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New strategies to create technologically relevant superomniphobic coatings on sol-gel base

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Background

- superomniphobic, self-cleaning surface coatings are interesting for various applications (windows, solar panels, facades)
- superhydrophobicity is obtained by hydrophobic surfaces with high roughness (hierarchical or fractal structure) [1]
  problem: mechanical stability
- superoleophobicity requires high roughness, high aspect ratio and re-entrant structures [2, 3]

Goal

- creation of superhydrophobic, oleophobic surface coatings by technologically relevant sol-gel process [4]with nanofillers
- systematic investigation of the correlations between surface topography / roughness and wettability
- test of mechanical stability

Methods

- preparation of coatings by sol-gel process with functional nanofillers
- investigation of morphology and roughness on different length scales by confocal microscopy, scanning electron microscopy (SEM), scanning force microscopy (AFM)
- measurement of advancing and receding contact angles of water, wather-ethanol mixtures and *n*-hexadecane
- wet abrasion test similar to DIN EN ISO 11998

preparation of the sol-gel coatings

basic formulation "H 1006"*

* commercial products by FEW Chemicals

basic formulation "H 5055"*

fluorine additives

inorganic pigments (microfillers)

fluoropolymer nanoparticles

sol-gel process

performed by FEW CHEMICALS

→ functional micro- and nanofillers to increase contact angles and roughness and create re-entrant structures

two-layer coatings H0-H4
base coat: blend of **"H 1006"**, inorganic fillers, polyethylene; sprayed, cross-linked (150°C)
→ roughness adjusted by particle size, mixing ratio
top coat: **"H 5055"**, sprayed, cross-linked (150°C)

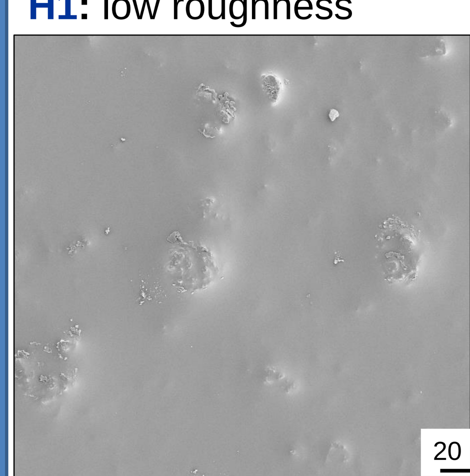
single-layer coatings R1-R3
acid-catalyzed hydrolysis and condensation products of functionalized (fluoro)silanes, fluorine additive and fluoropolymer nanoparticles, cross-linked (150°C)
prepared by doctor blade (variation of thickness)

single-layer coatings S1-S6, S7
acid-catalyzed hydrolysis and condensation products of functionalized (fluoro)silanes, fluorine additive and fluoropolymer nanoparticles, cross-linked (150°C)
prepared by spraying (variation of sprayed mass, temp.)

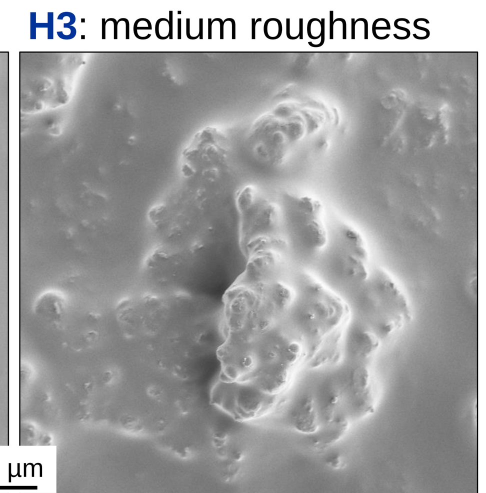
topography (SEM images of selected coatings)

