

Supplemental Information for:

Controlling the termination and photochemical reactivity of the SrTiO₃ (110) surface

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0. Overview

This document contains the supplemental information supporting the main text of the manuscript. Specifically, AFM images are given for samples annealed in air at 1200 °C for different lengths of time, after photo-reduction (S1) and before any photo-reaction (S2). These images are related to the images given in Figure 3 of the main text, showing photo-oxidation of the same surfaces. Also, AFM images are given for samples annealed in air at 1100 and 1000 °C, for both 0 and 6 h each, after photo-reduction (S2) and before any photo-reaction (S4). These images are related to the images given in Figure 4 of the main text showing photo-oxidation of the same surfaces. None of these samples were annealed with powder reservoirs. The images support the complementary nature of the photo-reactive surfaces and the different reactive nature of the two sets of terraces on the surface.

1. Silver photo-reduction for samples annealed at 1200 °C

Fig. S1 shows topographic AFM images after silver photo-reduction of four samples annealed for different amounts of time at 1200 °C in air, without powder reservoirs. The surfaces were imaged at the same locations as in Fig. 3 of the main text. The bright contrast in the images corresponds to silver deposits. The fractional coverages of silver (i.e., the photocathodic area fractions) are 53 , 40, 11, and 2 % for the samples annealed

for 0, 3, 12, and 24 h, respectively. When compared to Fig. 3, the surface reactivity is complementary: photo-reduction and photo-oxidation reactions happen on different terraces. Thus, while the photoanodic area fraction increases with annealing time, the photocathodic area fraction decreases with increasing annealing time.

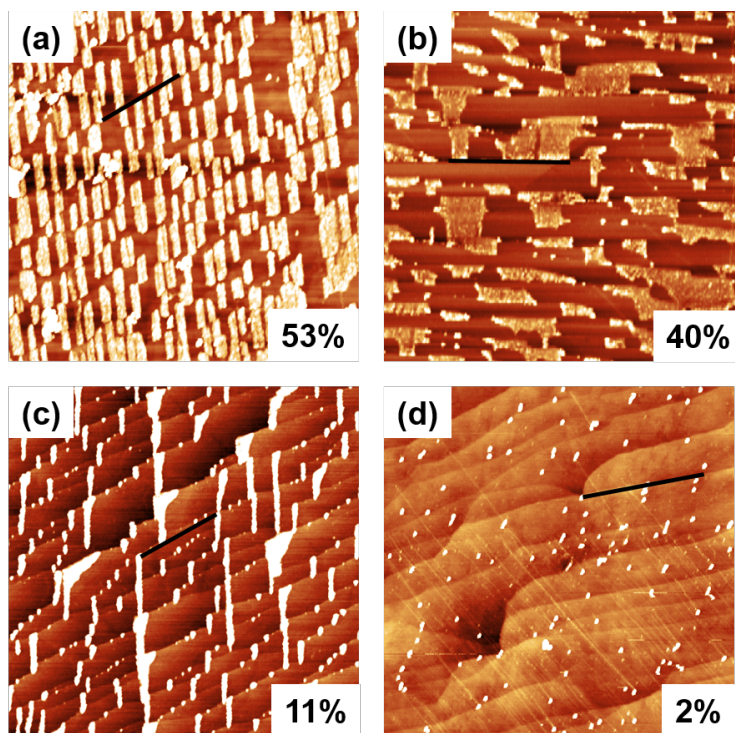


Figure S1. Surface topography AFM images of the photo-reduced silver distribution on samples annealed at 1200 °C for (a) 0 hour (b) 3 hours (c) 12 hours and (d) 24 hours. All images are 5 μm \times 5 μm laterally and the dark-to-light vertical scales are 0 – 4 nm. The percentage in lower corner marks the fractional coverage of photocathodic terraces in each image. The black lines mark the same locations that are marked in Fig. 3 and Fig. S2.

2. Surface topography for samples annealed at 1200 °C

Fig. S2 shows topographic AFM images of the clean, annealed surfaces of the same samples and in the same as the images of Fig. 3 and Fig. S1. The two sets of terraces (described in the main text for Fig. 2) are evident in Fig. S2(a) and (b). Again, the set of terraces with bright contrast in topography are reactive for photo-reduction (are

photocathodic). The topographic contrast is not as obvious in Fig. S2(c) and (d). In S2(c), the edges of terraces where the step edge changes direction is often brighter, and this does correspond to the reactivity in Fig. S1(c). But the relative area is only 11 % photocathodic, and thus these terraces are smaller and narrower, and less obvious. There is only one set of terraces in S2(d), and therefore no contrast; this surface is 100 % photoanodic (Fig. 3). The small (2 %) photocathodic activity observed in S1(d) is not correlated with any terrace feature.

