

Supporting Information

Facile fabrication of robust superhydrophobic surfaces: comparative investigation

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EXPERIMENTAL

Chemicals:

1H,1H,2H,2H-perfluorodecanethiol (Sigma Aldrich), *2-hydroxyethyl methacrylate* (Sigma Aldrich), *2,2-dimethoxy-2-phenylacetophenon* (Sigma Aldrich), *3-(trimethoxysilyl)propyl methacrylate* (Sigma Aldrich), *4-(dimethylamino)pyridine* (Novabiochem, Merck), *4-pentyoic acid* (Sigma Aldrich), *ammonia solution (28-30%, Merck)*, *azobisisobutyronitril (AIBN, Sigma Aldrich)*, *butyl methacrylate (Sigma Aldrich)*, *divinylbenzene (technical grade, Sigma Aldrich)*, *dodecyltrichlorosilane (95%, Sigma Aldrich)*, *ethylene dimethacrylate (Sigma Aldrich)*, *hydrochloric acid (1 M, Emsure, Merck)*, *N,N'-diisopropylcarbodiimide (Alfa Aesar, USA)*, *silica spheres (15 µm diameter, Silicycle Inc., Canada)*, *silicone dioxide nanoparticles (10-20 nm particle size, Sigma Aldrich)*, *sodium hydroxide (Carl Roth)*, *tetraethylorthosilicate (Sigma Aldrich)*, *tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane (95%, Chempur, Germany)*.

Coating procedures:

Rough polystyrene. A solution of polystyrene in tetrahydrofuran (70 mg/ml) was prepared as stock solution. To prepare the work solution ethanol (EtOH) (100%) was added in a ratio of 1,4:2 (v/v) and the mixture was vortexed until a clear solution was obtained. A few drops were added onto the cleaned smooth polystyrene for 5 s, removed and the substrate was immediately immersed in ethanol and dried at ambient conditions.

Nanoporous PDVB chalk. 2 g of divinylbenzene in 20 ml ethyl acetate (EtOAc) were stirred with 0,05 g of azobisisobutyronitril (AIBN) as initiator for 4 h at room temperature. The solution was heated under reflux at 80°C for 24 h. After cooling and slow evaporation of the solvent a white solid was obtained. Grinding with mortar and pestle led to the polymer chalk. To coat paper the chalk was simply wiped onto the paper surface.

Spray-deposited silica nanoparticles. 2 g of SiO₂ nanoparticles (10-20 nm particle size) were stirred in 40 ml of dried toluene. 1 ml of dodecyltrichlorosilane was added and the solution was heated to reflux for 3 h. After cooling and filtration, the particles were dried at 80°C and ground to a fine powder. 0.4 g of the hydrophobic silica powder was mixed with 20 ml ethanol, stirred for at least 30 min and sonicated for 20 min. With a glass vaporizer the suspension was sprayed onto paper and dried at ambient conditions overnight.

Dip-coating with silica-based sols and SAM. 4 ml of NH₄OH (28%) were added as a catalyst to 50 ml of EtOH (100%) and stirred for 30 min at 60°C. 3 ml of tetraethyl orthosilicate (TEOS) were added dropwise and the solution was stirred for further 90 min. The cleaned glass slides were dip-coated in a diluted solution of the produced sol (1:1 in EtOH), dried for 5 min in the fumehood and heat-treated at 80°C for 1,5 h. To modify the surface chemistry self-assembling monolayers were used. The dip-coated glass slides were immersed in a 0,1 M tridecafluoro-1,1,2,2-tetrahydrooctyldimethylchlorosilane (TFCS) solution in hexane for at least 6 h. After cleaning in EtOH (sonication for 5 min) the glass slides were dried in a nitrogen stream.

BMA-EDMA. A glass slide was first activated in 1 M NaOH for 1 h and in 1 M HCl for 30 min. After activation it was modified with 3-(trimethoxysilyl)propyl methacrylate (20%, v/v in ethanol) for 1 h. A mixture of butyl methacrylate (24 wt%), ethylene dimethacrylate (16 wt%), 1-decanol (40 wt%), cyclohexanol (20 wt%) and 2,2-dimethoxy-2-phenylacetophenone (1 wt% with respect to monomers) was applied between two modified glass slides. The thickness of the layer was controlled with 75 µm silica spheres, that separated the two glass slides. The photopolymerization was initiated by irradiating the glass slides with UV-light (260 nm, 5 mW/cm²) for 15 min. The two glass slides could be opened carefully with a razor blade. The porous polymer usually adheres to the top glass slide. The polymer was washed with methanol for 2 min and dried in nitrogen stream.

