

Means of control over Poly(4-vinylpyridine)-CoBr₂ complexes functional thin films formation in static and dynamic conditions

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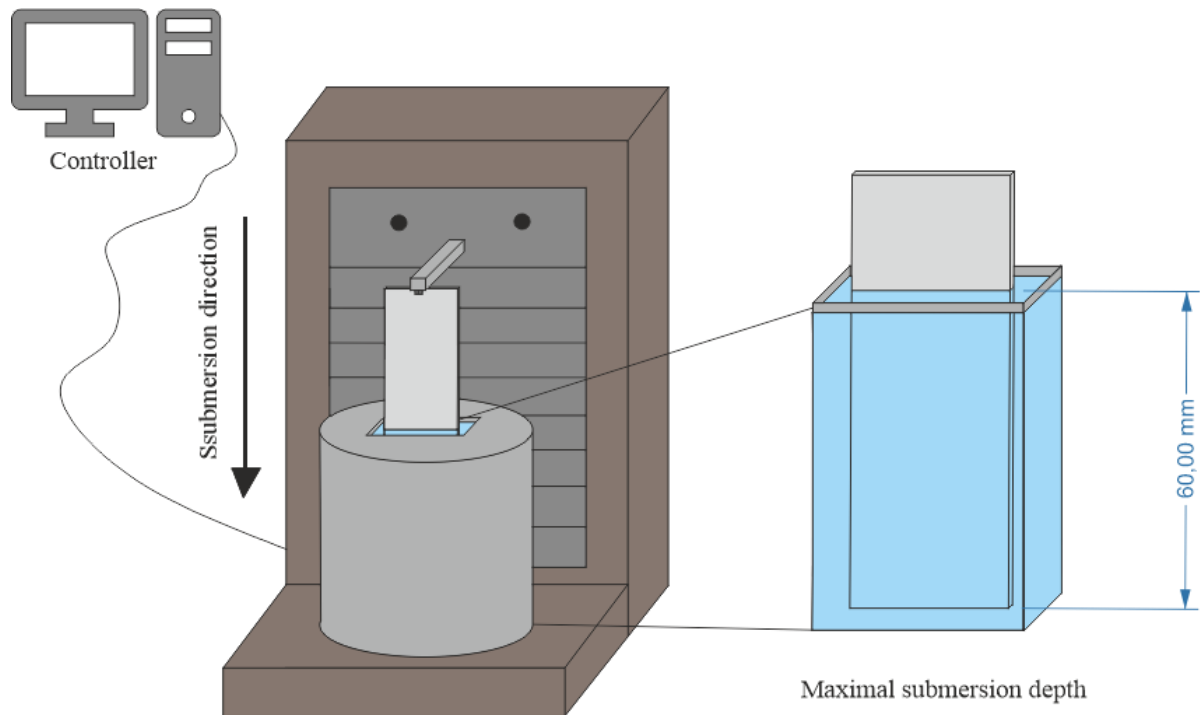
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1) Dynamic samples submersion process

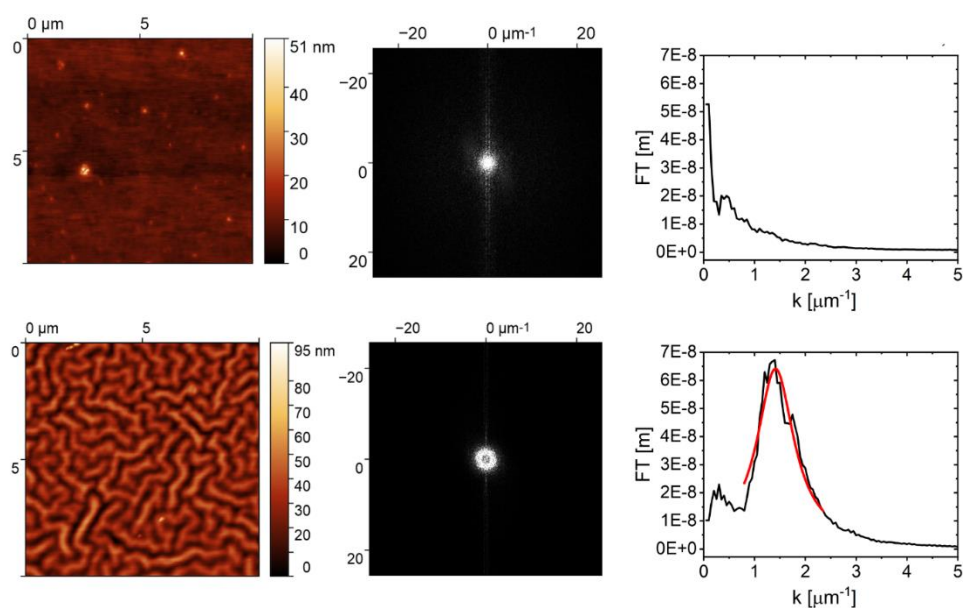


Suppl. Fig. 1 Schematic illustration of the dip coater for horizontal dipping used to modify dynamic samples by submerging them into CoBr_2 solution.

Modification of samples with submersion time gradient were carried out using a device with step motor. Microscopic slide with P4VP polymer layer were approached to surface of CoBr_2 solution and then submerged with speed from $1 \frac{\text{mm}}{\text{s}}$ to $0,2 \frac{\text{mm}}{\text{s}}$ and then immediately emerged with speed $20 \frac{\text{mm}}{\text{s}}$. The submersion distance was 60 mm. Samples were then rinsed with acetonitrile to remove salt residue and dried with nitrogen. The setup is illustrated schematically in Suppl. Fig. 1.

2) Methodology of Fourier Transform characteristics size determination.

