Supplementary Information for 'Structure of the Clean and Oxygen-covered Cu(100) Surface at Room Temperature in the Presence of Methanol Vapor in the 10 to 200 mTorr Pressure Range'

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We provide here additional images, spectra, and discussion supporting the main text.

1. Identification of gas phase species with mass spectroscopy

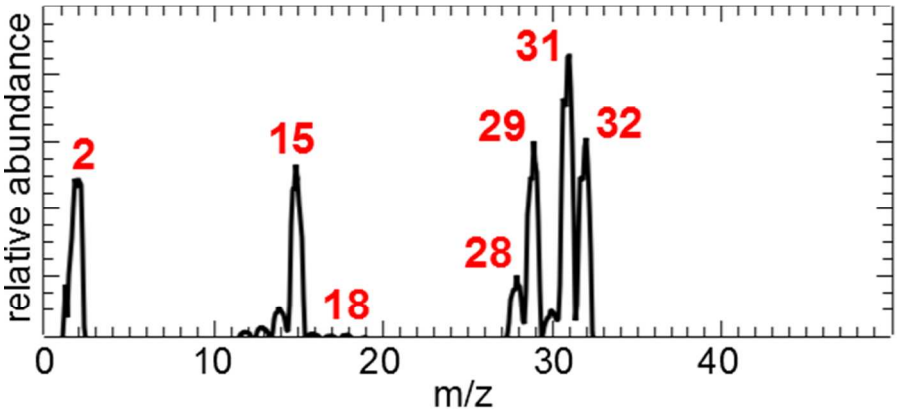

Figure S1 Mass spectrum showing the background gas composition after methanol is dosed into the HPSTM chamber. Except for H_2 (mass 2), CO (mass 28) and water (masses 18 and 17) peaks, all the

peaks arise from methanol (species with a m/z lower than 32 are due to dissociation via the ionizer filament). The CO peak is mostly due to dissociation of methanol by the ion pumps. The ion pumps and ion gauges were switched off during our experiments.

2. Cu(100) surface at 1×10^{-10} Torr

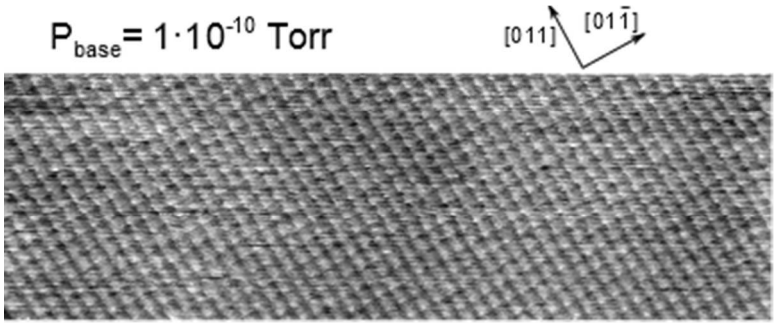

Figure S2 Atomically resolved STM image of the Cu(100) prepared at a base pressure of 1×10^{-10} Torr. Imaging parameters are V_s=0.3 V and I_t=3.6 nA.

