Electronic Supporting Information

Generation of 3-Dimensional Multi-Patches on Silica Particles via Printing with Wrinkled Stamps

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Materials and Methods

Poly(dimethylsiloxane) (PDMS) was obtained as Sylgard 184 elastomer kit from Dow Corning. 50 wt% aqueous solutions of linear polyethyleneimine (PEI) were purchased from Fulka Chemicals with a molecular weight distribution of 600 to 1000 kg mol^{-1}. Dry silica particles with a size of 5 µm were purchased from Polysciences Inc. and with a size of 20 µm from Microparticles. Ethanol was purchased from Th. Geyer (Chemsolute) and acetone from VWR (ACS reagent). Fluorescein isothiocyanate (FITC), rhodamine B isothiocyanate (RBITC) and n-octyltriethoxysilane was obtained from Sigma Aldrich.

Analysis

Scanning Force Microscopy (SFM): SFM measurements were done with a Dimension Icon of Bruker Corporation. For all samples Tapping Mode and OTESPA tips (k = 42 N/m, f_0 = 300 kHz) were used. The measurement itself was controlled by the software NanoScope (Version 9.1), whereas all data were analysed with NanoScope Analysis (Version 1.5).

Fluorescence microscopy: All light and fluorescence microscopic images were taken by the inverse microscope DMi8 of Leica Microsystems and analysed with the software Leica Application Suite X (LAS X).

Preparation of Wrinkles

For the fabrication of wrinkled substrates (see Fig. S1), PDMS was prepared by mixing prepolymer and curing agent of Sylgard 184 with a 10:1 mass ratio. The mixture was stirred and filled in a clean, plane petri dish with a film thickness of 3 mm. After degassing overnight, PDMS was cured for 2 h at 80°C. The crosslinked PDMS was cut in substrates with dimensions of 1 x 2.5 cm^2 and 2.5 x 5 cm^2. The surface pattern was induced by clamping and stretching the substrates with a custom-made stretching apparatus to 130 % of their original length. The surface was exposed to air plasma for 600 – 1200 s at 0.2 or 0.1 mbar (PlasmaFlecto 10, 100 W), following the relaxation of the elastomer to create a wrinkled surface pattern. These wrinkled substrates could be used directly for printing experiments or for manufacturing cast substrates. For casting these substrates (see Fig. S2), their surface must be inert for interactions with fresh PDMS. For this reason, the substrates were firstly modified with n-octyltriethoxysilane. Substrate and 0.5 mL of silane were placed in a desiccator and evacuated at 1.5 mbar. After the surface modification, the wrinkled substrate was poured with freshly mixed PDMS, degassed and cured for 2 h at 80°C. Original and cast substrate could be removed easily from each other and the cast substrate could be used for printing processes.

Ink Synthesis

In case of "sandwich"-printing processes, the inks have to be fluorescently marked before printing. For this, PEI was marked with FITC and RBITC. At first, an aqueous solution of PEI (4 wt%) was generated and referred to the amount of PEI, 2 wt% of the fluorescent dye were added. The mixture was stirred overnight at room temperature and could be used without further purification.

Intaglio Printing on Silica Particles

For intaglio printing, either original or cast substrates with different wavelength (1.5 or 3 µm) were used. Moreover, printing was done on bare silica particles with a diameter of 5 µm and 20 µm. In case of a standard printing from one side, the following steps were important: generation of a particle monolayer, loading of the stamps with PEI, printing on the particles, particle release from the stamps and fluorescent labeling of PEI.

Particle monolayers were generated by drop-casting or spin-coating of particle dispersions in ethanol with a concentration of 10 mg/mL (5 µm) or 50 mg/mL (20 µm). 40 µL of small silica particles were spin-coated via a two-step process (firstly 5 min at 300 rpm, secondly 1 min at 1500 rpm / Laurell WS-650-23B). 15-20 µL of large silica particles were drop-cast. The stamps (original and cast wrinkled substrates) were plasma activated (60 s, 300 W, 0.2 mbar / PlasmaFlecto 10) before spin-coating (1 min at 4000 rpm) of the PEI solution (2 or 4 wt%). After drying, the loaded stamps were pressed on top of the particles for a few seconds. The particles stuck to the stamps and were removed by ultra-sonication in ethanol or acetone. In case of ethanol, the particles were washed by centrifugation (10 min at 10000 rpm) and dispersion for one time, in case of acetone, the washing step was repeated once more with ethanol. For fluorescent labeling, the particles were dispersed in 100 µL FITC solution, sonicated for 10 min and then stirred for 20 min to complete the reaction between PEI and FITC. Afterwards, the labeled particles were washed three times by centrifugation and dispersion in ethanol.