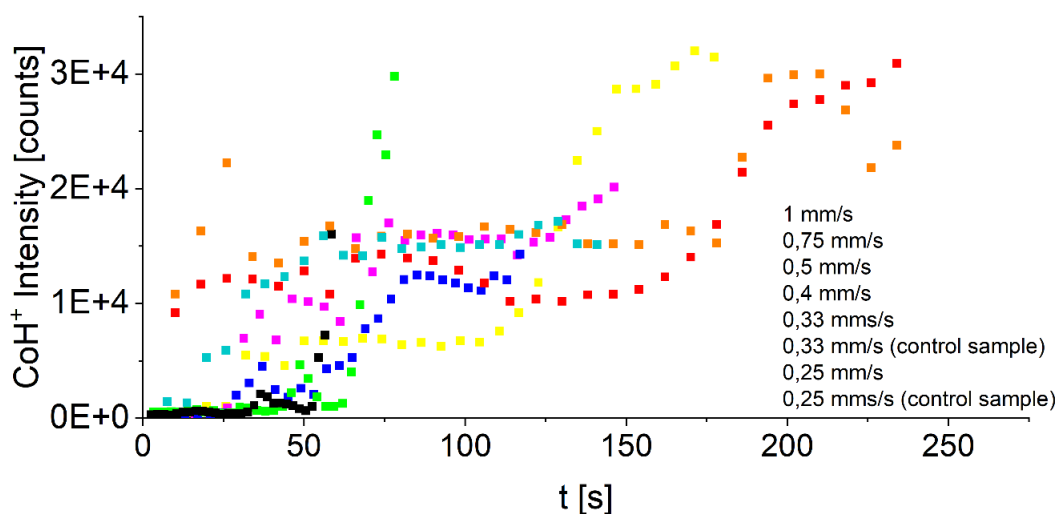
Using Gwyddion 2.61 software, two-dimensional Fast Fourier Transform (FFT) was performed on all obtained images resulting in rings characteristic for such structures. The radius of the ring corresponds to the characteristic size of the wrinkles in the image. It was obtained by extracting angularly averaged profiles and fitting the Lorentz function.¹ An example of image processing for wrinkle-free and wrinkled surface are shown in Suppl. Fig. 2.



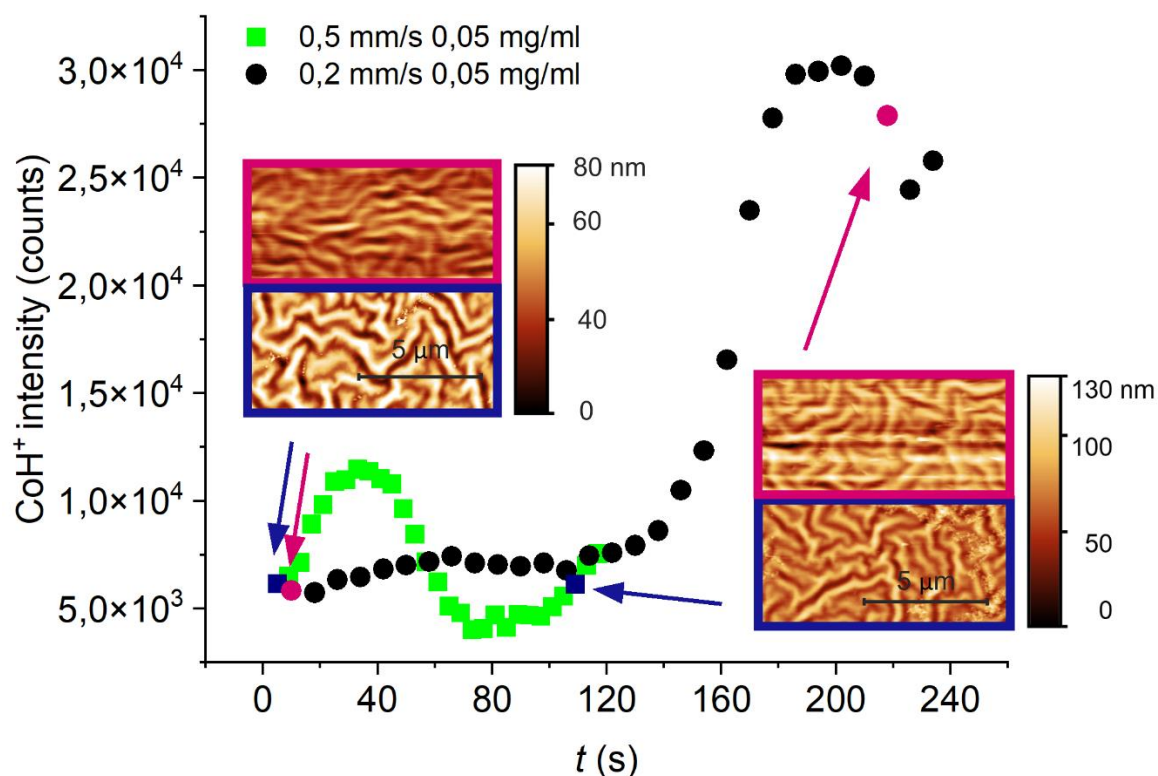
Suppl. Fig. 2 Example analysis of AFM images for sample submerged with speed 0,4 mm/s for 21,25 s (top) and 131,25 s (bottom) immersion time in 0,02 mg/ml CoBr₂ acetonitrile solution with corresponding Fourier Transforms and angularly averaged profiles. Lorentz function (red line) was fitted for surface with wrinkles.

3) Secondary Ion Mass Spectrometry (TOF-SIMS) for dynamic samples.

The samples were measured using Bi₃⁺ as primary ions with beam current 0,71 pA (70 scans, 128x128 px), Measurement was taken by setting the first one in 1,5 mm distance from the edge of the sample that was submerged first. Next, measurements were carried out every 2 mm moving up the sample. Knowing the measurement position and submersion velocity, time of submersion was calculated for each SIMS measurement on each sample and is presented in Suppl. Fig. 3.



