Supporting Information

Micromechanical Behavior of Polycrystalline Metal-Organic Framework Thin Films Synthesized by Electrochemical Reaction

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Experimental setup for electrochemical synthesis and processing parameters

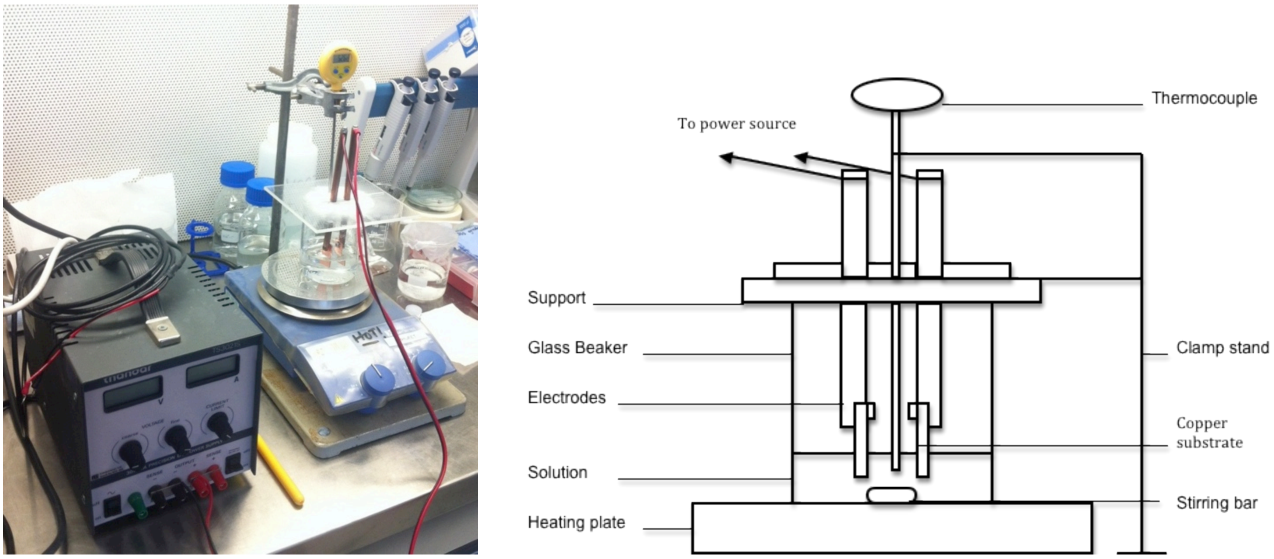


Figure S1. Electrochemical reaction set-up used in this study. The front of the substrates were arranged as the inside faces, facing each other at 1 cm separation. These substrates are screwed to the base of two copper electrodes, which are held in place by a support, designed to hold the substrates at the correct position within 100 mL of solution in a 250 mL beaker placed on a heated stirrer plate. The support also allowed a thermocouple to be placed into the solution, to monitor the temperature throughout the reaction. The electrodes were connected to a DC power supply.

Sample No.	8	11	12	13	14	15	16	17	18	19	20	21	22	25	26
Substrate Grinding (grit)	600	4000	2000	4000	4000	4000	2000	2000	2000	2000	4000	4000	2000	4000	2000
Substrate Polish (mi-crons)	-	1	1	-	-	-	-	-	-	-	1	6	-	1	-
Average Temper-ature (C)	56.2	56.4	49.0	52.6	55.5	55.8	53.3	54.6	65.0	58	59.9	55.5	59.8	57.3	56.6
Reaction Time (s)	180	180	180	180	180	180	300	240	600	90	180	180	420	600	240

Table S1. Sample preparation parameters. All reaction solutions consisted of 56 mL ethanol, 44 mL water, 1 g 1,3,5-benzenetricarboxylic acid (BTC) and 2 g MTBS. A DC waveform at 2.5 V was used for all reactions. Samples no. 19, 12, 18, 25 respectively correspond to coatings “A”, “B”, “C”, “D” reported in the manuscript.

HKUST-1 coating	Film thickness estimated from SEM images (nm)									
A	3013	1185	2667	2716	1334	1087	3013	3655	3358	1235
B	7340	3378	5301	4485	2854	2988	2338	3897	2209	2209
C	13800	11260	12600	8175	7103	12200	11660	8845	4513	8577
D	14660	5498	11000	9896	4765	10269	11730	12460	6964	9896

Table S2. Values used to calculate the mean film thickness via SEM for coatings A, B, C and D, in which 10 random sampling areas were obtained for each coating.

