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Surface nanostructuring of pine wood veneer chips by etching of self-assembled PS nanospheres via O_2 atmospheric plasma treatment

Sebastian Dahle[1,2,*], Alexandra Prowald[3], Wolfgang Viöl[2] and Wolfgang Maus-Friedrichs[1,4]

[1] Institut für Energieforschung und Physikalische Technologien, TU Clausthal, Leibnizstraße 4, Clausthal - Zellerfeld, D - 38678, Germany
[2] Hochschule für Angewandte Wissenschaft und Kunst, Fakultät für Naturwissenschaften und Technik, Von-Ossietzky-Straße 99, 37085 Göttingen, Germany
[3] Institut für Elektrochemie, TU Clausthal, Arnold-Sommerfeld-Straße 6, 38678 Clausthal-Zellerfeld, Germany
[4] Clausthaler Zentrum für Materialtechnik, TU Clausthal, Leibnizstr. 4, 38678 Clausthal-Zellerfeld, Germany

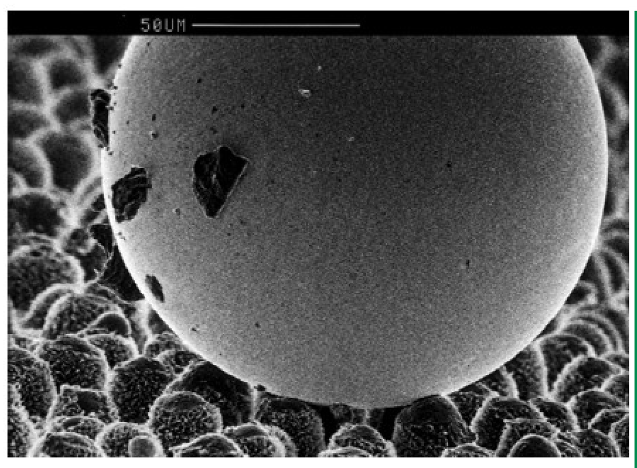
1. Introduction

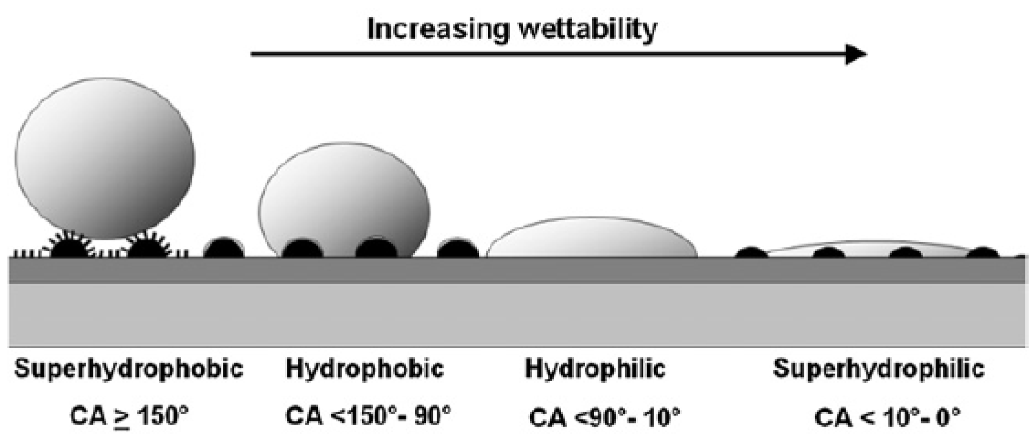
The hydrophobation of wood surfaces is of great technological interest and a variety of approaches is being followed to earn contact angles as large as possible. The high contact angles for both, polar and non-polar liquids that are found for Lotus leaves may thus be advantageous over current methods and may also bring in many new applications. Resembling the highly structured surfaces that induce those (super-)amphiphobic behaviour of the leaves (c.f. sect. 3) can be done using colloidal lithography via self-assembled layers as a template for etching and functionalization [1]. Usually, this technique is employing spin-coating deposition of one monolayer of the colloidal spheres on smooth, flat surfaces as PMMA. Regarding wood surfaces, the roughness inhibits the deposition of an ordered monolayer via spin-coating. Thus, a dip-coating procedure has been used that deposits a film of multiple ordered layers. This procedure has initially been developed for the fabrication of crystal structures e.g. for optical applications [2,3,4].

