

## HIERARCHICALLY STRUCTURED SELF-ADAPTIVE SURFACES

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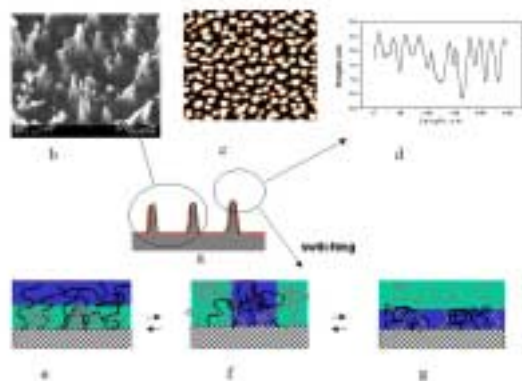
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### Introduction

Wettability of solid surfaces is of great importance for many mechanisms in alive nature and for numerous industrial applications. Particular, ultrahydrophobic materials, strongly repelling water with very small contact angle hysteresis when water drops move spontaneously on near-horizontal surfaces, are used in nature for building of self-cleaning surfaces of plants and insects<sup>1</sup> and are getting increasing applications in modern synthetic materials<sup>2,3</sup>. Advantages of hydrophobic surfaces useful for self-cleaning and water repelling mechanisms can turn to disadvantages in the case of particular applications, for example, interactions with human body (clothes, implants, catheters), technical applications (static electricity, poor adhesion and dyeability). A possibility to combine in the same material both water repelling properties and wettability would extend the range of applications of synthetic materials. Wettability can be regulated by chemical composition and roughness<sup>2-6</sup>. Here we report the design and the fabrication of hierarchically structured smart surfaces capable for the reversible switching between hydrophilic and ultrahydrophobic states upon external stimuli, combining those two methods of the wettability regulation. We show several examples how this behavior can be used to reversibly switch wettability, adhesion and to pattern solid substrates. We use the "grafting to" approach to synthesize switchable mixed polymer brushes<sup>7</sup> on the surface of radio-frequency plasma etched poly(tetrafluoroethylene) (PTFE) film. The mixed brush exhibits switching properties caused by interplay between lateral and perpendicular to the substrate phase segregation.<sup>8,9</sup> The range of switching is substantially amplified by the composite surface built by a pin-like highly rough morphology of the etched PTFE substrate.

### Results and discussion

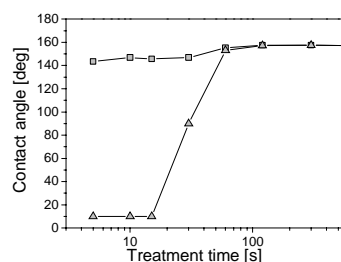
Our approach to regulate and switch wettability is outlined in **Figure 1**. Central to our surface design is the ability to switch between different morphologies at the nanometer scale by applying an external stimuli (solvent, pH, temperature) while the microscopic morphology (roughness) at the micrometer scale, responsible for the formation of a composite surface, is left unchanged.



**Figure 1.** Switching properties of the hierarchically structured SAS: schematic representation of the two-level morphology of the polymer film (a) consisting from the pin-like PTFE substrate illustrated with SEM  $20 \times 20 \mu\text{m}^2$  image (b), the switchable mixed polymer brush illustrated with AFM  $1 \times 1 \mu\text{m}^2$  image (c), and its cross-section (d). Pictures e, f and g schematically explain the switching properties of the mixed brush in solvent selective for black chains, nonselective solvent and solvent selective for gray chains, respectively.

The first step of our procedure comprises the fabrication of the composite surface with functional groups required for further modification steps. We use a PTFE film as a substrate to fabricate the smart coating. The radio-frequency oxygen plasma etching is used to create the rough PTFE surface with the large scale of features ( $1-2 \mu\text{m}$  in both lateral and vertical dimensions). During the plasma treatment the original morphology is replaced by pin-like features (**Figure 1b**). The increase of treatment time from 60 s to 300 s yields an increase of the surface roughness from 150 nm to  $1 \mu\text{m}$ , as it was obtained from atomic force microscopy (AFM) measurements. XPS investigations (emission angle  $45^\circ$ ) of the plasma etched surface (treatment time 600s) revealed only minor changes in the C:F ratio and only small amount of oxygen on the surface. Obviously, under the applied plasma conditions a fast etching process predominates the chemical surface modification and especially the introduction of oxygen. **Figure 2** shows the dynamic contact angles for different etching times. Immediately after the start of the etching procedure the receding contact angle ( $\theta_r$ ) drops to a very low value of about  $10^\circ$ , while the advancing contact angle ( $\theta_a$ ) is slightly increasing. For longer etching times advancing and receding contact angles are about  $160^\circ$ , i.e. the contact angle hysteresis disappears. A reason for the intermediate increase of the contact angle hysteresis is the transition from a relatively flat surface to a rough and chemically heterogeneous surface (Wenzel regime). After 150 s of plasma treatment we approached a composite surface with ultrahydrophobic properties. The large structures form a composite surface due to trapped air. A drop of liquid in such a surface is in the contact with a surface composed of solid and air (Cassie regime).

Then the PTFE samples were treated by ammonium plasma for a short period of time (20 s). We observed some increase of film roughness after this treatment. XPS spectra proved the incorporation of amine groups on the surface (16 % of nitrogen). The advancing and receding contact angles have dropped dramatically to  $100^\circ$  and  $45^\circ$ , respectively, showing large hysteresis. Optimizing the conditions of plasma reactions we approached: (a) PTFE surface morphology with the desired level of roughness, (b) covalent incorporation of  $-\text{OH}$  and  $-\text{NH}_2$  functional groups.



