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Momentum for Catalysis: How Surface Reactions Shape the RuO<sub>2</sub> Flat Surface State

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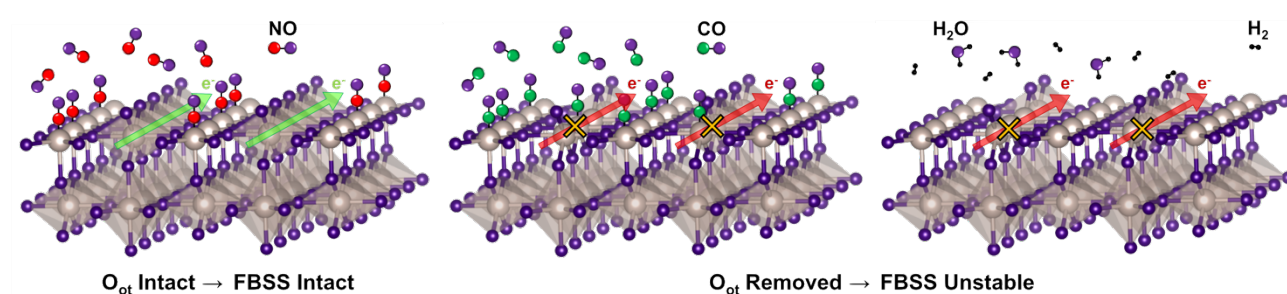
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## Momentum for Catalysis: How Surface Reactions Shape the RuO<sub>2</sub> Flat Surface State

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The active (110) surface of the benchmark oxygen evolution catalyst RuO<sub>2</sub> spans a flat-band surface state (FBSS) between the surface projections of its Dirac nodal lines (DNL) that define the electronic properties of this functional semimetal. Monitoring well known surface adsorption processes of H<sub>2</sub>, O<sub>2</sub>, NO and CO by *in-operando* angle resolved photoemission spectroscopy, we selectively modify the oxidation state of individual Ru surface sites and

identify the electronic nature of the FBSS: Stabilized by bridging oxygen  $O_{br}$   $p_z$ , the FBSS disperses along  $\langle 001 \rangle$  oriented chains of bridging  $Ru_{br}$   $4d_{z^2}$  orbitals, collapses upon  $O_{br}$  removal, yet, remains surprisingly unaffected by the oxidation state of the undercoordinated 1f-cus-Ru species. This directly reflects in the ability of  $RuO_2$  (110) to oxidize CO and  $H_2$  along with its inability to oxidize NO, demonstrating the FBSS's active role in catalytic charge transfer processes at the oxygen bridge sites. Our synergetic approach provides momentum resolved insights to the interplay of a catalyst's delocalized electronic structure and the localized orbitals of its surface reactants – a route towards a microscopic understanding of heterogeneous catalysis.

**Keywords.** – Ruthenium dioxide ( $RuO_2$ ), angle resolved photoemission spectroscopy (ARPES), density functional theory (DFT), flat band surface state (FBSS), Dirac nodal lines (DNL),  $H_2$  oxidation, CO oxidation, NO adsorption

**Introduction.** – The (110) surface of ruthenium dioxide ( $RuO_2$ ) serves as a useful study ground for a variety of catalytic oxidation and dehydrogenation reactions, summarized in two exemplar reviews by Over<sup>1</sup> and Weaver.<sup>2</sup>  $RuO_2$  (110) is easily reduced in UHV and has been investigated as a prototypical oxidation catalyst for carbon monoxide (CO)<sup>3</sup> and nitrogen oxides ( $NO_x$ ).<sup>4,5</sup>  $RuO_2$  degrades alcohols,<sup>6</sup> and dehydrogenates ammonia ( $NH_3$ ),<sup>7</sup> valuable properties to remediate wastewater.<sup>8,9</sup> The exceptional activity of  $RuO_2$  (110) in the anodic evolution of chlorine is industrially exploited in the Deacon process, an energy neutral recycling method of  $Cl_2$  from hydrochloric acid (HCl),<sup>10–14</sup> capable of replacing energy intense conventional recycling methods based on electrolysis.<sup>1,15</sup> With low overpotentials and – if alloyed with iridium<sup>16</sup> – high resilience in the anodic evolution of oxygen,  $RuO_2$  has become the “gold standard co-catalyst” of electrolytic<sup>17</sup> and photocatalytic<sup>18</sup> water splitting, as well as of the electrochemical reduction of carbon dioxide ( $CO_2$ ).<sup>19</sup>

