Electronic Supplementary Information

Preparation of PDMS Ultrathin Films and Patterned Surface Modification with Cellulose

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1. Quartz crystal microbalance with dissipation (QCM-D)

A QCM-D device (model E4 from Q-Sense, Gothenburg, Sweden) was used to determine the film thickness, mass and stability of the PDMS coated surfaces. The QCM-D method is based on the piezoelectric effect of a quartz sensor. Basically, QCM-D records the change in responses of frequency and dissipation of the freely oscillating sensor. The oscillation frequency is decreased when the material is coated on the sensor surface. These changes in frequency can be directly related to the adsorbed mass on the sensor surface using the Sauerbrey equation.

$$\Delta f = -\frac{C\,\Delta m}{n} \qquad (1)$$

Where Δf describes the frequency shift, Δm is the mass change, C is the Sauerbrey constant (17.7 ng Hz^{-1} at $f = 5$ MHz) and n is the number of the overtone ($n = 1, 3, 5$, etc.) of oscillation. Equation 3 is applicable only for thin and rigid films, which are fully coupled to the oscillation motion of the quartz sensor. In our case, equation 1 was used to calculate the dry mass of the coated PDMS film. For that purpose, the third overtone resonance frequency of the crystal before and after film deposition was measured for at least 10 minutes. Furthermore, it is possible to calculate the effective layer thickness (d_{eff}) using the Sauerbrey mass if the density of the coated layer is known (equation 2). A density value of 970 kg m^{-3} was taken for the thickness calculation.[1] All calculations were carried out using the software package QTools 3.0.12 (Q-Sense).

$$d_{\mathrm{eff}} = \frac{\Delta m}{\rho_{\mathrm{eff}}} \qquad (2)$$

Stability measurement: In each experiment, Au-sensors coated with PDMS thin films were mounted into the QCM-D flow cell and the initial resonance frequency of the sensor was determined for at least 10 min. The films were equilibrated with MQ-water until a constant frequency signal was obtained. After this, solutions with different pH values (3, 5, 7, 9) each 150 mM sodium chloride were pumped through the QCM-D cells for 60 min followed by rinsing with water for 30 min. The measurement was terminated at this stage. The flow rate of the solution was kept at 0.1 ml min^{-1} throughout the experiments. All measurements were performed at 21 ± 0.1 °C. Three independent coated sensors were used for each experiment.

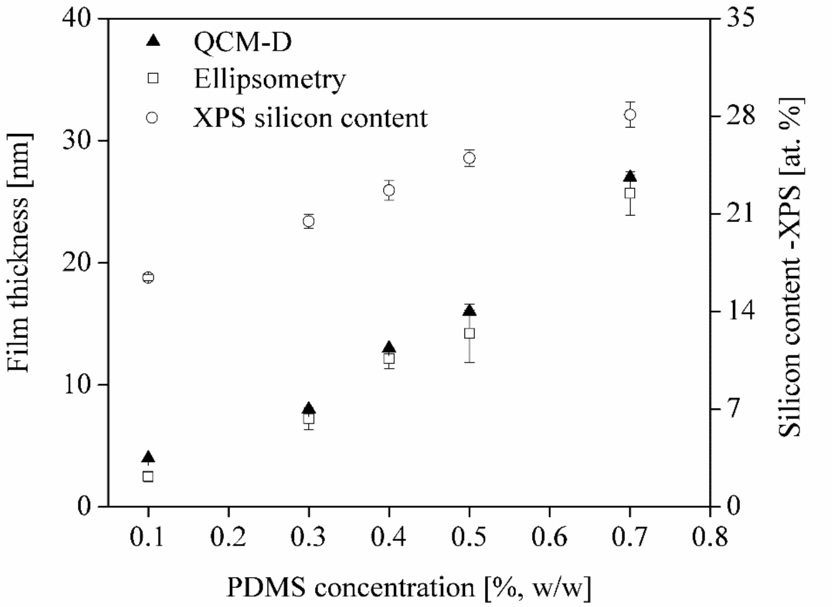


Fig. S1 Comparison of the film thickness determined using QCM-D and ellipsometry with the silicon content from XPS analysis as a function of PDMS concentration

