the utility of identification and quantification of surface carbon contaminants in studying the intrinsic hydrophilicity of TiO₂.²⁰ Stoerzinger et al. have provided a rigorous accounting of surface carbon contamination in their experiments of water vapor at perovskite surfaces.^{9,10,19} In those works, surface hydroxylation preceded formation of surface carbonates, which displaced hydroxyl groups prior to molecular water adsorption.¹⁰ The surface carbonate coverage was found to increase with increasing relative humidity (isobar experiments at 0.1 Torr water vapor pressure), reaching a surface coverage of 0.2-0.3 monolayers at 0.1% RH. For these

materials, where the catalytic activity for water splitting was found to be intimately related to the surface termination and wetting,^{9,19} these studies demonstrate that the influence of surface carbon species on the desired material properties cannot be ignored.

Cracking of gas-phase species over the hot ion gauge filament (typically thoria/yttria-coated iridium or tungsten) during APXPS experiments, while certainly possible, is rarely mentioned in the literature. Cracking of gas molecules over hot metals is also used intentionally in surface science studies in the production of atomic oxygen and hydrogen. In the case of water, cracking may facilitate surface hydroxylation at low water vapor pressures, although the prevalence and extent of this process over different surfaces is currently unknown.

Here, we will discuss some of these practical considerations of APXPS experiments with water vapor on polycrystalline CuO and Cu₂O, which provides an exemplary case study in the importance of considering experimental design and data analysis protocols in similar studies. In general, the copper oxides follow the trends observed on other metal oxide surfaces upon exposure to water vapor; namely, hydroxylation occurs readily at low relative humidities, and the surface hydroxyl coverage reaches ~1 monolayer when molecular water adsorption is observed. On both oxides, surface carbon contamination coverage increases with increasing relative humidity and accounts for most of the changes observed in the O 1s spectra. We also observe partial reduction of CuO upon water vapor exposure when the ion gauge is left on during the APXPS measurement at low water vapor pressures. Furthermore, surface hydroxylation appears to be facilitated on both CuO and Cu₂O with the ion gauge turned on.

2 Experimental

2.1 *Ambient-pressure X-ray photoelectron and near-edge X-ray absorption fine-structure spectroscopy.*

XPS and NEXAFS experiments were performed in the ambient-pressure XPS (APXPS-1)²⁷ endstation at beamline 11.0.2²⁸ at the Advanced Light Source at Lawrence Berkeley National Laboratory. Milli-Q purified water (18.2 M Ω cm) was mounted onto the APXPS analysis chamber in a glass vessel, degassed by three cycles of liquid nitrogen freeze-pump-thaw, and introduced into the XPS analysis chamber via a high-precision leak valve. The base pressure of the analysis chamber was 1×10^{-8} Torr or better for each experiment. Prior to moving the sample into the analysis chamber, the water leak valve was calibrated so that desired water vapor pressures below 1×10^{-3} Torr could be accessed with the ion pressure gauge turned off; this was accomplished by recording the number of turns opening the leak valve from the fully closed position that were required to reach a desired pressure. Calibration values were checked at least twice before each experiment to ensure reproducibility. Pressures of 1×10^{-3} Torr and higher were monitored with a 10 Torr capacitance manometer (Baratron®).

A ceramic heater embedded in the sample holder was used to heat the samples during oxide preparation and isobar measurements. The binding energy scale for XPS spectra was calibrated to the position of the Cu $2p_{3/2}$ main peak (932.9 eV for CuO² and 932.4 eV for Cu₂O²⁹). Spectra were analyzed with the KolXPD software package, using Voigt lineshapes and Shirley or linear backgrounds. More detailed information about XPS fitting procedures can be found in the Supporting Information. Spectra presented in the main text are from representative experiments where the carbon contamination was relatively low, however, isobar and isotherm experiments on both CuO and Cu₂O surfaces were performed at least three times each to confirm reproducibility.

To prevent beam-induced changes to the sample surface, the beam spot was defocused ($\sim 200 \times 200 \mu\text{m}^2$), its position on the sample was changed every 2-4 minutes (after collecting 2-4 spectra), and the X-ray beam was blocked with a shutter between measurements. On the timescale of the measurements presented here (~ 3 -4 min at each spot), no evidence of beam-induced changes was observed.

2.2 *Preparation of oxide surfaces.*

CuO and Cu₂O samples were prepared from high purity metal foils (Cu: 99.999% metals basis, Alfa Aesar, 0.5 mm thick). The Cu foil was cut into pieces ~ 1.5 cm in diameter and pre-cleaned by sequential sonication in acetone, isopropanol, and ethanol (20 min each), followed by blow-drying with nitrogen. Pre-cleaned Cu foils were oxidized in air, at 450 °C for CuO and 300 °C for Cu₂O, for 30 min, followed by sonication in ethanol. This treatment was repeated, giving a total of two oxidation-sonication cycles per sample. The foils were then treated further in the endstation sample preparation chamber to generate a single copper oxidation state. For CuO, samples were heated in 1 Torr O₂ for at least 30 min to remove adventitious carbon contamination and fully oxidize any Cu₂O present at the surface, cooled to ~ 200 °C in 1 Torr O₂, and then further cooled under vacuum to room temperature (~ 20 °C) before being transferred to the APXPS analysis chamber. For Cu₂O, the samples were heated under vacuum ($< 1 \times 10^{-8}$ Torr) for at least 30 min to remove adventitious carbon contamination and to reduce any CuO, then cooled to room temperature (~ 20 °C) in the preparation chamber before being transferred to the APXPS analysis chamber. The Cu oxidation state of the samples was confirmed by a combination of Cu 2p_{3/2} XPS and Cu L-edge NEXAFS, as described in our previous publication.² (See Supporting Information for these spectra.)