2. Experimental

The chemical analysis was carried out by X-ray Photoelectron Spectroscopy (XPS) using a commercial non-monochromatic X-ray source (Specs RQ20/38C) and a hemispherical analyzer (VSW HA100) using Al Kα at a photon energy of 1486.6 eV. Fit curves were gained with CasaXPS. Microscopic structures have been investigated with a Confocal Laser Scanning Microscope (LSM, Keyence VK-X200) and a Scanning Electron Microscope (SEM, Omicron NanoSAM). All SEM measurements have been done without any conductive cover layer on the samples surface.
The colloid template has been made from polystyrene (PS) nanospheres with an average diameter of 600nm (Optibind polystyrene microparticles, Duke Scientific Corporation), which have been dip-coated from a suspension in ethanol.
Plasma treatments have been carried out in O_2 (Linde Gas, 99.995%), employing alternating high voltage pulses with a peak voltage of 11 kV, a pulse duration of 0.6 µs and a pulse repetition rate of 10 kHz.

3. The structure dependence of contact angles

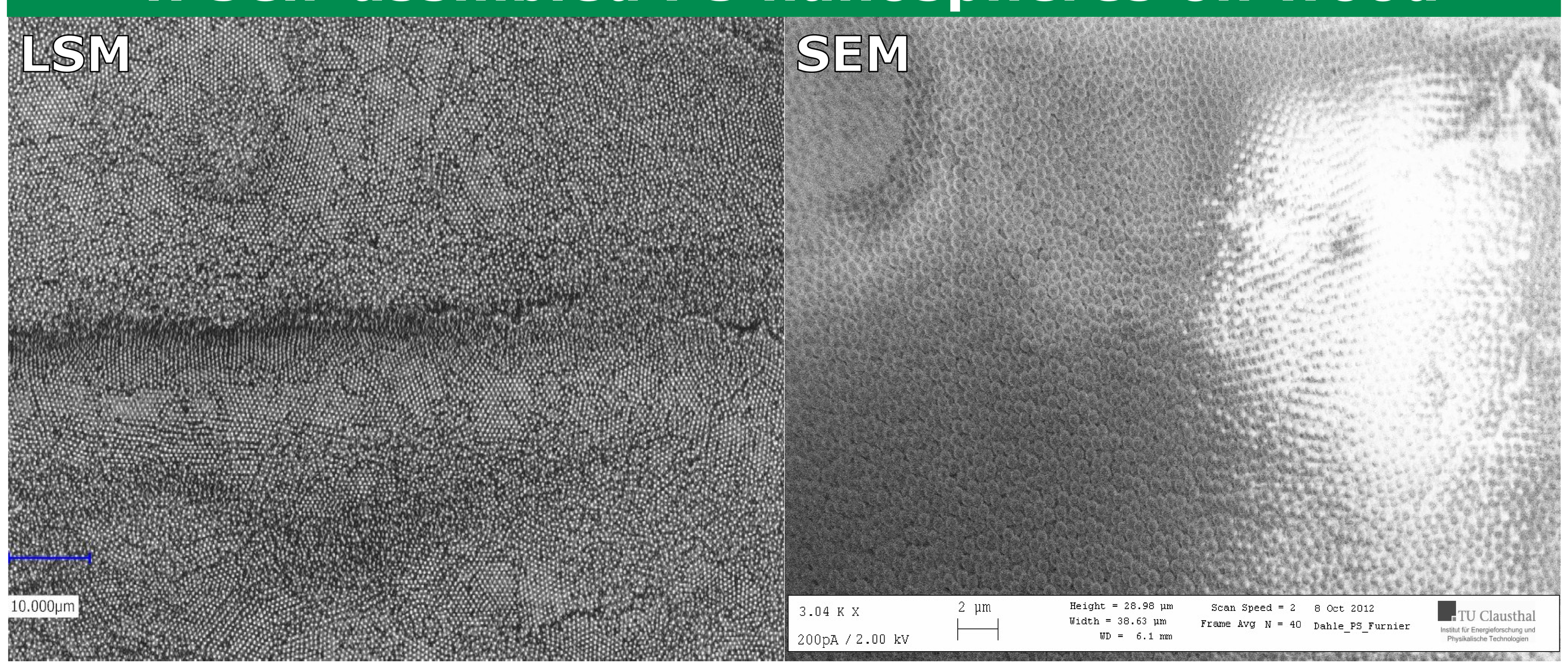

SEM image of a water droplet on a Lotus leaf [5]

