From Superhydrophobicity and Water Repellency to Superhydrophilicity: Smart Polymer-Functionalized Surfaces

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Experimental Section

2-(diisopropylamino)ethyl methacrylate (DPAEMA) was purchased from Scientific Polymer Products and was passed through an inhibitor-removing column, DHR-4, before use. 2-(diethylamino)ethyl methacrylate (DEAEMA, 99%), copper (I) bromide (CuBr, 99.999%), 1,1,4,7,10,10-hexamethyl-triethylenetetramine (HMTETA, 97%) and ethyl 2-bromoisobutyrate (EBIB, 98%) were obtained form Aldrich. Methanol (Sigma-Aldrich), *N,N*-dimethyl formaminde (DMF, Riedel-de Haën) and tetrahydrofuran (THF, Riedel-de Haën) were used without further purification. The surface-bound initiator, 3-(2-bromoisobutyramido)propyl(trimethoxy)silane was synthesized using the procedure developed by Klok and co-workers.[1]

Structuring of polished Si substrate surfaces by ultrafast lasers[2] under reactive gas (SF_6) atmosphere was chosen as the method of surface micro- and nano-structuring because it produces surface morphologies exhibiting two length scales with a simple one-step process. The irradiating source was a regenerative amplified Ti:Sapphire laser (λ=800 nm) delivering 180 femtosecond (fs) pulses at a repetition rate of 1 kHz. The laser pulse fluence was 2.47 J/cm^2 and the SF_6 gas pressure was 500 Torr. Details of the structuring process can be found elsewhere.[3] Following irradiation, the samples were first cleaned in ultrasonic baths of

trichloroethylene, acetone and methanol followed by a 10% HF aqueous treatment in order to remove the oxide grown on the surface. Then, they were thermally oxidized at 1000 °C for 20 min to obtain a ~20nm conformal silicon oxide coating; this resulted in a fully hydrophilic surface. The samples were morphologically characterized by field emission scanning electron microscopy (FESEM; JEOL JSM 7000F) after being sputter-coated with a less than 20 nm thick Au/Pd coating.

The hierarchically structured surfaces were functionalized (**Fig. S2**) by "grafting from" pH-responsive polymer brushes using surface-initiated atom transfer radical polymerization (ATRP). First, the initiator self-assembled monolayer (SAM) was formed by immersing overnight a thermally oxidized silicon substrate in a vial containing a 40 mM solution of the 3-(2-bromoisobutyramido)propyl(trimethoxy)silane initiator in anhydrous THF. After the incubation period, the substrate was rinsed extensively with anhydrous THF, dried under a stream of nitrogen and transferred to the polymerization flask. Surface-initiated ATRP of DPAEMA and DEAEMA monomers was carried out from the initiator-modified silicon substrates. A typical polymerization protocol for the growth of the PDPAEMA brushes is given below. A flat and a rough silicon substrate modified with the ATRP initiator were placed in a reaction flask under a nitrogen atmosphere. In a separate flask DPAEMA (2 g, 9.345 mmol) was dissolved in DMF (10 mL). Copper (I) bromide (0.0717 g, 0.499 mmol) and HMTETA (136 μL, 0.499 mmol) were added next and the solution was purged with nitrogen. After stirring for 20 minutes at room temperature the solution was transferred to the flask containing the substrates. EBIB free initiator (8.16 μL, 0.055 mmol) was also added to the polymerization mixture, which resulted in the formation of free polymer in solution. The polymerization was allowed to proceed for 24 h at 70 °C before the reaction was quenched by exposure to air. The substrates were cleaned by extensive washing with DMF and acetone, followed by sonication in an ultrasonic bath. The ATRP catalyst was removed from the reaction medium by passing the solution through a basic alumina column. Excess solvent was

removed under vacuum using a rotary evaporator before precipitating the polymer in water. A similar protocol was employed for the ATRP of DEAEMA in methanol at room temperature, using copper (I) bromide and HMTETA as the catalyst system.

A variable-angle spectroscopic ellipsometer (VASE, Woollam Co., Inc.) was used to determine the dry layer thickness and the refractive index of the polymer film grafted on the flat silicon substrate. The measurements were performed at three different angles of incidence 60°, 70° and 75° in the wavelength range 450-1200 nm. Gel permeation chromatography (GPC) (Thermo Finnigan, equipped with two Polymer Laboratory columns, PL-Mixed-D and PL-Mixed-E) using tetrahydrofuran (THF) as the mobile phase was employed to determine the molecular weight of the free polymer in solution. The grafting density σ (chains/nm^2) defined as the number of grafted polymer chains per unit of surface area was calculated as[4] $\sigma = h \rho N_A/M_n$, where h is the dry polymer layer thickness, ρ is the bulk density of the attached polymer (assumed to be 1 g/cm^3), N_A is Avogadro's number and M_n (g/mol) is the number-average molecular weight of the polymer chains on the surface (assumed to be the same as that of the polymer chains synthesized in solution). Polymer molecular weights 15 Kg/mol and 33 Kg/mol and anchoring densities σ=0.78 chains/nm^2 and 0.28 chains/nm^2 were obtained for the PDPAEMA and PDEAEMA brushes, respectively. The samples were also morphologically characterized by SEM after being sputter-coated with a less than 20 nm thick Au/Pd coating.