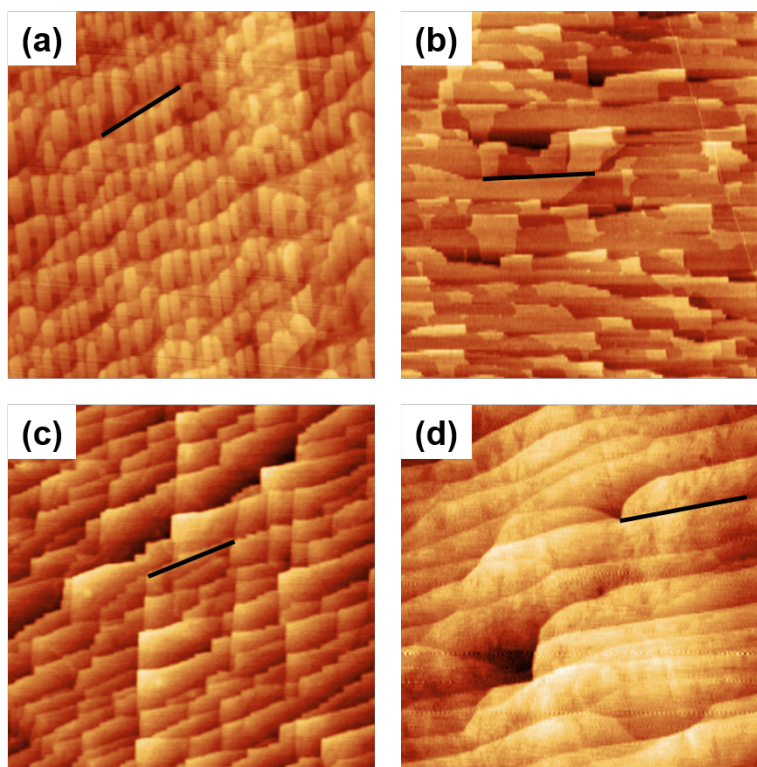


Figure S2. Surface topography AFM image of clean surfaces of samples annealed at 1200 °C for (a) 0 hour (b) 3 hours (c) 12 hours and (d) 24 hours. All images are 5 $\mu\text{m} \times 5 \mu\text{m}$ laterally and the dark-to-light vertical scales are 0 – 2 nm. The black lines mark the same locations that are marked in Fig. 3 and Fig. S1.

3. Silver photo-reduction for samples annealed at 1100 °C and 1000 °C

Figures S3(a) and (b) (Figures S3(c) and (d)) show topographic images of samples heated to 1100 °C (1000 °C) for 0 h and 6 h, respectively, after the photo-reduction of

silver. Images show the same locations as in the images in Fig. 4 of the main text. The bright contrast corresponds to the silver deposits. The sample shown in Fig. S3(c) has the smallest terraces and, because the size of the silver particles produced after reaction are significant in comparison to the terrace width, the terrace contrast becomes grainy. The fractional coverage of photocathodic terraces decreases with annealing time, from 60 to 32 % (80 to 65 %) for 0 h and 6 h anneals at 1100 °C (1000 °C). When compared to Fig. 4, the surface reactivity is complementary: photo-reduction and photo-oxidation reactions happen on different terraces and the photocathodic area fraction decreases with the annealing time (and temperature).