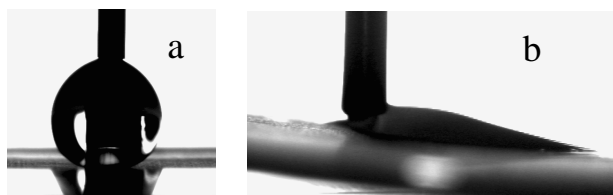
**Figure 2.** Dynamic contact angles of water on the PTFE surface as a function of etching times:  $\theta_a$ -circles,  $\theta_r$ -triangles.

The second level of heterogeneous morphology is created via grafting of two carboxy terminated incompatible polymers of different polarity: poly(styrene-co-2,3,4,5,6-pentafluorostyrene) (PSF-COOH) (0.75:0.25) and poly(2-vinylpyridine) (P2VP-COOH). Polymer chains of these two polymers are attached to the PTFE substrate by end functional groups and randomly distributed on the surface. Hydroxyl and amino functionalities, introduced by plasma treatment, are used to graft the mixed polymer brush. The brush was fabricated using two-step "grafting to" procedure<sup>7</sup>. In the first step a thin film (10 nm) of carboxy terminated PSF-COOH was spin-coated on the surface of the PTFE film and heated for 6 hours at  $150^\circ\text{C}$  to graft the polymer from melt. Nongrafted polymer was removed with Soxhlet extraction and the second polymer P2VP was grafted using the same procedure to fabricate the sample ( $S_{\text{comp}}$ ) with the smart switchable film. The spectroscopic measurements (Fourier transform infrared spectroscopy in the attenuated total reflection FTIR ATR) support the grafting of both polymers: characteristic bands of PSF-COOH ( $1601$ ,  $2923$ , and  $3027 \text{ cm}^{-1}$ ) and P2VP-COOH ( $1586$  and  $1590 \text{ cm}^{-1}$ ) were identified in the spectra. Control experiments show that at these conditions about  $3.5 \text{ mg/m}^2$  of each polymer can be grafted to the substrate which corresponds to the 6 nm thick switchable film. We also prepared the *reference* sample

( $S_{\text{refer}}$ ) using the same protocol but the first step of the treatment with oxygen plasma was short (60 s) to have the sample with a smaller roughness (below 100 nm).

Covalent binding to the substrate surface irreversibly prevents macrophase separation in the mixed brush and, as it was recently shown<sup>8,9</sup>, the chains self-assemble into two dimensional structures with lateral periodicity. Simultaneously, the chains segregate perpendicular to the surface. Interplay between the lateral and perpendicular segregation effects the film morphology and switching properties (**Figure 1e-g**). Upon exposure to selective solvent a top of the film is enriched by a favored component and the unfavored component forms clusters dipped into the film. Upon exposure to toluene P2VP builds round domains in the matrix of PSF (**Figure 1c, 1e**). The inverse situation was observed upon exposure to water with pH=3. In the latter case PSF forms clusters dipped into P2VP matrix (**Figure 1g**). Upon exposure to 1,4-dioxane we observe domains of both polymers on the surface (**Figure 1f**). Contact angle measurements support the switching of the surface composition: we obtained the water contact angles on the surface of the control sample  $S_{\text{refer}}$  (not composite surface): 118° after toluene, 25° after water (pH=3), and 75° after ethanol.

The dramatic change of the switching properties was observed for the sample  $S_{\text{comp}}$  upon exposure to different solvents: 160° after toluene, when the drop of water rolls on the surface showing very small hysteresis (**Figure 3a**). After treatment by water (pH=3) for several minutes the surface switches to hydrophilic properties. A drop of water spreads on the surface because of capillary penetration effect (**Figure 1b, 3b**). Such an increase of the switching range is caused by the hierarchical morphology of the film: the combination of the large and small structures and an interplay between the structures of the mixed brush.



**Figure 3.** A water drop on PTFE surfaces after exposure of the sample toluene (a) and water at pH=3 (b).

The switching of SAS results in the switching of various types of interaction mechanisms with surroundings, particular, van der Waals interactions which can be used to regulate adhesion. We performed a simple adhesion test in which we adhered a polymer film to the SAS sample with a patterned surface. The sample was switched to ultrahydrophobic state with toluene and patterned with water to switch particular areas to hydrophilic state. The plot in **Figure 4** represents the force of the film defoliation from the SAS-substrate vs. distance of the defoliation along the sample. The sharp decrease of adhesion was observed at the point of crossing the border between the ultrahydrophobic and hydrophilic areas on the sample.

### Conclusions

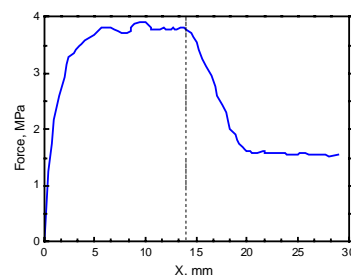
We have demonstrated that combination of the two level hierarchical organization of polymer films at macroscopic and nanoscopic levels resulted in the formation of SAS switchable in controlled environment from ultrahydrophobic to hydrophilic energetic states.

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**Figure 4.** Plot of a force to defoliate the polymer film adhered to SAS on PTFE substrate vs. length of the defoliation path. The dot line indicates the border between hydrophilic (left) and hydrophobic (right) areas of the SAS prepared by patterning of the substrate upon exposure to water and toluene, respectively.