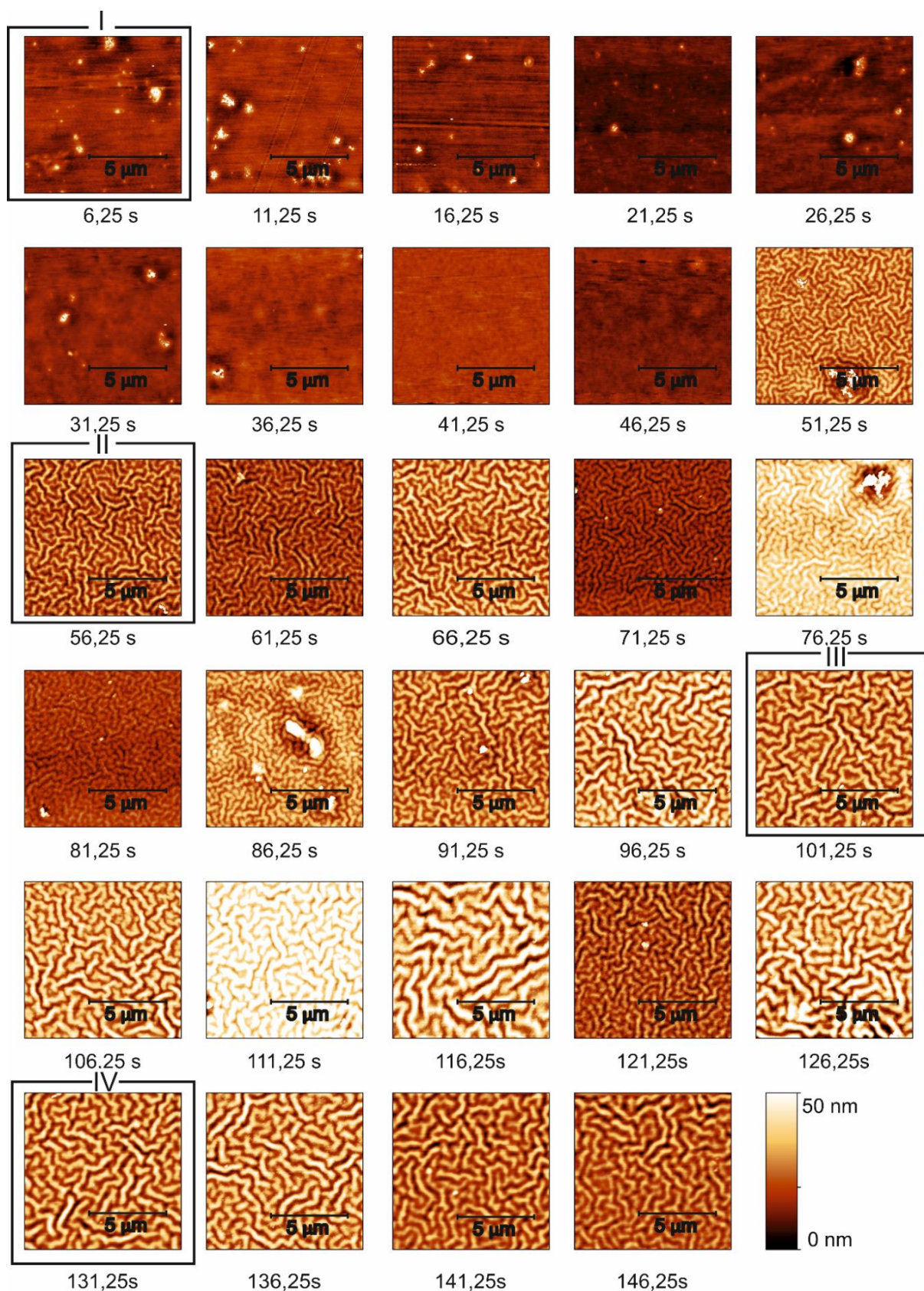
Suppl. Fig. 3 Intensity of CoH⁺ signal obtained by the SIMS technique for samples submerged with all available velocities (0,25 mm/s to 1 mm/s) in 0,02 mg/ml CoBr₂ acetonitrile solution.



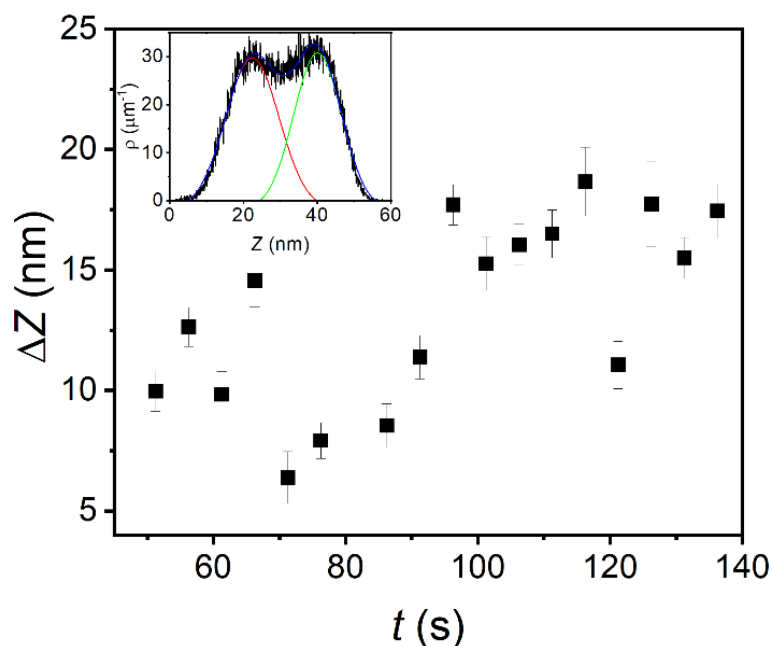
Suppl. Fig. 4 Intensity of CoH^+ signal obtained by the SIMS technique for samples submerged in 0,05 mg/ml solution with speeds of 0,2 and 0,5 mm/s. Insets: AFM topography images taken at marked points.