3. More images and spectra on the oxygen covered surface

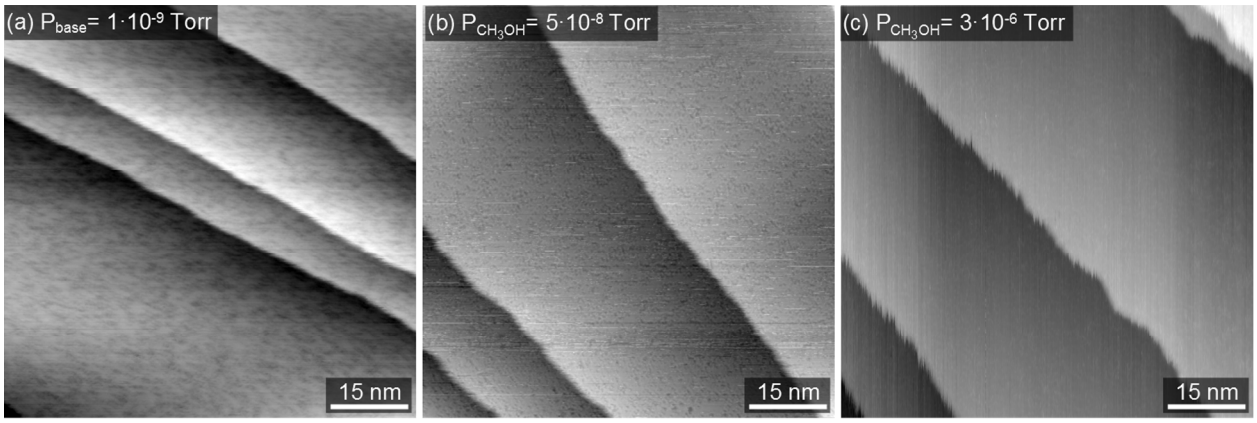

Figure S3 STM images of the Cu(100) surface at 298 K: (a) after preparation at a base pressure of 1×10^{-9} Torr (mostly water in the background), in the presence of (b) 5×10^{-8} Torr and (c) 3×10^{-6} Torr of gas phase methanol, respectively. (a) and (b) were scanned in the horizontal direction, whereas (c) was scanned in the vertical direction. As the pressure is increased, black spots due to atomic oxygen and OH are removed from the surface by reaction with methanol producing methoxy and formate, which are both mobile on

the surface and result in fuzzy step edges. Imaging parameters are V_s=0.5 V and I_t=0.5 nA for all the images.