3 Results and Discussion

3.1 *Fitting of APXPS spectra and identification of surface species.*

Representative XPS data for isotherm (20 °C) experiments with CuO and Cu₂O are shown in Figure 1. The spectra are normalized on the y-axis to the oxygen lattice peak O_{lat}, near 529.9 eV and 530.4 eV for CuO and Cu₂O, respectively, and a Shirley-type background has been subtracted from each. Relative to the metal oxide peak, increasing intensity is observed with increasing water vapor pressure in the binding energy region between 531-534 eV, associated with an increase in OH, carbonaceous (C-O_x), and molecular water species. At higher relative humidity values, a peak for water vapor (H₂O_(v)) is observed above 535 eV. In the Cu₂O spectra, a small peak near 529 eV is also observed. This peak has been previously identified as either adsorbed oxygen on the Cu₂O surface, subsurface oxygen, or some other surface defect.²²⁻²⁴ We note that the binding energy position of this peak is very similar to that of CuO; however, we do not see any evidence in the Cu 2p_{3/2}, valence band, or Cu L-edge NEXAFS spectra to suggest that a significant population of Cu²⁺ sites is present (see spectra in the Supporting Information). This peak decreases with increasing water vapor pressure, which could indicate either that these sites are reacting with surface adsorbates and are being consumed or that they are simply being covered by surface adsorbates. Spectra collected during isobar (0.1 Torr) experiments appear similar, although typically with lower intensity in the region associated with carbonaceous species, as heating the surface can decrease adsorption of carbon contaminants. No changes were observed in the Cu 2p_{3/2} or Cu L-edge NEXAFS spectra on either surface upon water exposure (see Supporting Information).

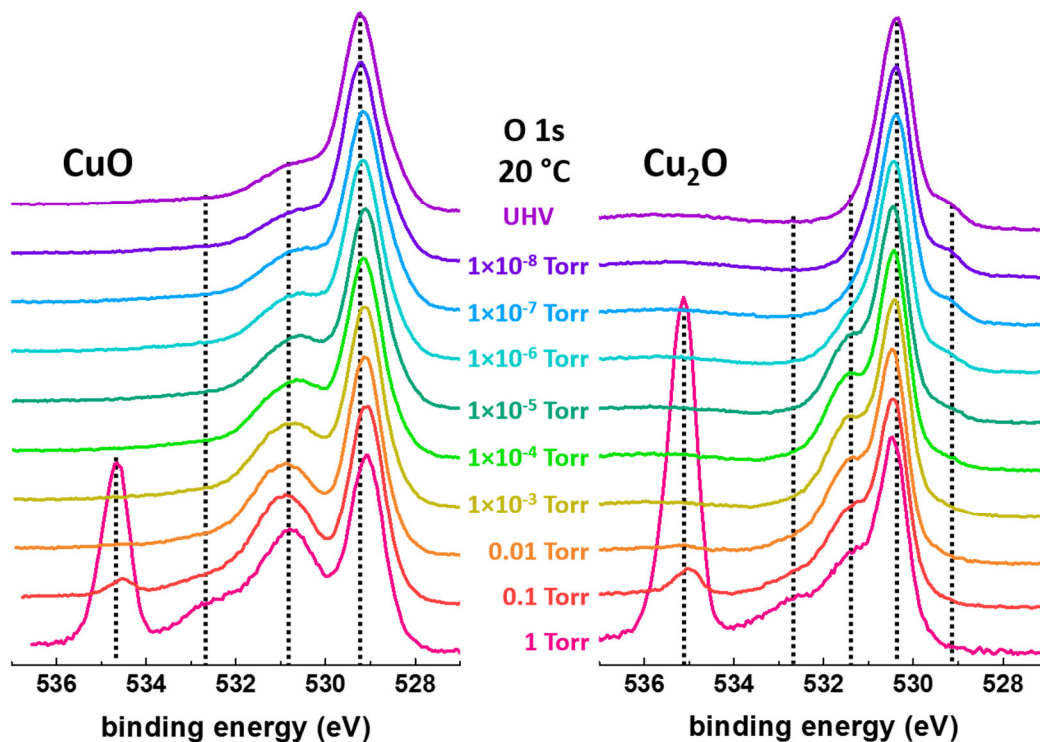


Figure 1. O 1s spectra for CuO (left) and Cu₂O (right) samples exposed to increasing water vapor pressures (at 20°C) from UHV conditions ($<1 \times 10^{-8}$ Torr) up to $\sim 6\%$ RH. Dotted vertical lines behind the data are guides for the eye to highlight changing intensities. Spectra are normalized to the CuO or Cu₂O oxygen lattice peaks, and the binding energy scales are calibrated to the position of the Cu $2p_{3/2}$ main peak.