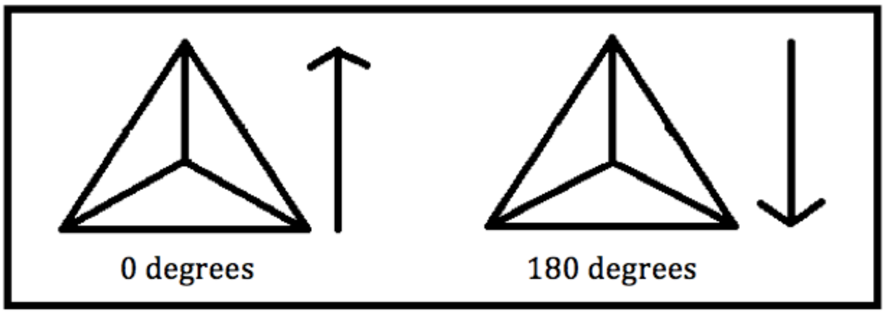


Figure S2. The movement of the Berkovich indenter tip in nanoscratch experiments designated as 0° and 180° orientations, respectively.

X-Ray diffraction (XRD) of HKUST-1 thin film coatings of different thicknesses

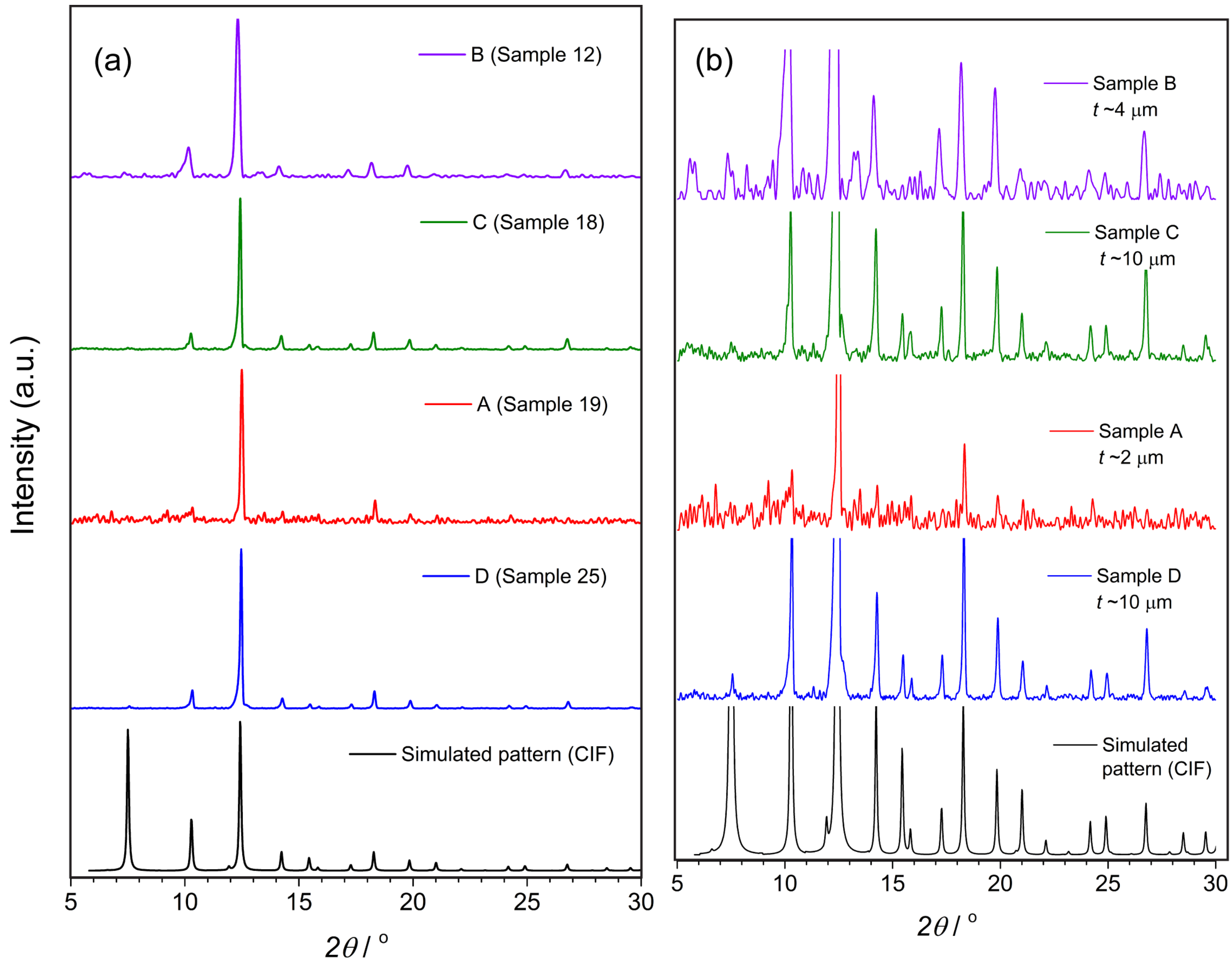


Figure S3. The XRD patterns of the HKUST-1 thin-film coatings for 2θ up to 30°. The diffraction data are consistent with published crystallographic structure (CIF: FIQCEN)[1], confirming the coatings to be HKUST-1 [$Cu_2(BTC)_3$]. As expected thinner films have relatively lower intensities than their thicker counterparts. Panel (b) is used to better highlight the relatively low intensity regions in panel (a).

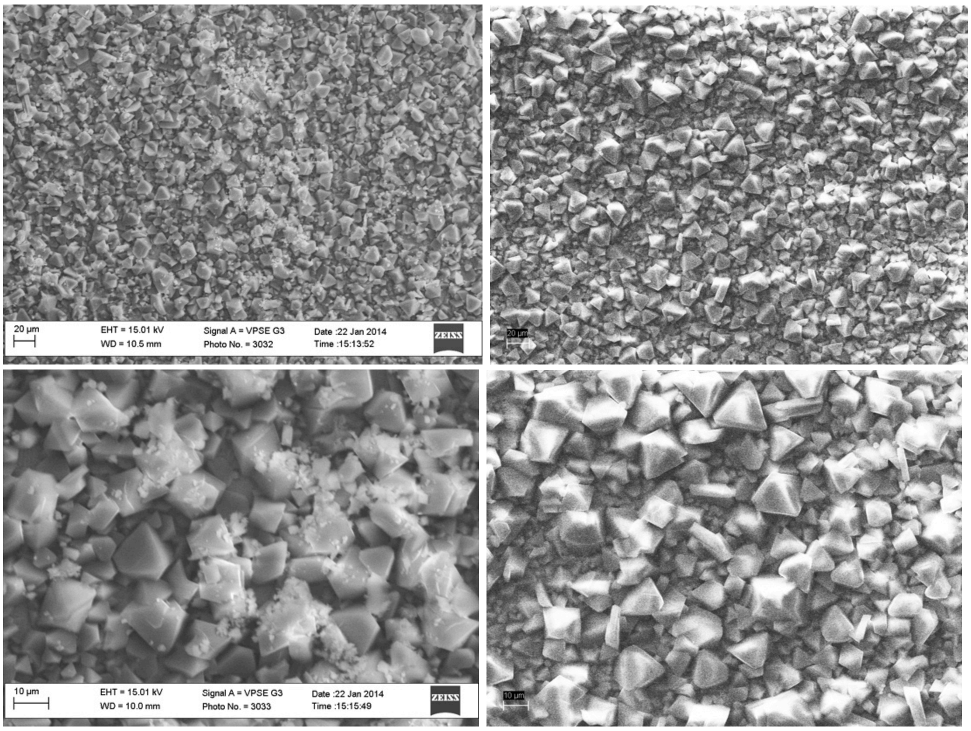


Figure S4. Effect of substrate polishing on the morphology of polycrystalline 'thick' films (t ~10 μm), indicated via comparison of SEM micrographs of coating C (left panels) and coating D (right panels). Bottom panels show micrographs taken at a higher magnification.

