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Water-hydroxyl phases on an open metal surface: breaking the ice rules

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Supporting Information:

High coverage [1 $\bar{1}$0] H_2O:OH chains.

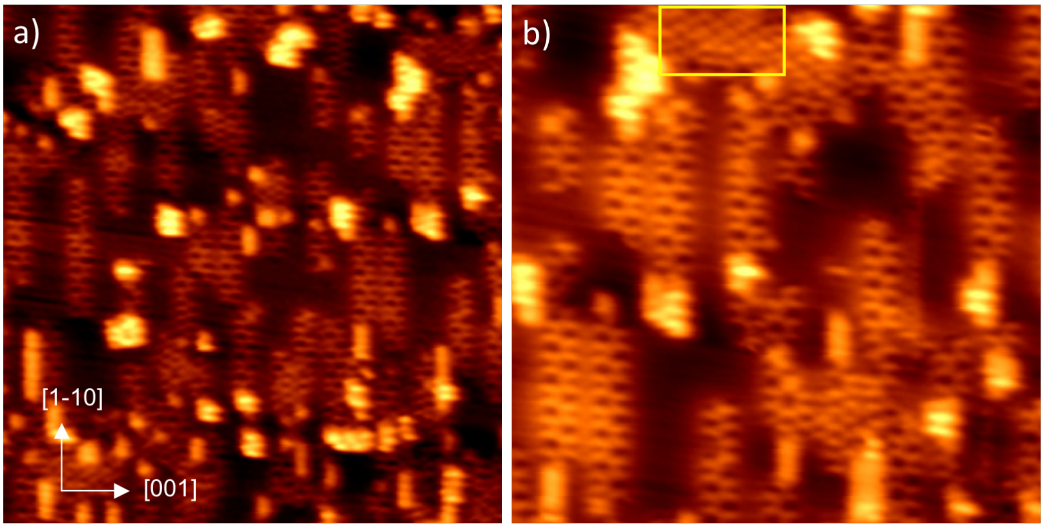

Figure S1. STM images of a high coverage surface formed by dosing water onto an O pre-treated Cu(110) surface at T<200 K. (a) 250 × 260 Å^2 and (b) 160 × 155 Å^2 respectively. The rectangle at the top of (b) shows a region of the c(2 × 2) structure. Bright features are second layer water adsorbed above hydroxyl/water structures. I= -0.35 nA, V= - 190 mV.

When water is adsorbed on a surface whose initial O coverage is above ca. 0.1 ML, the TPD peaks at 185 K and 220 K, associated with decomposition of the c(2 × 2) 2H_2O:1OH structure and 1H_2O:1OH chains respectively, are replaced by a single peak near 200 K, whose shape becomes extremely sensitive to the O coverage. In order to test if any new water/hydroxyl phase is formed under these conditions, we imaged the structures formed by reaction at higher initial oxygen coverage. Figure S1 shows the surface after dosing water onto ca. 0.13 ML of O as the surface is cooled below 200 K. The surface shows 1D chains and islands of the c(2 × 2) structure (e.g. rectangle in Figure S1b), as well as bright clusters of second layer water adsorbed on top of the chains. Although short sections of Z type chain are present, the majority of the $[1\bar{1}0]$ chains are P type, having a $4a_{Cu}$ repeat along $[1\bar{1}0]$. Adjacent chains show no regular separation on the [001] direction, or registry in the $[1\bar{1}0]$ direction, indicating that the chains do not interact directly with each other. This behaviour is consistent with termination of the chains by OH preventing any direct H bonding between adjacent chains. The preponderance of P type chains might suggest that these are slightly more stable than the Z type, but DFT does not predict a significant difference in adsorption energy. Although the ordering of the c(2 × 2) structure and $[1\bar{1}0]$ chains is often incomplete, no new structural motifs are observed.

Growth of c(2 × 2) structure from $[1\bar{1}0]$ H_2O:OH chains.

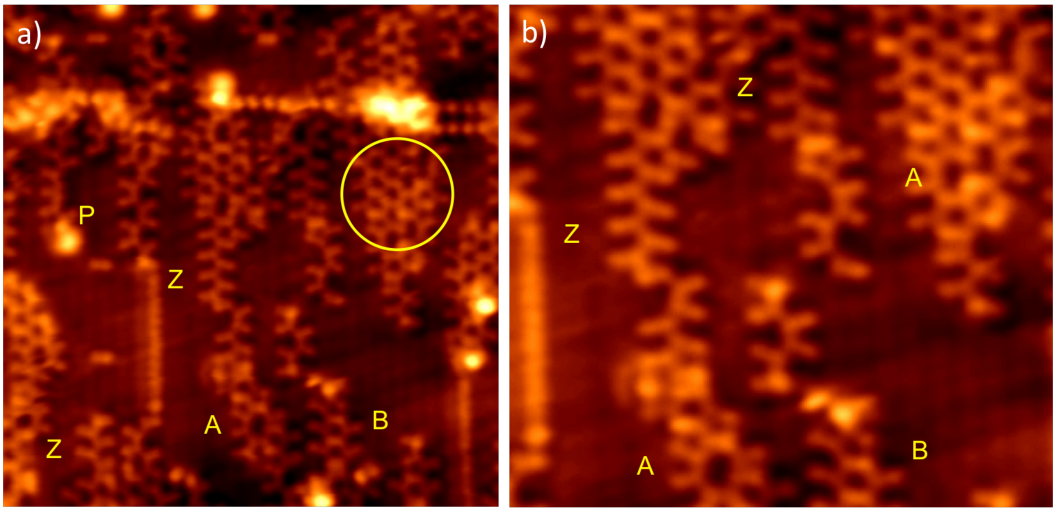

Figure S2. STM images (a and b) showing co-existing dissociated water structures on Cu(110). Water was dosed onto an oxygen pre-treated Cu(110) surface at 110 K. Image shows unreacted CuO chains (top right in a), regions of the c(2 × 2) structure (circled), ring type defects (marked A), as well as the Z and P type chains. In addition we see and linear features related to the $[1\bar{1}0]$ H_2O:OH chains but with a hexagonal backbone in place of the simple linear water chain (marked B). (114 × 112 $Å^2$ and 75 × 70 $Å^2$, respectively. $I_t = -0.38$ nA, $V_t = -196$ meV. Axes as shown in figure S1.)

