A Full Monolayer of Superoxide: Oxygen Activation on the Unmodified $Ca_3Ru_2O_7(001)$ Surface

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Supplementary Information

Impurities

The compositions of two samples of the same batch were determined via inductively coupled plasma mass spectroscopy (ICP-MS) using laser ablation for direct analysis of the solid samples. Several impurities (Ti, Sr, Ba and Mg) were found; their mass fractions are listed in Table S1. Both samples had comparable impurity contents, the main impurities being Ti and Sr. This is consistent with the observation of point defects in STM images of as-cleaved samples. The amount of impurities observed by STM usually varies when measuring samples from different batches.

Element	Sample 17	Sample 22
Ti [ppm]	135.6 ± 0.20	135.3 ± 0.39
Sr [ppm]	79.9 ± 1.43	80.1 ± 0.77
Ba [ppm]	4.4 ± 0.19	4.2 ± 0.13
Mg [ppm]	13.4 ± 0.27	14.6 ± 1.12

Table S1: Mass fractions of impurities measured by ICP-MS. Quantification by NIST612 and ^{44}Ca as internal standard.

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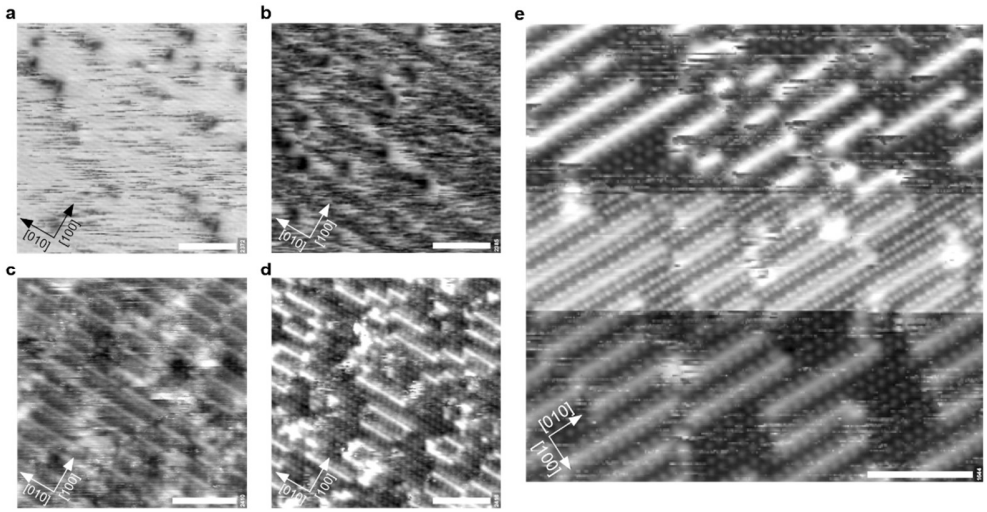

Figure S1: STM images of increasing O_2^- coverage. The cumulative doses of O_2 at 110 K in panels a, b, c and d are 0.075, 0.15, 0.4 and 0.6 L, respectively. Common STM parameters: V_{sample} = +1.0 V, T_{sample} = 78 K. All scale bars correspond to 5 nm. (a) The O_2^- appear as streaks across surface defects and on the pristine surface. STM parameters: I_{tunnel} = 0.1 nA. (b) The streak density increases, small parts of the pristine surface (bright areas) are still visible. STM parameters: I_{tunnel} = 0.025 nA. (c) The streak density decreases. O_2^- arranged in rows of bright spots along the [010] direction become visible. Uncovered substrate lines appear as bright rows in [010] direction. STM parameters: I_{tunnel} = 0.05 nA. (d) O_2^- is clearly visible, locally forming the (2×1) overlayer (see Figure 5) and covering most of the sample. Here one O_2^- molecule appears as one bright spot, instead of the usual pair of bright and dark spot. The tip change between the one-spot and two-spot contrast is shown in panel (e). Uncovered substrate lines appear as bright rows of various lengths in [010] direction. STM parameters: I_{tunnel} = 0.05 nA. (e) STM image showing a tip change between the one-spot and two-spot contrast of the O_2^- molecules arranged in the (2×1) configuration. STM parameters: V_{sample} = +1.5 V, I_{tunnel} = 0.1 nA.

Tip-induced diffusion of O_2^-

When scanning at higher sample bias voltages of roughly -1 or +2 V the O_2^- is desorbed by the tip and the pristine surface is revealed, see Figure S2. After desorbing the O_2^- from a specific area by scanning at higher bias voltage, molecules from the surrounding area diffuse back to the area again during subsequent STM images taken at the usual, lower sample bias voltage, see Movie S1. The movie shows 16 sequential STM images. STM parameters: V_{sample} = +0.8 V (frame 2 and 6: V_{sample} = +0.4 V), I_{tunnel} = 0.1 nA, T_{sample} = 78 K;