Representative fits of the isotherm data at a water vapor pressure of 0.1 Torr are shown in Figure 2. In the case of Cu₂O, a feature at higher binding energies near the background is present in all spectra (see Figure 1) and is shown in the Figure 2 fit as a dashed curve. In our spectra, this feature is fit well by fixing the binding energy difference between it and the main Cu₂O oxide peak, as well as the relative areas of these two peaks. This feature has been observed previously,^{29,30} but to the best of our knowledge, its origin has not been discussed in detail. (It is also at the high-end of the range where O 1s spectra are typically collected, and thus may often be overlooked. In this study, we have extended the collection window to include the feature for gas-

phase H₂O.) The position and intensity relative to the main oxide peak could be consistent with a shake-up excitation of an electron in the final-state from the conduction band to the valence band; similar O 1s features are commonly observed in polymers arising from HOMO→LUMO final-state excitations.³¹

The remaining features in the O 1s spectra are labeled in Figure 2 and correspond to the oxide lattice atoms O_{lat}, surface hydroxyl groups OH, and surface carbon contamination C-O_x. During fitting, the area of the C-O_x peak was constrained based on the area of the C 1s peaks corresponding to oxidized carbon species and relative sensitivity factors calculated from measurement of gas-phase CO₂. The protocol for fitting the C-O_x peak will be discussed in more detail below. As shown in Figure 2, at room temperature and a water vapor pressure of 0.1 Torr, the spectra are well fit with only these species and there is no obvious chemical signature for molecular water, which is typically expected between 532-534 eV (i.e. between the surface OH peak and the gas-phase water peak). The C-O_x peak would appear to be perhaps a misidentified H₂O peak, but as we will explain below, this assignment is not the case for these measurements.

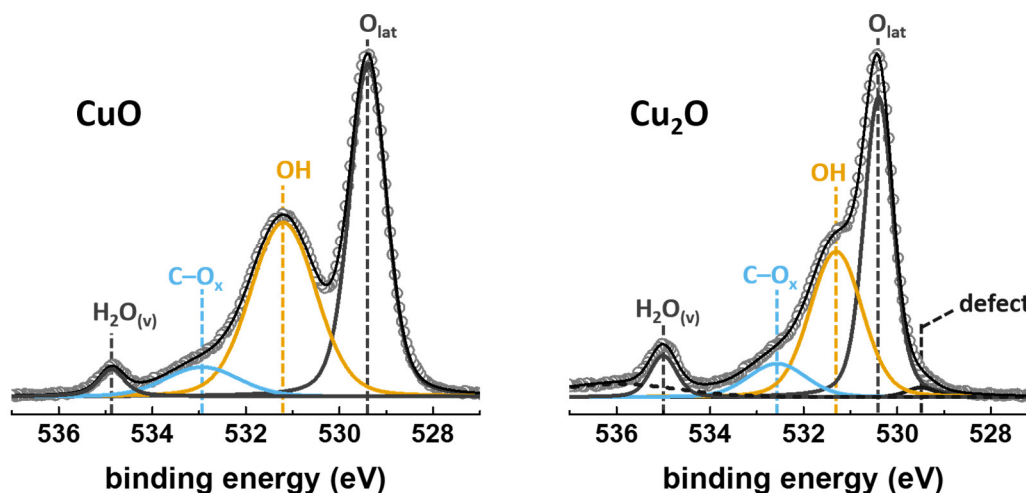


Figure 2. Representative fits for O 1s spectra under 0.1 Torr water vapor pressure at 20 °C (~0.001% RH) for Cu₂O (left) and CuO (right). Fitted peaks for individual species are shown with thick solid lines, the sum of the fitted peaks is shown as a thin solid black line, and the data points are shown as grey circles. The small peak in the Cu₂O spectrum shown as a black dashed curve represents a component present in all

spectra that scales with the O_{lat} intensity and likely represents a shake-up feature from the O_{lat} peak. More information can be found in the Supporting Information file.

We will now briefly explain the protocol for including the $C-O_x$ peak shown in Figure 2. In the case of the copper oxide surfaces studied here, the quantification of adventitious surface carbon is a point which cannot be ignored. Figure 3 shows the C 1s spectra collected immediately after the O 1s spectra plotted in Figure 2. On both surfaces, the spectra are fit well by three peaks. The binding energy values for the different peaks show that the majority of the surface carbon contamination is in an oxidized state (peaks near 288 eV and 287 eV), with a small population of aliphatic C-H species (near 285 eV). These spectra are representative of the carbon species observed across multiple experiments performed across several experimental runs, spanning more than half a year. Presumably, the adventitious carbon species in the chamber background are relatively constant throughout any one day during a measurement. The consistency in the appearance of the C 1s spectra across samples and experimental runs, which all show that the peak near 287 eV is smaller for Cu_2O relative to CuO , suggests that there is some difference in either affinity or reactivity of certain carbon species between the two oxide surfaces.

There are multiple different carbon-containing moieties which typically fall in the binding energy region between 287-288 eV, including various carbonyl, carboxyl, ether, and alcohol groups.³¹ Since the O 1s spectrum is dominated by signal originating from the oxide substrate, conclusive identification of the surface carbon species on each surface is not possible only by APXPS. We can however draw some general conclusions about these carbon-containing species; namely, they likely contain between one and two oxygen atoms per carbon atom, and the corresponding O 1s peaks likely occur in the region between 532-534 eV. (See the Supporting Information for more detail.) These general guides are helpful in deciding how to appropriately place and constrain the $C-O_x$ peak during fitting of the O 1s spectra.