Partial reaction of O with water at lower temperatures (110 K) creates complex structures, including structures intermediate between the $[1\bar{1}0]$ H_2O:OH chains and the c(2 × 2) structure, Figure S2. As well as Z and P type chains, ring defects (marked ‘A’) and small clusters elongated along the $[1\bar{1}0]$ direction are observed, marked ‘B’ in Figure S2. These B chains have the same edge termination as the Z chains and c(2 × 2) islands, but instead of having a single chain of water forming the backbone, the chains are one hexagonal unit wide. These clusters represent an intermediate structure in the growth of 1D chains into the c(2 × 2) structure, and are metastable, not being present in higher temperature images. Again, apart from such metastable clusters, no distinct new structural features were observed that were not related to the $[1\ \bar{1}0]$ (H_2O:OH) chains and c(2 × 2) ($2H_2O$:OH) structure.

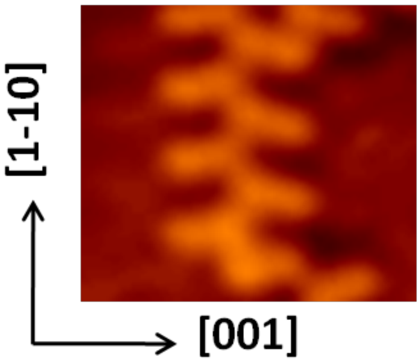

Figure S3. Expansion of a section of Z type chain from Fig. S2 showing how the side branches point slightly along the chain rather than exactly perpendicular along [001].

Registry of the c(2 × 2) structure and $[1\ \bar{1}0]$ H_2O:OH chains

Figure S2(a), taken with the scan direction perpendicular to the chain structures, shows several sections of Z type chain with different orientation, the one in the centre of the image having the branches pointing ‘down’ the chain while that in the lower left corner has the branches pointing ‘up’ the chain. Figure S3 shows an expanded image of the former, emphasising the orientation of the branches along the chain. In fact we find the edge termination of all the mixed water/hydroxyl structures shows an $a_{Cu}/2$ offset between the location of the edge groups and the position of the closed hexagonal rings.

Figure S4 shows the centre portion of Figure S2a with the Cu lattice sites marked, these are interpolated from the position of the (2 × 1) CuO added row chain at the top of the image, assuming the bright spots imaged are the Cu atoms of the -CuO- chains.[1] On this basis, the backbone of both the P and Z type chains lies directly above the Cu close packed rows, as does the c(2 × 2) network, consistent with the structures found from DFT. The registry of features along the $[1\ \bar{1}0]$ direction is more difficult to define exactly from these images, since the individual molecules are not imaged as separate features and the separation of atop and bridge sites (1.2 Å) can be masked by thermal drift in the variable temperature STM. Nevertheless, the location of the c(2 × 2) structure in the centre of the image is consistent with an atop H_2O/OH adsorption site[2] while the branches of the 1D chains are displaced towards the bridge site; in both cases this is consistent with the calculated minimum energy structures.

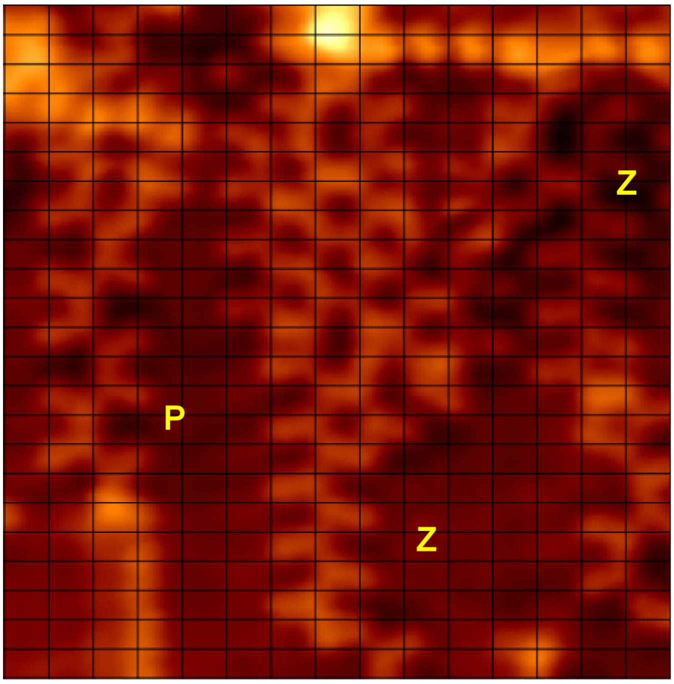

Figure S4. Section of Fig. S2a showing the Cu lattice sites interpolated from the CuO chains at the top of the image superimposed on the P and Z type H_2O:OH chains and the c(2 × 2) (2H2O:OH) structure. (Alignment as Fig. S1, 55 × 60 Å^2).

References

1. Ruan, L.; Besenbacher, F.; Stensgaard, I.; Laegsgaard, E., Phys. Rev. Lett. 1993, 70, 4079.
2. Forster, M.; Raval, R.; Hodgson, A.; Carrasco, J.; Michaelides, A., Phys. Rev. Lett. 2011, 106, 046103.