

Two-Level Structured Self-Adaptive Surfaces with Reversibly Tunable Properties

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Abstract: We report a route to fabricate two-level structured self-adaptive surfaces (SAS) of polymer materials. The first level of structure is built by a rough polymer film that consists of needlelike structures of micrometer size. The second level of structure is formed by the nanoscopic self-assembled domains of a demixed polymer brush irreversibly grafted onto the needles. By exposing the surface to solvents that are selective to one of the components of the brush, we reversibly tune the surface properties. The large-scale surface structure amplifies the response and enables us to control wettability, adhesion, and chemical composition of the surface over a wide range.

Introduction

Controlling the wettability of solid surfaces is of abiding importance for many processes in living organisms (e.g., ultra-water-repellent materials are found in self-cleaning surfaces of plants and insects¹) and for numerous industrial applications.² Advantages of ultrahydrophobic surfaces, however, can turn into disadvantages: the self-cleaning properties of a surface may result in static electric charges or poor adhesion or dyeability. The ability to reversibly switch the properties of the *same material* from strongly water-repellent to hydrophilic would allow a diverse range of applications. In general, however, a polymer surface has fixed properties and the design of switchable coatings is a formidable challenge.^{2h,j-1}

Wettability can be regulated by chemical surface composition.¹⁻³ On a flat polymer film, the contact angle of a liquid drop is determined by the balance of tensions at the contact line between the polymer film, the liquid, and its vapor, which

results in Young's equation:

$$\cos \Theta_0 = (\gamma_{sv} - \gamma_{sl})/\gamma$$

where Θ_0 is the bare contact angle of water (on a flat surface), γ is the surface tension of water, and γ_{vs} and γ_{ls} are the surface tension of the solid-vapor and the solid-liquid (water) interfaces, respectively. Roughness of the surface can strongly amplify hydrophobicity or hydrophilicity.^{3b,3c,4}

If the bare contact angle on a flat surface is very small, the liquid might fill the grooves of the rough surface and only the upper part of the relief, which comprises a fraction ϕ_s of the total area, is not in contact with the liquid. This occurs if the wicking criterion^{4g}

$$\cos \Theta_0 > (1 - \phi_s)/(r - \phi_s)$$

is fulfilled. r denotes the ratio between the increased contact area of the rough surface and the corresponding projected area.

If the bare contact angle is smaller than 90° but the wicking criterion is not fulfilled, the liquid fills the grooves of the rough surface only below a droplet, and Wenzel's equation^{3b} holds, which takes due account of the increased contact area between the liquid and the surface:

$$\cos \Theta = r(\gamma_{sv} - \gamma_{sl})/\gamma = r \cos \Theta_0$$

where Θ is contact angle of water on a rough surface.

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If the bare contact angle is larger than 90° , air can be trapped below a drop and the rough surface acts like a fakir carpet;^{4a} i.e., the liquid is only in contact with the upper part of the relief of the rough surface. In this limit (Cassie regime⁵) the contact angle is given by

$$\cos \Theta = -1 + \phi_S(1 + \cos \Theta_0)$$

where ϕ_S is the fraction of the upper part of the relief, which itself depends on Θ_0 . Superhydrophobic surfaces⁴ often possess surface textures that trap air between the liquid and the surface.

Thus the ability of a surface to repel a liquid or to make it spread can be tuned by surface design. For the fixed liquid (e.g., water), wettability may be regulated by appropriate surface texture and/or ($\gamma_{sv} - \gamma_{sl}$) value. Careful studies on model surfaces,⁴ which consist of regular structures such as spikes, pillars, or stripes, reveal that if the contact angle on a flat surface is less than 90° , roughness amplifies hydrophilicity, while it enhances hydrophobicity otherwise. The very same mechanism is also employed in biological systems (e.g., plant leaves¹). Details, however, depend on the geometrical properties of the surface as well as on the ability of the structures to pin the three-phase contact line between liquid, vapor, and substrate.⁴

In the present work we take advantage of the amplification of hydrophilicity or hydrophobicity by the roughness of an etched substrate. In the following we shall demonstrate that wettability is amplified by the rather irregular structure of the plasma-etched surface. The combination of controlling of the wetting properties of mixed polymer brushes and its strong amplification by roughness enables us to effectively fabricate surfaces with a wide span of reversibly tunable surface properties. A detailed study of how the geometric surface structure depends on the etching procedure and how this, in turn, influences the amplification effect is beyond the scope of the present work. We note, however, that our fabrication scheme is rather robust with respect to etching conditions.