low magnification

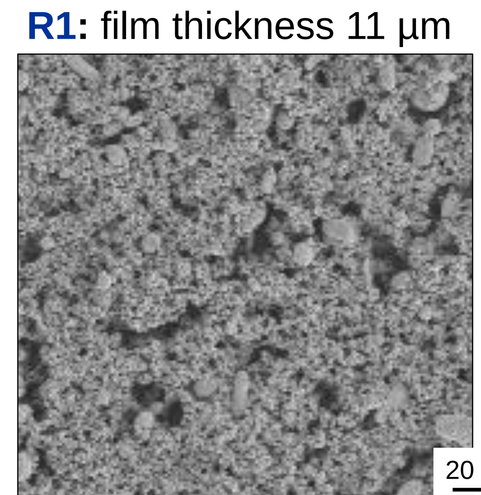
H1: low roughness



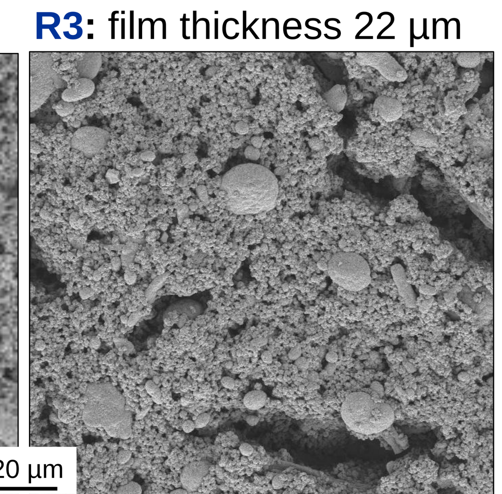
H3: medium roughness



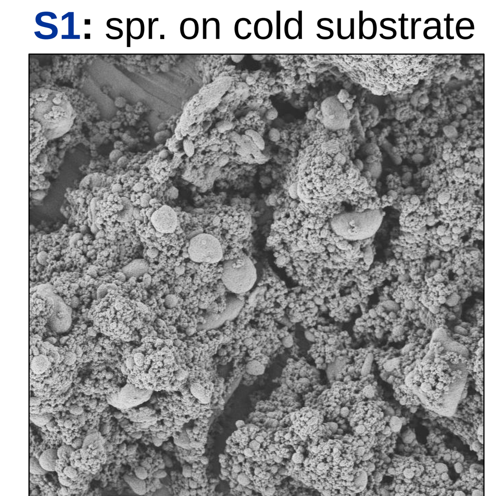
R1: film thickness 11 µm



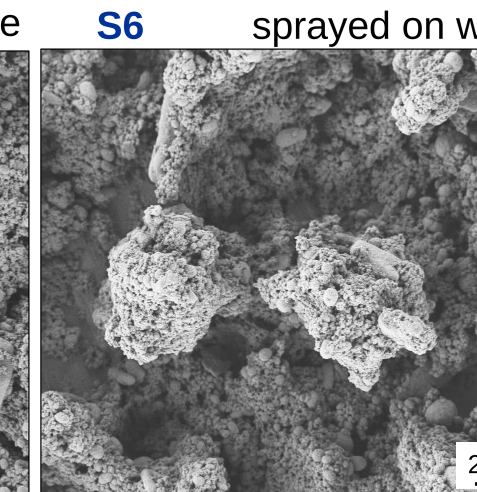
