Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information for:

Investigations on Sub-Structures within Cavities of Surface Imprinted Polymers using AFM and PF-QNM

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Materials

Styrene, divinylbenzene (DVB) and trimethoxyvinylsilane (TMVS) were purchased from Merck KGaA, toluene and 2,2'-azoisobutyronitrile (AIBN) from Sigma Aldrich, bis(2-hydroxyethyl)-3-aminopropyltriethoxysilane (62% in ethanol) from ABCR GmbH & Co. KG and 1µm silica nanospheres (standard, NanoXact) from NanoComposix.

Accuracy of AFM size measurements determined on a calibration standard

AFM imaging to determine the accuracy of size measurements took place in tapping mode using a Multi Mode 8 AFM (Bruker Corporation) and TESPA-V2 tips (Bruker Corporation; k = 42 N/m; f0 = 320 kHz) to acquire 20 µm x 20 µms scan of the 5 µm repeating circular pit area of a HS-100MG silicon dioxide calibration standard (BudgetSensors; 5 µm repeating structures; step height of 100nm). Gwyddion 2.50 , an open-source software, was used for data processing and evaluation. Curvature was flattened by subtracting polynomial background (2nd degree) from the image. Accuracy of size measurements on the slow scan axis (y-axis), fast scan axis (x-axis) and pit height were determined with N = 3.

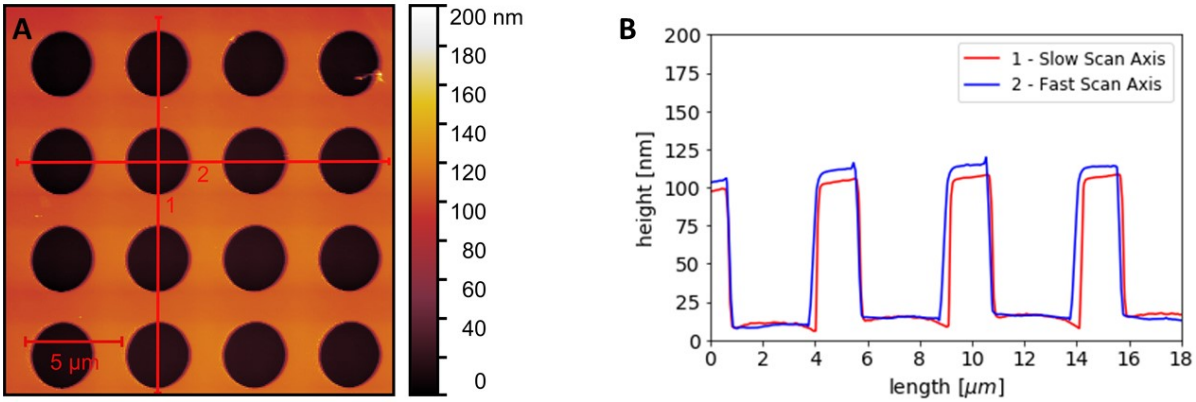

Figure S 1: AFM topography image (20 µm x 20 µm) of the 5 µm repeating circular pit area of a HS-100MG silicon dioxide calibration standard with sections (marked in red) on the slow scan axis (1) and fast scan axis (2) (A); Height profiles of the sections on the slow scan axis (1) and the fast scan axis (2)

Table S 1: Determine accuracy of AFM size measurements using a 5 µm repeating circular pit area of a HS-100MG silicon dioxide calibration standard

	Reference Size of AFM calibration standard	Measured Size	Difference [%]
Slow Scan Axis	5 µm	5.03 µm ± 0.04 µm	0.6
Fast Scan Axis	5 µm	4.97 µm ± 0.04 µm	0.6
Pit Height	100 nm	98 nm ± 1 nm	2

N=3 for each axis

Non-imprinted polymer (NIP) thin film as a reference for SIP thin film

NIP thin film synthesis relied on the protocol of SIP thin film synthesis, but applied an unmodified glass slide instead of a bacteria stamp. First, a glass slide was activated with oxidative plasma and functionalized with TMVS (4 h incubation in 163 mM TMVS in toluene). For pre-polymer synthesis, styrene and DVB (v/v = 50:50) were oligomerized for 30 min at 70°C using 1.8% (w/v) AIBN as radical initiator. The thin film was generated by covering the functionalized glass slide with the pre-polymer and pressing an unmodified glass slide onto the pre-polymer thin film. After hardening the polymer over night at 37°C, the unmodified glass slide was removed.

