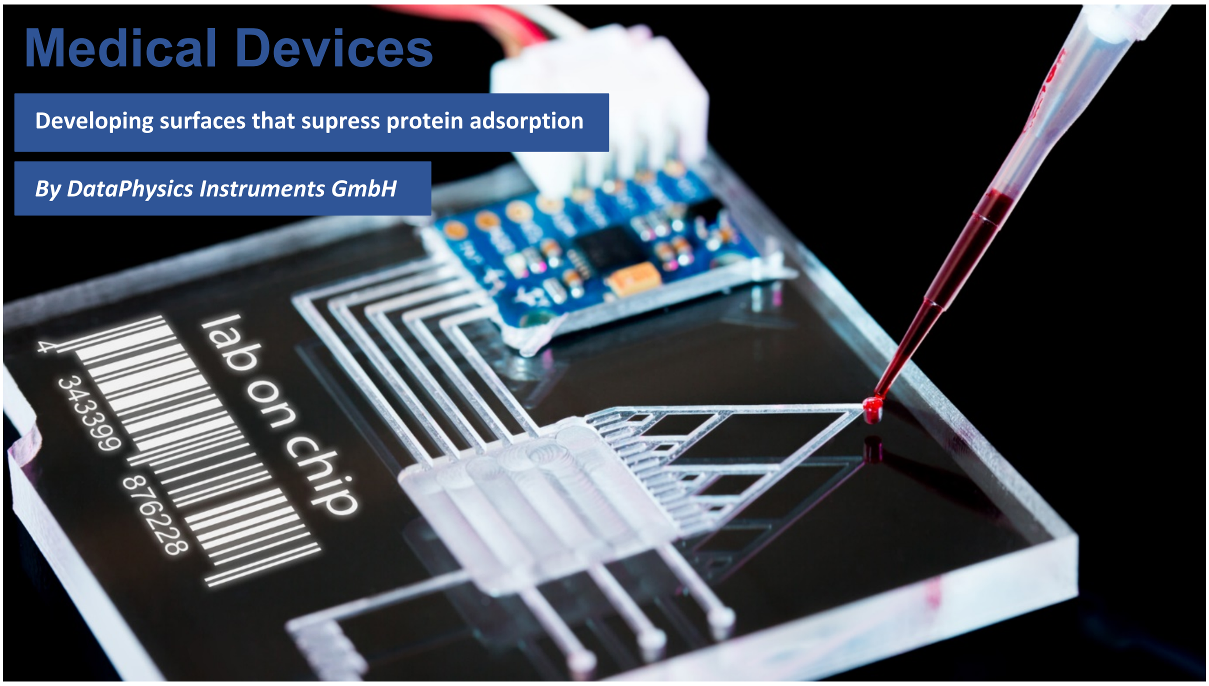
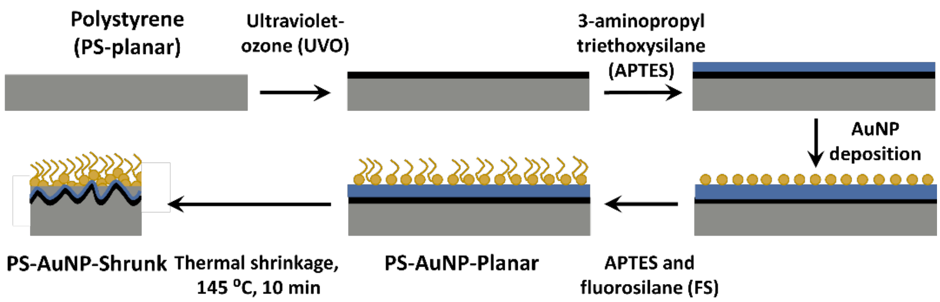
How shrinking a surface can increase its hydrophobicity.



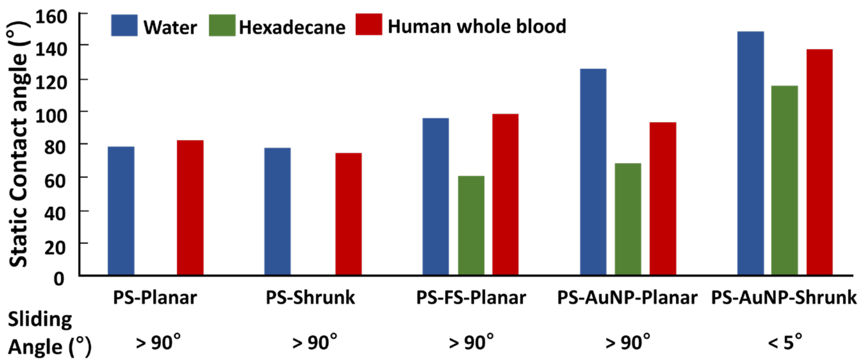
One of the biggest challenges for biomedical devices is to avoid biofouling, coagulation and thrombosis caused by a non-specific protein adsorption on the device surfaces. Anticoagulants, like heparin, were used to solve these problems. However, due to the limited activity of anticoagulants and the potential risk caused by anticoagulants themselves, more effective strategies need to be sought after to keep surfaces in medical devices clean from biocompounds. Promising strategies involve specially designed surfaces with anti-biofouling ability under blood flow to minimize the administration of anticoagulants. In particular, surfaces with hierarchical micro-/nanostructures are promising candidates. Theoretically, the formation of these hierarchical structures can effectively reduce the available surface area and decrease the shear stress at the surface, thus reducing the proteins adhesion. In most studies, these hierarchical structures were made using advanced technologies like laser ablation or electrodeposition, which are typically costly, material dependent and difficult-to-scale. Recently, Sara and coworkers have applied an easily scalable strategy based on nanoparticle-induced microscale wrinkling (NMW)—for preparing liquid repellent surfaces with good performance of preventing blood adhesion and clot formation which makes it an attractive way to improve the surface of medical devices.