4) Detailed topography analysis of sample modified with CoBr_2 with gradient of submersion time.

For the sample submerged with speed of $0,4 \frac{\text{mm}}{\text{s}}$, a detailed analysis of topography was carried out. AFM images were taken for places on the sample corresponding to the times measured using the SIMS technique. They are shown in Suppl. Fig. 5.



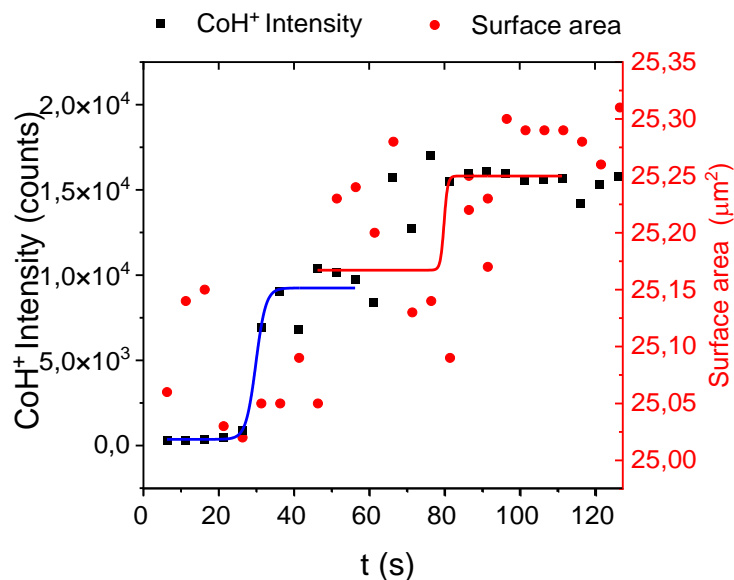
Suppl. Fig. 5 AFM topography images for CoBr₂-modified sample submerged with 0,4 $\frac{mm}{s}$ at different time points in 0,02 mg/ml CoBr₂ acetonitrile solution. Roman numerals highlight the images shown in Fig. 1 in the main text.



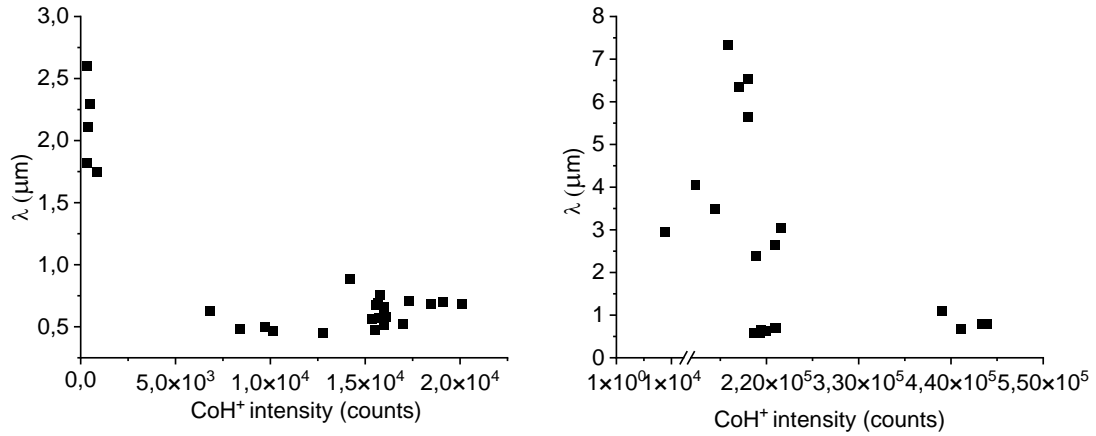
Suppl. Fig. 6 Depth of wrinkles vs. time spent in 0.02 mg/ml CoBr_2 solution ($v = 0.4$ mm/s) obtained by fitting a sum of Gaussian profiles to height distributions of AFM topography images measured at each time point – example in inset for $t = 96.25$ s.

In Suppl. Fig. 7, the intensity of CoH^+ obtained by the SIMS technique and surface area is presented as a function of immersion time. Actual surface area of $5 \times 5 \mu\text{m}$ was computed by simple triangulation using Gwyddion 2.61 software.²

Characteristic size as a function of CoH^+ intensity for both the dynamic and static studies is presented in Suppl. Fig. 8.



