

## **Supporting information**

# **Methanol Oxidation Catalyzed by Copper Nanoclusters Incorporated in Vacuum-Deposited HKUST-1 Thin Films**

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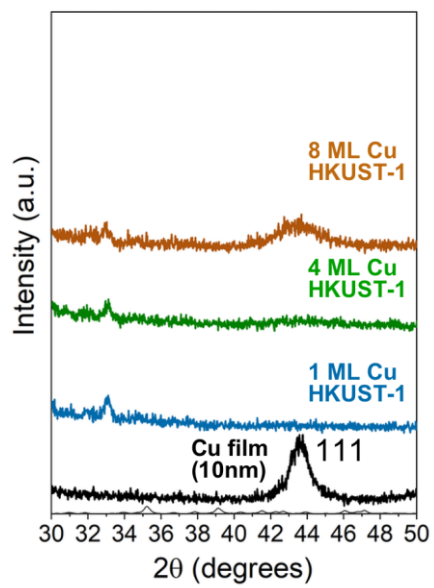


Figure S1. XRD patterns of a polycrystalline Cu film (10 nm thick), 1 ML, 4 ML, and 8 ML Cu-HKUST-1 films in the range of 30° – 50° of 2θ.

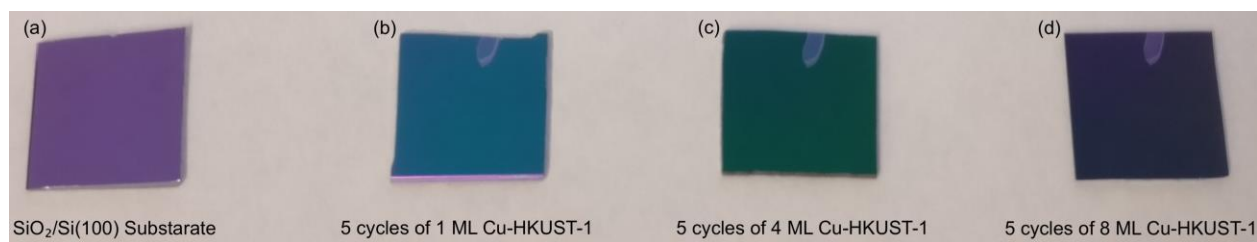
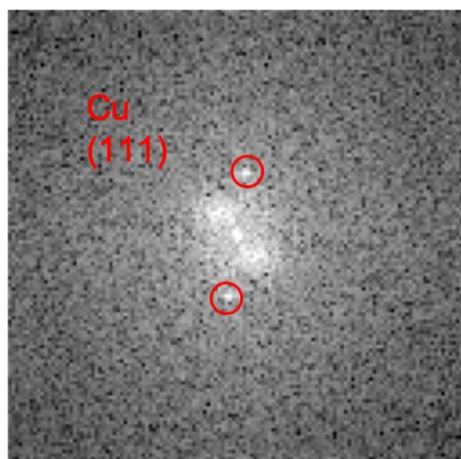
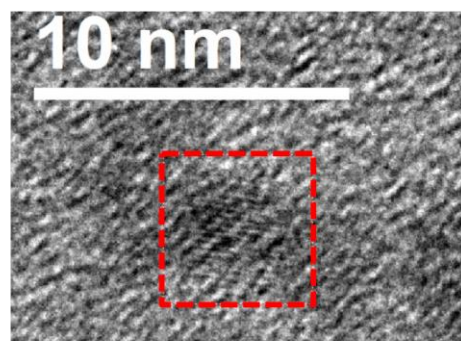


Figure S2. Color variations of 5 cycled HKUST-1 thin films depending on the amount of deposited Cu. (a) SiO<sub>2</sub>/Si(100) substrate, (b) 5 cycles of 1 ML Cu-HKUST-1, (c) 5 cycles of 4 ML Cu-HKUST-1, and (d) 5 cycles of 8 ML Cu-HKUST-1.