The hydrophobic/hydrophilic nature of the surfaces was switched by dipping the polymer functionalized surfaces sequentially into the high and low pH aqueous solution for 1 min (except for the immersion time dependent measurements). For the PDPAEMA brushes, solutions at pH 8.5 and pH 2.5 were utilized (pK_α of PDPAEMA in solution is[5] 6.3) whereas, for the PDEAEMA brushes, solutions at pH 10 and pH 3 were used (pK_α of PDEAEMA in

solution is[6] 7.3). The surfaces were then dried with N_2 gas following the immersion in the appropriate solution before the contact angle measurement.

Static contact angle measurements were performed by an automated tensionmeter, using the sessile drop method.[7] A 2 μL Milli-Q water droplet was gently positioned on the surface using a microsyringe and images were captured to measure the angle formed at the liquid-solid interface. The mean value was calculated from at least five individual measurements. Successive measurements were reproducible within ±1°. The error bars presented in the text are associated with multiple measurements on different spots on the same surface. The measured contact angle values are stable with time until the surface is immersed again in a solution of different pH. A tilt stage assembly, with an extendable lever arm that permitted continuous inclination of the surface from horizontal, was used in order to determine the angle at which a drop starts to move,[8] i.e., the sliding angle. Depending on the variability of the data, a mean sliding angle value was calculated from five to ten individual measurements. The advancing and receding angles were determined from the drop-snapshot just before slippage occurred; on a drop about to slide, the wetting angle on the lower edge is the advancing angle whereas that on the upper edge is the receding angle. The sliding angle data shown in Figure 3 were measured for water droplets of 10 μL volume (drop radius R=1.35mm). The dynamic behavior of water droplets free falling on flat or patterned surfaces was followed using a high-speed camera at a frame rate of up to 1000Hz. The velocities before and after each shock were calculated either from the distance traveled between successive snapshots (at high impact speeds) or from the corresponding maximum heights attained (at low impact speeds). The restitution coefficient data shown in Figure 4 were measured for water droplets of 10 μL volume (drop radius R=1.35mm).