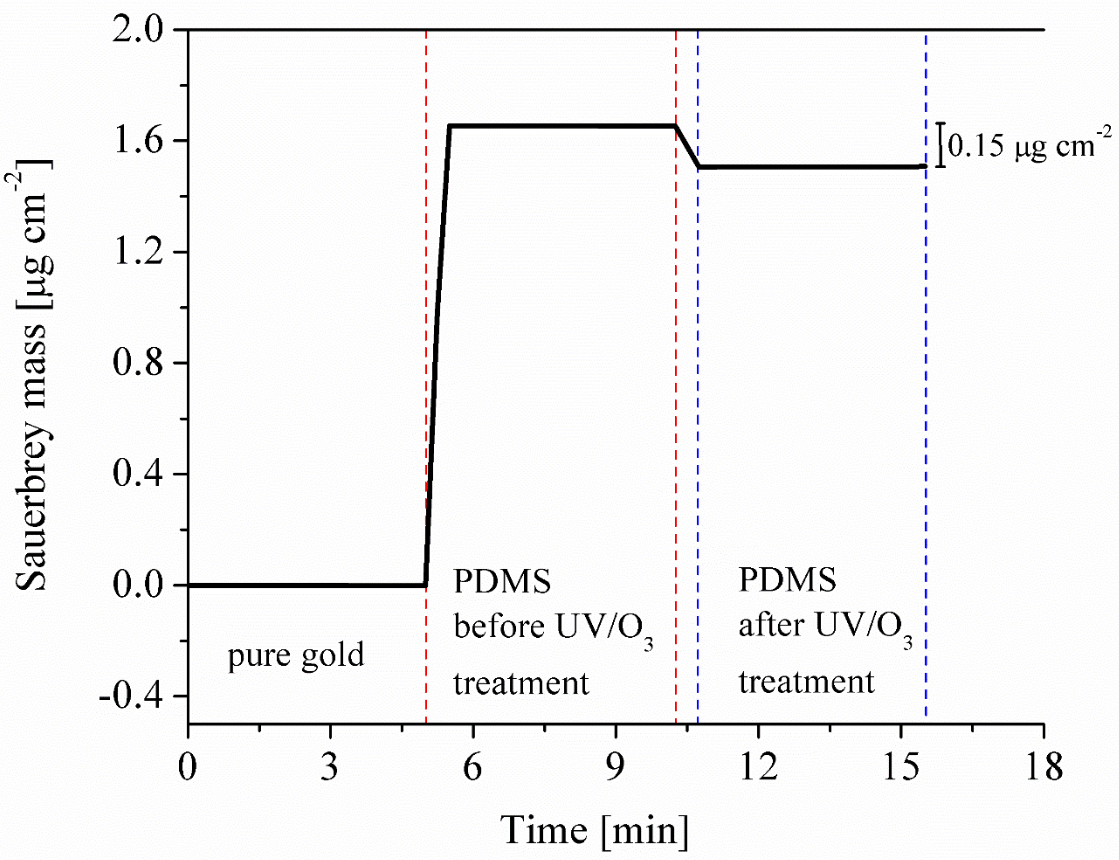


Fig. S2 Sauerbrey mass of PDMS films (coated on gold substrate) before and after UV/ozone treatment determined using QCM-D.

1.1 Stability of the PDMS films

In order to test their stability, films manufactured from 0.5% (w/w) were rinsed with water at different pH values (3-9) and 150 mM NaCl, for 60 min in the QCM-D cell. It has been found that, rinsing did not significantly increase frequency (third overtone) at all pH values, implying that films are not detached from the base substrate and are very stable under the given environment. This is an important factor if one aims to apply thin PDMS films for diverse solid-liquid interaction studies under different external stimuli (e.g. pH, ionic strength, etc.).