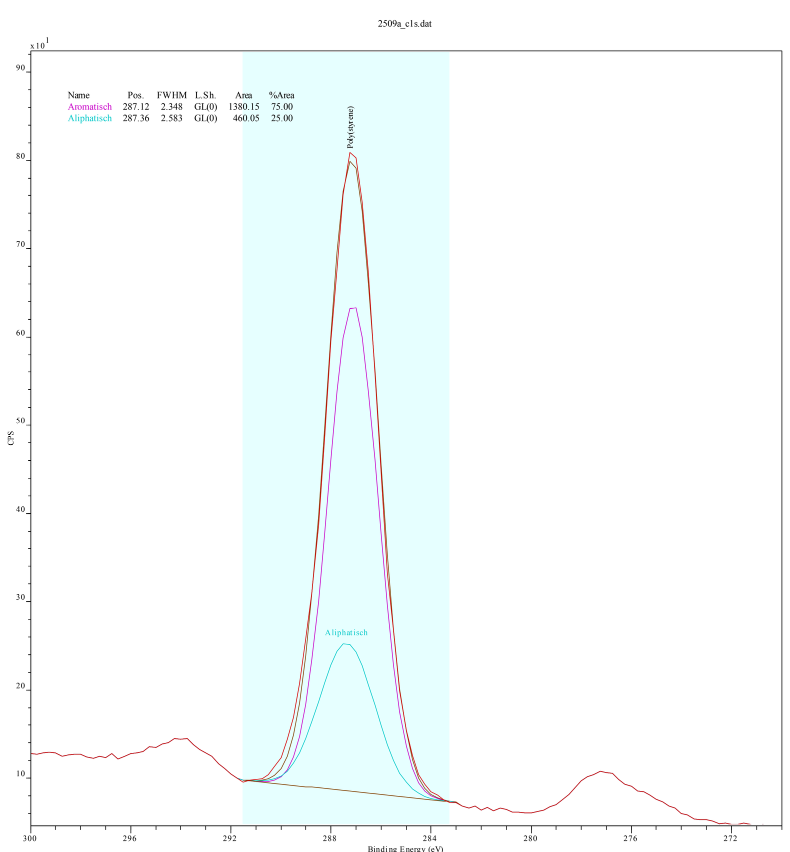


Schematic sketch of highly structured surfaces found on different plants' leaves as well as the corresponding water contact angles [6]

The typical water repelling leaves reveal a hydrophobicity which is not only duet to wax coatings but also very much due to the geometrically structured surfaces. Especially high values of water repellence are achieved by structures upon the surface that are tall but narrow. On this structures, the water is inhibited to wet the voids between the adstructures due to contact angle reasons. When the effective contact area determining the energy gain upon surface wetting gets rather small, the contact angles behave just alike.
This structural hydrophobicity can be increased furthermore, when the surface is structured hierarchical over several orders of magnitude. This is represented by convex cells, papillas, hairs and 3D wax structures on the surface of the leaves.
A similar hierarchical surface structuring might be implemented by the combination of self-assembled nanospheres with hydrophobic, chain-like molecules attached all around.