“Sandwich” Intaglio Printing

The “sandwich” printing process was similar to the intaglio printing process from one side. In general, the steps - generation of a particle monolayer and loading of the stamps with ink (PEI with FITC or PEI with RBITC) - were done by the same procedure. The concentration of PEI was always 4 wt% and only silica particles with a diameter of 20 µm were used. After printing onto one side of the silica particles such as it was described before, the second loaded stamp was pressed on the other side of the particles for a few seconds. The particles now stuck to both stamps and were removed by ultra-sonication in acetone. Finally, the particles were washed three times by centrifugation and dispersion in ethanol.

Printing Type

Initially, we had to identify the type of printing process. From literature, two possible printing techniques are known: microcontact printing and intaglio printing (see Fig. S3).[41,42] In case of intaglio printing, in comparison to microcontact printing, the ink is not transferred directly at the contact area but from the hollow parts of the wrinkled stamps. Proofing the printing type was done by SFM measurements of the stamps before and after loading with the ink (see Fig. S4). It shows a clear decrease of the amplitude compared to the unloaded stamp. PEI is not spread as a thin and homogeneous film over the whole wrinkled stamp but is mainly located in the grooves. That means for the printing process, that the interaction between ink and particle surface does not take place at the contact area of particle and stamp; instead, the contact area restricts the ink/particle interaction area.

Supplementary Pictures

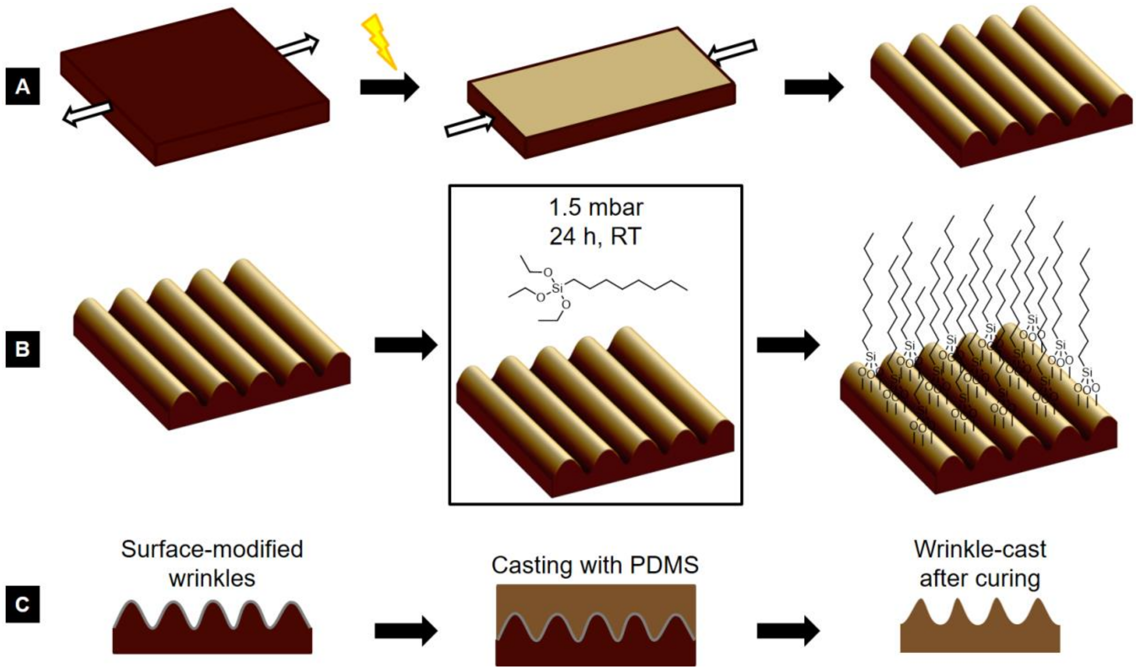

Figure S1 Principle of the generation of wrinkles and cast wrinkles. A: Stretched PDMS is treated with air plasma to generate a hard silicon oxide top layer. Release of the stress induces the formation of wrinkles. B: Surface modification with n-octyltriethoxysilane via chemical vapor deposition. C: Modified substrate is poured with freshly mixed PDMS and cured at elevated temperatures.