R3: film thickness 22 µm

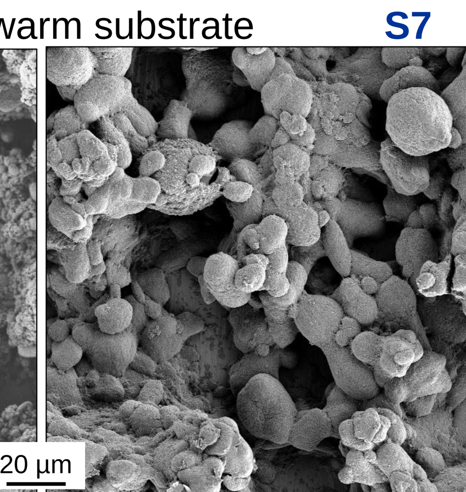


S1: spr. on cold substrate



S6 sprayed on warm substrate **S7**

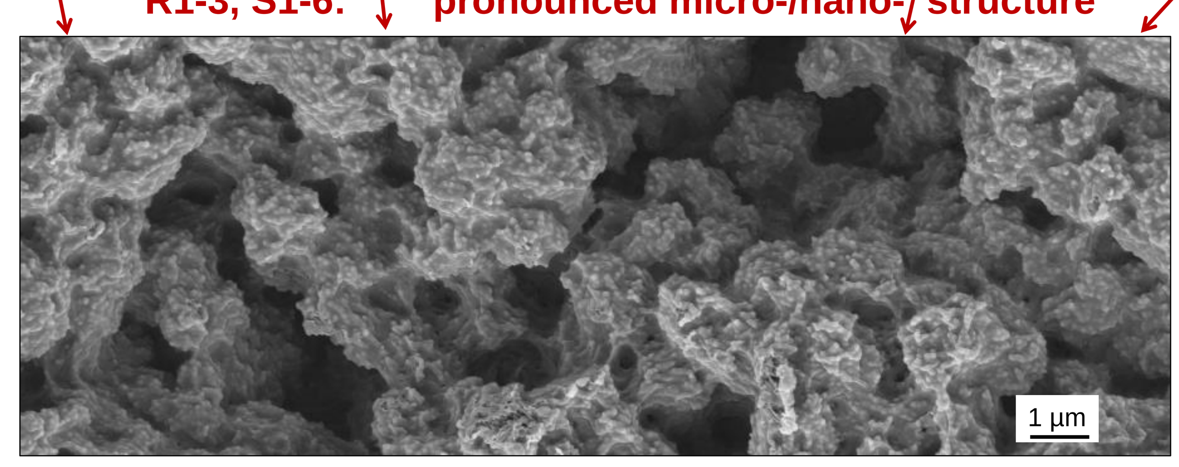




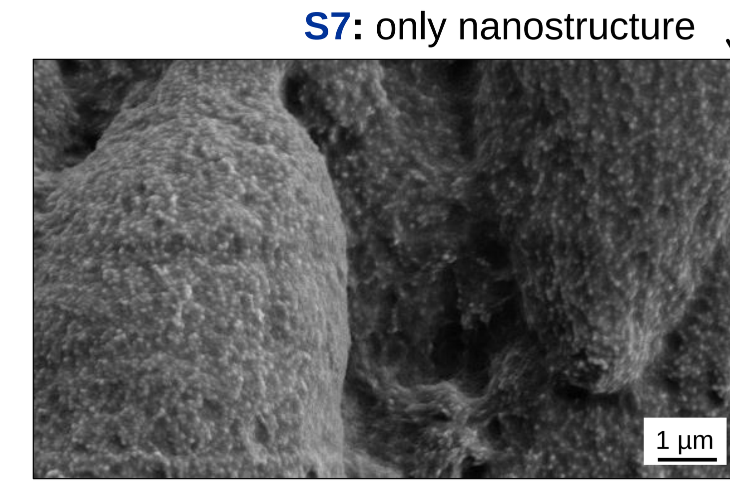
high magnification

H0-4: no micro-/nanostructure