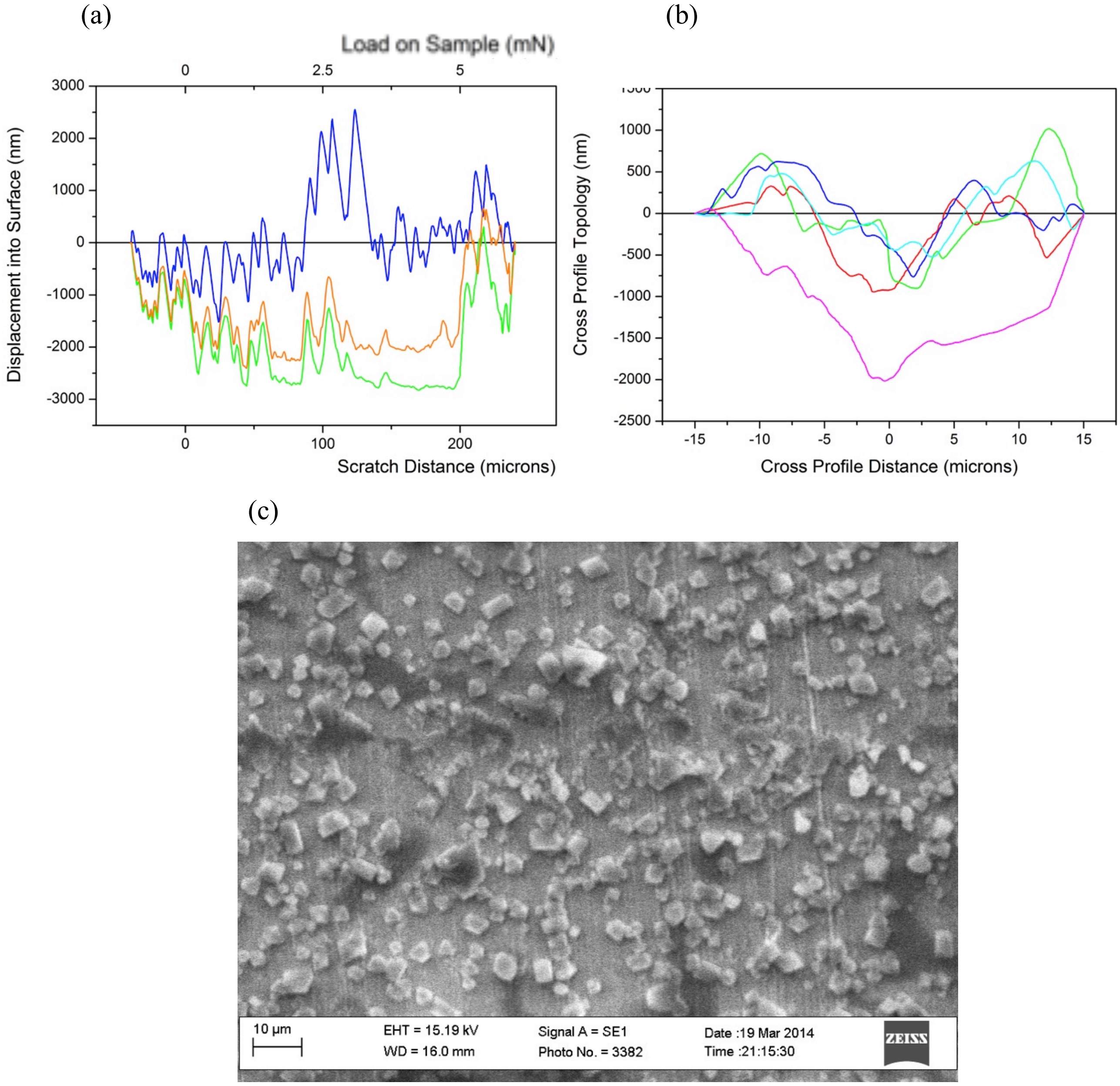
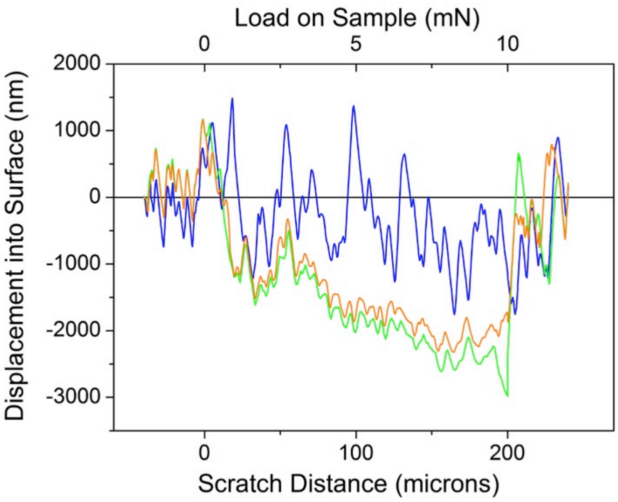
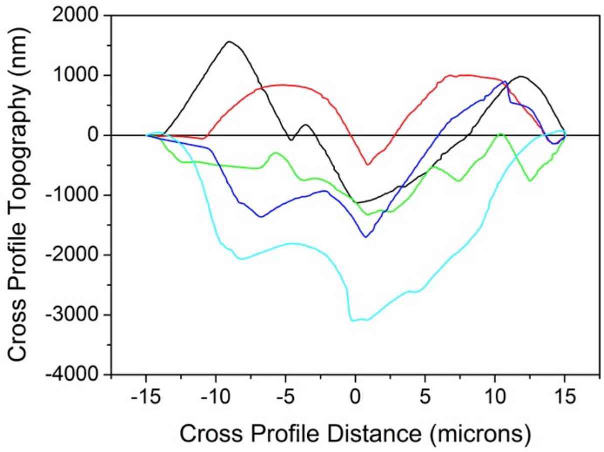