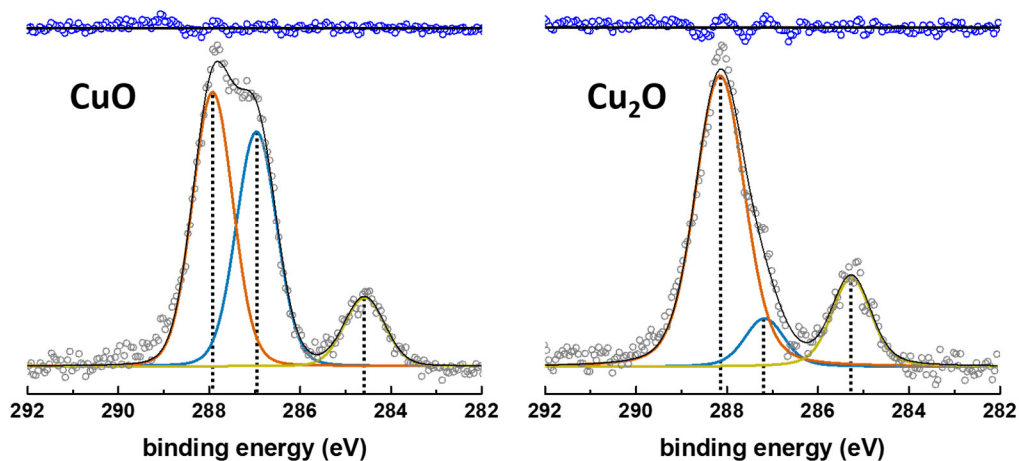


Figure 3. C 1s spectra taken immediately after the O 1s spectra shown in Figure 2 (at 20 °C and 0.1 Torr water vapor pressure). Peaks for oxidized carbon species are observed near 287 eV and 288 eV (blue and orange, respectively) and aliphatic carbon appears near 285 eV (gold). Fitted peaks for individual species are shown with thick solid lines, the sum of the fitted peaks is shown as a thin solid black line, and the data points are shown as grey circles. Difference spectra between the data points and the total fit are shown at the same scale in blue at the top.

Figure 4 compares several fits of a single O 1s spectrum collected for CuO at 20 °C under 0.1 Torr of water vapor. In each fit, different parameters were used for fitting the C-O_x peak and, when necessary, an additional peak for adsorbed molecular water was included. In Figure 4a, no peak is included for C-O_x and the water peak increases in intensity to fit this part of the spectrum. This fit gives a peak position for water of 533.8 eV, which is similar to that reported by Deng et al. where no peak was included for carbonaceous species during fitting.²²

The remaining fits in Figure 4b-e all include a peak for C-O_x and demonstrate the effect of constraining the peak area using different assumptions. By measuring CO₂ gas phase spectra, relative sensitivity factors for the C:O area ratio were established. (See Supporting Information). Based on the previous discussion of C 1s binding energies, it is likely that each carbon atom accounted for in the peaks near 287 eV and 288 eV is associated with one or two oxygen atoms. If we add a peak for these C-O_x species and assume the maximum of 2 O atoms per C atom while allowing the peak position to vary in a reasonable range, we obtain the fit shown in Figure 4b. The

difference spectrum between the data points and the total fit show clearly that some intensity (shaded) is not accounted for by the C-O_x peak in the region between 533-534 eV, which is exactly the region where we expect molecular water to appear.