In this work the authors fabricated an innovative surface (PS-AuNP-shrunk) by a NMW process (**Picture 1**) and some control surfaces including untreated PS (PS-planar), a PS substrate after shrinking (PS-shrunk), a PS substrate after fluorosilinizaiton (PS-FS-Planar), and unshrunken surface (PS-AuNP-Planar).



Picture 1. *Fabrication process of liquid repellant surfaces*

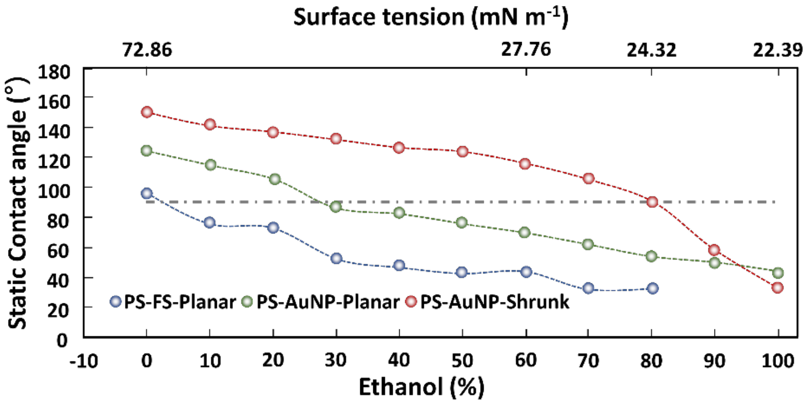
To demonstrate the hydrophobicity and oleophobicity of the testsurfaces, contact angle (CA) measurements with water, hexadecane and human whole blood were done (**Picture 2**). While unmodified PS-Planar and PS-Shrunk were both hydrophilic, the CAs progressively increased upon gradual introduction of fluorosilane (FS) (PS-FS-Planar, 96 ± 3.8°), gold nanoparticles (PS-AuNP-Planar, 127 ± 9.4°) and shrinkage (PS-AuNP-Shrunk, 149.5 ± 4°). This is for the following reason: FS reduces the surface energy, nanoparticles increase the surface roughness to create an effective Cassie wetting state, and the hierarchical structures further contribute to elevated CAs.



Picture 2. *The CAs of different surfaces for water, hexadecane, and human whole blood.*

In addition, unmodified PS-Planar and PS-Shrunk were both oleophilic, and the introduction of FS and AuNPs increased the CAs while still keeping oleophilic (PS-FS-Planar, 62 ± 2.4°; PS-AuNP-Planar, 69 ± 6°). However, the hierarchical structures completely changed the surface into an oleophobic one (PS-AuNP-Shrunk, 116 ± 3°). Furthermore, the CA of human whole blood, obviously increased from 83 ± 4.5° (PS-Planar) to 138 ± 3.1°(PS-AuNP-Shrunk). Moreover, only PS-AuNP-Shrunk possessed a sliding angle below 5° upon the formation of the Cassie state, in which the trapped air helped decreased adhesive forces and thus liquid droplets could easily detach from the surface. All above results show that chemical modification and hierarchical structures dramatically improved the surface repellency for various liquids.

To further understand how the liquid surface tension influences the surface repellency, formulations with different ethanol/water concentrations and thus a varying surface tension were used for CA measurements (**Picture 3**). In details, when the surface tension was higher than 24.32 mN m^{-1}, PS-AuNP-Shrunk already exhibited a hydrophobic behavior. In comparison, PS-FS-Planar and PS-AuNP-Planar displayed hydrophilicity when ethanol concentration was higher than 0% and 30%, respectively. 60% ethanol has a similar surface tension with hexadecane but with a different polarity; still similar CAs was observed both on PS-AuNP-Shrunk (120°) and PS-AuNP-Planar (70°). However, this was not the case for PS-FS-Planar which shows that there a synergistic effects form micro-/nanostructures and surface chemistry. Furthermore, the authors illustrated that PS-AuNP-Shrunk has the best performance in preventing blood coagulation and contamination (surface tension of human whole blood ≈55 mN m^{-1}). Finally, they combined superhydrophobic and hydrophilic surfaces to a patterned substrate, which showed selective digitization of liquids in high throughput assays, and successfully created a fluorescence biosensor for analyzing Interleukin 6.



Picture 3. *The CAs of different surfaces for various ethanol/water concentrations (%v/v) with different surface tension.*

Overall, this work presents a scalable and low-cost strategy to fabricate highly repellent surfaces. PS-AuNP-Shrunk which combines both chemical modification (polyfluorinated surface) and hierarchical structures (Nanoparticles and microstructures from shrinkage) demonstrated the best anti-adhesion behavior for blood making it a promising material for the surfaces of medical devices.

An optical contour analysis system OCA (DataPhysics Instruments GmbH, Germany) was used in this research.

For more information, please refer to the following article:

Hierarchical Structures, with Submillimeter Patterns, Micrometer Wrinkles, and Nanoscale Decorations, Suppress Biofouling and Enable Rapid Droplet Digitization; Sara M. Imani, Roderick Maclachlan, Yuting Chan, Amid Shakeri, Leyla Soleymani, and Tohid F. Didar, *Small* ***2020**, 2004886*; DOI: 10.1002/smll.202004886