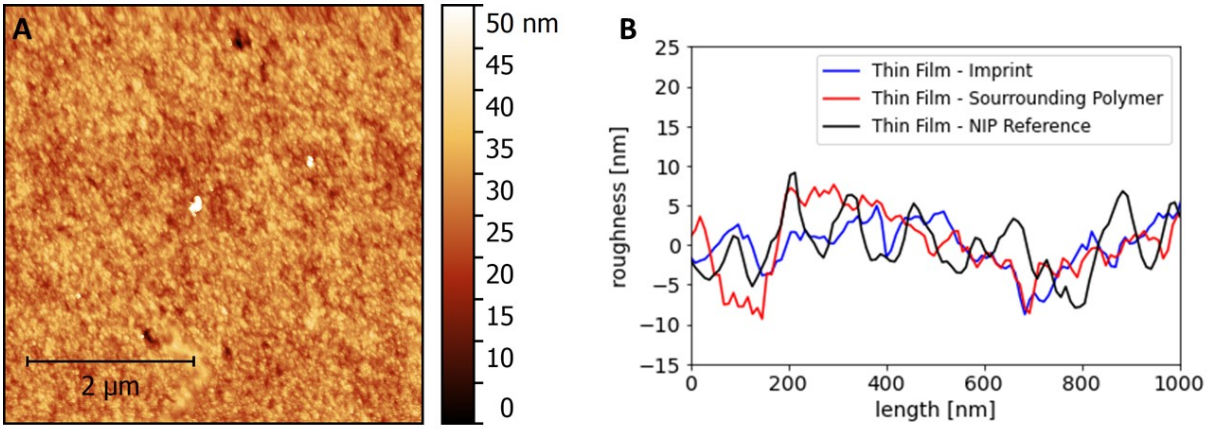

Figure S 2: AFM topography image (5 µm x 5 µm) of a NIP thin film (A); Typical roughness profiles of 1 µm sections on SIP thin film in imprints, on the surrounding polymer and on a NIP thin film as reference (B)

Reference SIP beads using functionalized silica nanospheres as template

When synthesizing SIP beads via polymerization in Pickering emulsions, one needs to stabilize the emulsion with particles. Therefore, it is not possible to synthesize a "clean" NIP bead reference. However, using a completely different template during Pickering emulsion, such as functionalized silica nanospheres, opens up the possibility to obtain a non-imprinted reference. For that purpose, 10mg silica nanospheres were treated with oxidative plasma and functionalized with bis-(2-hydroxyethyl)-3-aminopropyltriethoxysilane (200 mM in toluene) for 18 h on a tube rotator (20 rpm). SIP bead synthesis took place using the same protocol as for SIP bead synthesis with bacterial cells. First, the oil phase was prepared by mixing 0.5 mL styrene, 0.5 mL DVB and 1.8% (w/v) AIBN and pre-polymerizing for 30 min at 70°C. The aqueous phase was prepared by suspending the functionalized silica nanospheres in 1.2mL water. The two phases were emulsified by vigorous shaking and the formed pre-polymer droplets were further polymerized at 37°C. The synthesized polymer beads were separated from the aqueous phase and rinsed with water. To remove the silica nanospheres from the SIP surface, the beads were boiled for 30 min in 1M NaOH and afterwards rinsed with water.