Figure S5. (a) 5 mN ramp-load test (tip oriented at 180°) nanoscratch data for coating A, (b) midway cross profiles (2.5 mN), (c) SEM image of the scratch path after test completion.

(a)



(b)



(c)

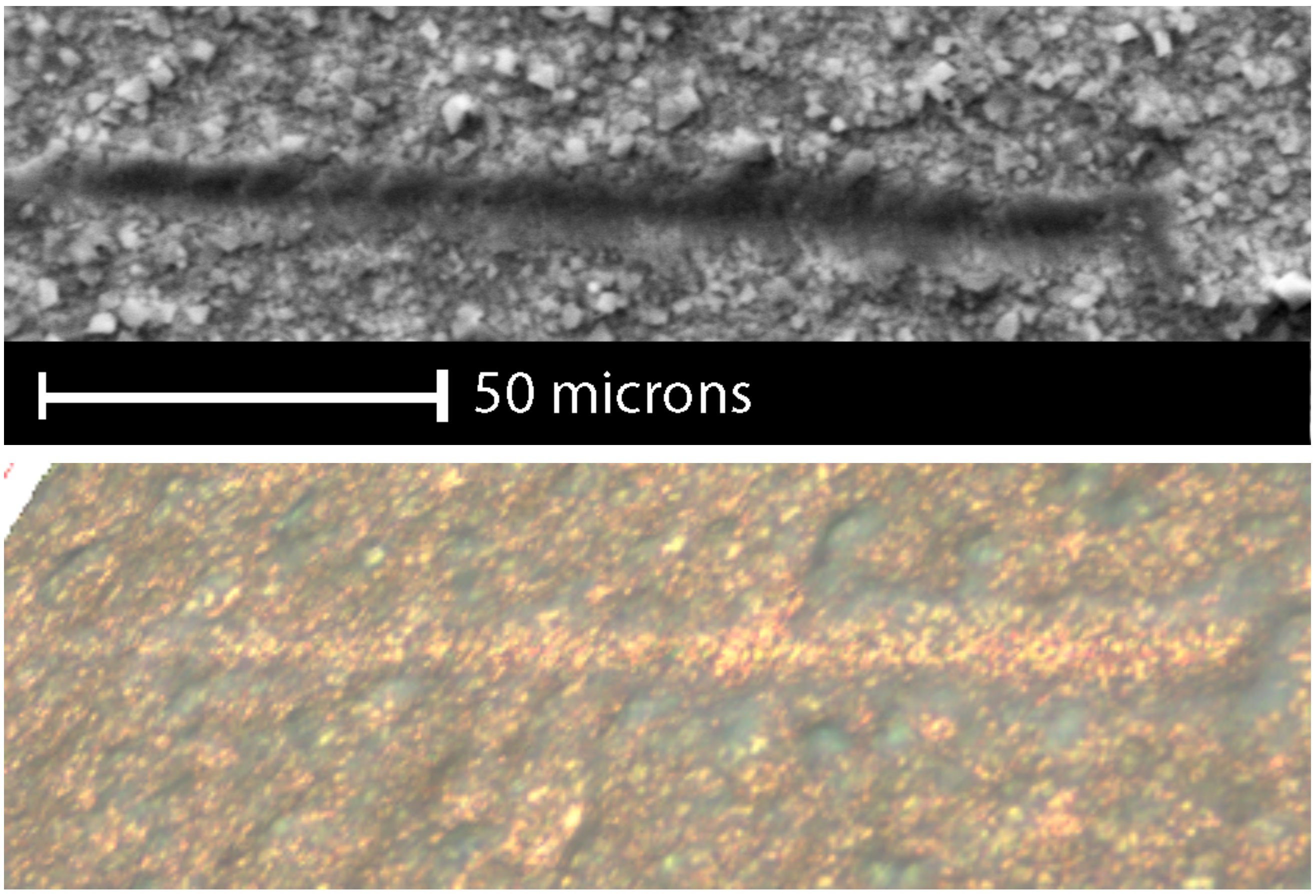
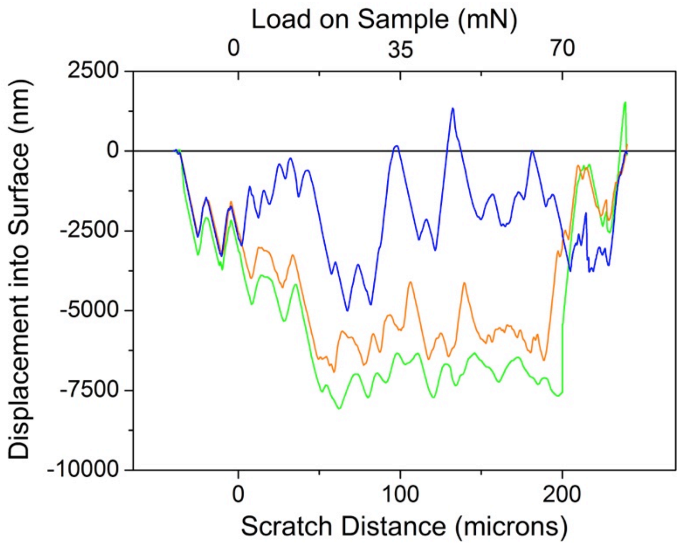
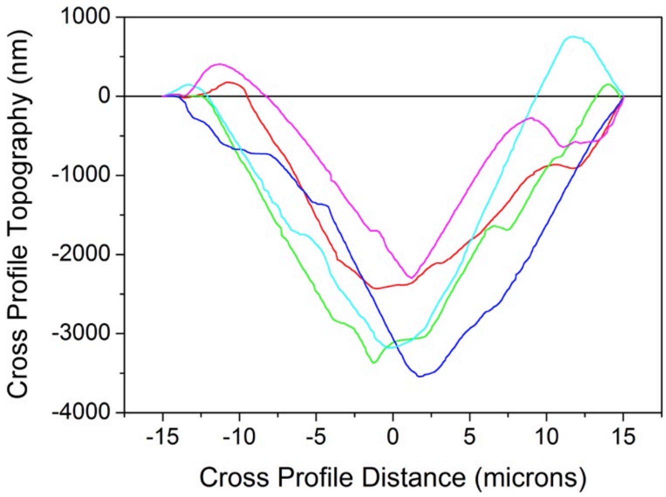