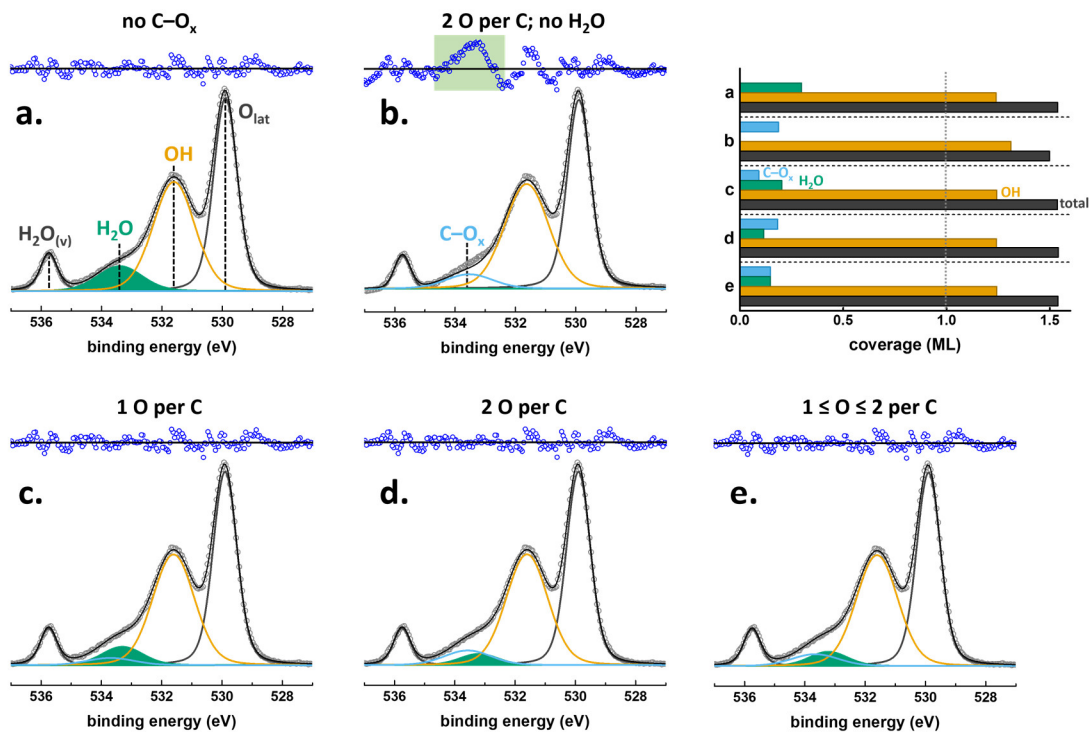


Figure 4. Fits of a single O 1s spectrum (CuO, 20 °C, 0.1 Torr water vapor) demonstrating the effect of changing the assumptions made about the quantity of oxidized carbon contaminants. (a) No peak is included for carbon contaminants, leaving only adsorbed molecular water (shaded peak) and gas-phase water (H₂O_(v)) above 533 eV. (b) The area of the C-O_x peak is fixed, assuming 2 O atoms for each C atom. The difference spectrum at the top shows that the fit is inadequate, indicating that an additional peak is required for adsorbed molecular water. (c) The area of the C-O_x peak is fixed, assuming 1 O atom per C atom, and a peak for adsorbed molecular water is included. (d) The area of the C-O_x peak is fixed, assuming 2 O atoms per C atom. (e) The area of the C-O_x peak is allowed to vary during fitting in the range between 1-2 O atoms per C atom. Note that the difference spectra for (a) and (c-e) are nearly identical. The bar graph in the upper right corner compares calculated coverages in monolayers (ML) of surface species for each fit condition (a-e). Depending on the assumptions made, the coverage of molecular water can vary by more than a factor of 2.

Figures 4 c-e show fits when an additional peak for water is included and the C-O_x peak area is given different constraints. All three of these fits, as well as the fit in Figure 4a, give nearly identical difference spectra. In Figure 4c, only one O atom per C atom is assumed, while in Figure 4d, we assumed two O atoms per C atom. Figure 4e shows the best fit where the area of the C-O_x

peak is constrained to be between one and two O atoms per C atom. In Figure 4e, the best fit gives an area intermediate of one O atom per C atom and two O atoms per C atom. This fit is physically and chemically reasonable, as a mixture of carbonaceous species containing one or two oxygen atoms is entirely possible. The bar graph in Figure 4 shows the different surface coverages calculated for OH, water, C-O_x, and the total surface coverage in monolayers (ML) for each of the fits in Fig. 4a-e. In the following sections, we use the fitting protocol demonstrated in Figure 4e, where the C-O_x peak area is constrained to between one and two O atoms per C atom, to calculate surface coverages.

The data in Figure 4 demonstrate, however, that an equally good fit can be obtained by assuming no carbon contamination, or the high and low cases of 2:1 and 1:1 O:C atom ratio. When we take into account also the inherent uncertainty in peak fitting and the calculated relative sensitivity factors (on the order of 15-20%), the calculated coverages should be taken only as a reasonable approximation based on identification and accounting of the surface carbon contaminants.

3.2 *Effect of the hot ion gauge filament on measurements in the presence of water vapor.*

Pressures in the mTorr range and higher can be measured by absolute capacitance manometers. For pressures up to 1×10^{-4} Torr, we require the use of an ion pressure gauge during isotherm measurements. Cracking of gas-phase molecules over the hot metal filament of the gauge should always be considered during experiments, as cracking products may be more reactive than the parent molecule. Here, we demonstrate the difference in surface chemistry as a result of water cracking on the hot pressure-gauge filament.

Figure 5a compares Cu 2p_{3/2} spectra collected for CuO and Cu₂O using the water leak-valve calibration method described in the experimental section (ion gauge is off during XPS

measurements). The Cu 2p_{3/2} spectra measured at 1×10⁻⁸ Torr and 1×10⁻⁴ Torr are identical. In Figure 5b, the Cu 2p_{3/2} spectrum for CuO shows distinct changes between these two pressure conditions when the ion gauge is left on. The main peak of the Cu 2p_{3/2} region shifts to lower binding energy and narrows, while the satellite features at higher binding energy become smaller. Together, these changes indicate a partial reduction of Cu²⁺ surface sites to Cu⁺. In contrast, no changes are observed in the Cu₂O Cu 2p_{3/2} spectrum. The extent of surface hydroxylation also seems to be affected by the ion gauge. In Figure 5c, the hydroxyl coverage at 1×10⁻⁴ Torr is greater when the ion gauge is left on during exposure to water vapor. This trend was consistent across the pressure range measured with the ion gauge on (10⁻⁸ – 10⁻⁴ Torr). For both surfaces, it is clear that the hot filament is reacting with gas phase water and thus subsequently affecting the surface chemistry of the oxides.