R1-3, S1-6: pronounced micro-/nano-structure



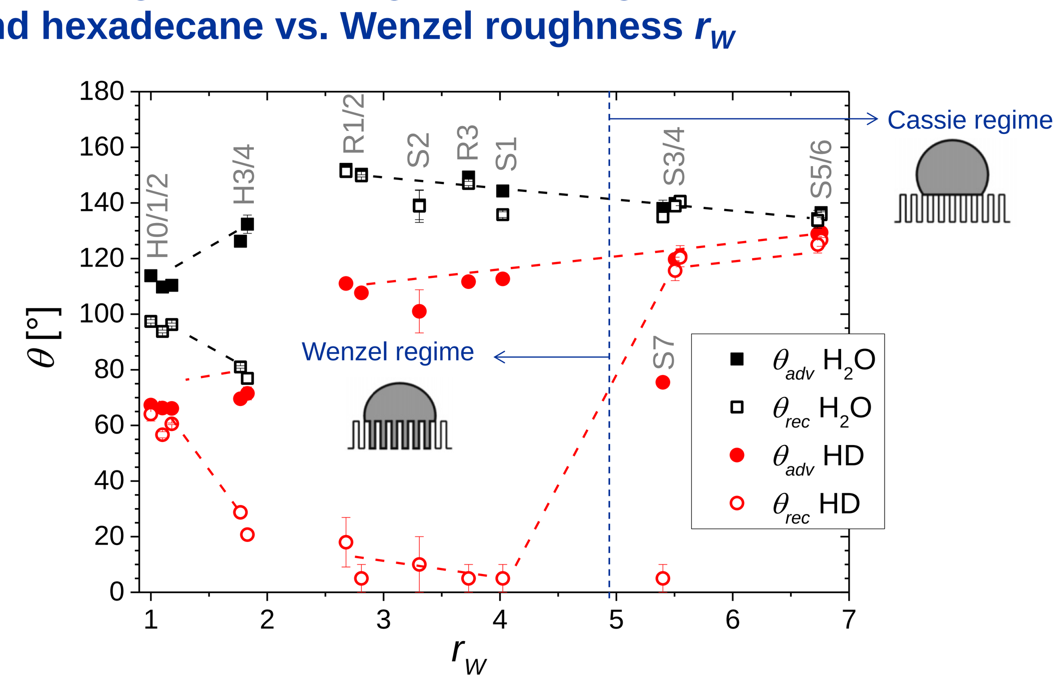
S7: only nanostructure



wetting

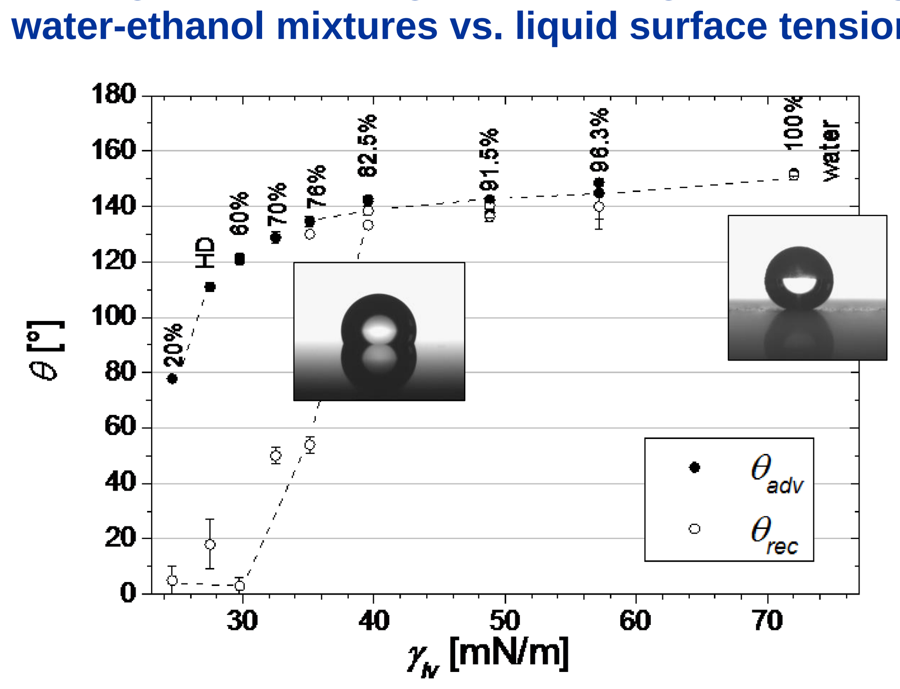
mechanical stability

advancing and receding contact angles of water and hexadecane vs. Wenzel roughness r_W