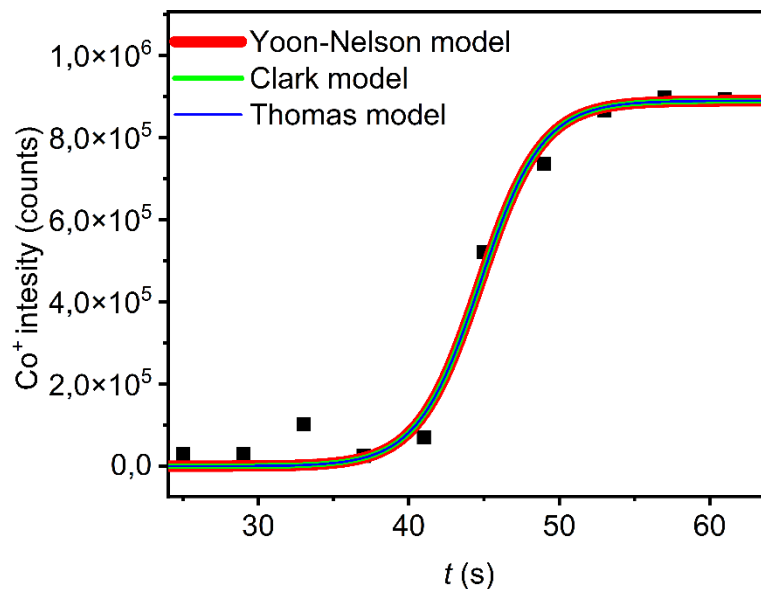
Suppl. Fig. 7 Intensity of CoH^+ signal obtained by the SIMS technique (black squares) with Yoon-Nelson model fitted to data (solid lines) along with the actual surface of $5 \times 5 \mu\text{m}$ area (red squares) for sample submerged with speed 0,4 mm/s in 0,02 mg/ml CoBr_2 acetonitrile solution.



Suppl. Fig. 8 Characteristic size of both dynamic (left) and static (right) sample surfaces versus intensity of CoH^+ signal obtained by the SIMS technique. The differences between CoH^+ intensity are caused by different doses.

5) Thomas, Clark and Yoon-Nelson models comparison

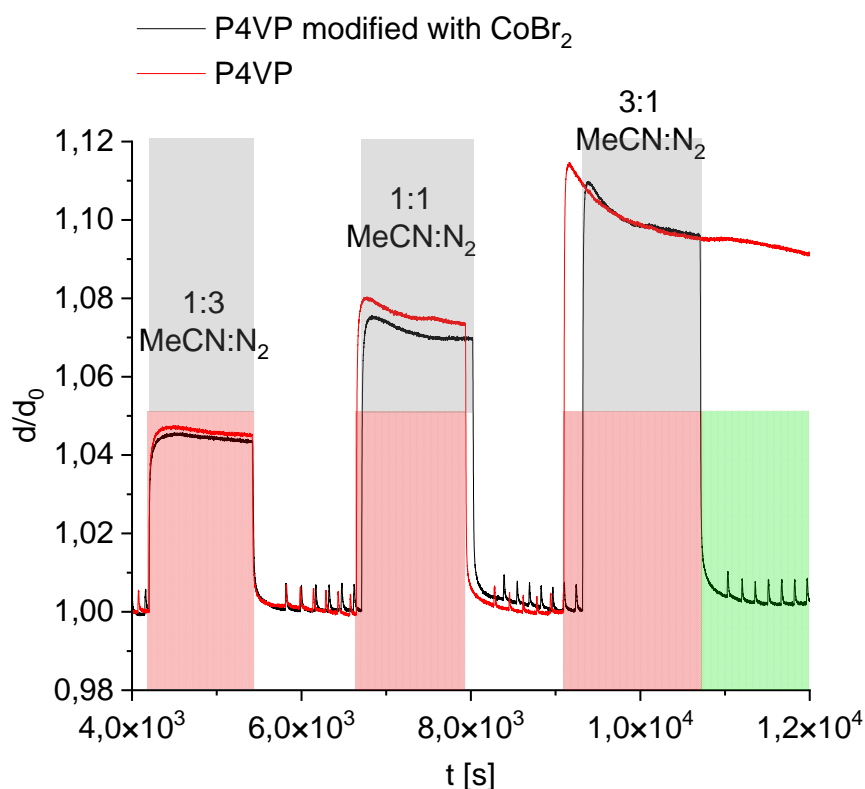
A comparison of models describing sigmoidal or S-like shaped curves included Thomas³, Clark⁴ and Yoon-Nelson⁵ models. Fitting each of them, respectively, resulted in an adjusted R-square equal to 0,98323 for Thomas model, 0,98083 for Clark and 0,98509 for Yoon-Nelson model. Given these results, the simplicity of the Yoon Nelson model, and the fact that it provides information on the time at which the curve is half saturated ($\tau_{1/2}$) - which is useful for determining the effect of immersion velocity on the adsorption kinetics of cobalt salts - this model was chosen as the optimal one for the analysis of the obtained data.



Suppl. Fig. 9 Intensity of CoH^+ signal obtained by the SIMS technique for sample submerged with $v = 0.5$ mm/s in 0,02 mg/ml CoBr_2 acetonitrile solution (points) with fits of the Yoon-Nelson, Clark and Thomas models to the data (solid lines).

6) Swelling of P4VP in acetonitrile vapors

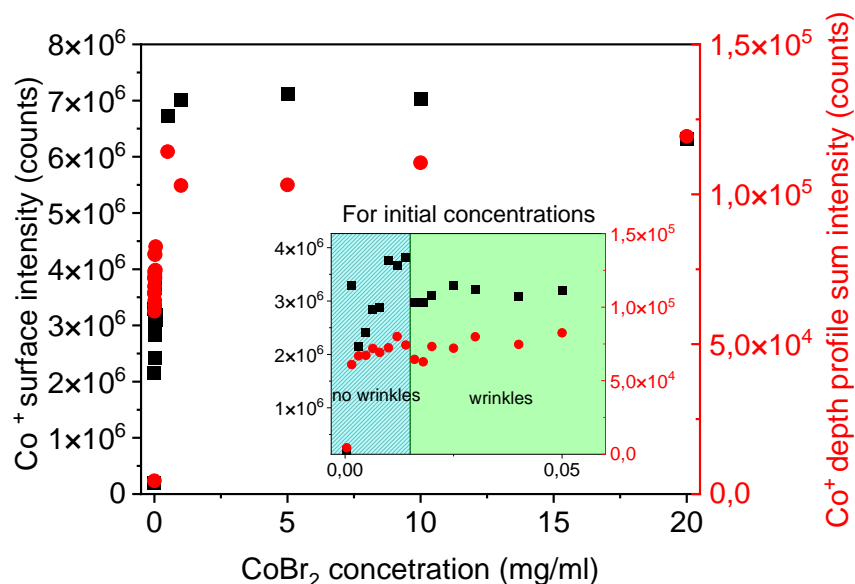
Swelling of P4VP and P4VP modified with CoBr_2 in acetonitrile was measured using white light reflectance spectrometry technique while passing acetonitrile vapors and nitrogen in ratio 1:3, 1:1 and 3:1 through the chamber in which the samples were located. Each time acetonitrile vapors (in respected ratio with nitrogen) were fed into the system for twenty minutes, after that time pure nitrogen was driven through the system for twenty minutes to dry the sample. Gas flow was controlled with rotameters and delivered to the system.⁶