Experimental Section

Materials. Poly(tetrafluoroethylene) (PTFE) foils, 0.5 mm thick, were purchased from PTFE Nünchritz GmbH, Germany. The material as received was cut into pieces of $2 \times 2 \text{ cm}^2$ and subsequently cleaned in CHCl_3 for 10 min in an ultrasonic bath to remove any contaminants. Highly polished silicon wafers (obtained from Wacker-Chemitronics) were first cleaned in an ultrasonic bath for 30 min with dichloromethane, placed in cleaning solution (prepared from NH_4OH and H_2O_2) at 60°C for 1 h, and then rinsed several times with Millipore water ($18 \text{ M}\Omega\cdot\text{cm}^{-1}$). Carboxyl-terminated poly(styrene-*co*-2,3,4,5,6-pentafluorostyrene) (PSF-COOH; styrene units:pentafluorostyrene units = 0.75:0.25; $M_n = 16\,000 \text{ g/mol}$ and $M_w = 29\,500 \text{ g/mol}$) was synthesized by free radical polymerization in THF solution with 4,4'-azobis(4-cyanopentanoic acid) as initiator. Carboxyl-terminated poly(2-vinylpyridine) (PVP-COOH; $M_n = 39\,200 \text{ g/mol}$ and $M_w = 41\,500 \text{ g/mol}$) was purchased from Polymer Source, Inc (synthesized by anionic polymerization). Toluene and tetrahydrofuran (THF) were distilled after drying over sodium. Dichloromethane was dried on molecular sieves. 3-Glycidoxypropyl trimethoxysilane (GPS) ABCR (Karlsruhe, Germany) was used as received. Oxygen and ammonia for plasma treatment with purities of 99.95% and 99.999%, respectively, were purchased from Messer Griesheim, Germany.

Plasma Treatment. For plasma etching of PTFE, a cylindrical vacuum chamber made of stainless steel with a diameter of 250 mm

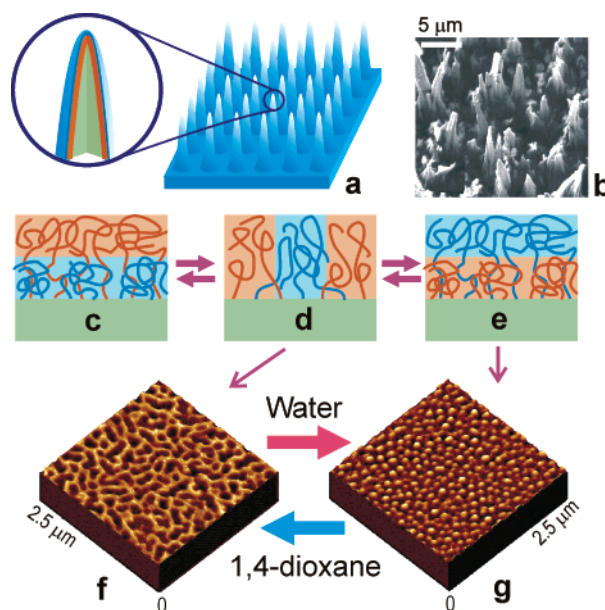


Figure 1. Two-level structure of self-adaptive surfaces (SAS): Schematic representation of needlelike surface morphology of the PTFE surface (first level) (a) and SEM image of the PTFE film after 600 s of plasma etching (b). Each needle is covered by a covalently grafted mixed brush that consists of hydrophobic and hydrophilic polymers (second level) depicted schematically in panels c–e. Its morphology results from an interplay between lateral and vertical phase segregation of the polymers, which switches the morphology and surface properties upon exposure to different solvents. In selective solvents the preferred polymers preferentially occupies the top of the surface (c and e), while in nonselective solvents, both polymers are present in the top layer (d). The lower panels (f and g) show AFM images (model smooth substrate) of the different grafted morphologies after exposure to different solvents.

and a height of 250 mm was used. The base pressure obtained with a turbomolecular pump was $<10^{-6}$ mbar. Oxygen was introduced into the chamber via a gas flow control system. The samples were introduced by a load-lock system and placed on an aluminum holder near the center of the chamber, which was coupled capacitively to a 13.56 MHz radio frequency (RF) generator, Caesar 136 (Derssler, Germany), via an automatic matching network. The metallic wall of the whole chamber worked as a grounded electrode, i.e., the electrode configuration was highly asymmetric, causing significant self-bias voltages and ion energies at the RF electrode. The following parameters were used: oxygen flow 10 sccm, pressure 2×10^{-2} mbar, effective RF power 200 W. The resulting self-bias voltage as displayed at the RF generator was approximately 1000 V. After plasma etching, the samples were rinsed in an ultrasonic bath for 10 min in CHCl_3 .