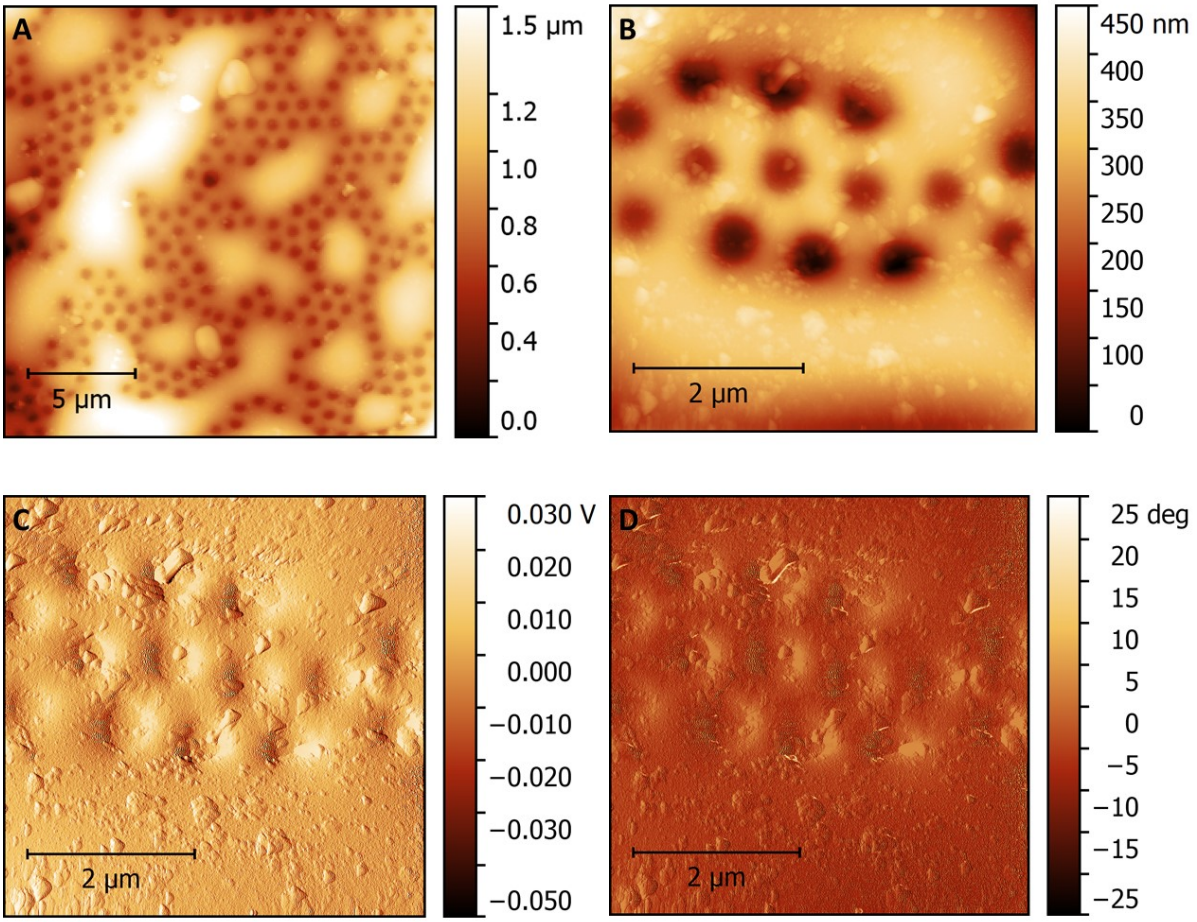

Figure S 3: AFM scan (20 µm x 20 µm) topography image of imprints on SIP- beads synthesized with functionalized silica nanospheres as reference template (A); AFM scan (5 µm x 5 µm) topography image of imprints on SIP- beads synthesized with functionalized silica nanospheres as reference template (B); AFM scan (5 µm x 5 µm) error image (C); AFM scan (5 µm x 5 µm) phase shift (D)