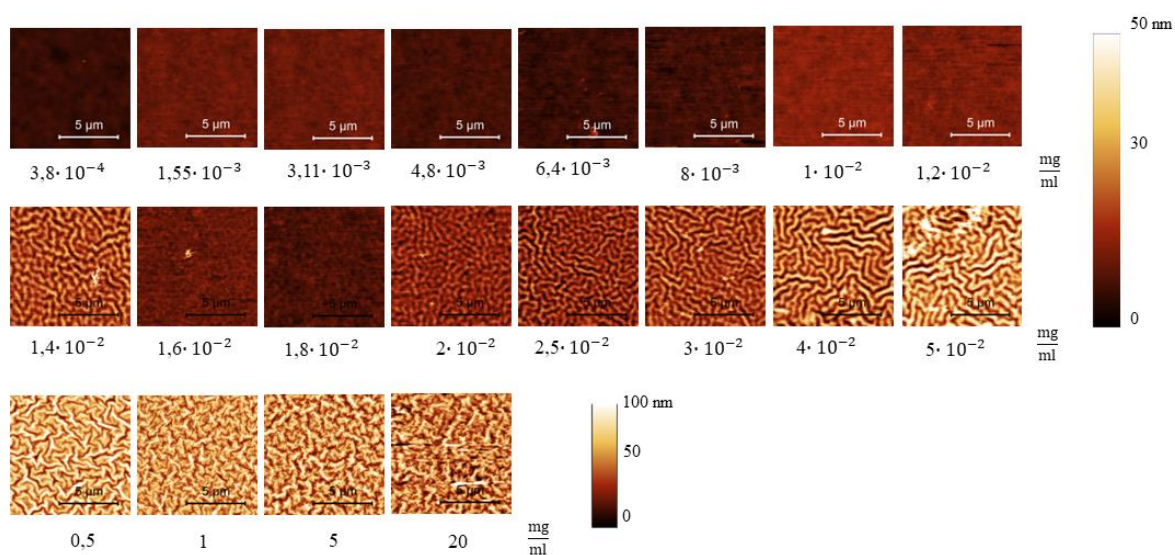
Suppl. Fig. 10 Relative thickness of thin films of P4VP and P4VP modified with CoBr_2 obtained via white light reflectance spectrometry versus time in acetonitrile vapors and nitrogen in ratio 1:3, 1:1 and 3:1. The red region corresponds to dosing acetonitrile vapors to the system for P4VP sample, the gray area marks the time when acetonitrile vapors were fed to the system for the sample modified with cobalt bromide. The system was purged with nitrogen between periods of dosing acetonitrile vapors. The green area corresponds to the P4VP layer remaining without purging with nitrogen after acetonitrile application.

7) SIMS measurements and detailed topography analysis of static samples

SIMS measurements were taken in 4 random places on each sample. Mean value of those is presented in Suppl. Fig. 11 along with sum of signal for obtained profiles (main text Fig. 5) for comparison. AFM images that were taken in random places on each sample are shown in Suppl. Fig. 11. Images were processed similarly to those obtained for dynamic samples.

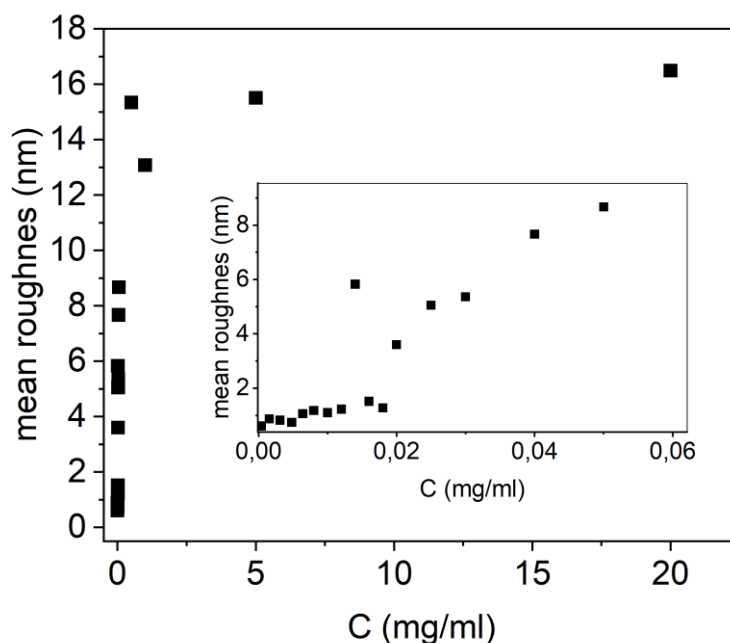


Suppl. Fig. 11 Co⁺ intensity signal as a sum of the depth profile (red squares) and from the surface (black squares) for all static samples.