Acknowledgements

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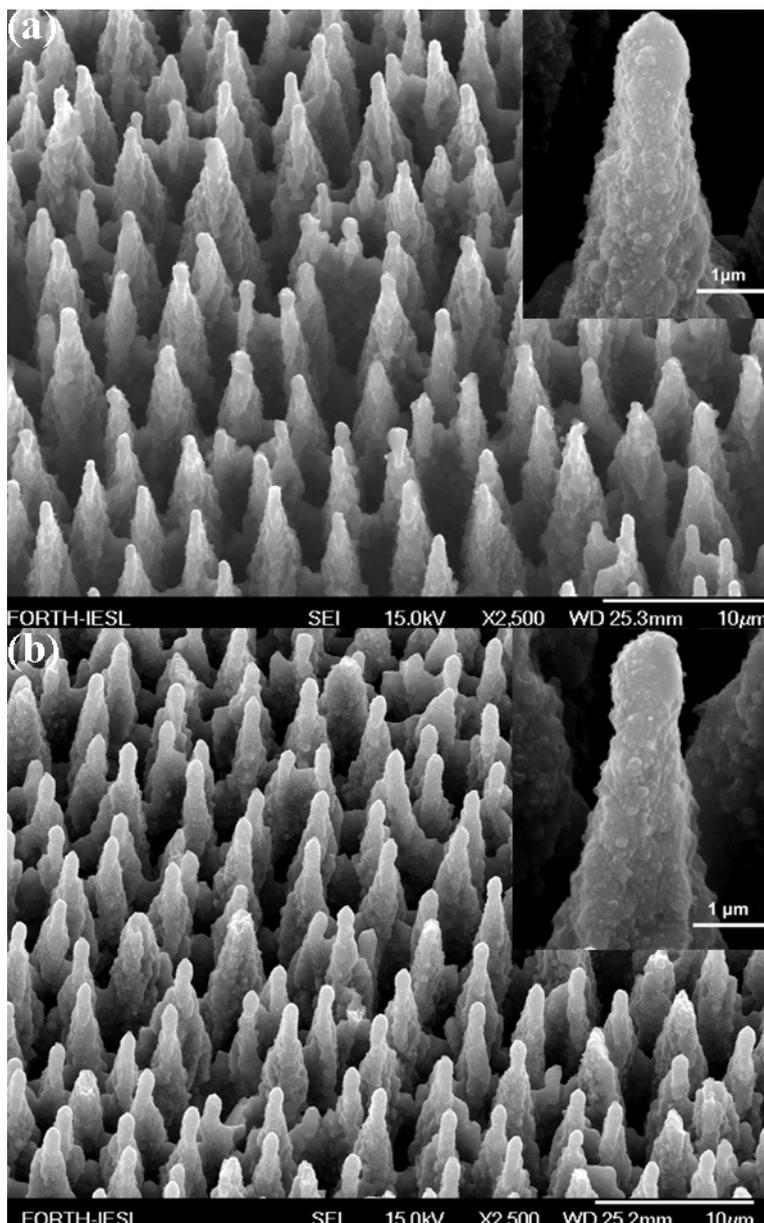
Figure S1. (a) SEM image of the artificially structured silicon surface comprising protrusions with conical or pyramidal asperities with average sizes of ~10 μm and surface density 5.0×10^6 cm^{-2} (scale bar 10 μm). Inset: high magnification SEM image of a single protrusion depicting nanostructures of sizes up to few hundred nanometers on the slopes of the protrusions (scale bar 1 μm). The surface was structured in the presence of 500 Torr SF$_6$ at a laser fluence of 2.47 J cm^{-2} with an average of 500 pulses. (b) SEM image of the PDPAEMA brush functionalized artificially structured surface (σ=0.78 chains/nm^2) after ten pH cycles, where the protrusions remain unperturbed (scale bar 10 μm). Inset: high magnification SEM image of a single protrusion depicting that the few hundred nanometer nanostructures on the slopes of the protrusions remain unperturbed as well (scale bar 1 μm).
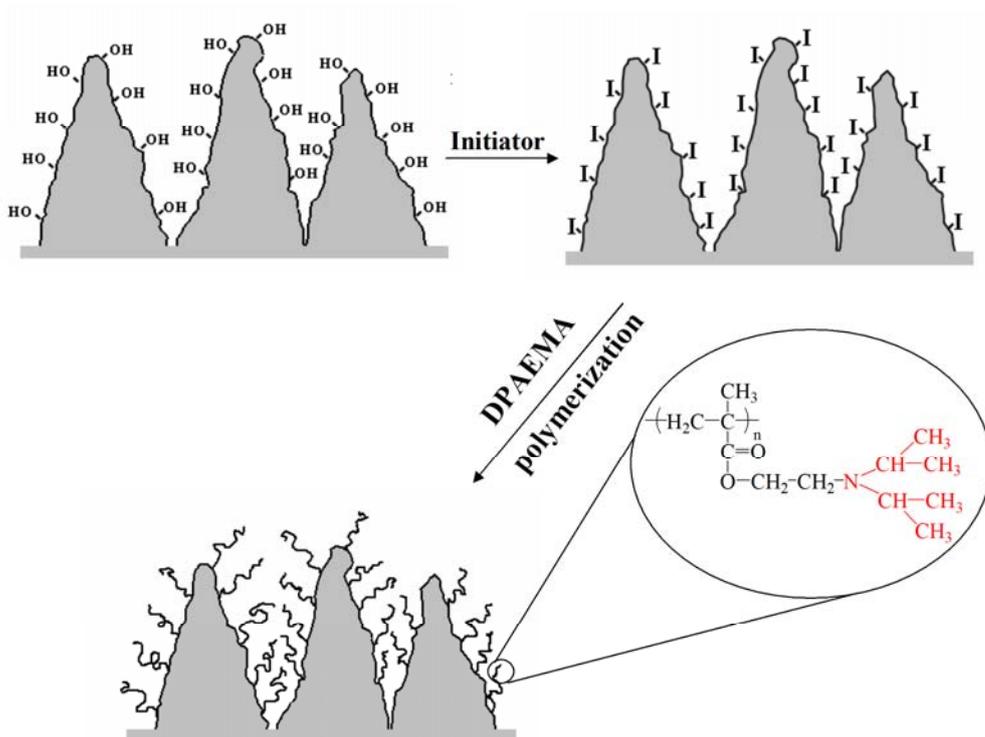
Figure S2. Schematic representation of the functionalization process of the hierarchically structured artificial surface. The initiator self-assembled monolayer is formed on top of the HF-treated hydrophilic silicon surface. A pH-responsive polymer brush is grown using surface-initiated atom transfer radical polymerization of PDPAEMA monomer.

Captions for Movies S1, S2

Movie S1. Impact of a water drop of 1.35 mm radius (drop volume: 10 μL) on the PDPAEMA functionalized artificially structured surface following immersion in a solution at pH 8.5. Drop velocity at first impact: 0.44 m/s. Dimensionless Weber number: $We = 3.5$. The drop comes to rest after several rebounds.

Movie S2. Complete wetting of the PDPAEMA functionalized artificially structured surface following immersion in a solution at pH 2.5. Drop volume: 2.5 μL.