(a) 4 ML Cu-HKUST-1



(b) 8 ML Cu-HKUST-1

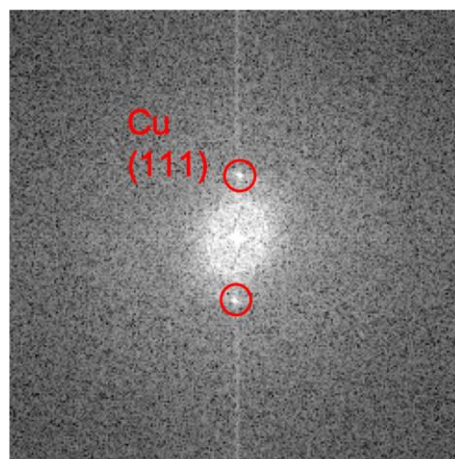
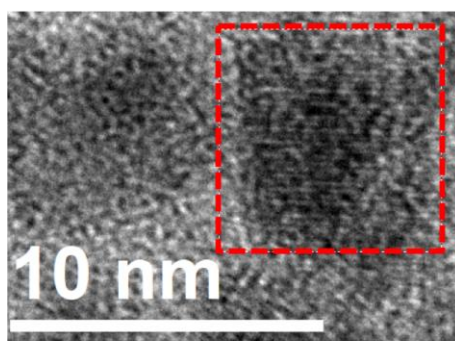
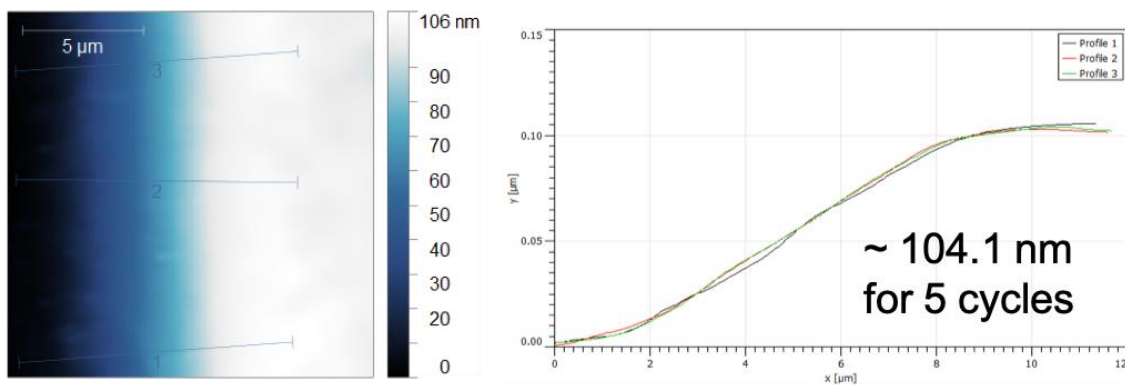
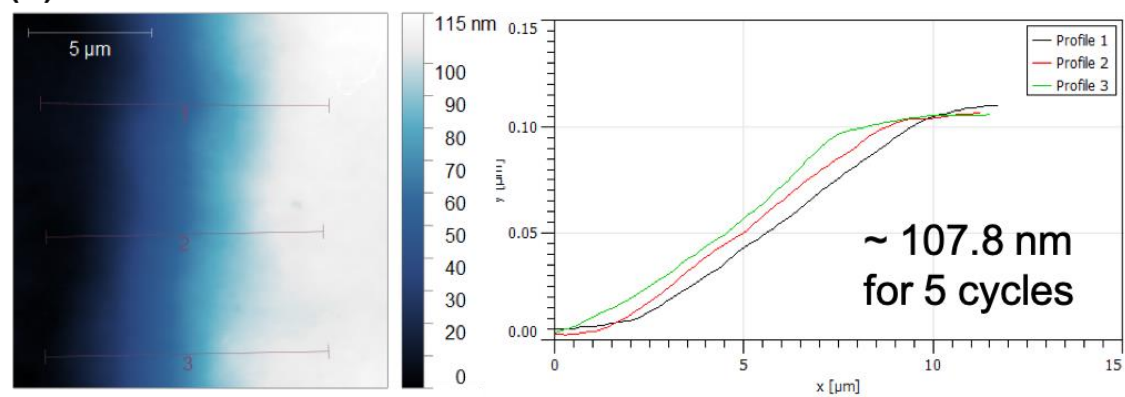


Figure S3. Magnified TEM images of (a) 4 ML Cu-HKUST-1 (b) 8 ML Cu-HKUST-1 with FFT of their lattice fringes (red square box in each TEM images)