For ammonia plasma treatment of PTFE, a cylindrical vacuum chamber made of stainless steel with a diameter of 350 mm and a height of 350 mm was used. The base pressure obtained with a turbomolecular pump was $<10^{-7}$ mbar. On the top of the chamber a 2.46 GHz electron cyclotron resonance (ECR) plasma source RR160 (Roth & Rau, Germany) with a diameter of 160 mm and a maximum power of 800 W was mounted. Ammonia was introduced into the active volume of the plasma source via a gas flow control system. The samples were introduced by a load-lock system and placed on a grounded aluminum holder near the center of the chamber. The distance between the sample and the excitation volume of the plasma source was about 200 mm. The following parameters were used: ammonia flow 15 sccm, pressure 7×10^{-3} mbar, power 220 W, treatment time varied from 20 s up to 120 s.

Preparation of the Binary Brushes. Polymer chains of PSF-COOH and PVP-COOH were attached to the PTFE substrate by end functional groups. Hydroxyl and amino functional groups, introduced covalently by ammonia plasma treatment into the PTFE surface, were used to

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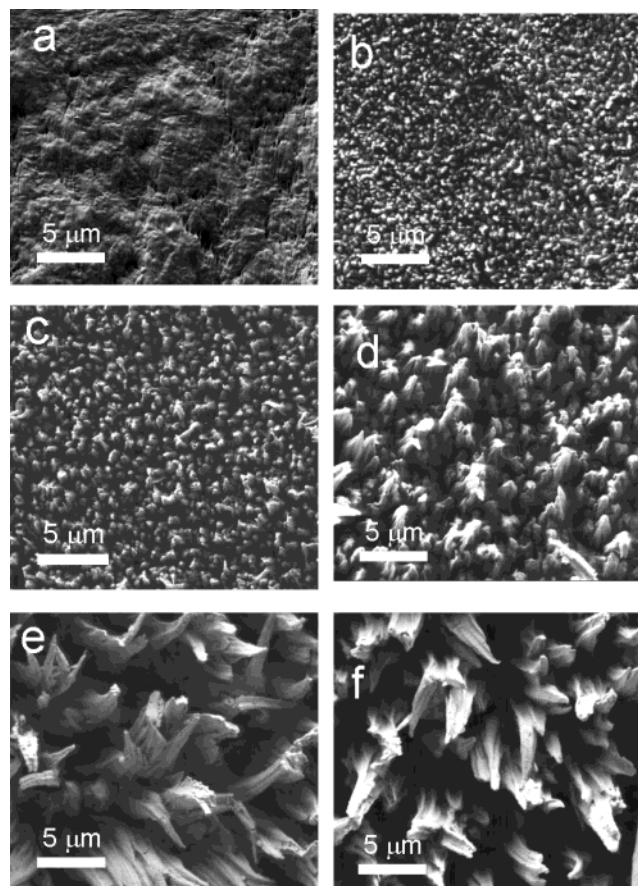


Figure 2. Scanning electron micrographs of PTFE foils: untreated (a); treated with oxygen plasma for 60 s (b), 120 s (c), 5 min (d), or 10 min (e); and treated with oxygen plasma for 10 min + NH_3 for 1 min (f).