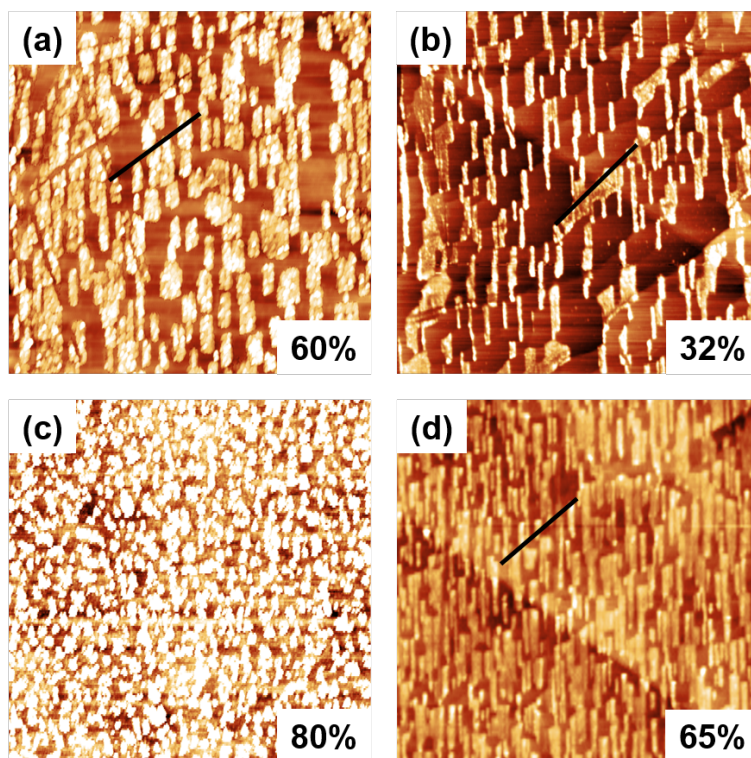


Figure S3. Surface topography AFM images after silver photo-reduction for samples annealed at 1100 °C for (a) 0 hour (b) 6 hours and samples annealed at 1000 °C for (c) 0 hour (d) 6 hours. (a), (b), and (d) are 5 $\mu\text{m} \times 5 \mu\text{m}$ and (c) is 3 $\mu\text{m} \times 3 \mu\text{m}$ laterally. The dark-to-light vertical scales are 0 – 4 nm. The black lines mark the same locations that are marked in Fig. 4 and Fig. S4.

4. Surface topography for samples annealed at 1100 °C and 1000 °C

Fig. S4 shows topographic AFM images of the clean annealed surfaces of the same samples and at the same locations as in Fig. 4 and Fig. S3. The two sets of terraces (described in the main text for Fig. 2) are evident for all samples in Fig. S4. One set of terraces exhibits a range of bright contrast, and these terraces sit upon another set of terraces that exhibit a darker range of contrast. The scratches (straight dark lines) in Fig. S4(d) were inadvertently introduced during handling, and thus was not present when the images in Fig. 4(d) and Fig. S3(d) were recorded. Comparing Fig. S4, S3, and 4, it is clear that the bright set of terraces in topography are reactive for photo-reduction (are photocathodic), while the darker set of terraces in topography are reactive for photo-oxidation (are photoanodic). This correlation is less clear for the sample shown in Fig. (c) (for each figure), because its terraces are narrow and the distribution of reaction products make the image appear grainy.

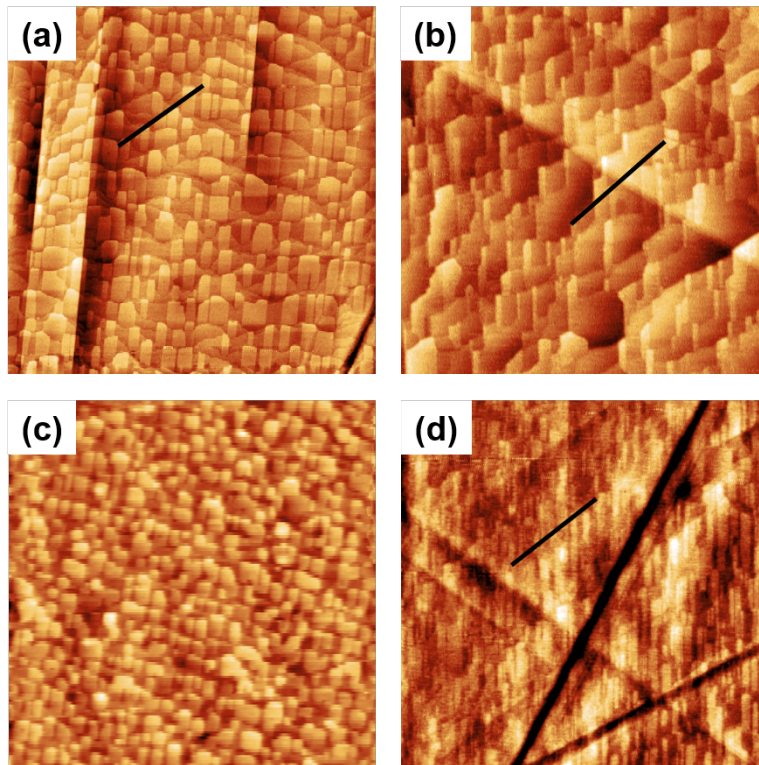


Figure S4. Surface topography AFM images of clean surfaces of samples annealed at 1100 °C for (a) 0 hours and (b) 6 hours and samples annealed at 1000 °C for (c) 0 hours and (d) 6 hours. The dimensions of the images are: (a), (b), and (d) 5 $\mu\text{m} \times 5 \mu\text{m}$ and (c) 3 $\mu\text{m} \times 3 \mu\text{m}$ laterally. The dark-to-light vertical scales are 0 – 2 nm. The black lines mark the same locations that are marked in Fig. 4 and Fig. S3.