(a) 1 ML Cu-HKUST-1



(b) 4 ML Cu-HKUST-1



(c) 8 ML Cu-HKUST-1

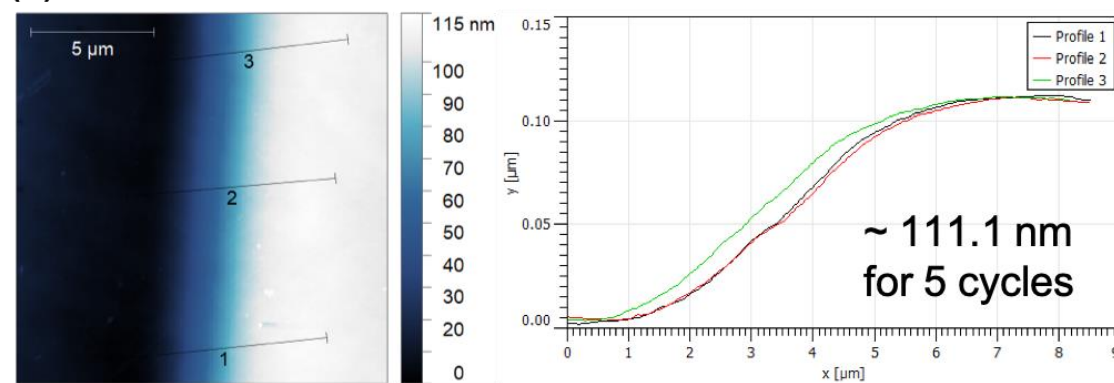


Figure S4. The thickness of (a) 1 ML Cu-HKUST-1, (b) 4 ML Cu-HKUST-1, and (c) 8 ML Cu-HKUST-1 films (5 growth cycles in each film) measured by AFM.