Figure 3. Plot of rms roughness of PTFE surfaces over the treatment time in oxygen plasma. Rms values were calculated from a scan size of $20 \times 20 \mu\text{m}^2$.

graft the mixed polymer brush. The brush was fabricated by a two-step “grafting to” procedure^{6a} based on the “grafting to” approach suggested by Luzinov et al.^{6b–d} In the first step, a thin film of PSF-COOH was spin-coated on the surface of the PTFE foil and heated for 6 h at 150 °C to graft the polymer from melt. Nongrafted polymer was removed with Soxhlet extraction, and the second polymer PVP-COOH was grafted by the same procedure. The amount of grafted polymer on the rough surface of PTFE substrate cannot be determined. However,

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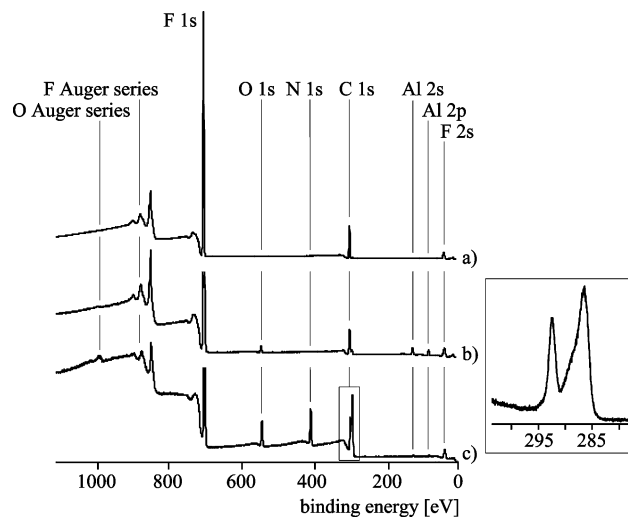


Figure 4. XPS survey spectra of PTFE: untreated (a), treated with oxygen plasma for 600 s (b), plus ammonia plasma treatment for 60 s (c). The inset shows the high-resolution C 1s spectrum of the sample.

we performed control experiments on the surface of Si wafers with covalently attached GPS. Epoxy groups of GPS were transformed to amino groups by treatments with ethylenediamine. In this way we prepared a model surface modified with hydroxyl and amino groups. The control experiments show that under these conditions about 3.5 mg/m^2 of each polymer can be grafted onto the Si wafer, which corresponds to a total thickness of 7 nm for the mixed polymer brush.

Sample Characterization:

(A) **Ellipsometry.** Layer thickness and grafted amount in the control experiments on Si wafers were evaluated at $\lambda = 633 \text{ nm}$ and an angle of incidence of 70° with Multiscopie Optrel (Berlin, Germany). The measurements were performed for each sample and after each step of the modification. The measurements of the previous steps were used as a reference for the simulation of the ellipsometric data as it is described elsewhere.^{6a}

(B) **XPS** experiments were performed with an Axis Ultra spectrometer (Kratos Analytical, England) equipped with a monochromized Al $K\alpha$ X-ray source of 300 W at 20 mA. The analyzer’s pass energy was set to 160 eV to record survey spectra and 20 eV to take high-resolution spectra.

(C) **FTIR-ATR** (Fourier transform infrared spectroscopic measurements in the attenuated total reflection mode) spectra were taken with an IFS 55 (Bruker) spectrometer.

(D) **SEM** (scanning electron microscopy) images were obtained without metallization of the sample at a beam voltage of 1 kV with a low-voltage scanning electron microscope, Gemini LEO/DSM 982.

(E) **AFM** studies were performed on a Dimension 3100 (Digital Instruments, Inc., California) microscope. The tapping and phase modes were used to map the film morphology under ambient conditions. Silicon tips with spring constant 1.5–6.3 N/m and frequency 63–100 kHz were used. Root-mean-square roughness (rms) S_q of the images was evaluated with commercial software. It is per definition the standard deviation of the elevation, z values, within the given area and is calculated from

$$S_q = \sqrt{\frac{1}{MN} \sum_{j=1}^N \sum_{i=1}^M |z^2(x_i, y_j)|}$$

Images of the PTFE surfaces were obtained at three different locations ($20 \times 20 \mu\text{m}^2$) and the average rms roughness and the error bars were determined for a particular surface-treated PTFE sample based on these images from three different locations.

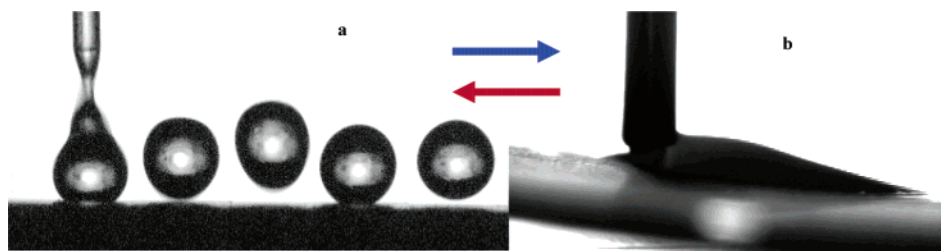


Figure 5. Photograph of a water drop deposited onto the SAS: the stroboscopic image shows that a water drop jumps and rolls on the ultrahydrophobic surface obtained after exposure of the sample to toluene (a). In contrast, exposure to acidic water switches the sample to a hydrophilic state and the water drop spreads on the substrate (b).