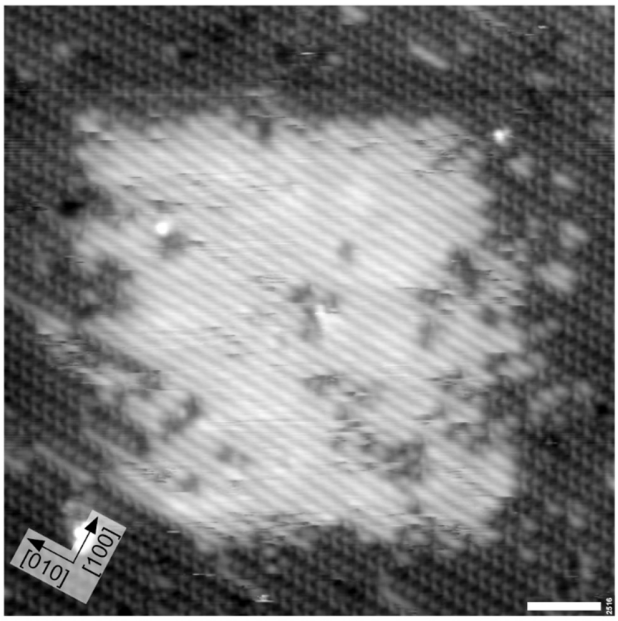

Figure S2: STM image after scanning a part of a (2×1) overlayer with a bias voltage of +2.0 V, removing the majority of O_2^- and revealing the uncovered surface. The few molecules remaining in the previously scanned area are influenced by the tip and appear streaky. The scale bar corresponds to 3 nm. STM parameters: V_{sample} = +1.0 V, I_{tunnel} = 0.1 nA, T_{sample} = 78 K.

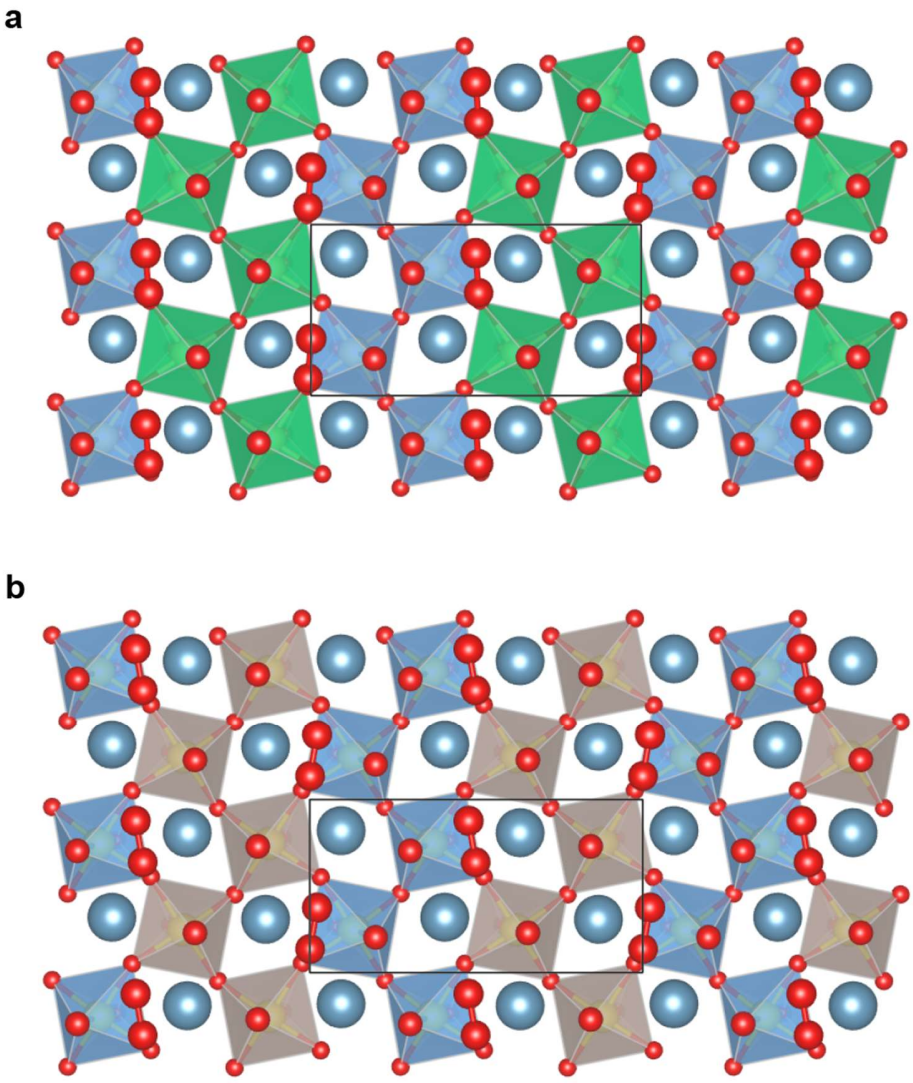

Figure S3: (2×1) overlayer. The color marks volume changes of the RuO_6 octahedra compared to the pristine surface: blue – contraction, green – expansion, grey – negligible change. (a) HSE06 model, contraction 5.2 %, expansion 3.0 %. (b) vdW-DFT model, contraction 3.2 %.