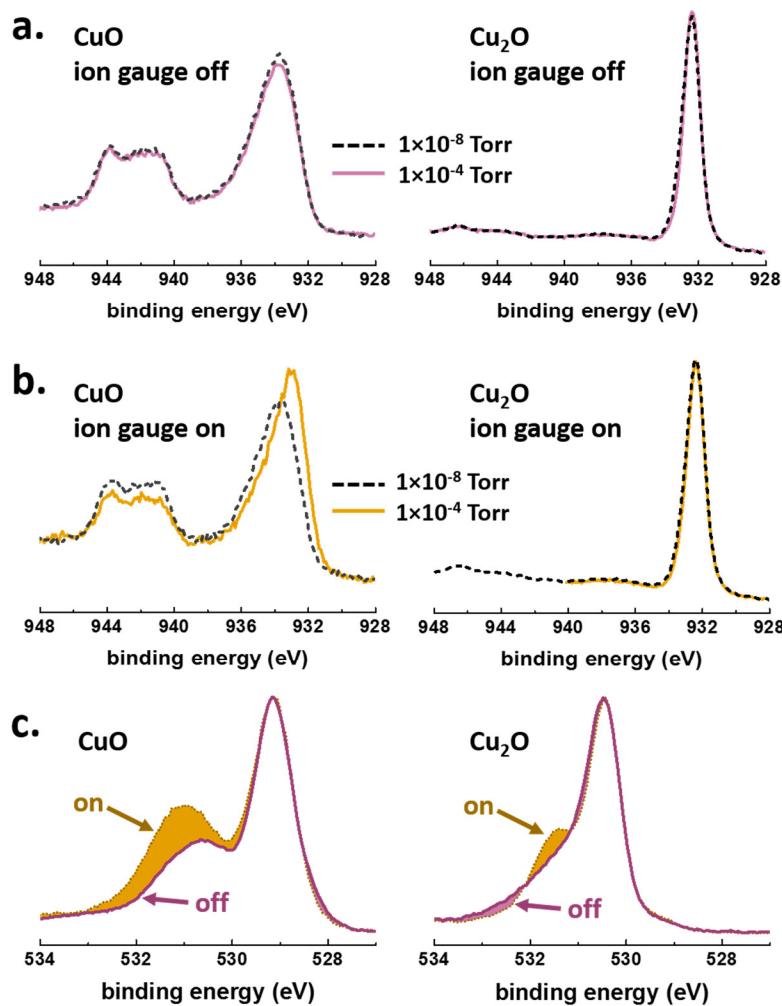


Figure 5. (a-b) Cu 2p_{3/2} spectra demonstrating the effect of leaving the ion gauge on during water exposure measurements. In (a), the ion gauge was left off during water exposure, and on both Cu₂O and CuO, no significant change is observed when the water vapor pressure is increased from 1×10⁻⁸ Torr to 1×10⁻⁴ Torr. In (b), the ion gauge was turned on during water exposure, and while no change is observed for Cu₂O when the water vapor pressure is increased, the CuO spectra indicate partial reduction of Cu²⁺ to Cu⁺. (c) O 1s spectra collected at a water vapor pressure of 1×10⁻⁴ Torr showing that the amount of hydroxyl groups on the surface is higher on both CuO and Cu₂O when the ion gauge is left on during water exposure. The shaded regions highlight differences between the on and off conditions.

3.3 Comparison of isobar and isotherm experiments.

Controlling the relative humidity at the sample surface can be done under constant pressure or constant temperature conditions, and each of these methods has advantages and disadvantages.

For isotherm measurements, much lower RH conditions can be accessed by beginning at UHV and slowly increasing the water vapor pressure. This approach can be helpful for determining the initial onset of surface hydroxylation, which for many oxide surfaces occurs even under UHV conditions due to reaction with low levels of water vapor in the background.^{3,8} Isotherm measurements also avoid problems associated with chemical changes to the surface due to decomposition of the substrate at elevated temperatures. On the other hand, the adventitious carbon contaminates the surface more quickly in isotherm experiments, particularly at higher water vapor pressures where turbo pumps must be isolated and pumping is reduced (here, $\geq 1 \times 10^{-3}$ Torr). Mild heating of the substrate can help prevent accumulation of contaminants on the surface, which may block or compete with water for adsorption sites, thus making isobar experiments where the sample starts hot and is gradually cooled typically “cleaner” than isotherms collected over the same RH range.

Figure 6 compares one isobar and one isotherm dataset each for CuO and Cu₂O. During isobar experiments where the sample is heated, the hydroxyl coverage is typically lower than that measured at room temperature under the same RH. This trend holds until higher RH ($> \sim 0.1\%$ RH) values are reached.

When isobar and isotherm measurements agree with each other, one can assume equilibrium conditions for water adsorption/desorption. When isobar and isotherm data do not converge, this mismatch could be caused by deviations of the true RH at the sample surface from calculated values in isobar experiments, where the gas phase temperature T_{gas} is in general lower than that of the surface (T_{surf}), leading to lower collision frequencies in adsorption. This situation can be taken into account by using an effective water vapor pressure $p' = p(T_{\text{gas}}/T_{\text{surf}})^{1/2}$ for the calculation of the RH, as described in Ref. 12. The RH scale in Figure 6 was calculated without using this correction since the actual gas phase temperature in the very vicinity of the sample is

not known. The deviation of isobar and isotherm data in Figure 6 is, however, not due to calculation of the RH for the isobar data, which would give an underestimate of the true RH and thus produce the opposite effect of that observed in Figure 6. The difference in isobar and isotherm measurements in this case also cannot be due to a difference in total water exposure (in Langmuir). Even though the isotherm experiments have a longer time between each measurement than the isobar experiments, the total water vapor exposure (in Langmuir, L) in isobar experiments is still higher due to the much larger partial pressure of water vapor (e.g. at $\sim 5 \times 10^{-4}$ % RH: isotherm, 15 min, 9×10^4 L; isobar, 2 min, 1.2×10^7 L). There also appears to be no consistent correlation between the difference in OH coverage and the amount of carbon contamination. In the case of CuO, there is indeed a higher coverage of C-O_x in isotherm experiments where the OH coverage is higher. On the other hand, the C-O_x coverage on Cu₂O is not always lower for isotherm experiments, and the OH gap between the isobar and isotherm curves is still prominent.