Interestingly, the application of water at pH 3 resulted in slightly reduced frequency and it is even more pronounced at pH 9. This behavior can be attributed to the swelling of the film as a result surface hydrolysis.[2] Similar results were observed for films coated on the SiO_2 substrates. Similar results were observed for films coated on the SiO_2 substrates (data not shown)

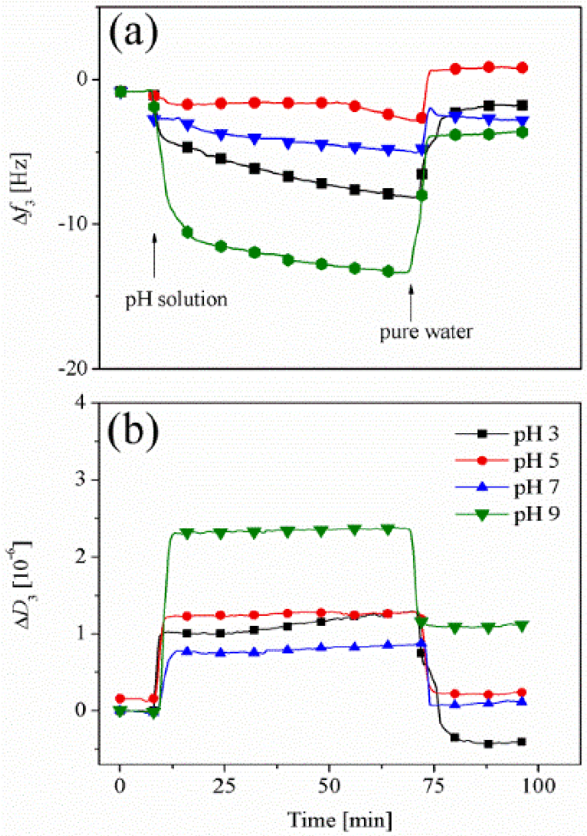


Fig. S3 QCM-D change in frequency of the PDMS thin film incubated with different pH solution in 150 mM NaCl.

2. Contact angle measurements

Advancing and receding contact angle: For an ideal surfaces *i.e.* flat, inert and chemical homogeneous, an equilibrium liquid contact angle can be applied without any constrains by Young's equation.[3] However, in general, the real surfaces are neither perfectly flat nor chemically homogeneous. In that case, the observed contact angle differ from the Young's angle due to the roughness and/or chemical heterogeneity of the surfaces. The knowledge about surface topography can be established by measuring the advancing (θ_A) and receding contact angle (θ_R). The difference between (θ_A) and (θ_R) is referred as contact angle hysteresis ($\Delta\theta = \theta_A - \theta_R$) which can be influenced by surface roughness and chemical heterogeneity. On smooth and homogeneous surfaces, the contact angle hysteresis is lower and liquid droplet can move easily under even little perturbation. Whereas, rough surfaces with high contact angle hysteresis are very adhesive to liquid droplets. The detailed description of contact angle hysteresis, advancing/receding contact angle can be found elsewhere.[4, 5]

Table 1. Static contact angle values of the silicon wafer and thin films of PDMS coated from different concentrations.

	Water [deg]	Ethyleneglycol [deg]	Diiodomethane [deg]	Formamide [deg]
Silicon wafer	19.8 ± 0.9	8.5 ± 1.5	43.9 ± 4.5	28.7 ± 1.9
PDMS 0.1 %	105.2 ± 0.5	88.2 ± 1.4	73.4 ± 0.9	92.5 ± 1.4
PDMS 0.3 %	109.7 ± 0.3	96.0 ± 0.6	78.0 ± 0.4	101.8 ± 0.6
PDMS 0.4 %	110.3 ± 0.8	95.3 ± 1.4	78.5 ± 1.2	103.2 ± 0.4
PDMS 0.5 %	110.5 ± 0.4	98.0 ± 0.6	79.6 ± 0.5	104.1 ± 0.6
PDMS 0.7 %	111.5 ± 0.7	98.1 ± 0.4	80.8 ± 0.8	104.9 ± 0.7

Table 2. Wettability of the surfaces of PDMS and cellulose coated surfaces. Contact angle hysteresis (advancing contact angle – receding contact angle).