Modified HEMA-EDMA. The activation and modification of the glass slide with 3-(trimethoxysilyl)propyl methacrylate was performed according to the BMA-EDMA protocol above. The modified glass slide was coated with 70 μ l of a polymerization mixture consisting of 2-hydroxyethyl methacrylate (24 wt%), ethylene dimethacrylate (16 wt%), 1-decanol (12 wt%), cyclohexanol (48 wt%) and 2,2-dimethoxy-2-phenylacetophenon (1 wt% with respect to the monomers), covered with a fluorinated glass slide and irradiated for 15 min with UV-light (260 nm, 5 mW/cm²). To control the thickness of the layer, the glass slides were separated by silica spheres with 15 μ m diameter. The porous HEMA-EDMA surface was functionalized by esterification with a solution in dichloromethane consisting of 0.15% 4-pentynoic acid, 0.06% 4-(dimethylamino)pyridine and 0.15% *N,N'*-diisopropylcarbodiimide that was stirred at 0°C for 4 h. After extensive washing with acetone the slides were kept in ethanol for several minutes and dried in nitrogen stream. In the last step a solution of 5% 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (v/v in aceton) was degassed and spread on the polymer surface. The glass slide was covered with a fluorinated glass slide and irradiated with UV-light (260 nm, 5 mW/cm²) for 60 s. The surface was washed with acetone and dried in nitrogen stream.

Candle soot. A glass slide was held above the flame of a paraffin candle until it turned black from the soot.

Commercial coating. UltraTech International (Florida, USA) kindly provided samples of their coating Ultra-Ever Dry on a ceramic tile. These sample tiles were used without further treatment. For the SEM and UV/vis-measurements the coating was produced on glass substrate according to the instruction manual.

Optics Inc. (USA).

COMPARISON AND SUMMARY

Tape test:

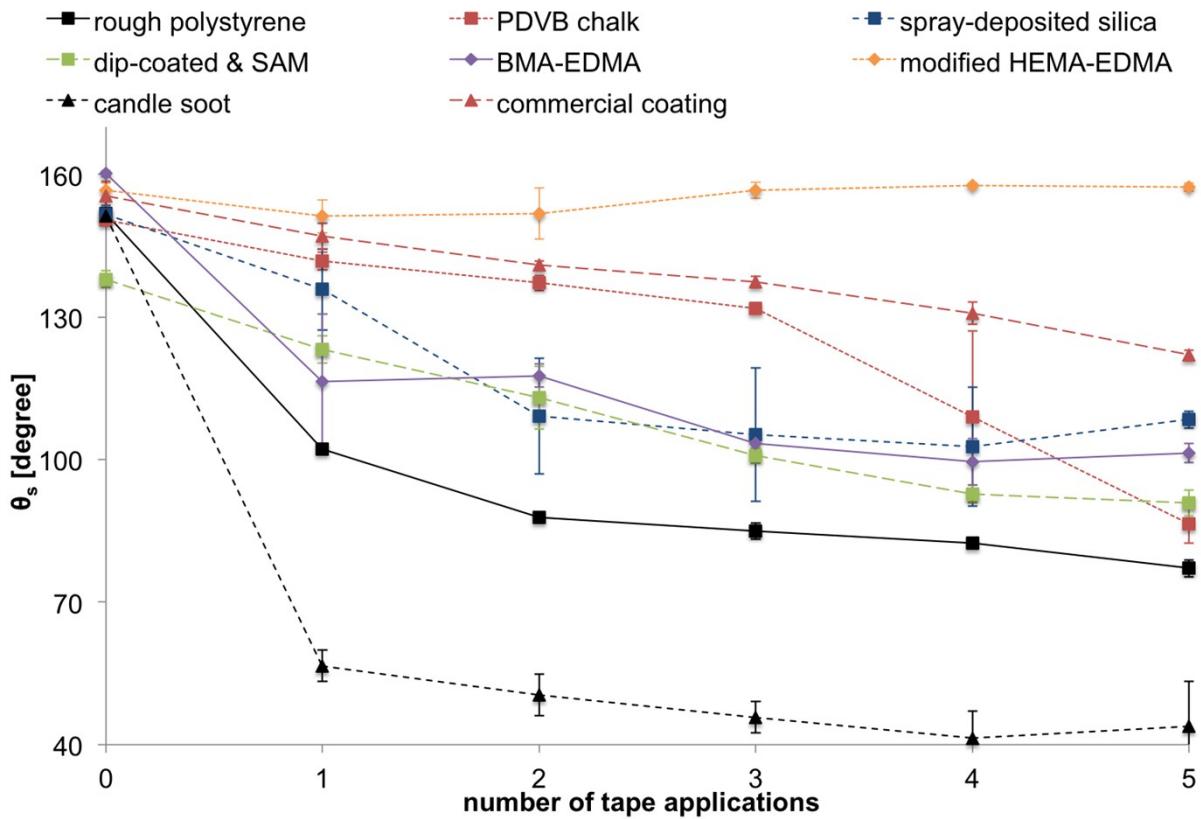


Figure 1. Results of the tape test. The different surfaces were treated with adhesive tape for five times, whilst measuring θ_s . The values represent the average and the error bars indicate the standard deviation.