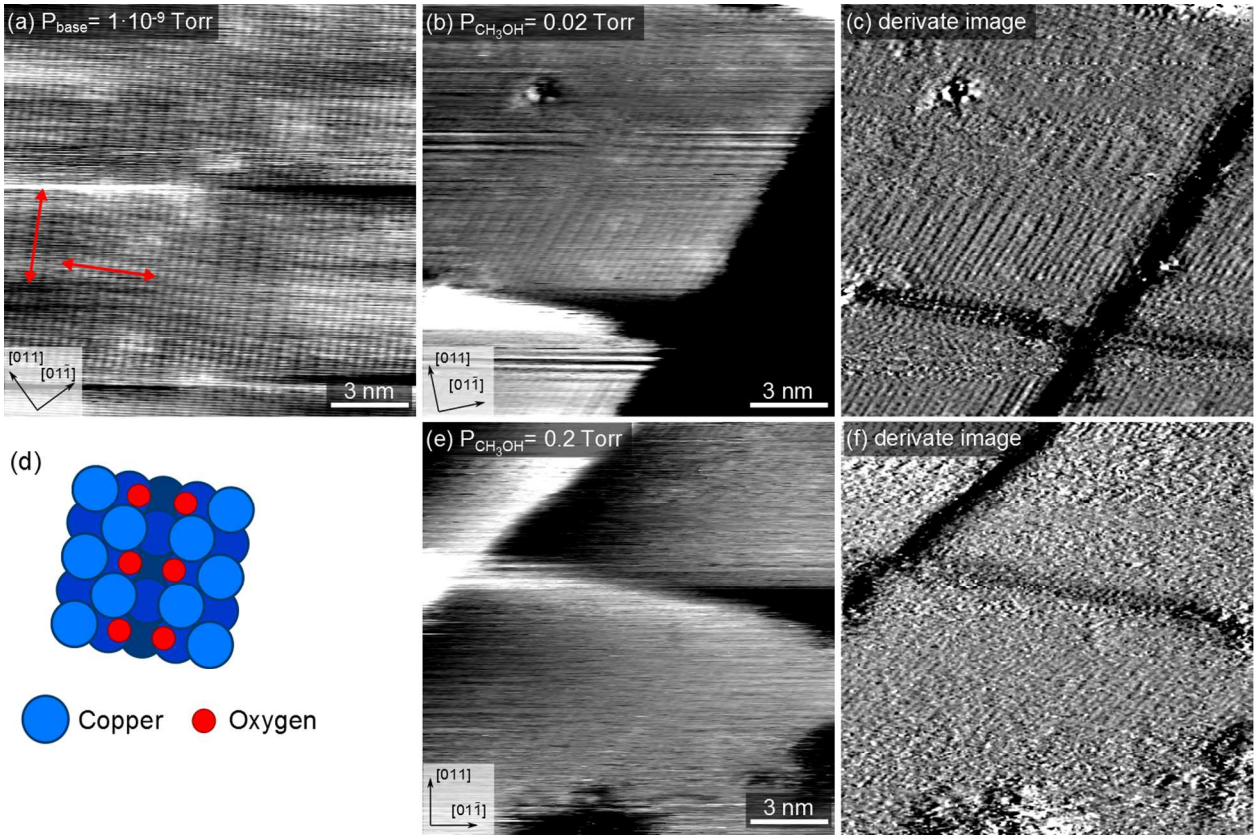

Figure S4 (a) Atomically-resolved STM image of the Cu(100)-(2√2×√2)R45°-O (also referred to as the 'missing row' because one of every for atomic rows is missing) surface at a base pressure of 1×10^{-9} Torr. (d) is the ball model of this surface structure. As indicated by the arrows in (a), this surface structure can be found along the equivalent <001> directions. (b-c) Although the resolution gets worse in the presence of CH_3OH in the gas phase, this structure appears intact after exposure to 0.02 Torr CH_3OH for 0.5 hours. (e-f) The structure also remained intact 5 minutes after the CH_3OH pressure was increased to 0.2 Torr. (d) and (f) are the derivate images of (c) and (e), to enhance the resolution on terraces. Imaging parameters are V_s=0.5 V and I_t=0.5 nA for all the images.

We also provide spectroscopic evidence of the intactness of the Cu(100)-(2√2×√2)R45°-O structure with APXPS.

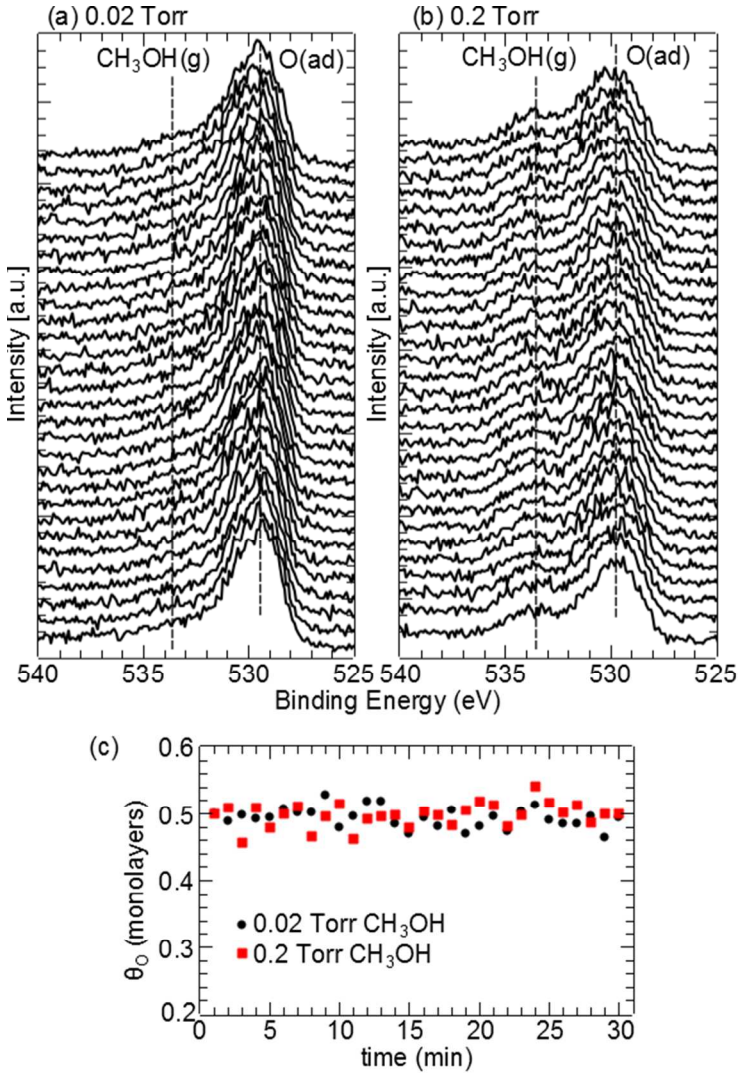

Figure S5 O 1s region of XPS spectra of Cu(100)-(2√2×√2)R45°-O in the presence of (a) 0.02 and (b) 0.02 Torr CH_3OH at 298 K, recorded at one minute intervals (upward direction for increasing duration). (c) The change in the atomic oxygen coverage over time.