	Static contact angle (deg)	Advancing contact angle (deg)	Receding contact angle (deg)	Contact angle hysteresis (deg)
PDMS 0.1 %	19.8 ± 0.9	111 ± 0.5	95 ± 0.2	16 ± 0.3
PDMS 0.3 %	105.2 ± 0.5	112 ± 0.7	97 ± 0.3	15 ± 0.4
PDMS 0.4 %	109.7 ± 0.3	115 ± 0.2	99 ± 0.8	16 ± 0.6
PDMS 0.5 %	110.3 ± 0.8	115 ± 0.4	100 ± 0.7	15 ± 0.3
PDMS 0.7 %	110.5 ± 0.4	117 ± 0.6	80 ± 0.2	37 ± 0.4
Cellulose spin coated	32 ± 1	46 ± 0.4	21 ± 0.6	25 ± 0.2
Cellulose spray coated	48 ± 1.7	52 ± 0.7	26 ± 0.2	26 ± 0.5

Table 3. Surface free energy (SFE) values and the individual components of the silicon wafer and thin films of PDMS coated from different concentrations. All SFE components are given in mJ m^{-2}.

	SFE	LW	γ+	γ-
Silicon wafer	44.5 ± 5.3	26.9 ± 2	1.18 ± 0.4	65.56 ± 1
PDMS 0.1 %	19.0 ± 0.8	19.0 ± 0.5	0 ±0.0	1.61 ± 0.3
PDMS 0.3 %	16.0 ± 0.3	16.0 ± 0.2	0 ± 0.0	1.00 ± 0.1
PDMS 0.4 %	16.1 ± 1.0	16.1 ± 0.6	0 ±0.0	3.50 ± 0.5
PDMS 0.5 %	15.8 ± 0.7	15.8 ± 0.3	0 ±0.0	3.33 ± 0.3
PDMS 0.7 %	12.8 ± 0.5	12.8 ± 0.4	0 ± 0.0	1.05 ±0.2

3. Field emission scanning electron microscopy (FESEM)

PDMS films coated on silicon wafers were mounted on sample holders. A Carl Zeiss FE-SEM SUPRA 35 VP electron microscope was used for observation of the images of PDMS coated films. The images were recorded with an acceleration voltage of 1 kV. No sputtering on sample surfaces was performed.