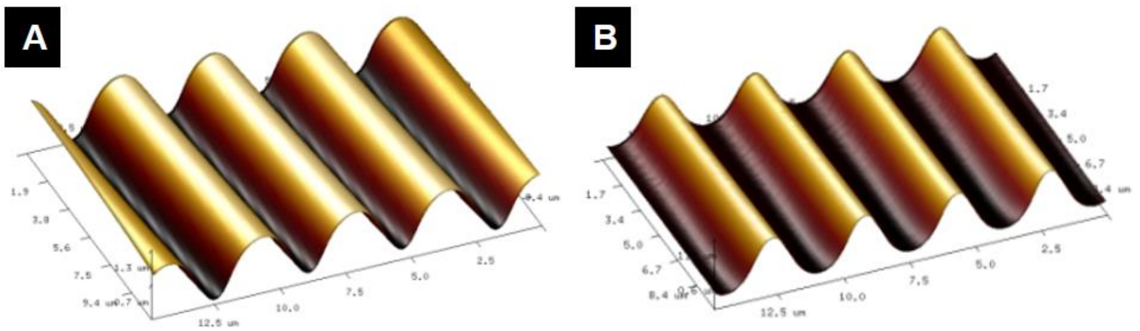

Figure S2 Three-dimensional topographic SFM images of the original (A) and cast (B) wrinkled substrate for detection of structural variations.

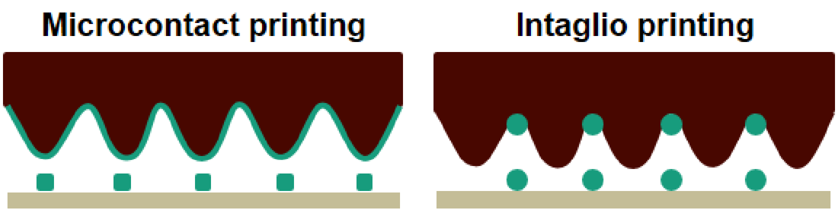

Figure S3 Schematic depiction of the two possible printing techniques: microcontact printing (µCP) and intaglio printing.

