Mussel-Inspired Polyglycerols as Surface Coatings with Controllable Wettability

Dissertation zur Erlangung des akademischen Grades des

Doktors der Naturwissenschaften (Dr. rer. nat.)

vorgelegt von

Christoph Schlaich

aus Schramberg

Institut für Organische Chemie

Fachbereich Biologie, Chemie, Pharmazie

Freie Universität Berlin

2017

Diese Arbeit wurde unter der Anleitung von Prof. Dr. Rainer Haag im Zeitraum von September 2014 bis Oktober 2017 am Institut für Chemie und Biochemie der Freien Universität Berlin angefertigt.

1. Referent: Prof. Dr. Rainer Haag.

2. Referent: Prof. Dr. Christoph A. Schalley

Disputation am: 14.12.2017

Content

1 Introduction

In the millions of years of evolution, nature has developed a variety of high performance materials that function from the nanoscale to the macroscale. The understanding of these functions provided by nature can guide us to imitate and fabricate micro and nanomaterials that not only increase our standard of living but can also contribute towards sustainability and environmental protection. In general, the adaption or inspiration from biology for technical applications is referred as biomimetics. It involves the understanding of biological functions, natural structures, and principles for the purpose of fabricating artificial materials with similar properties. Living organisms are composed out of numerous interfaces that are highly organized in hierarchical structures. The interplay in nature between surface structures and physical and chemical properties results in a variety of different functionalities. In the last decade, scientists from chemistry, biology, physics, and material science have prepared various materials with outstanding properties that have been inspired by nature. In most of these cases, the wettability plays a key role as the most fundamental parameter of interfacial materials regarding the functionality of a surface. Especially in the area of materials with special wettability states (e.g., superhydrophobicity or superhydrophilicity), there has been incredible progress since the discovery of the lotus effect.[1] Nowadays, we consider superhydrophobicity only one part of a broad spectrum of different extreme superphilic or superphobic wetting states in the concept of superwettability. Based on the broad concept of superwettability, many surfaces for various applications have been reported, including self-cleaning, drag reduction in fluid flow, anti-reflective, anti-icing, anti-bacterial, anti-corrosion, and self-healing materials.[2-3] Therefore, a variety of novel chemical and physical methods have been explored for fabricating functional surfaces with special wetting properties. Although a large number of reported applications and fabrication protocols have been published, the broad industrial and technological distribution has remained on a low level, mainly due to three points. First, most of the reported fabrication protocols involve a tedious multistep protocol and/or specialized equipment. Second, most of the reported surface coatings are substrate-specific and heavily rely on the underlying materials' properties. Third, there is still a fundamental problem with the long-term durability of coatings with superwettability.

A process in nature, whose mimicry could possibly solve all these above-mentioned problems, is the adhesion process of mussels. While commercial adhesives hardly adhere under water, the mussel is able to adhere on all kinds of surfaces (e.g., rocks, ships, ropes) under extreme conditions, such as saltwater conditions, in an amazingly short time. The secret of this

unique adhesion lies in an extremely sticky mixture of so-called mussel foot protein (mfp) in the mussel byssus that is secreted by the mussel foot (see Figure 1). In the last two decades, research has focused on understanding this complex adhesion mechanism as well as the characterization and imitations of these mussel foot proteins to develop a synthetic underwater adhesive. Additionally, mussel-inspired materials have also received great attention in the field of surface coatings because of their substrate-independent, strong, and robust adhesion to the substrate.

A combination of two separate and biomimetic concepts of mussel-inspired adhesion and highly hierarchical lotus-like surface structures will be presented in the first part of this thesis. Therefore, both concepts will be introduced in the theoretical part of this work. Building on this knowledge, an entirely substrate-independent and universal fabrication method for various super-wetting systems on any kind of material will be presented. In the second part, new applications of coatings with superwettability and simplification of the coating processes will be discussed.
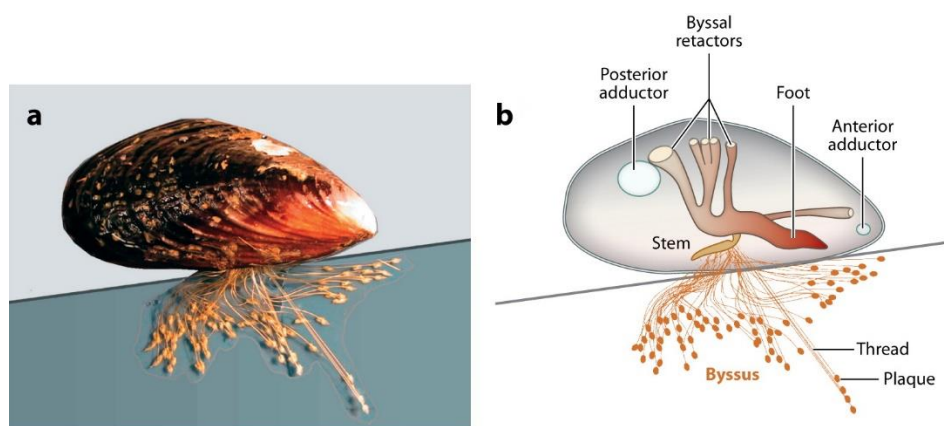
Figure 1. (a) Mussel with an extensive byssus attached to a substrate. (b) Schematic illustration of a mussel. The byssus consist out of a bundle of threads with adhesive plaques. Reprint from with permission ref. [4]. Copyright 2011 Copyright Clearance Center.