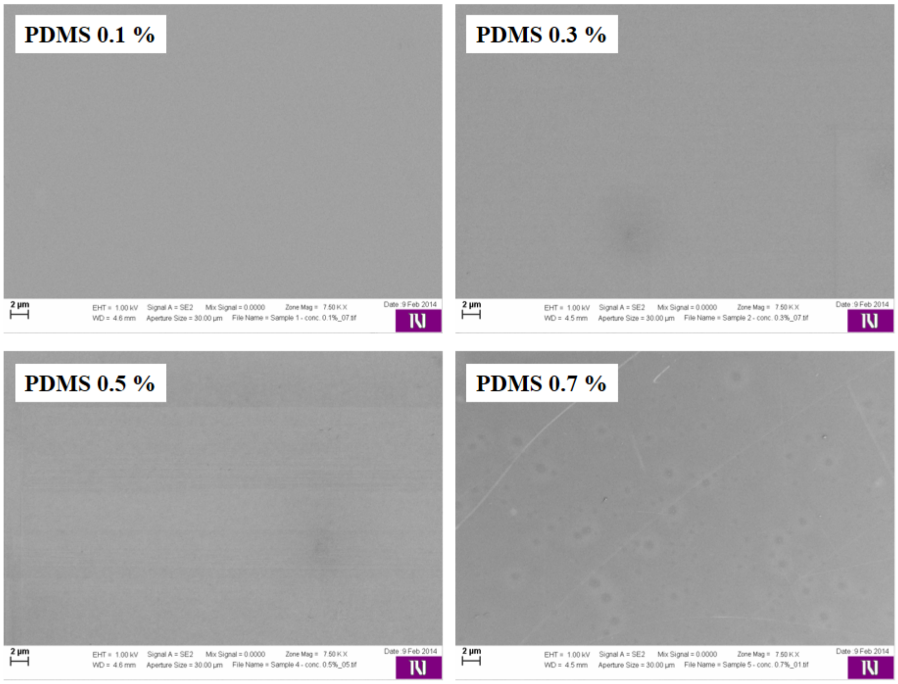


Fig. S4 Scanning electron microscopy images of PDMS films spin coated from different concentration on silicon substrates. All concentrations are given in w/w.

4. Atomic force microscopy

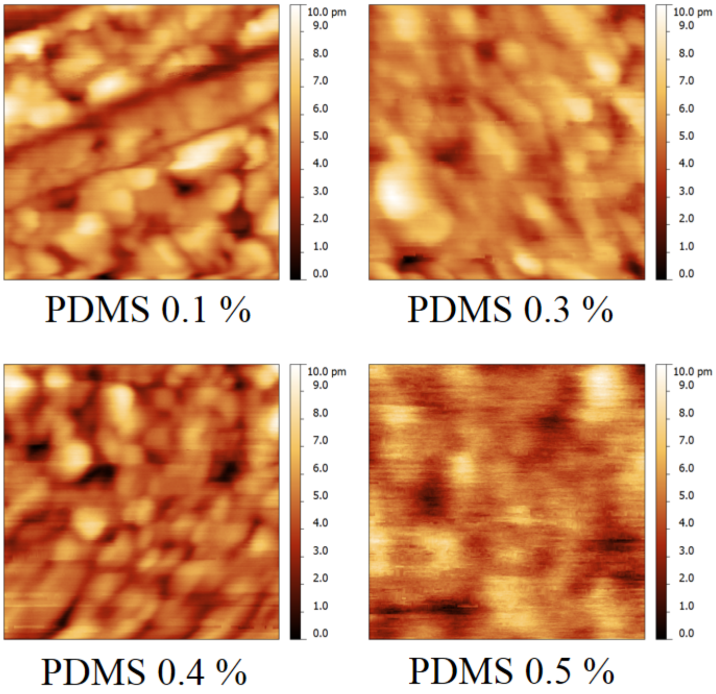
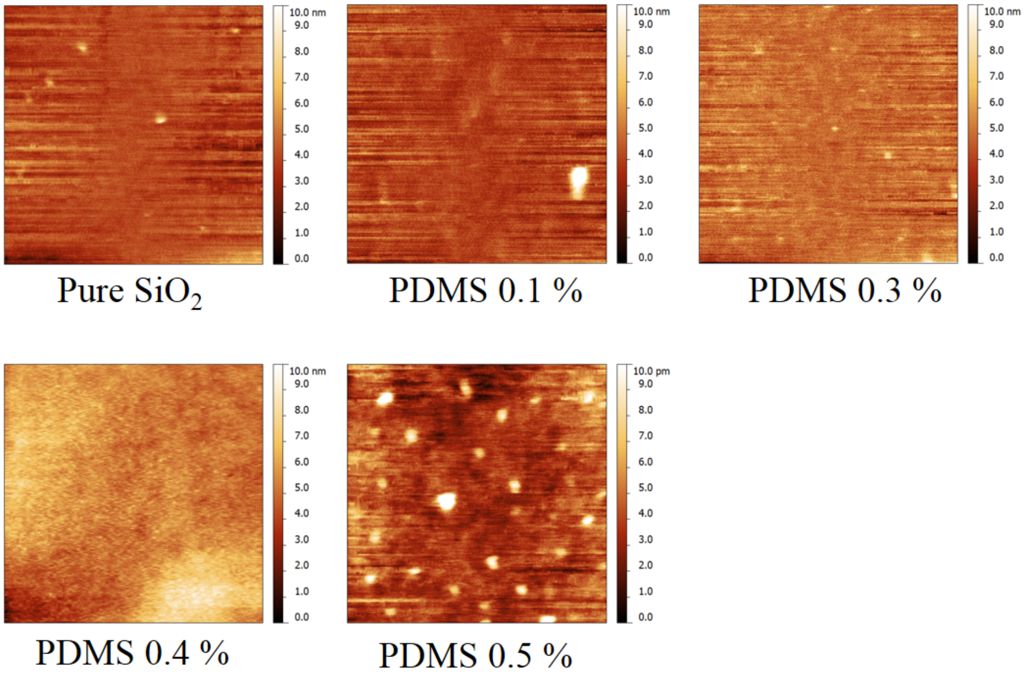