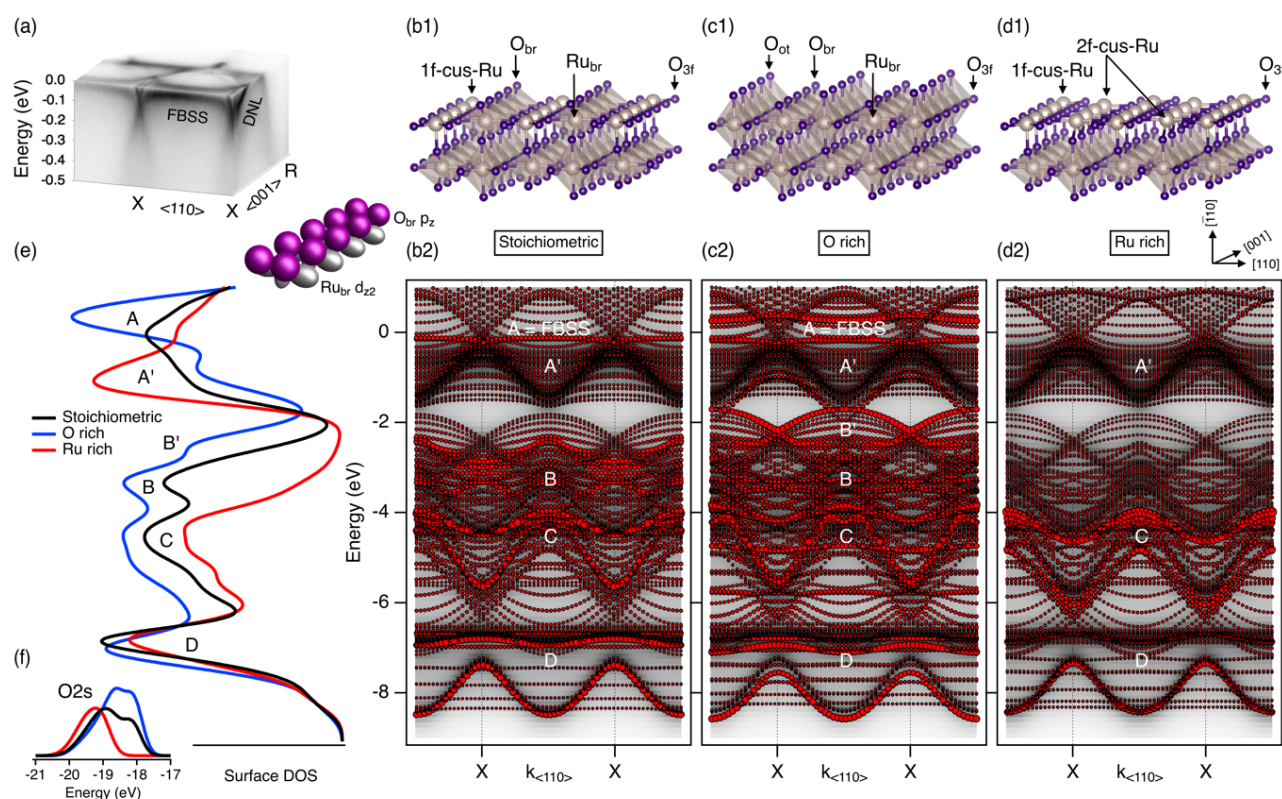
Recently, the fundamental electronic and magnetic structure of RuO<sub>2</sub> has also gained attention due to the appearance of unusual and previously inaccessible physical phenomena such as colinear antiferromagnetism,<sup>20–22</sup> the crystal Hall effect<sup>23,24</sup> and Dirac Nodal lines (DNLs).<sup>25–27</sup> The latter underpin the semi-metallicity of this functional oxide and serve as anchors for a quasi-one-dimensional flat-band surface state (FBSS) at the (110) surface of RuO<sub>2</sub>, which exhibits exaggerated – van Hove singularity like – density of states (DOS) right at the Fermi level (see Fig. 1a). The potential of this FBSS to act as a correlated reservoir of charge and spin<sup>22,28</sup> made us speculate about its role in surface catalytic charge transfer reactions,<sup>27</sup> however, a systematic experimental and theoretical study of its orbital origin and its interaction with surface reactants has remained elusive to date.

Here, we exploit four well characterized redox reactions to site selectively control the oxidation state of individual RuO<sub>2</sub> (110) surface atoms,<sup>1,2</sup> while we monitor the response of the valence electronic band structure *in-operando* by state-of-the-art angle resolved photoemission (ARPES): Hydrogen (H<sub>2</sub>) and carbon monoxide (CO) act as reducing agents for surface Ru bridge sites (Ru<sub>br</sub>) and destabilize the FBSS. Oxygen (O<sub>2</sub>) and nitric oxide (NO) on the other hand adsorb on undercoordinated 1f-cus-Ru sites and leave the Ru<sub>br</sub> sites and the FBSS unaffected. This demonstrates the FBSS to propagate along <001> oriented chains formed by bridging RuO<sub>6</sub> octahedra, where it actively participates in surface catalytic processes.

***Stoichiometric RuO<sub>2</sub> (110).*** – Bulk rutile RuO<sub>2</sub> is comprised of 6-fold coordinated Ru<sup>4+</sup> cations and 3-fold coordinated O<sup>2-</sup> anions. *In vacuo* cleaving of slightly *n*-type, 7% Ir doped, bulk RuO<sub>2</sub> single crystals with a ceramic top pin produces small (~50 μm), clean facets of a mostly stoichiometric (110) surface.<sup>26,27</sup> The *stoichiometric (110) surface* is depicted in Figure 1 (b1), exposing rows of fully (3-fold) coordinated oxygen (O<sub>3f</sub>) and 2-fold coordinated bridging

oxygen ( $O_{br}$ ) species, as well as the 5-fold coordinated, i.e., 1-fold “coordinatively unsaturated” and partially reduced 1f-cus-Ru sites.

We have studied the electronic structure of this surface by micro-focused angle resolved photoemission spectroscopy (ARPES) with 69 eV photons and discussed the results in detail in Refs. 26 and 27. As summarized in the ARPES data of Figure 1(a), the FBSS disperses along the  $\langle 001 \rangle$  direction but remains mostly localized, i.e., a flat band, along the perpendicular  $\langle 110 \rangle$  direction. Density functional theory (DFT) calculations (see details in the method section) on a stoichiometric  $RuO_2$  (110) surface slab (panel (b2)) in Fig. 1 and Supporting Figs. 2-4) identify the predominant in-plane surface  $Ru_{br}$   $d_{z^2}$  and  $O_{br}$   $p_z$  orbital character of the FBSS (inset), generating feature A in the surface DOS of panel (e) (see also Supporting Fig. 1).



**Figure 1: The FBSS on  $RuO_2$  (110).** (a) ARPES Fermi surface and maps along the  $XX$  and  $XR$  direction measured with 69 eV photons,<sup>26,27</sup> marking the DNLs and the FBSS that is spanned in between. (b-d) Crystal structure (1) and electronic DFT band structure (2) of the stoichiometric (b), the oxygen rich (c), and the ruthenium rich  $RuO_2$  (110) surface (d). The marker size indicates the surface oxygen character, i.e., the

projection of the electronic bands onto the topmost O atomic orbitals to which ARPES at 69 eV (panel a) is most sensitive. The gray background is the surface projection of the bulk band structure. (e) Valence and (f) O 2s surface DOS of the stoichiometric (black), the oxygen rich (blue), and the ruthenium rich RuO<sub>2</sub> (110) surface (red) calculated by DFT. Feature “A” labels DOS of preliminary Ru 4d<sub>z<sup>2</sup></sub> character that forms the FBSS, feature “A’ ” the DOS composed of undersaturated Ru 4d states. Features “B”, “B’ ” and “C” are of predominantly O 2p character and feature “D” of mixed orbital character (see supporting information).