(F) Wettability of the surfaces was characterized by contact angle measurements with sessile water droplets. Two techniques were applied, a goniometer technique and an axisymmetric drop shape analysis—profile (ADSA-P). By use of a goniometer, DSA10 of Krüss, advancing (θ_a) and receding (θ_r) contact angles from six individual drops placed on six new surface areas were measured by adding or withdrawing a small volume of water through a syringe. The needle was maintained in contact with the drop during the experiments. All readings were then averaged to give a mean advancing and receding contact angle for each sample. The accuracy of this technique is on the order of $\pm 2^\circ$. ADSA-P is a technique to determine liquid–fluid interfacial tensions and contact angles from the shape of axisymmetric menisci, i.e., from sessile as well as pendant drops. Details of the methodology and experimental setup can be found elsewhere.⁷ During the experiments the temperature and relative humidity were maintained at $23 \pm 0.5^\circ\text{C}$ and about 40%, respectively.

Results and Discussion

Our approach for the design and the fabrication of two-level structured surfaces, which are capable of reversible switching from hydrophilic to ultrahydrophobic states upon external stimuli (solvent selectivity, acidity, or temperature) is outlined in Figure 1. Using plasma etching, we produce a PTFE film with roughness on the micrometer scale. Then, we employ the “grafting to” technique to synthesize a mixed polymer brush^{6a} onto this rough surface. The mixed brush forms domains of nanometer size and its (average) surface composition stems from an intricate interplay between lateral and perpendicular segregation.^{4i,6a,8} Exposing this mixed brush to different environments, we can reversibly modify its surface properties, and the range of switching is substantially amplified by the needlelike, micrometer roughness of the etched PTFE substrate.

The first step of our procedure comprises the fabrication of the composite surface with functional groups required for further modification steps. The radio frequency oxygen plasma etching is used to create a rough PTFE surface with large-scale features of $1\text{--}2\ \mu\text{m}$ in lateral as well as vertical dimensions. During the plasma treatment the originally flat morphology is replaced by needlelike structures (Figure 2). The prolongation of etching time from 60 to 300 s yields an increase of the surface roughness from 150 nm to $1\ \mu\text{m}$, as measured by AFM (Figure 3). XPS investigations of the plasma-etched surface for different periods of time revealed only small amount of oxygen (Figure 4). Under the applied conditions, a fast etching process dominates and

there is only a minor chemical modification of the surface. For etching time in excess of 100 s, advancing and receding contact angles were both about 160° and no contact angle hysteresis was observed.

After the plasma treatment we obtain a composite surface with ultrahydrophobic properties. The large structures (at the micrometer scale) of the surface trap air below a drop of liquid. Such a drop on the surface is in contact with the solid surface and air. Then, the PTFE samples were treated by microwave ammonium plasma for a short period of time (20 s). We observed some additional increase of the film roughness after this treatment. XPS spectra indicate the incorporation of amine groups into the surface (16% nitrogen) (Figure 4c). Advancing and receding contact angles decrease substantially to 100° and 45° , respectively, showing large hysteresis. The hydroxyl and amino functional groups, which have been introduced by the plasma treatment, are subsequently used to create the second level of surface structure: a mixed brush consisting of two carboxyl-terminated incompatible polymers PSF-COOH and P2VP-COOH. The brush was fabricated by a two-step “grafting to” procedure.^{6a} In the first step PSF-COOH was spin-coated on the surface of the PTFE film and heated for 6 h at 150°C to graft the first polymer PSF-COOH from the melt. Nongrafted polymer was removed with Soxhlet extraction. Then the second polymer P2VP-COOH was grafted by the same procedure. FTIR ATR spectra give evidence for the grafting of both polymers: characteristic bands of PSF-COOH (1601 , 2923 , and $3027\ \text{cm}^{-1}$) and PVP-COOH (1586 and $1590\ \text{cm}^{-1}$) were identified in the spectra. Quantitative evaluation by XPS and FTIR-ATR spectra gives the composition of the mixed brush $50:50 \pm 10\%$.