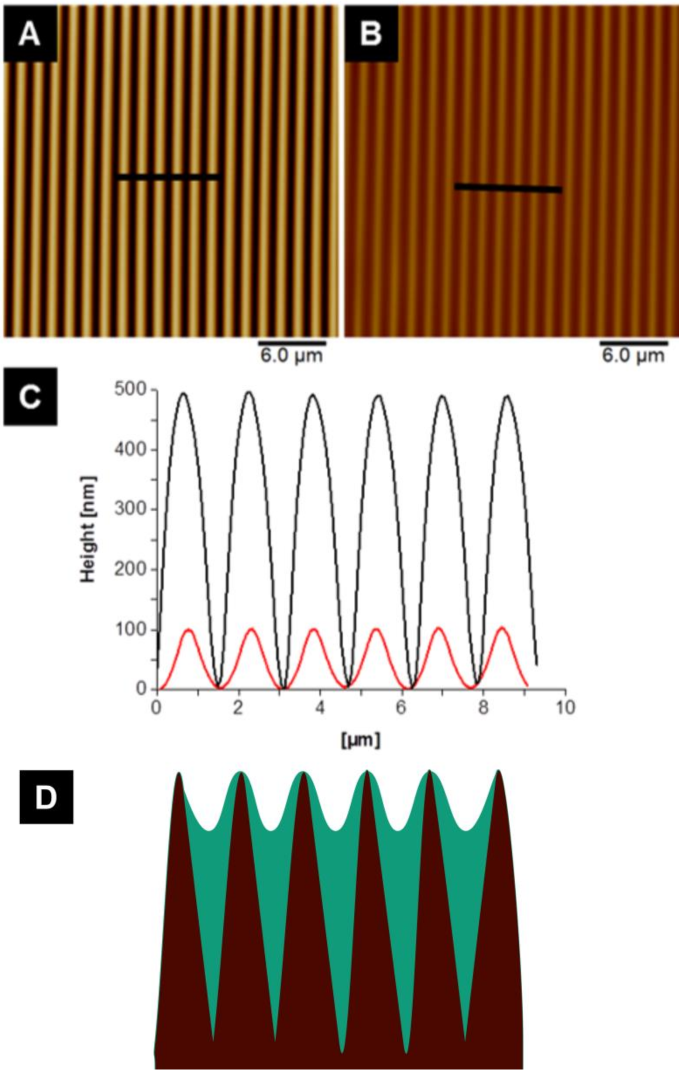

Figure S4 SFM images with same height scale of wrinkled stamps before (A) and after (B) loading with PEI (4 wt%). C: Cross sections of indicated black lines from SFM image. Black curve shows stamp profile before loading with PEI with amplitude around 500nm. The red line indicates the stamp profile after loading with PEI, where the amplitude decreases to around 100nm. D: Scheme indicates the filling of the wrinkle grooves with PEI (green) and therefore the decrease of amplitude.

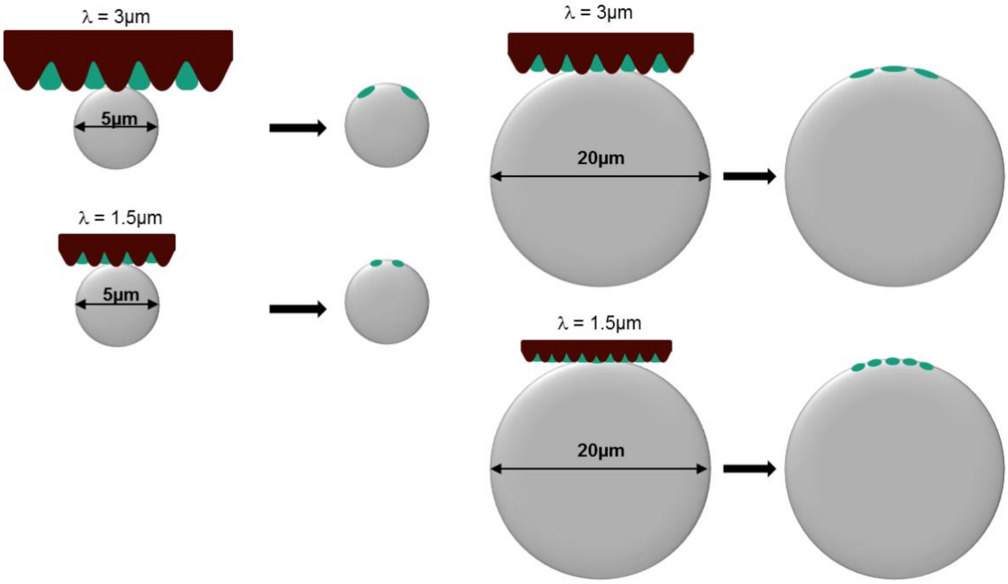

Figure S5 This Schematic shows a depiction of the size ratio between particle diameter (5 and 10 µm) and wavelength (1.5 and 3 µm), as well as resulting patch-geometry (2 / 3 / 5 patches).