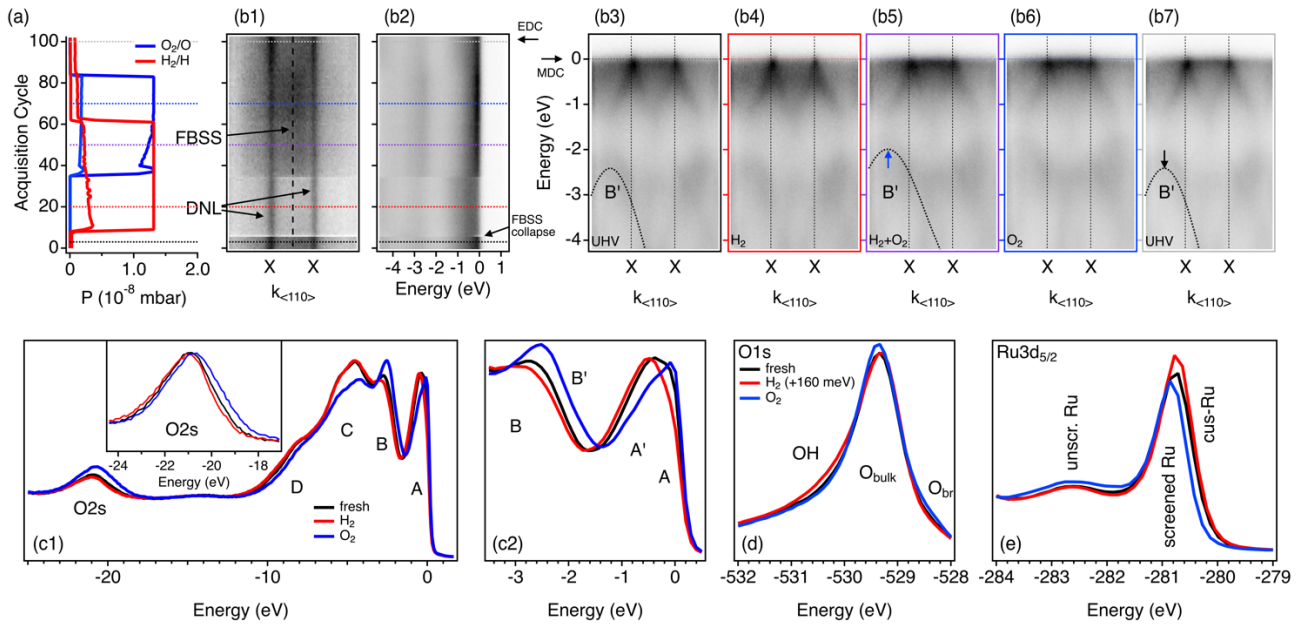
***Non-stoichiometric RuO<sub>2</sub> (110).*** – The under-coordinated 1f-cus-Ru sites have both electron donating and electron accepting character, and thus serve as active catalytic centers to bind a variety of surface reactants.<sup>1,2</sup> In particular, the 1f-cus-Ru site can bind 2-fold under-coordinated O<sub>ot</sub> species via dissociative adsorption of molecular oxygen (O<sub>2</sub>), resulting in an *oxygen rich surface* (Figure 1(c1)) that is expected to intensify the FBSS as well as the O<sub>3f</sub> derived feature B’ in the electronic band structure (Figure 1(c2) and (e)). Both O<sub>ot</sub> as well as O<sub>br</sub> act as proton acceptors that can be easily hydroxylated and – via subsequent diffusion, water formation and desorption<sup>29,30</sup> – removed by molecular hydrogen (H<sub>2</sub>). This results in a *ruthenium rich surface* (Figure 1(d1)), leaving Ru<sub>br</sub> sites exposed and reduced to 4-fold coordinated 2f-cus-Ru centers. The FBSS feature A as well as band B’ are now expected to disappear, while the O<sub>3f</sub> states condense into the higher energy band manifold C (see electronic properties in Fig. 1(d2) and Fig. 1(e)).

Having laid out the theoretical foundation, we now exploit this well-studied redox-process<sup>1,2</sup> to study the relationship of surface stoichiometry and the FBSS experimentally. The evolution of the RuO<sub>2</sub> (110) surface electronic structure upon room temperature H<sub>2</sub> exposure is summarized in Figure 2. We start from a freshly cleaved RuO<sub>2</sub> (110) surface in <10<sup>-10</sup> mbar UHV, aligned by ARPES along the reciprocal XX direction (cf. Fig. 1(a)). This surface is now exposed to ~1.3 × 10<sup>-8</sup> mbar of H<sub>2</sub> (red), subsequently admixed and replaced by about the same amount of O<sub>2</sub> (blue) before the sample is pumped back to UHV. The temporal evolution of the partial gas pressures, tracked by a rest gas analyzer (RGA), is shown in panel (a) of

Figure 2. Simultaneously, we monitor the evolution of the ARPES signature close to the Fermi level (b1)–(b7), as well as the angle integrated photoemission signal up to 25 eV binding energy (c1) and (c2), *in operando* with 69 eV photons.