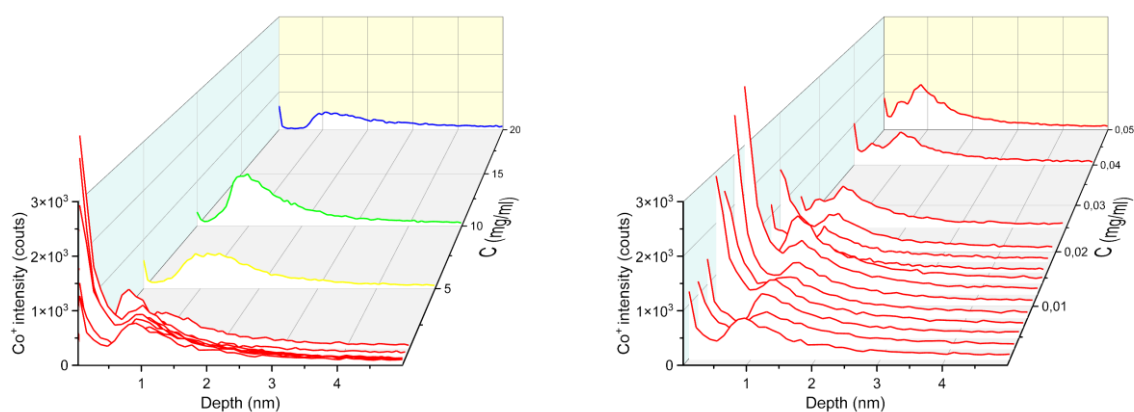


Suppl. Fig. 12 AFM topography images for CoBr₂ - modified sample submerged in acetonitrile solutions of different concentrations for 24 hours.

To check where in the polymer film the majority of adsorption takes place, concentration profiles were obtained using sputtering technique (Suppl. Fig. 14). Depths were calculated by measuring thickness of samples with DektakXT (Bruker). Times needed to completely sputter the sample were determined by the Si^+ signal. Constant sputtering rate was assumed in calculations.



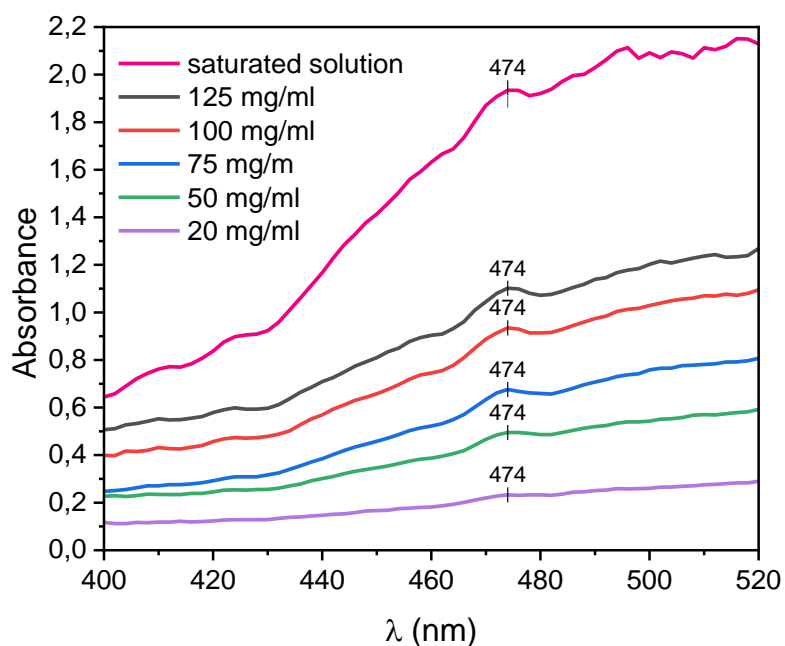
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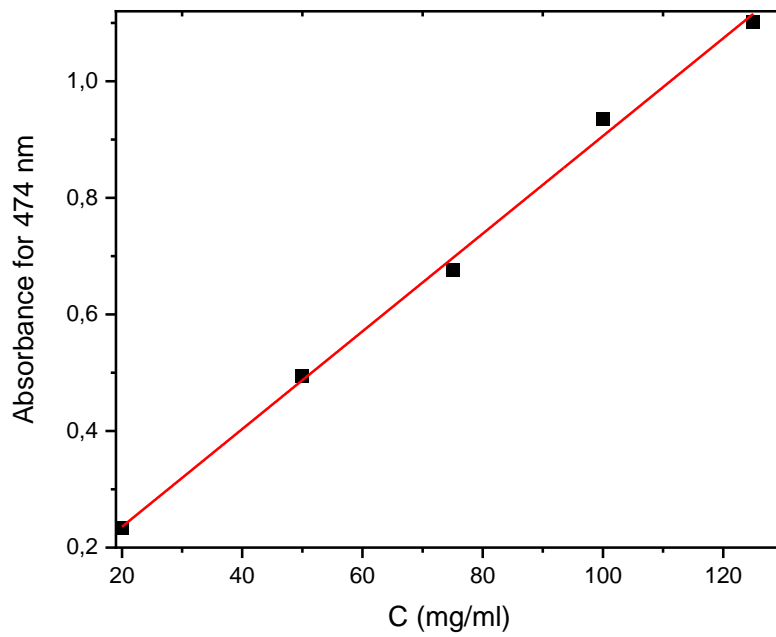
Suppl. Fig. 14 TOF-SIMS depth profiles of Co^+ for samples submerged in different cobalt salt concentrations for 24 hours. On the left full range of concentrations and on the right small concentrations zoomed in for clarity.

8) Determination of the solubility limit of cobalt bromide in acetonitrile using UV-Vis spectroscopy.