4. Transient changes on the Cu(100) surface after dosing methanol

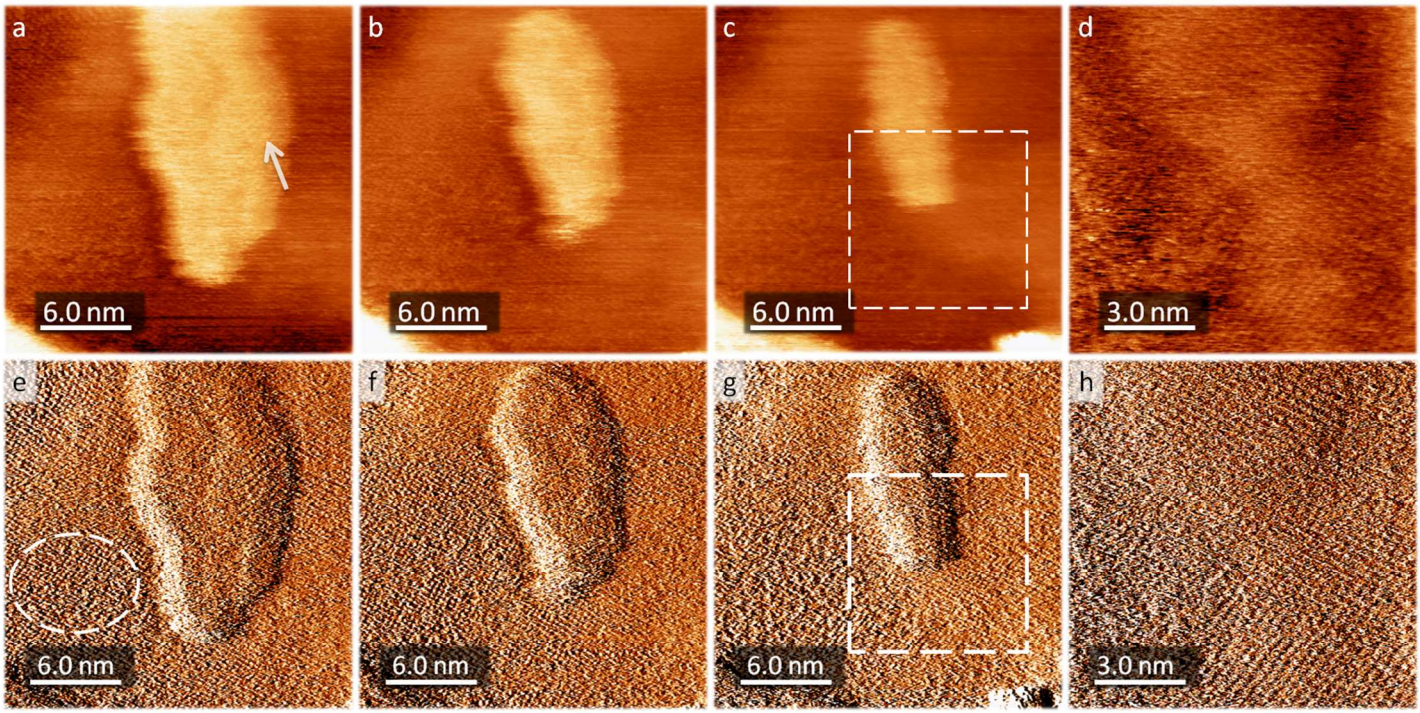

Figure S6 Time-lapse STM images revealing the transient changes in the surface structure after dosing 0.02 Torr methanol (The first image is taken approximately 2 hours after dosing methanol). T=0 s, 346 s, 692 s, and 2338 s, respectively from a to d. e-h are the derivative images of the corresponding topography images above, which enhances the resolution of the inner structure. The arrow in a points out to the faint ordered 'transient' structure; the oval shows a location with clear resolution of the steady state structure in images e, f, and g. The dashed box inside c marks the position of the image in d. The transient structure, which appears 50-60 pm higher in apparent STM height than the rest of the surface, disappears after some time when the steady-state is reached. Imaging parameters are V_s=0.3 V and I_t=0.5 nA for all the images.

5. XPS Binding energy scale table

Table S1 Approximate (±0.3 eV) XPS binding energies of all the species discussed in the main text. Exact positions differ for adsorbed species due to interaction with the neighboring species. Position of the gas phase components also differ due to the changes in the sample work function.

Species	**C 1s**	**O 1s**
Methoxy	**285.3 eV**	**530.3 eV**
Formate	287.5 eV	531.4 eV
Methanol (gas)	288 eV	534.2 eV
Molecular methanol (adsorbed)	287.4 eV	533.8 eV
Molecular methanol (multilayers)	287.9 eV	534.5 eV
Atomic oxygen	-	529.6 eV
Hydroxyl	-	531.1 eV
Molecular water	-	534 eV
Formaldehyde (gas)	290 eV	534.5 eV
Oxygen (gas)	-	539 eV
Carbonate	289.3 eV	532 eV
CO2 (gas)	292.8 eV	536.5 eV

As it can be seen in this table, the methoxy species, which dominate both the C 1s and O 1s spectra, are well separated from all the other species.