Panel (b1) shows the evolution of a momentum distribution curve (MDC) at the Fermi energy, i.e., the Fermi surface cut along XX; panel (b2) the evolution of an energy distribution curve (EDC) at a momentum right in between the two X points (vertical dashed line in b1). Panels (b3)–(b7) are representative ARPES images (cf. Fig. 1(a)) along the *colored horizontal lines* in panels (a), (b1) and (b2): specifically, for the pristine- (b3, black), the H<sub>2</sub>- (b4, red), the H<sub>2</sub>+O<sub>2</sub>- (b5, purple) and the O<sub>2</sub> exposed surface (b6, blue), as well as the final measurement in UHV (b7, gray). While the bulk derived DNLs at X are robust upon all gas exposure (b1), the FBSS collapses upon exposure to H<sub>2</sub> (b1, b2, b4), but recovers upon admixture of O<sub>2</sub> (b1, b2, b5). As expected from theory (Fig. 1(c2)), dissociation of O<sub>2</sub> to O<sub>ot</sub> shifts valence band spectral weight B' centered at -3.5 eV (black dotted guide to the eye in (b3)) upwards by ~ 0.5 eV (blue arrow in (b5)). This oxidation step is somewhat reverted in the final UHV step (b5), a sign of photo-stimulated O<sub>ot</sub> desorption due to the collimated x-ray beam.<sup>31</sup>





**Figure 2: Dissociation of H<sub>2</sub> and O<sub>2</sub> on RuO<sub>2</sub> (110).** (a) Evolution of H<sub>2</sub> and O<sub>2</sub> partial pressures in the ARPES chamber. One acquisition cycle corresponds to ~45 seconds. (b1) Evolution of the Fermi surface MDC along XX measured with 69 eV photons. (b2) Evolution of the EDC taken along the dashed vertical line in (b1). Panels (b3-b7) show representative ARPES images in UHV (b3, b7), in H<sub>2</sub> (b4), in H<sub>2</sub> + O<sub>2</sub> (b5) and O<sub>2</sub> (b6), taken along the color-coded horizontal lines in panels (a, b1, b2). Panels (c1, c2) show representative angle integrated spectra in UHV (black), in H<sub>2</sub> (red), and in O<sub>2</sub> (blue), taken at the color-coded horizontal lines in panels (a, b1, b2). (d) O1s and (e) Ru3d<sub>5/2</sub> core levels measured with 650 eV photons. The red spectrum in (d) was shifted by +160 meV.

Panel (c1) shows representative angle integrated photoemission spectra, revealing changes of the four major contributions to the valence surface DOS that were predicted by theory in Fig. 1(e): at ~-9 eV (feature D); at ~-5 eV (feature C); at ~-2.2 eV (feature B); and close to the Fermi level, feature A, the latter two which split into (A,A') and (B,B') upon closer inspection (c2). While H<sub>2</sub> (red) leaves peak C unaffected with respect to the freshly cleaved surface (black), it significantly suppresses upon O<sub>2</sub> exposure (blue). Feature B – built mostly from spectral weight of the dispersive band B in panels (b3)–(b7) – is slightly suppressed by H<sub>2</sub>, but greatly enhanced and shifted by ~0.1 eV upon O<sub>2</sub> exposure (c2), forming the high energy shoulder B' predicted by DFT. Further, H<sub>2</sub> considerably depletes Fermi level spectral weight of feature A (c2), which recovers and significantly sharpens at the expense of A' (i.e., undersaturated Ru 4d states) upon exposure to O<sub>2</sub>, as reflected in (b3)–(b7). The surface

sensitive O 2s peak at  $\sim -20.6$  eV (the mean free path of photoelectrons at 50 eV kinetic energy is  $\sim 5$  Å) is slightly reduced by H<sub>2</sub> but is greatly enhanced and broadened towards low energy by O<sub>2</sub>, indicating additional surface oxygen as predicted in Fig. 1(f).

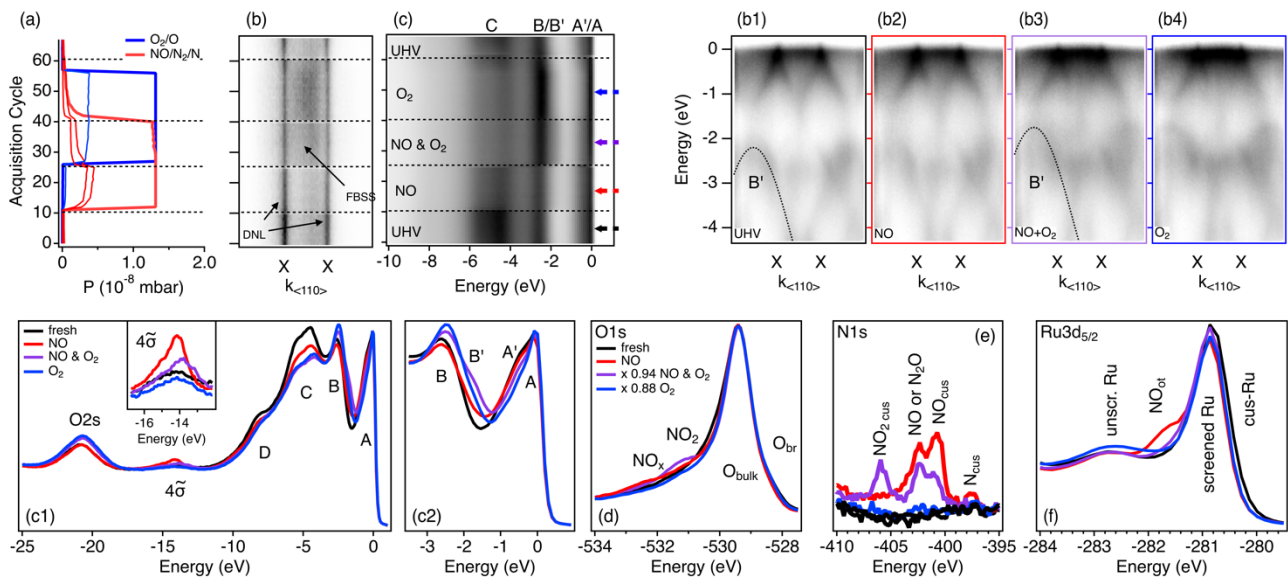
To check the surface stoichiometry more accurately, we repeat this gas dosing experiment on a fresh surface, this time monitoring the O 1s (panel (d)) and Ru 3d core levels (panel (e)) with 650 eV photons. With respect to the pristine surface (black), H<sub>2</sub> (red) shifts the O 1s peak in panel (d) towards 160 meV higher energy and produces a high energy shoulder, indicative of OH-group formation. O<sub>2</sub> removes these OH-groups, and – similar to the O 2s peak – enhances the O 1s main peak (the mean free path at this kinetic energy is less surface sensitive as for O 2s:  $\sim 10$  Å), while simultaneously producing a small low energy shoulder indicative of additional surface oxygen.<sup>29,30</sup> In the Ru 3d<sub>5/2</sub> manifold of panel (e), H<sub>2</sub> considerably enhances the screened main peak and its low energy shoulder, but leaves the unscreened satellite mostly unaffected, a sign of increased surface metallicity.<sup>32</sup> O<sub>2</sub> on the other hand re-oxidizes the surface, removes the 1f-cus-Ru-derived low energy shoulder and lowers the main peak in favor of the unscreened satellite.<sup>33,34</sup>