Solutions of 20, 50, 75, 100, 125 mg/ml were prepared. Spectra were measured with a Spectrostar Nano spectroscope in the range from 220 to 1000 nm. A wavelength of 474 nm was chosen for analysis due to the linear dependence of absorbance on concentration in the higher ranges of c_p . Spectrum for saturated solution of cobalt bromide (solution collected above the undissolved salt from a vial of 300 mg of CoBr_2 placed to dissolve in 1 ml of acetonitrile) was also measured. The resulting spectra zoomed in to clearly present the aforementioned peak are shown in Suppl. Fig. 14. Resulting from the obtained calibration curve (Suppl. Fig. 15), the concentration of the saturated solution is estimated to be 222(15) mg/ml.

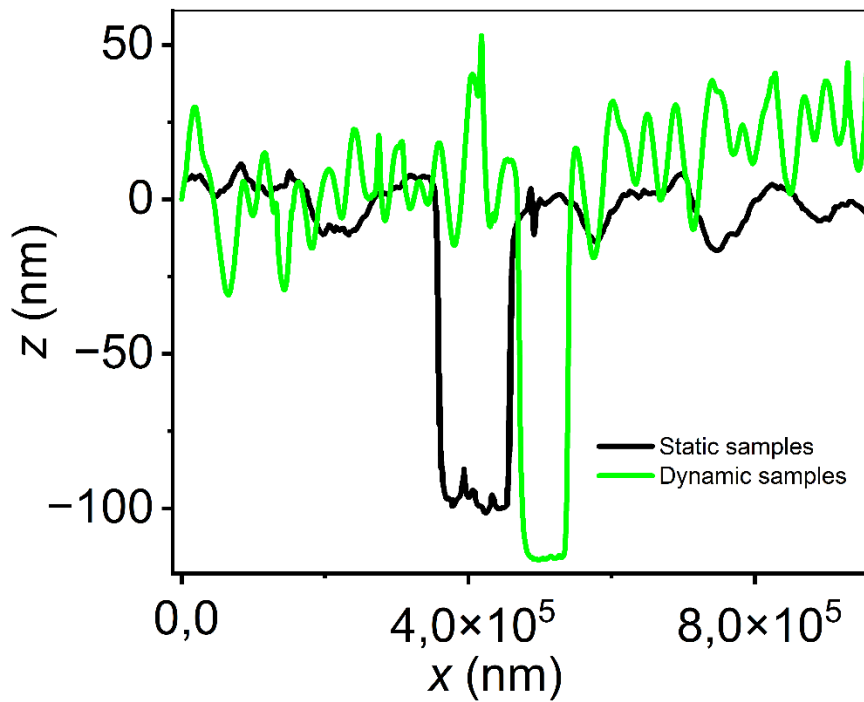


Suppl. Fig. 15 UV-Vis absorbance spectra of CoBr_2 solutions in acetonitrile for all considered concentrations for wavelengths 400-520 nm with marked values for 474 nm.

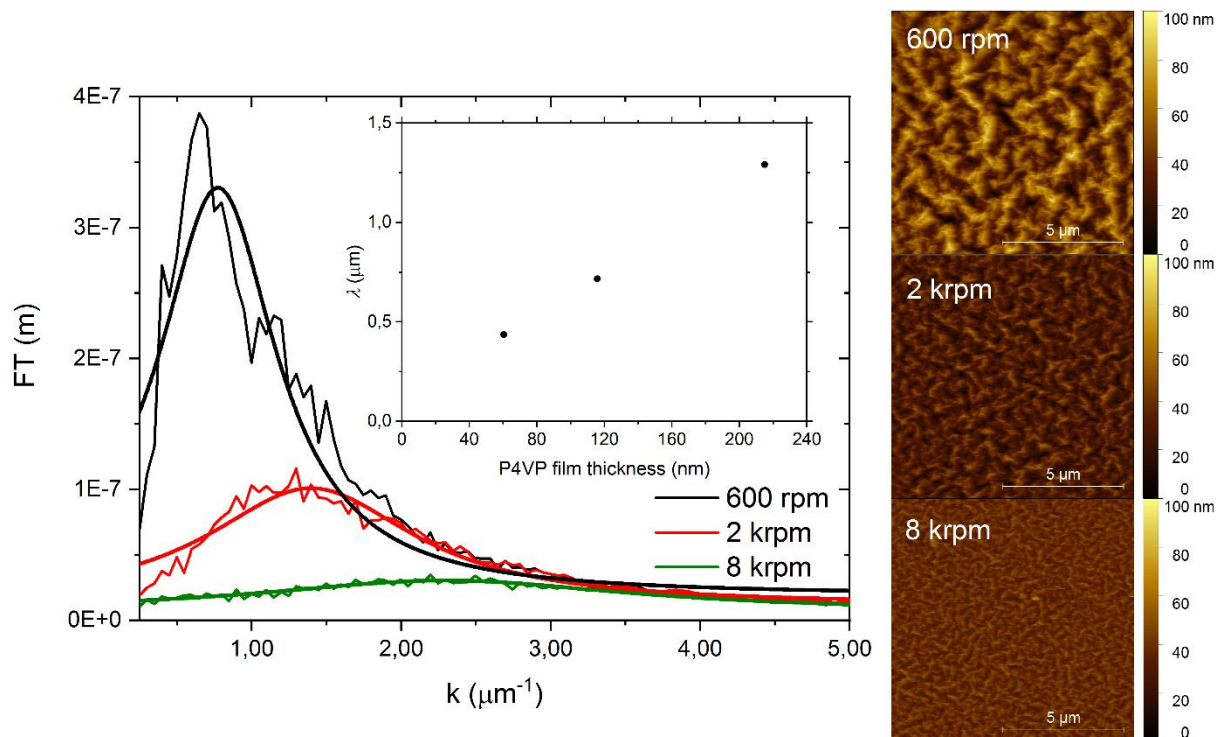


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