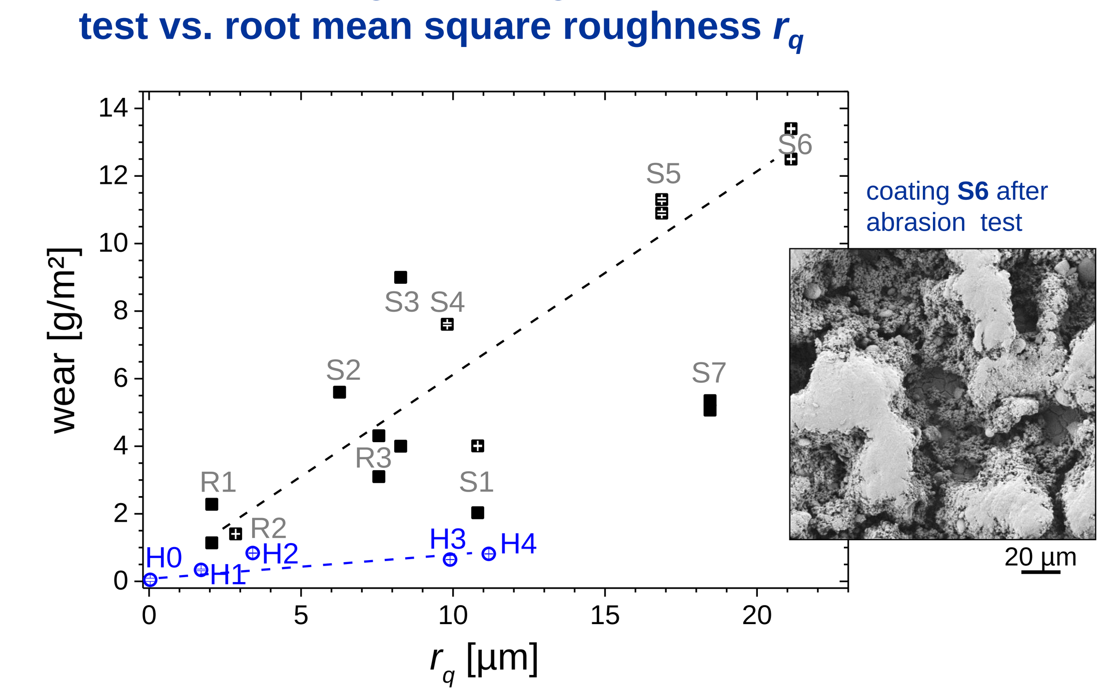
two-layer systems H0-4: contact angle hysteresis of water and hexadecane increases with roughness → Wenzel regime
single-layer systems *with microstructure* R1-3, S1-6:
water: Cassie regime; hexadecane: transition from Wenzel to Cassie regime for $r_W > 5$ (not for S7!)

coating R1: advancing and receding contact angles of water-ethanol mixtures vs. liquid surface tension γ_{lv}



macroscopically smooth blade-coated single-layer coating R1 *with microstructure* repels all liquids with surface tensions $\gamma_{lv} > 40$ mN/m (Cassie regime)

wear of the sol-gel coatings after wet abrasion test vs. root mean square roughness r_q



mechanical stability decreases with increasing roughness;
- lower wear for coatings without microstructure (H0-4, S7)
- asperities of sprayed coatings protect microstructure in the voids → coating remains superhydrophobic, oleophobic

summary

Superomniphobic coatings can be prepared on technical scale by sol-gel technique with additives and nanofillers.

single-layer coatings with nanofillers:
- hierarchical structure on various length scales
- superhydrophobic, oleophobic behavior

single-layer coatings sprayed on heated substrate:
- high aspect ratio, pronounced microstructure, re-entrant structures, low defect density

⇒ superhydrophobic, superoleophobic behavior, (if full surface coverage, low defect density)

superomniphobicity reached with micro- and nanostructured coatings sprayed on heated substrates

two-layer systems:
\+ low fluorine content, better mechanical stability
– insatisfactory wetting behavior

mechanical stability
- decreases with increasing roughness, aspect ratio and microstructure
- roughness has to be optimized with regard to wetting behavior
- asperities act as "sacrificial layer", protect microstructure in the voids → superhydrophobicity is maintained after wet abrasion test

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