Figure S6. (a) 10 mN ramp-load test (180°) nanoscratch data for coating B, (b) midway cross profiles, (c) SEM image of the scratch path after test completion and (shown below) the corresponding 3D optical profilometry image.

(a)



(b)



(c)

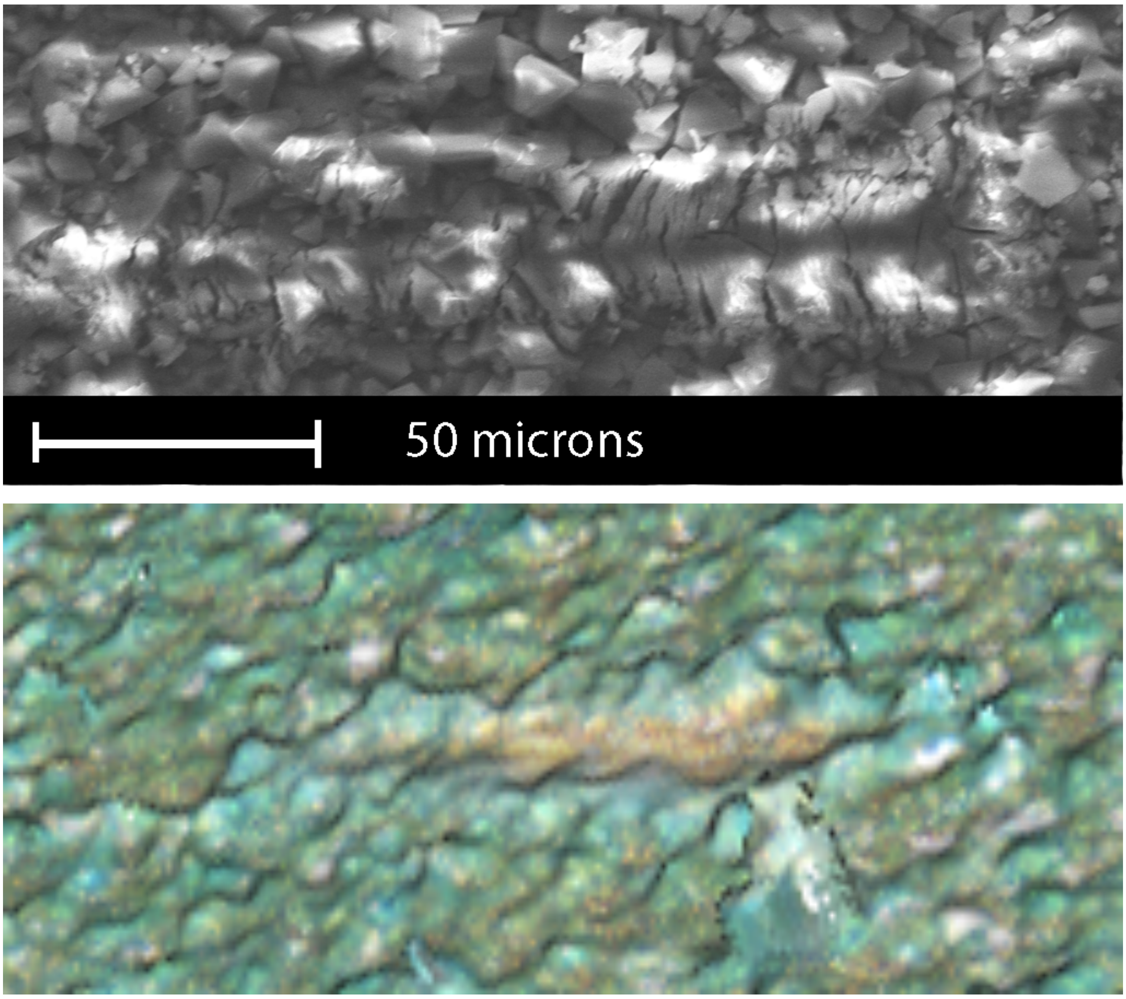