Fig. S5 Atomic force microscope (AFM) height images (1 x 1 μm^2) of PDMS (dissolved in tetrahydrofuron) films spin coated from different concentration on gold substrate. All concentrations are given in w/w.



Pure SiO_2

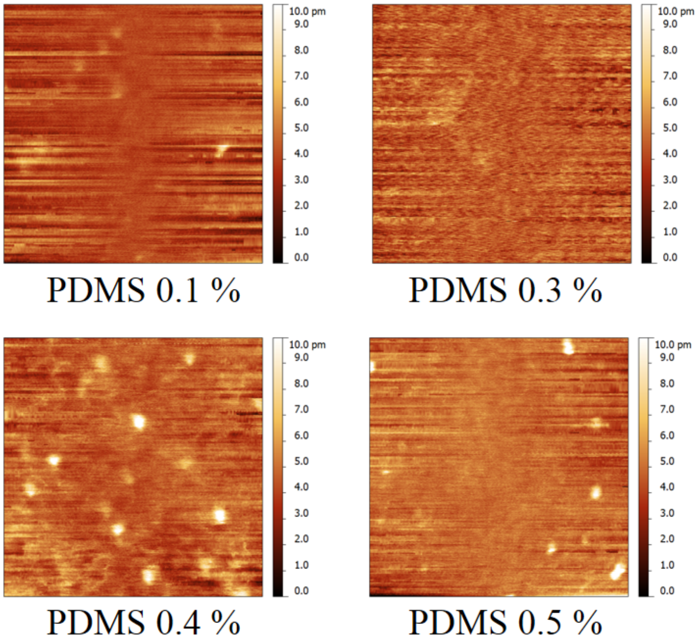
PDMS 0.1 %

PDMS 0.3 %

PDMS 0.4 %

PDMS 0.5 %

Fig. S6 Atomic force microscope (AFM) height images (1 x 1 μm^2) of pure SiO_2 and of PDMS (dissolved in tetrahydrofuron) films spin coated from different concentration on SiO_2 substrate.



PDMS 0.1 %

PDMS 0.3 %

PDMS 0.4 %

PDMS 0.5 %

Fig. S7 Atomic force microscope (AFM) height images (1 x 1 μm^2) of PDMS (dissolved in toluene) films spin coated from different concentration on SiO_2 substrate.

References:

1. J. E. Mark, *New York, NY: Oxford University Press.*, 1999.
2. Gaëlle Ducom, Baptiste Laubie, Aurélie Ohannessian, Claire Chottier, Patrick Germain and V. Chatain, *Water Science Technology*, 2013, **68**, 813-820.
3. T. Young, *Philosophical Transactions of the Royal Society of London*, 1805, **95**, 65-87.
4. H. B. Eral, D. J. C. M. 't Mannetje and J. M. Oh, *Colloid Polym Sci*, 2013, **291**, 247-260.
5. J. W. Krumpfer and T. J. McCarthy, *Faraday Discussions*, 2010, **146**, 103-111.