One possibility is that for the isobar measurements, the lower RH data points are collected when the sample is hot, and some reorientation of the exposed crystal facets at the sample surface could occur upon heating. It has been shown that for many metals and metal oxides, including Cu and TiO₂, changing the exposed crystal facet can have a marked effect on water adsorption and dissociation.^{8,32,33} The effects of crystallographic surface termination is a point which requires further investigation for these and other polycrystalline samples.

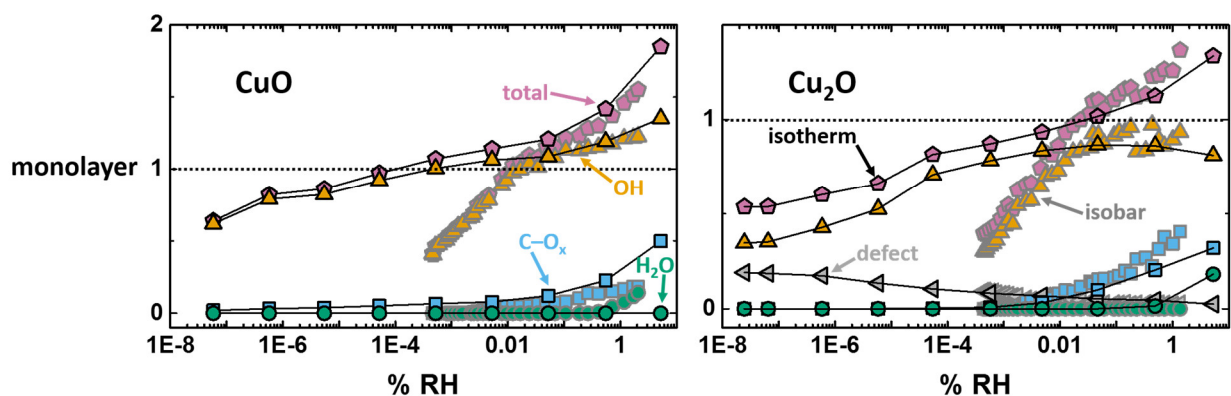


Figure 6. Comparison of isobar (0.1 Torr water vapor pressure, grey outlined symbols) and isotherm (20°C, symbols connected by black lines) water exposure experiments for polycrystalline CuO and Cu₂O surfaces. Below ~0.01% RH, the isotherm measurements show significantly higher OH coverages on both oxides. This OH gap between the isobar and isotherm curves may be due to differences in the crystallite orientations when the samples are held at higher temperatures.

In isobar experiments, the sample surfaces are expected to remain cleaner at a given RH condition, as the adventitious carbon species are less likely to react with the surface before water vapor is introduced. The data in Figure 6 demonstrate that the CuO samples consistently show lower coverages of C-O_x species for isobar compared to isotherm measurements. However, we did not observe a similar trend for the Cu₂O samples, and sometimes, as shown in Figure 6, the isobar experiments showed slightly higher C-O_x coverages. In general, C-O_x species were first observed at higher RH on Cu₂O than on CuO, and only at RH values where the partial pressure of water vapor required reduced pumping to the XPS analysis chamber (i.e. above 1×10^{-4} Torr). The higher RH required for onset of C-O_x adsorption on Cu₂O, even for similarly low background concentrations of adventitious carbon, suggests that CuO has a higher affinity for these species than Cu₂O. On both surfaces, there is a correlation between lower C-O_x coverage and higher coverages of molecular water. These data therefore suggest that the presence of adventitious carbon contaminants suppresses molecular water adsorption on these surfaces. However, the range of RH values accessible in this study has an upper limit just at the point where molecular water is

observed. Additional experiments with a wider RH window would help to clarify this point, but would require a method to cool the sample to lower temperatures than were available in our experimental setup. Since the preparation of the CuO_x surfaces requires heating in O_2 in the end station, a method for being able to both heat and significantly cool the sample (such that the sample is the coldest point in the chamber) would be required. Qualitatively, both of the copper oxide surfaces appear to have a higher affinity for carbon contaminants than other metal oxides we have studied, and the different C 1s binding energies measured on the two different oxides suggest that the same background contaminants may undergo different reactions depending on the copper oxidation state. Thus, at least in the case of the copper oxides, the reactivity of the surface with environmental background carbon should be taken into account when considering possible mechanisms of water adsorption and dissociation.

When considering the effects of both adventitious surface carbon and water cracking over the ion-gauge filament, one can build a convincing case for isobar measurements that start with a hot sample as the preferred method for comparing these two oxide surfaces side-by-side. In this way, the presence of surface carbon species, while not completely unavoidable, are at least partially controlled, and we can more comfortably assume that the surface hydroxylation is primarily a result of interactions with molecular water rather than other, more reactive gas-phase species.