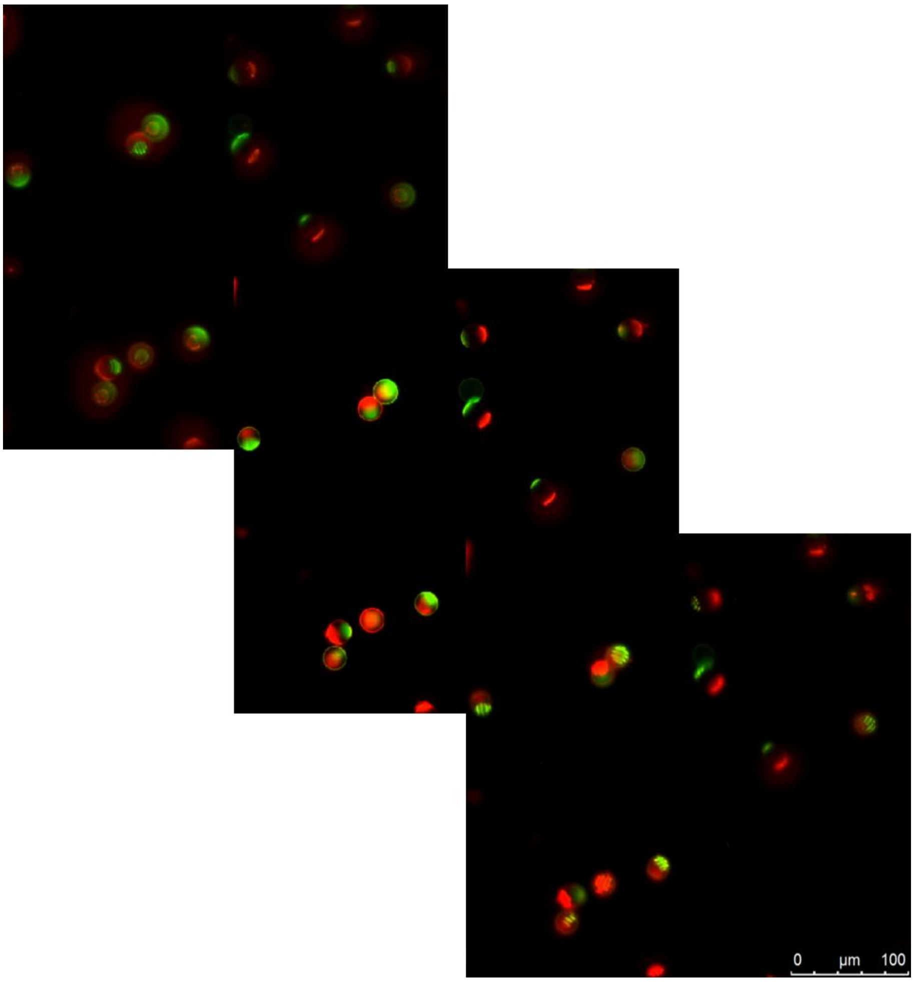

Figure S6 Fluorescence microscopy images of silica particles (20 µm) in three different focus planes after “sandwich” printing with wrinkled stamps ($\lambda = 3$ µm). The stamps were loaded with PEI/FITC (green) and PEI/RBITC (red). Particle release was conducted using acetone.

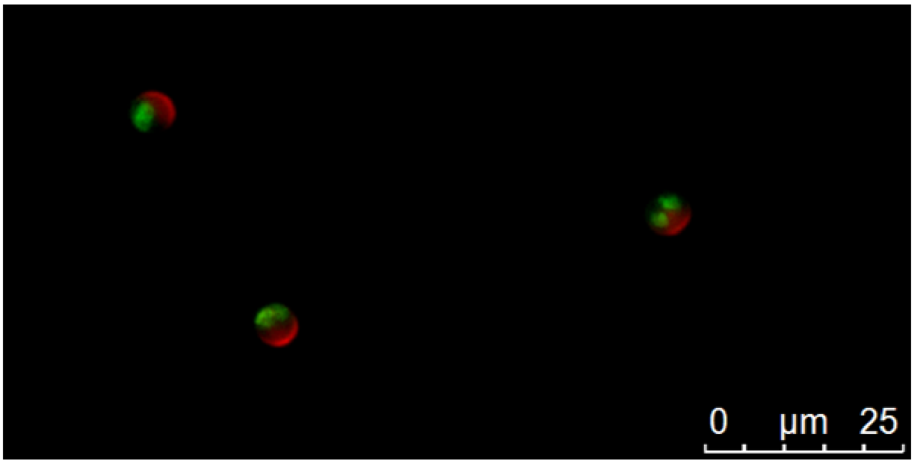

Figure S7 Fluorescence microscopy images of silica particles (5 µm) after „sandwich“-intaglio printing with wrinkled stamps ($\lambda = 3$ µm). Ink is PEI-FITC (green) and PEI-RBITC (red).