We also prepared a reference sample using the same protocol except for a much shorter treatment (60 s) in oxygen plasma, which resulted in a surface roughness of less than 100 nm.

Covalent binding to the substrate surface prevents macrophase separation in the mixed brush and, the chains self-assemble laterally into domains that are of the molecule’s (50 nm) size.^{4i,6a,8} Simultaneously, the chains segregate perpendicular to the grafting surface. There is a subtle interplay between lateral and perpendicular segregation that affects the film morphology and its surface properties. This switching of morphology was recently proved on the basis of X-ray photoemission electron microscopy experiments.^{8a} Upon exposure to a selective solvent, we can enrich the favored component at the top of the polymer film, while the other component collapses into dense dimples in the interior of the polymer film (Figure 1c–e). Upon exposure to toluene, P2VP builds round domains in the matrix of PSF (Figure 1g). The inverse situation was observed upon exposure to acid water (pH 3). In the latter case PSF forms clusters buried

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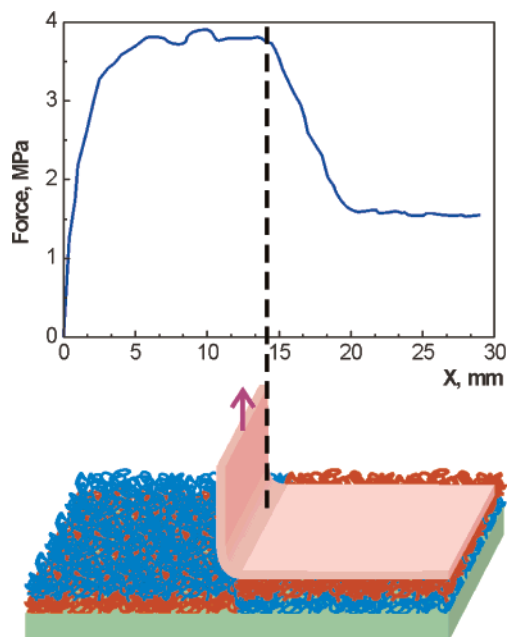


Figure 6. Switching adhesion with SAS: the plot presents the change of the force applied to the Tesa band defoliated from SAS vs distance (X) from the starting point. The dashed line marks the border between ultrahydrophobic (orange) and hydrophilic (blue) areas on SAS.

in the P2VP matrix. Upon exposure of the sample to 1,4-dioxane, we observe lamellarlike domains of both polymers on the surface (Figure 1f). Contact angle measurements confirm the switching of surface composition.

The advancing contact angle of water on the control sample was measured to be 118° after exposure to toluene, 25° after exposure to water (pH 3), and 75° after exposure to 1,4-dioxane. In contrast, a much more pronounced modification of surface properties was observed for the two-level structured surface. An advancing contact angle of 160° was measured after

exposure to toluene. A drop of water rolls easily on the surface, a fact that indicates also a very small hysteresis of the contact angle (Figure 5a). After we immerse the same sample in an acid (pH 3) water bath for several minutes and dry the sample, however, a drop of water spreads on the surface because of the wicking effect (Figure 5b). These observations demonstrate the usefulness of combining large-scale roughness (scale of micrometers) with the self-assembled structure of a binary polymer brush in the range of nanometers, and it reflects the “smart” properties of the self-adaptive surface (SAS).

It is noteworthy that after the treatment with toluene the wetting hysteresis depends on the time of the water drop contact with the substrate. After 30 s the difference between advancing and receding contact angles is within the error of the measurement ($\pm 2^\circ$), while in several minutes the difference increases dramatically due to the slow switching of the surface composition to a more hydrophilic state.

SAS can be employed for constructing sophisticated functional materials. Switching of SAS results in tuning of various kinds of interaction mechanisms with its surroundings. An example of practical importance is van der Waals interaction, which can be used to regulate adhesion.

As an illustration, we performed a simple adhesion test in which we glue Tesa tape to the plate with SAS. Half the plate is in the hydrophilic state and the other half is in the hydrophobic state. A sharp decrease of adhesion was observed when we cross the border between the ultrahydrophobic and hydrophilic areas on the sample (Figure 6).

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