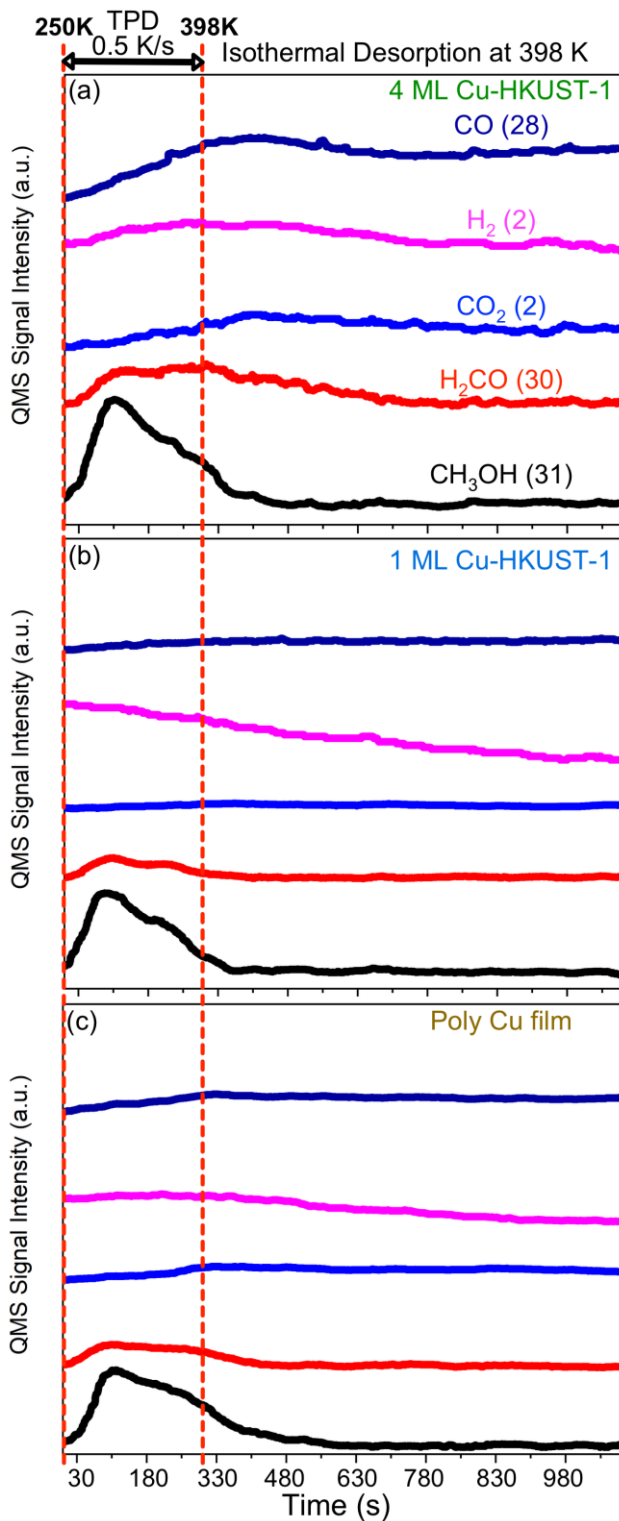


Figure S5. The desorption spectra of CH<sub>3</sub>OH (black), H<sub>2</sub>CO (red), CO<sub>2</sub> (blue), H<sub>2</sub> (magenta), CO (dark blue) from (a) 4 ML Cu-HKUST-1, (b) 1 ML Cu-HKUST-1 films (5 growth cycles in each), and (c) polycrystalline Cu film (10 nm thick). They were treated with  $1.0 \times 10^{-6}$  Torr of O<sub>2</sub> at 300 K for 3 minutes and then were exposed to  $5.0 \times 10^{-7}$  Torr of methanol at 250 K for 20 minutes. The sample were heated from 250 K to 398 K at a rate of 0.5 K/s, and they were isothermally held at 398 K for 15 minutes.

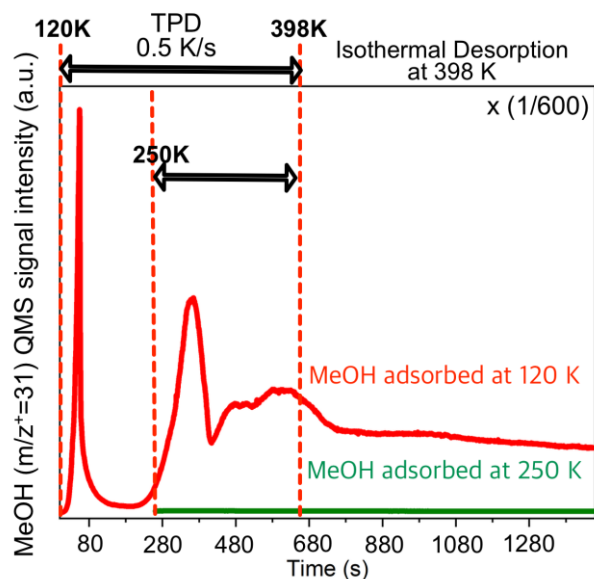


Figure S6. The desorption spectra of CH<sub>3</sub>OH from the 5 cycled 4 ML Cu-HKUST-1 thin film. They were treated with  $1.0 \times 10^{-6}$  Torr of O<sub>2</sub> at 300 K for 3 minutes and then were exposed to  $5.0 \times 10^{-7}$  Torr of methanol at 120 K (red) and 250 K (green) for 20 minutes. The sample were heated from 120 K (red) and 250 K (green) to 398 K at a rate of 0.5 K/s, and they were isothermally held at 398 K for 15 minutes. The y-axis scale of this figure is 1/600 compared to other TPD spectra in this study.

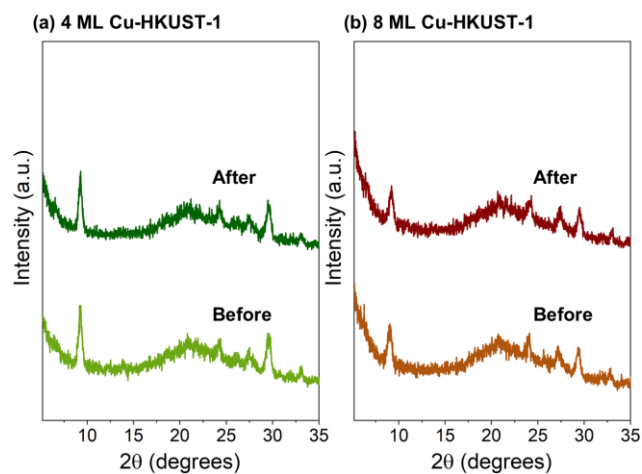


Figure S7. XRD patterns regarding HKUST-1 structures on the 5 cycled 4 ML and 8 ML Cu-HKUST-1 thin films before and after the methanol oxidation experiment.