These observations are fully aligned with the expected redox scenario<sup>1,2,35</sup> and our theory: The initial hydroxylation of surface oxygen (OH-shoulder in O 1s peak) triggers the formation and desorption of water, removing surface oxygen species and producing a ruthenium rich surface (1f-cus-Ru shoulder in Ru 3d<sub>5/2</sub>). The FBSS collapses and only recovers upon subsequent exposure to O<sub>2</sub>, well known to bidentately adsorb and dissociate on neighboring 1f-cus Ru sites with reported O<sub>ot</sub> coverages  $>86\%$ , while efficiently replenishing O<sub>br</sub> vacancies.<sup>30</sup> The Ru 3d<sub>5/2</sub> low energy shoulder hence diminishes<sup>33,34</sup> in panel (e) in favor of the low energy O 1s and O 2s edges in panels (c1) and (d).<sup>29,30</sup> The consequent decrease in surface metallicity reduces screening and enhances the unscreened Ru 3d<sub>5/2</sub> satellite.

The consistency of our experimental observations and theory allows us to conclude on the FBSS to stabilize on the stoichiometric and oxygen rich surfaces, but to collapse upon removal of  $O_{br}$  species. We can now further identify the  $O_{3f}$  derived surface DOS feature C as a useful indicator for the presence of coordinatively unsaturated cus-Ru sites, while B' foremost monitors the amount of on-top surface oxygen.

***NO adsorption.*** – The adsorption of NO to the  $RuO_2$  (110) surface is important for the understanding of catalytic oxidation of ammonia or  $NO_x$  exhaust emissions and is quite well understood:<sup>2,35,36</sup> Upon exposure to small amounts, NO molecules adsorb and bond strongly at 1f-cus-Ru species with the molecular axis oriented normally to the surface and nitrogen pointing towards ruthenium.<sup>37–40</sup> This bonding mechanism is commonly rationalized by purely local pictures within the Blyholder<sup>41</sup> or more accurate three-orbital models.<sup>36</sup> In a nutshell, NO transfers charge from its  $5\sigma$  to the Ru 4d states, an antibonding interaction that is counterbalanced by a bonding back-donation to the NO  $2\pi^*$  orbital. The dissociation of NO on two adjacent 1f-cus-Ru sites can produce adsorbed atomic nitrogen and oxygen species, which in principal – dependent on the reaction conditions – can react to adsorbed  $N_2$ , to  $N_2O$  as well as to  $NO_x$  and  $NO_2$ .<sup>2,42</sup>

We exploit this mechanism and monitor the response of the  $RuO_2$  surface electronic structure to the adsorption of NO at room temperature in Fig. 3. In analogy to  $H_2$  dosing, we start from a freshly cleaved, i.e., an essentially stoichiometric  $RuO_2$  (110) surface in  $<10^{-10}$  mbar UHV (black). This time, the surface is exposed to  $\sim 1.3 \times 10^{-8}$  mbar of NO gas (red), successively admixed (purple) and replaced (blue) by about the same amount of  $O_2$  before the chamber is pumped back to UHV. The partial pressure evolution measured by the RGA is shown in panel (a). As in the  $H_2$  experiment, we monitor the ARPES signature close to the Fermi level (panels (b), (b1)–(b4)) as well as the integrated photoemission signal up to  $\sim 25$  eV binding energy (panels (c), (c1) and (c2)) with 69 eV photons.



**Figure 3: Adsorption of NO on RuO<sub>2</sub> (110).** (a) Evolution of NO and O<sub>2</sub> partial pressures in the ARPES chamber. One acquisition cycle corresponds to ~49 seconds. (b) Evolution of a Fermi surface cut along XX measured with 69 eV photons. Panels (b1-b4) show representative ARPES images in UHV (b1), in NO (b2), in NO + O<sub>2</sub> (b3) and O<sub>2</sub> (b4), taken along the color-coded arrows panel (c). (c) Evolution of the angle integrated photoemission signal measured with 69 eV photons. Panels (c1, c2) show representative spectra in UHV (black), in NO (red), in NO + O<sub>2</sub> (purple) and in O<sub>2</sub> (blue), taken along the color-coded arrows in panel (c). (d) O1s, (e) N1s and (e) Ru3d<sub>5/2</sub> core levels measured with 650 eV photons. The blue and purple spectra in (d) were scaled by indicated factors.

Panel (b) shows the evolution of the Fermi surface MDC along XX and panels (b1)–(b4) are representative ARPES cuts of the pristine- (b1), the NO- (b2) the NO+O<sub>2</sub>- (b3) as well as the merely O<sub>2</sub> exposed surface (b4). While the DNLs *and, this time, the FBSS* remain robust upon NO exposure, O<sub>2</sub> intensifies the FBSS and shifts feature B' upwards by ~500 meV. Four representative angle-integrated spectra in panels (c1) and (c2) reveal the response of the valence band to individual gases (colored arrows in (c)). In contrast to H<sub>2</sub>, NO (red) significantly suppresses feature C with respect to the fresh surface (black), a trend that continues upon further exposure to O<sub>2</sub> (blue). Peak B is slightly reduced by NO, but greatly enhances and shifts by ~0.1 eV upon O<sub>2</sub> exposure (c2), forming a high energy shoulder B' that mimics the shift of feature B' in panel (b3). Feature A, composed mostly of the FBSS,

remains robust upon NO exposure (red in panel (c2)), but sharpens considerably with admixture of oxygen (purple, blue in panel (c2)).