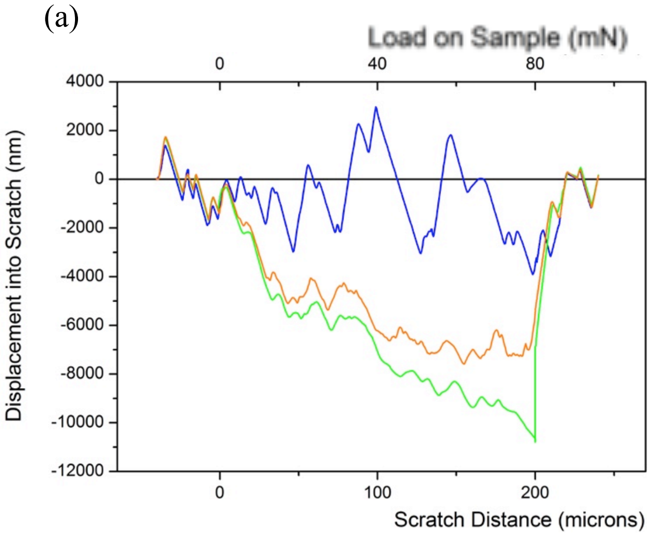
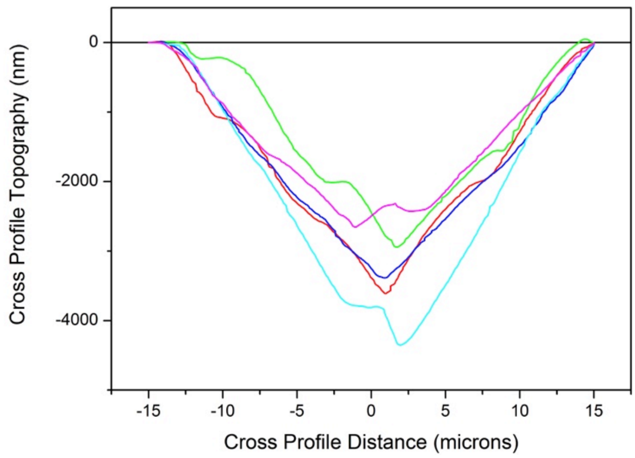


Figure S7. (a) 70 mN ramp-load test (180°) nanoscratch data for coating C, (b) midway cross profiles, (c) SEM image of the scratch path after test completion and (shown below) the corresponding 3D optical profilometry image.