4. Self-assmbled PS nanospheres on wood



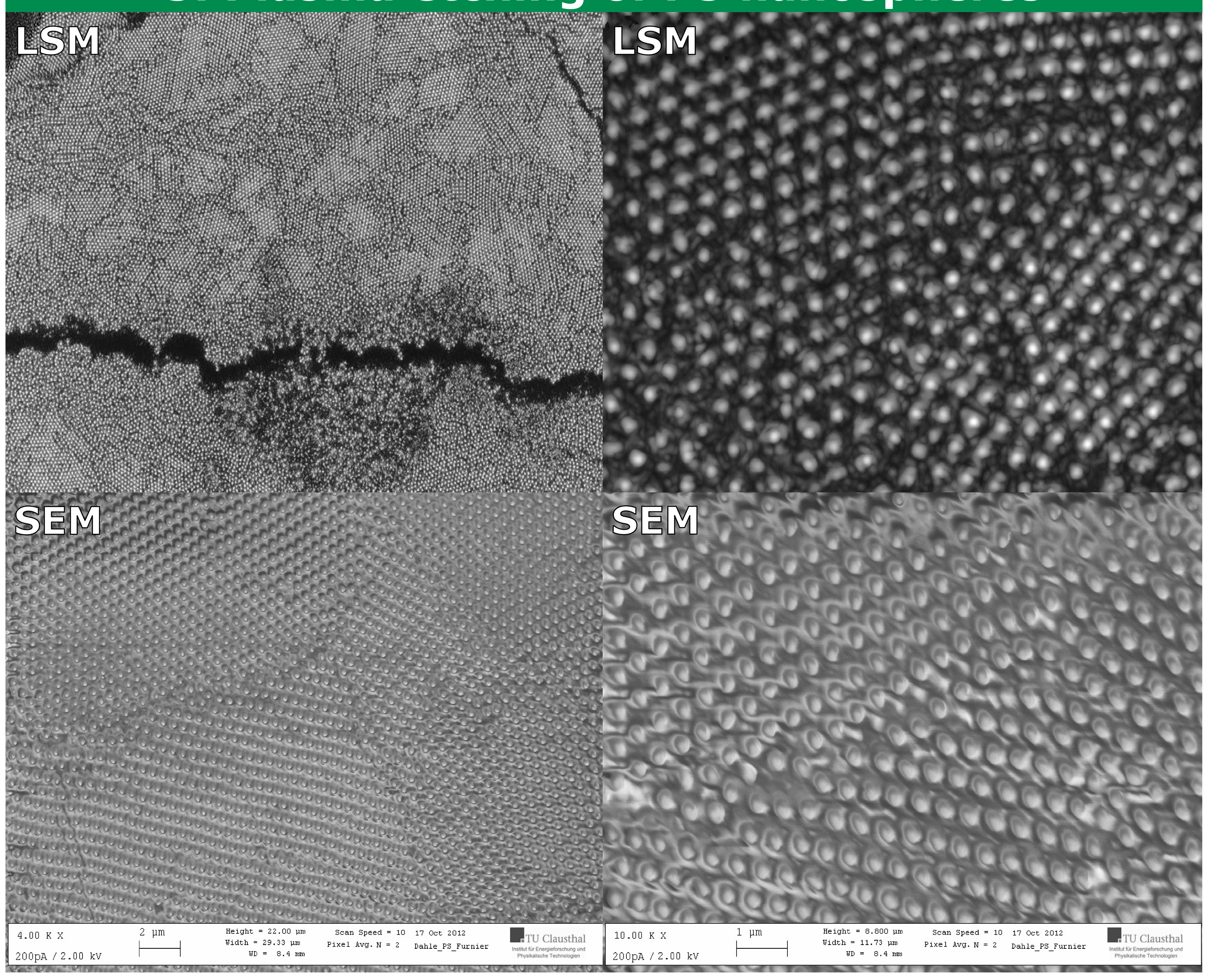


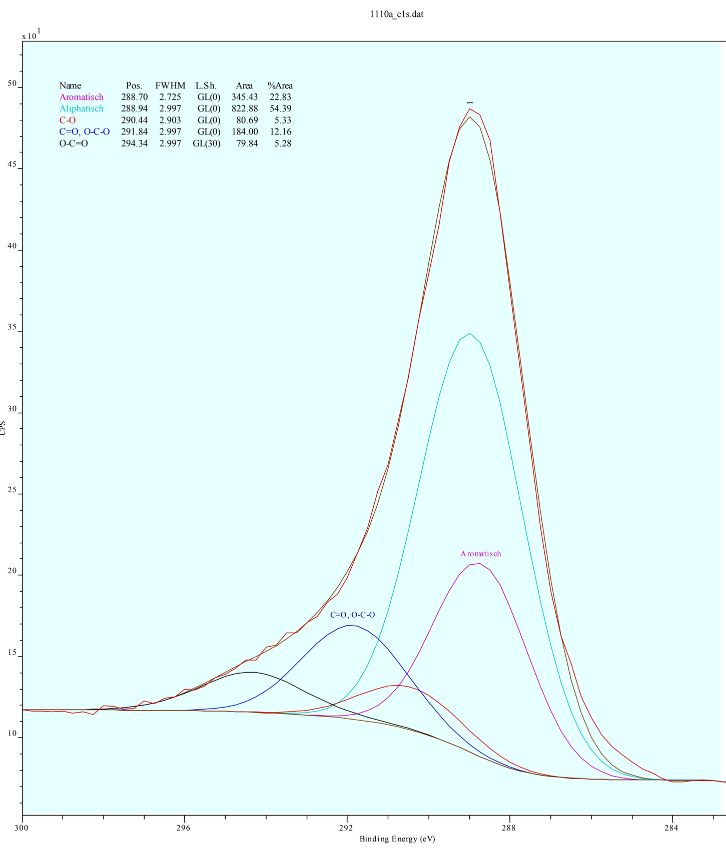
The LSM image reveals…
- A good self-assembling behavior of the PS nanospheres despite the roughness of the wood surface.
- A partly polycrystalline, hexagonal closed packed structure of the PS nanospheres.

The SEM image confirms…
- The complete coverage of the pine wood veneer chip's surface.
- The dense structure of the PS nanospheres

The XPS results (only C1s region shown)…
- Perfectly resemble the structure of polystyrene.
- Indicate a multilayer system of self-assmbled PS nanosphere layers by the absence of any wood-related structures.

5. Plasma etching of PS nanospheres





The SEM image reveals…
- A successfull etching of the PS nanospheres by the O_2 plasma.
- A reduction of the PS nanospheres' diameters by about half of its original value.
- The conservation of the structure and lattice constant of the PS nanosphere polycrystals.

The LSM image confirms the SEM interpretation, excluding any significant influence of electric charging on the SEM image.

The XPS results (only C1s region shown) show an oxidation of the PS nanospheres' surfaces by the attachment of hydroxy, alkoxy, carbonyl and carboxyl groups.

6. Summary and Outlook

We succesfully demonstrated the application of colloidal templates on wood surfaces using multilayers of self-assembled PS nanospheres. Etching in an oxygen plasma has been shown to efficiently reduce the PS nanospheres' diameters, while contemporarily loading their surfaces with polar groups. The predicted influence of the surface structuring on the wettability still has to be verified by contact angle measurements.

The next steps towards a superamphiphobical modification of wood surfaces will then be:
- The optimization of the particles' and voids' sizes for liquid repelling behavior.
- The improvement of the film's mechanical properties via thermal or plasma processing.
- The attachment of chain-like organic molecules to maximize the repellence of all liquids via hierarchical surface structuring.

7. Literature

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*Email: s.dahle@pe.tu-clausthal.de

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