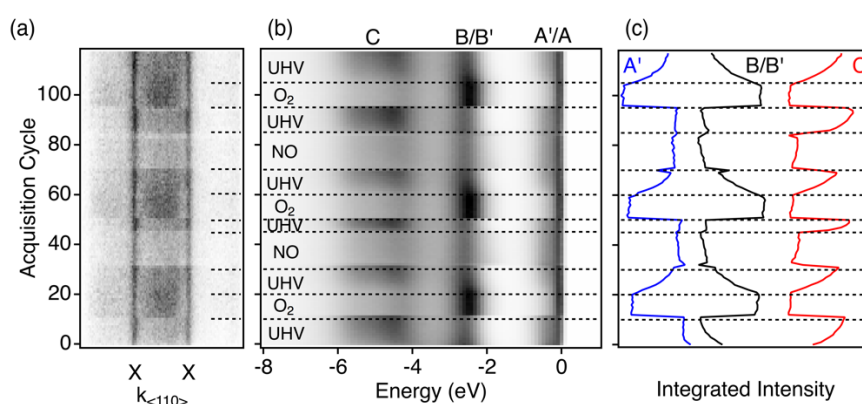
At  $\sim -14.2$  eV, NO produces a feature attributed to  $4\bar{\sigma}$  states of NO molecules bound to 1f-cus-Ru sites.<sup>37–39</sup> This peak is suppressed and shifted by  $\sim 500$  meV upon O<sub>2</sub> admixture (purple, blue, inset in panel c1), marking a change in the surface bond. The O 2s peak at  $\sim -20.6$  eV remains unaffected by NO but intensifies and forms a low energy tail upon surface oxidation.

To gain further insight on the origin of this behavior, we monitor the O 1s (d), the N 1s (e) as well as the Ru 3d (f) core levels on a fresh surface with 650 eV photons. Exemplary spectra are shown for the fresh (black) as well as the NO- (red), the NO & O<sub>2</sub>- (purple) and the O<sub>2</sub> exposed surface, respectively. With respect to the pristine surface, NO slightly lowers the O<sub>br</sub> tail of the O 1s peak, which recovers via surface re-oxidation by O<sub>2</sub>.<sup>29,30</sup> NO further produces a broad high-energy shoulder, that accumulates at  $\sim -531.36$  eV upon simultaneous exposure to O<sub>2</sub> (purple) and flattens once NO is removed from the chamber (blue). This shoulder is indicative of various NO<sub>x</sub> species, which we identify in more detail in the N1s spectra of panel (e):

Features at  $-402.4$  eV and  $-400.6$  eV appear upon NO exposure (red) and are identified with adsorbed NO (the former peak might also point to N<sub>2</sub>O).<sup>43,44</sup> A smaller peak at  $\sim -397.4$  eV is consistent with atomic nitrogen stemming from NO dissociation on 1f-cus-Ru sites.<sup>44</sup> The admixture of O<sub>2</sub> removes this N-peak, lowers (in particular) the  $-400.6$  eV NO peak and produces an additional (non-volatile) NO<sub>2</sub> peak at  $-406$  eV,<sup>43</sup> all of which are completely suppressed by oxygen (blue).

The bonding sites of these NO<sub>x</sub> species are identified in the Ru 3d<sub>5/2</sub> spectra of panel (e). A pronounced shoulder on the low energy side of the Ru 3d<sub>5/2</sub> indicates the large amount of

under-coordinated 1f-cus-Ru sites on the pristine surface (black).<sup>32–34</sup> Upon exposure to NO (red), this shoulder is removed in favor of a pronounced structure on the high energy side along with a reduction of the main Ru 3d<sub>5/2</sub> peak, confirming NO molecules to bind on top of 1f-cus-Ru (NO<sub>ot</sub>). The admixture of O<sub>2</sub> (purple) leads to a competition of NO and O<sub>2</sub> for 1f-cus-Ru sites,<sup>35</sup> which reduces and – upon removal of NO – completely removes this shoulder. The final O<sub>2</sub> step (blue) almost fully oxidizes the surface, which lowers the main Ru 3d<sub>5/2</sub> peak but enhances its unscreened satellite due to the decreased surface metallicity.<sup>32</sup>



**Figure 4: Cyclic adsorption of NO and O<sub>2</sub> on RuO<sub>2</sub> (110).** (a) Evolution of a Fermi surface cut along XX measured with 69 eV photons. One acquisition cycle corresponds to ~49 seconds. (b) Evolution of the angle integrated photoemission signal measured with 69 eV photons. (c) Integrated spectral evolution of peaks C, B and the shoulder A'.

Interestingly, NO does not affect the FBSS, but only lowers valence peak C, a measure of the quantity of 1f-cus-Ru sites as we saw in the last section and as is confirmed in the behavior of the Ru 3d<sub>5/2</sub> high energy shoulder. In contrast to hydrogen, NO *does not remove* O<sub>br</sub>, strong experimental evidence for the FBSS to localize only along the <001> chains formed by O<sub>br</sub> and Ru<sub>br</sub>.