(a)



(b)



(c)

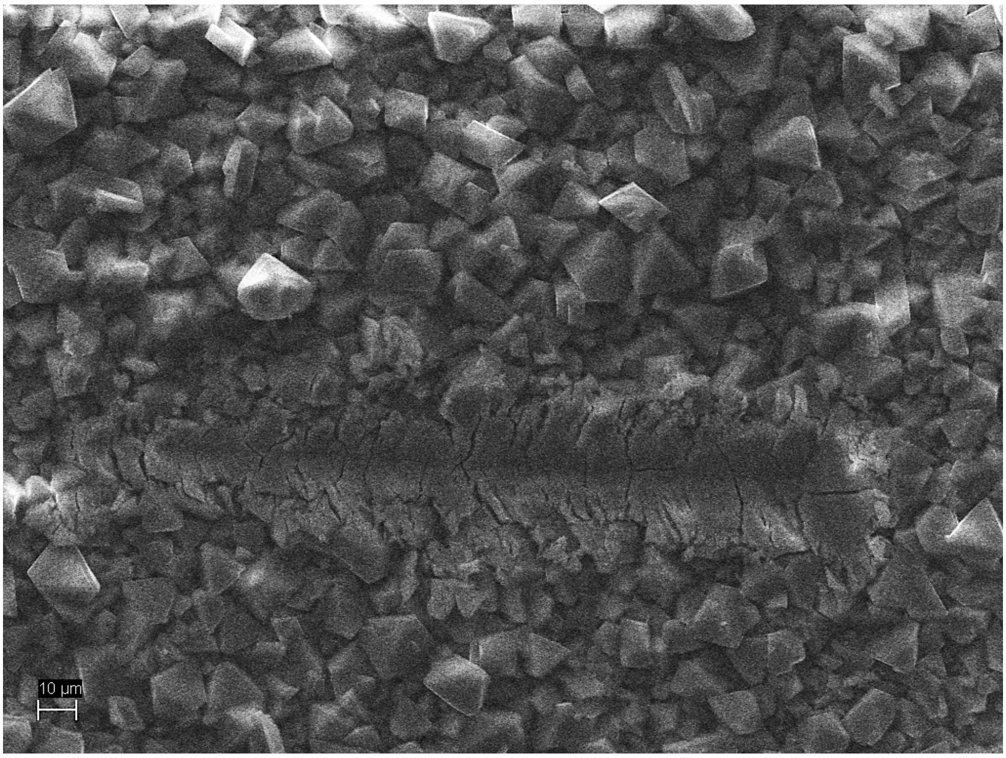


Figure S8. (a) 80 mN ramp test nanoscratch data (180°) for thin film coating D, (b) midway cross profiles, (c) SEM image of the scratch track.

Thin Film Coating	Nanoscratch Ramp-Load Test	Film Thickness via Nanoscratch Ramp Tests (µm)				
A	5mN 0°	2.5	2.0	3.0	1.5	1.5
A	5mN 180°	4.5	2.0	2.5	3.0	2.0
A	10mN 0°	3.0	1.5	1.5	2.5	2.0
A	10mN 180°	3.5	2.5	3.5	2.5	2.5
A	15mN 0°	3.0	2.0	2.0	2.0	1.5
A	15mN 180°	2.0	3.5	2.0	2.0	4.0
B	50mN 0°	3.5	X	3.5	X	3.0
B	50mN 180°	8.0	4.0	4.0	3.5	X
B	100mN 0°	4.5	6.0	4.5	7.0	6.0
B	100mN 180°	5.0	8.0	4.5	4.5	7.0
C	70mN 0°	7.0	7.0	7.0	7.0	7.0
C	70mN 180°	8.0	4.5	7.0	9.0	6.5
C	80mN 180°	12.0	13.5	X	9.5	12.0
C	100mN 180°	15.0	13.5	15.5	10.0	16.0
C	120mN 180°	20.0	15.0	15.0	X	15.0
C	150mN 0°	25.0	18.0	17.0	18.0	X
C	150mN 180°	20.0	18.0	15.0	20.0	X
D	60mN 180°	8.5	8.0	9.0	7.0	7.0
D	80mN 180°	9.0	9.0	11.0	9.0	7.0
D	100mN 180°	11.0	9.0	9.5	13.0	12.0

Table S3. Values used for calculating the film thickness via nanoscratch experiments for coatings A, B, C and D.

References

(1) Chui, S. S.; Lo, S. M.; Charmant, J. P.; Orpen, A. G.; Williams, I. D., *Science* **1999,** 283, (5405), 1148-50.