Figure 7 shows sets of isobar data for CuO and Cu_2O . Both surfaces show that in the region between ~ 0.01 - 0.1 % RH, the hydroxyl coverage reaches approximately 1 ML and then plateaus. The total coverage continues to increase, primarily due to accumulation of surface carbon species. However, in the case of CuO , molecular water absorption is observed, with onset occurring around 1% RH. No molecular water is observed on Cu_2O in our isobar experiments. Based on our isotherm

experiments and those reported previously by Deng et al.,²² we do expect molecular water accumulation on Cu₂O at higher RH values that are outside the scope of the range attainable in our experimental configuration. However, were the C-O_x species not accounted for, one could mistakenly calculate ~0.5 ML of molecular water on Cu₂O and ~0.4 ML on CuO at 1% RH. This situation may be the case in the previous work of Deng et al. with Cu₂O, where the issue of carbon contamination is not discussed.²² Taking caution to account for surface carbon shows that the actual surface coverage of molecular water is significantly lower, even when being conservative in calculating the area of the C-O_x peak (see Figure 4 and corresponding discussion).

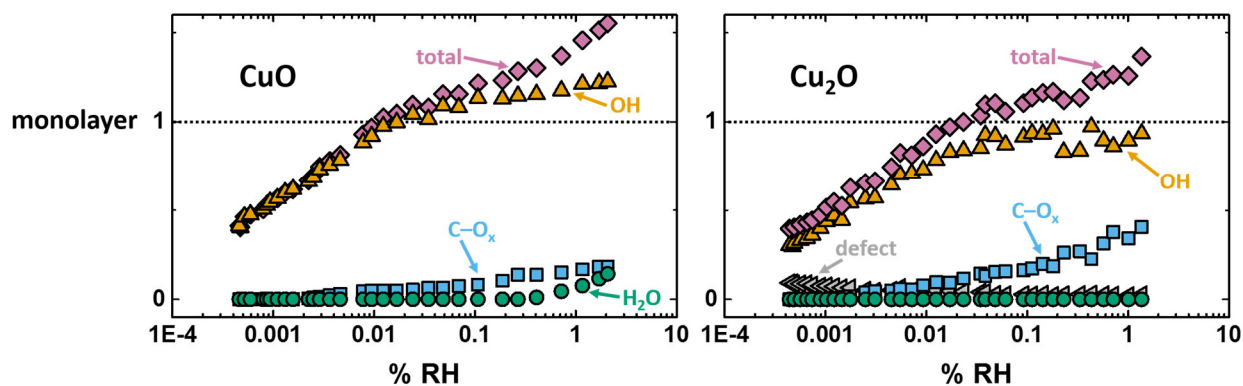


Figure 7. Surface coverage calculations from isobar ($p_{\text{H}_2\text{O}} = 0.1$ Torr) measurements on Cu₂O and CuO. The total coverage of surfaces species was calculated based on attenuation of the O_{lat} oxide peak using the procedure outlined in ref. 18 (more detail is available in the Supporting Information). Fractional coverages of other species were calculated by multiplying the total coverage by the fraction of the total peak area corresponding to that species.

5. Conclusions

We have studied the initial hydroxylation of copper oxide surfaces in the presence of water vapor. On both CuO and Cu₂O, the surfaces readily hydroxylated at low relative humidities, with the OH coverage approaching one monolayer below 0.1% RH. Molecular water adsorption is only observed once a full monolayer of OH has formed, which is consistent with general reactivity trends observed on other metal oxide surfaces. Adventitious carbon species also readily adsorb to

these surfaces, with coverages approaching 0.5 ML on Cu₂O at 1% RH, even when precautions are taken to keep the as-prepared surfaces free of carbon. We have demonstrated that quantification of carbonaceous surfaces species is necessary to avoid overestimating the coverage of adsorbed molecular water on these surfaces. We have also demonstrated that cracking of water on the ion gauge filament can affect surface chemistry during APXPS experiments. We found that CuO surfaces were partially reduced when the ion pressure gauge was turned on during water exposure, and both CuO and Cu₂O surfaces hydroxylated more readily. Apart from the technical APXPS considerations detailed here, the initial hydroxylation and hydration of copper oxide surfaces are important chemical processes in numerous technical applications and environmental systems. This work adds to the library of metal oxide surfaces studied by APXPS in order to shed light on inherent reactivity trends of these surfaces under environmentally relevant conditions.

Supporting Information Available

Supplementary discussions, figures, and tables. This material is available free of charge via the Internet at pubs.acs.org.

Acknowledgments

This work was supported by the Department of Defense through the Defense Threat Reduction Agency under grant number HDTRA11510005. L.K. acknowledges support from the Danish Research Council for Independent Research and Innovation Fund Denmark (under the National Initiative for Advanced Graphene Coatings and Composites). S.P., H.T., and T.H. acknowledge financial support by Research Foundation – Flanders (FWO) under project number SB-19-151. H.B. acknowledges support by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences of the US Department of

Energy under Contract No. DE-AC02-05CH11231. The ALS and the MES beamline 11.0.2 are supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy at the Lawrence Berkeley National Laboratory under Contract No. DE-AC02-05CH11231.

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TOC Graphic

O 1s XPS spectra at ~0.001% RH