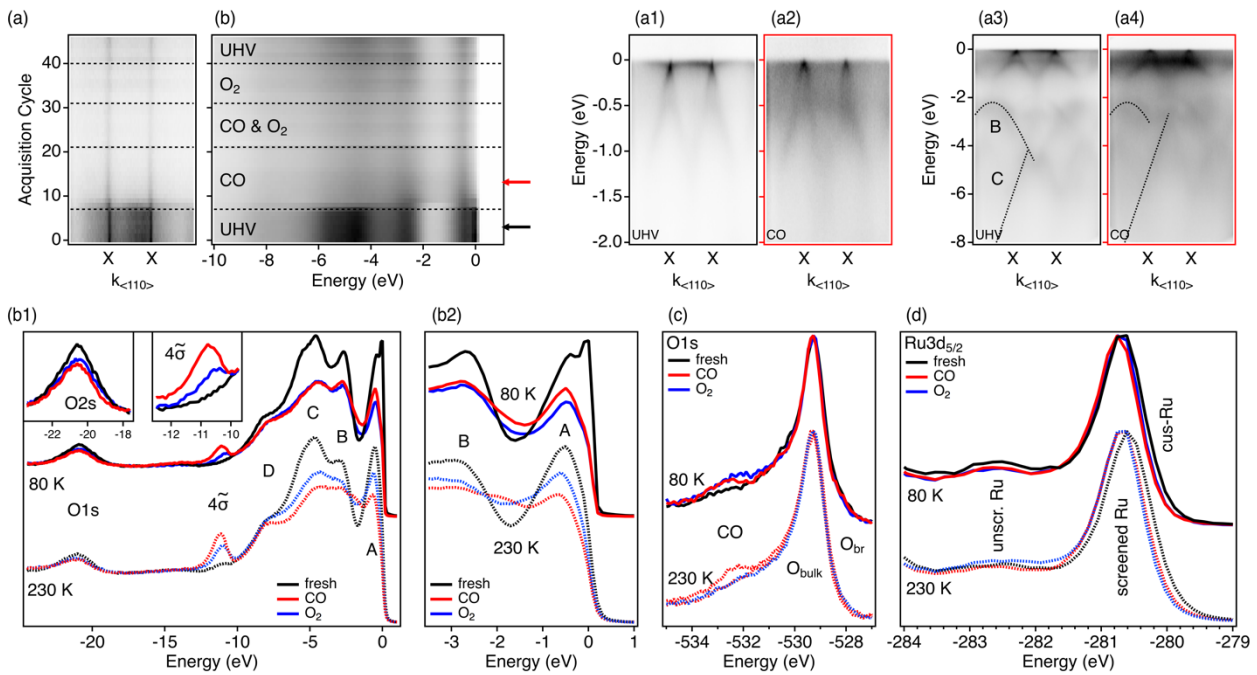
Rather than oxidizing NO, RuO<sub>2</sub> (110) was predicted to be an effective and reversible NO adsorber.<sup>35</sup> We thus test the reversibility of NO adsorption in Figure 4. The experiment is

similar as above, but now built from several cycles of O<sub>2</sub> and NO exposure, interrupted by pumping cycles to ~10<sup>-10</sup> mbar UHV. Panel (a) shows the evolution of the Fermi surface cut along the XX-line, panel (b) the evolution of the integrated valence band, and panel (c) the integrated signal of features A' (shoulder of A), B/B' and C. Additional valence band and core level data are consistent with our previous observations and shown in the supporting information.

We again start with a pristine surface with a pronounced shoulder A' to the FBSS A and a pronounced VB feature C. The first oxidation step instantly suppresses C and A', however, it enhances peak B (related to O<sub>br</sub> species), indicative of an efficient oxidation of the 1f-cus-Ru surface sites. Assisted by the x-ray beam<sup>31</sup> and thermal energy,<sup>30</sup> the follow up UHV cycle reverts this process indicating beam assisted O<sub>ot</sub> desorption.

Upon exposure to NO, peak C instantly decreases, while peak B and shoulder A' hardly change, as NO occupies only 1f-cus-Ru sites. A subsequent UHV cycle desorbs NO, before a new O<sub>2</sub> cycle re-oxidizes the 1f-cus-Ru sites. This proves the RuO<sub>2</sub> (110) surface to be a reversible NO adsorber under UHV conditions.<sup>35</sup>

***CO adsorption and oxidation.*** – Another important model reaction catalyzed on the RuO<sub>2</sub> (110) surface is the oxidation of carbon monoxide.<sup>1,2,35</sup> CO has one electron less than NO but likewise strongly adsorbs with the C side down to 1f-cus-Ru through a donor-acceptor Blyholder mechanism.<sup>41</sup> Unlike NO, adsorbed CO – at sufficiently high temperatures – can react with both O<sub>ot</sub> and O<sub>br</sub> to volatile CO<sub>2</sub> species, which exposes 2f-cus-Ru sites that can bind further bridging CO.<sup>1,2</sup> We use this mechanism to reduce RuO<sub>2</sub> (110) and summarize its impact on the surface electronic structure in Figure 5.



**Figure 5: Adsorption of CO on RuO<sub>2</sub>(110).** (a) Evolution of a Fermi surface cut along XX measured with 69 eV photons. One acquisition cycle corresponds to ~56 seconds. Panels (a1-a4) show representative ARPES zoom-(a1, a2) and overview images (a3, a4) for UHV (a1, a3) and CO (a2, a4) exposure (color-coded arrows in panel b). (b) Evolution of the angle integrated photoemission signal measured with 69 eV photons. Panels (b1, b2) show representative overview (b1) and zoom in (b2) spectra in UHV (black), in NO (red), in NO + O<sub>2</sub> (purple) and in O<sub>2</sub> (blue) (color-coded arrows panel b), normalized to secondary electron background. (c) O1s (normalized to peak height) and (d) Ru3d<sub>5/2</sub> core levels measured with 650 eV photons.

Starting from a freshly cleaved and aligned RuO<sub>2</sub> (110) surface in  $<10^{-10}$  mbar UHV, we monitor both ARPES (panels (a), (a1) - (a4)) and angle integrated spectra (panels (b), (b1), (b2)) while the surface is exposed to  $\sim 1.3 \times 10^{-8}$  mbar of CO (red), subsequently admixed and replaced by an equivalent amount of O<sub>2</sub> (blue), before pumping back to UHV (black). We start with data acquired at ~80 K and compare it to results obtained at ~230 K (dotted lines in (b1), (b2), (c) and (d)): Upon dosage with CO, both the FBSS (panels (a), (a1)–(a4)) and the overall spectral weight instantly collapse (panel b), while the secondary electron background increases – a sign of CO induced surface disorder. In contrast to our experiments with H<sub>2</sub> and NO, however, the signal does not fully recover upon later exposure to O<sub>2</sub> – particularly not at 80 K.



Similar to NO, the angle integrated spectra in panel (b1) (here normalized to secondary background) develop a  $4\tilde{\pi}$  peak at  $\sim -10.8$  eV (red) indicative of CO molecules bound to 1f-cus-Ru sites.<sup>37–39</sup> This peak is – irrespective of temperature – suppressed and shifted by  $\sim 300$  meV, *but not removed* by O<sub>2</sub> (blue). A significant suppression of the O 2s peak at  $\sim 20.6$  eV indicates surface oxygen removal by CO (red), again remarkably unaffected by O<sub>2</sub> (blue), and again seen at both 80 and 230 K. This substitution of surface oxygen sites with CO is mimicked by the suppression of the valence features C, B and A, which only recover slightly upon O<sub>2</sub> exposure at 230 K. Interestingly, CO exposure shifts the dispersing band feature C in panels (a3) and (a4), a similar effect as we observed for surface oxidation in the previous sections.

In the 80 K O 1s core level of a fresh surface (solid lines in panel (c)), CO adsorption is reflected by the formation of a high energy tail (red), which gains weight upon further exposure to O<sub>2</sub> (blue). At 230 K, CO oxidation to volatile species is thermally more activated as compared to 80 K,<sup>2</sup> resulting in a reduction of the O 1s CO tail. The removal of the cus-Ru 3d<sub>5/2</sub> shoulder and the reduction of the screened Ru3d<sub>5/2</sub> satellite in panel (d) reflects the irreversible coordination of surface cus-Ru sites with CO molecules at 80 K, while slightly activated CO oxidation at 230 K allows for the surface to somewhat re-oxidize (blue).

**Impact.** – Our results for the drosophila system RuO<sub>2</sub> (110) underline two important aspects: First, the modification of an ordered catalyst's surface band structure through site selective surface reactions can be used to monitor catalytic processes *in operando* and with *momentum resolution*. Second, but more importantly, the delocalized surface electronic band structure of the catalyst, i.e., *momentum carrying Bloch states*, actively participate in the catalytic process.

Tapping into this resource sheds new light on traditional tenets of surface chemistry, such as the fully local Blyholder picture, and offers new tools to bridge the gap between fundamental solid-state physics, surface chemistry and heterogeneous catalysis. In particular, our approach will prove valuable with respect to catalysts based on transition metal oxides, whose electronically active  $d$ -electrons are often subject to inherent many body effects<sup>20,22,45</sup> that directly reflect in the one-electron removal spectral function measured by ARPES. The method further assists in quantum engineering approaches based on topological principles, promising a route towards more effective catalysts.<sup>46</sup>

Whether topology and/or correlation physics such as magnetism affect surface reactions on RuO<sub>2</sub>,<sup>22,28</sup> or other systems, is difficult to be answered experimentally and has yet to be shown. We point out, however, that such efforts will crucially depend on powerful spectroscopy tools based on VUV and soft X-rays that are available only at the synchrotron. In view of the current global upgrade to 4<sup>th</sup> generation diffraction limited storage rings of unprecedented brilliance along with novel end-stations, routine angle resolved experiments at near ambient conditions might become state-of-the-art in the long run. Endowed with additional time and spin resolution, such experiments could even give an *in operando* view on catalytic spin transfer and elucidate the role of surface magnetism in heterogeneous catalysis.<sup>47</sup>

## Methods:

***DFT-calculations.*** – Surface band structure calculations of the RuO<sub>2</sub> (110) surface were performed with the Vienna ab initio Simulation Package (VASP)<sup>48,49</sup> in the framework of Density Functional Theory, using the projector augmented wave method (PAW). Exchange and correlation effects were handled using the generalized gradient approximation (GGA) by

Perdew, Burke, and Ernzerhof (PBE).<sup>50</sup> While the effect of spin-polarization on the surface properties of RuO<sub>2</sub> is known from Ref. 28., we found satisfactory agreement with our ARPES results already at the non-spin-polarized level. Calculations have been performed using a plane wave cut-off of 600 eV on a  $4 \times 4 \times 1$  k-point mesh, and SOC was included self-consistently. The slab consisted of 10 octahedral RuO<sub>2</sub> layers which account for a thickness of 32 Å. More than 10 Å of vacuum were included to screen the interaction between the repeated images in the periodic boundary conditions setting. The dimensions of the unit cell was  $3.105 \times 6.359 \times 45.000$  Å<sup>3</sup> and contained 60 atoms (20 Ru + 40 O) in the stoichiometric case, 62 atoms (20 Ru + 42 O) in the oxygen rich case and 58 atoms (20 Ru + 38 O) in the ruthenium rich case. In every instance, the surface of the supercell has been relaxed such that the total force acting on each atom is smaller than 0.01 eV/Å. The width of the smearing is 0.2 eV and the Methfessel-Paxton method of order 1 has been used. Finally, DOS calculations have been performed using a  $16 \times 16 \times 1$  *k*-point mesh and the tetrahedron method (with Blöchl corrections).

***μARPES experiments.*** – were performed at the Microscopic and Electronic Structure Observatory (MAESTRO) of the Advanced Light Source (ALS) in Berkeley, USA. RuO<sub>2</sub> single crystals were grown by chemical vapor transport and are from the same batch as samples that we used in Refs. 26 and 27. Crystals were cleaved in ultra-high vacuum ( $< 5 \times 10^{11}$  mbar), exposing small (~50 μm) clean (110) surface domains, as confirmed by Laue diffraction. Details on extensive physico-chemical characterisation of the RuO<sub>2</sub> single crystals is provided in the supporting information of Ref. 26 and in Ref. 27.

Data was collected with p-polarized light, employing a hemispherical Scienta R4000 electron analyzer. The beam spot size was ~20 μm in the photon energy range below 200 eV. The analyzer slit was oriented along the [110] crystal axis, with the [110] surface vector pointing towards the analyzer. The total energy and momentum resolution of the experimental setup

was better than 20 meV and  $0.01 \text{ \AA}^{-1}$ , respectively. In operando dosing of high purity gases (99.999%) was performed through a leak valve up to a pressure of  $\sim 1.3 \times 10^{-8}$  mbar. The gas lines were purged prior to experiment. Gases in the chamber were monitored by a residual gas analyzer (RGA).

## Associated Content

**Supporting Information.** – The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx.

- Additional DFT slab calculations.
- Additional photoelectron spectroscopy data on NO cycling.

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