2 Theoretical Section

2.1 Wetting Behavior on Solid Surfaces

2.1.1 Wetting on Flat Surfaces

Young's equation is a way to determine the wetting of a perfectly smooth and chemically homogeneous solid surface.[5] The equation describes a thermodynamic equilibrium and allows one to calculate the theoretical contact angle (θ^0).

$$\cos \theta^0 = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad \text{(Eq. 1)}$$

In Eq. 1, the terms γ_{SV}, γ_{SL}, and γ_{LV} refer to the interfacial surface tensions of the solid-vapor, solid-liquid, and the liquid-vapor phase. According to Young's equation, 90° degrees is considered as the mathematic threshold to determine whether a solid material is hydrophilic or hydrophobic. From this classical point of view, it was assumed that any surface with $\theta < 90°$ was considered hydrophilic and any surface with a $\theta > 90°$ is hydrophobic. However, recent empirical and investigations studies have shown that a $\theta = 65°$ rather than 90° from the theoretical model determines the border between hydrophilic and hydrophobic.[6-7] This border is also called the intrinsic wetting threshold (IWS) and also known as the Berg limit.[8-9] Moreover, the border of 65° only applies for water and every single liquid has its own IWS that is dependent on the liquid's surface tension (Figure 2).[9] According to Equation 1, the hydrophobicity of a surface increases with a decrease of the free energy of the solid-vapor interface. A water contact angle of 120° was found for the lowest surface free energy of the solid-air interface material, e.g., perfluorinated materials such as Teflon. For an even further increase in hydrophobicity, the manipulation of surface roughness and topography is required.
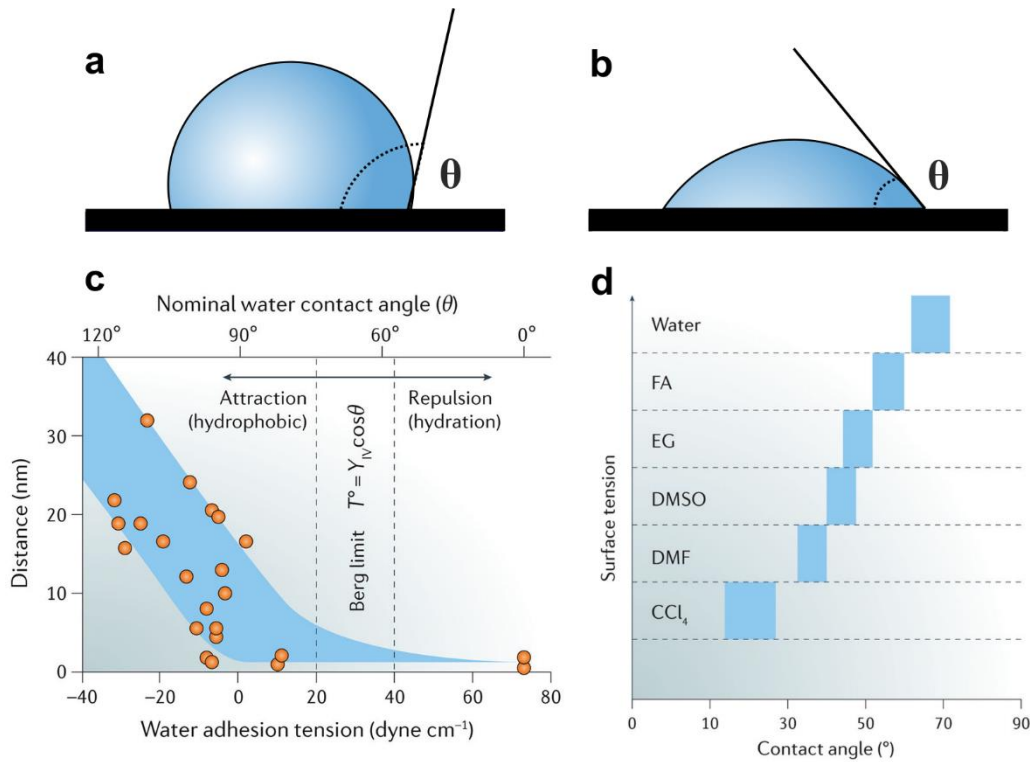
Figure 2. Schematic illustration of droplet placed on an (a) hydrophobic and (b) hydrophilic flat surface. (c) Quantitative definition of the terms 'hydrophobic' and 'hydrophilic' from surface force investigations. Attractive hydrophobic forces were observed between surfaces with a water contact angle of around 65°, which is termed the Berg limit. (d) The intrinsic wetting thresholds (IWT) for different liquids. Modified reprint with permission from ref. [10]. Copyright 2017 Nature Publishing Group.

2.1.2 Wetting on Rough Surfaces

In reality, most surfaces are not flat and completely homogeneous like in Young's theories. Rather the opposite, they show a certain degree of surface roughness and are covered with micro- and/or nanoscale rough grooves. The surface roughness strongly affects the wetting of a surface and plays a key role in the design of surfaces with extreme wettability. Wenzel, Cassie, and Baxter extensively studied the effect of roughness on wettability. Two basic models of wetting were established (Figure 3): Wenzel's mode (penetration state) and Cassie-Baxter mode (suspension state).[11-12] In the Wenzel state, a water droplet fully penetrates the rough grooves of a textured surface. Consequently, the effective contact area of a droplet with the surface increases and a roughness factor has to be considered (Equation 2).

$$\cos \theta^W = R_F \cos \theta^0 \hspace{4cm} \text{(Eq. 2)}$$

In Equation 2, θ^W corresponds to the apparent contact angle, θ^0 represents the contact angle on the ideal flat surface, and R_F represents the roughness factor. The R_F is given by the ratio of the solid-liquid area to its projection on a flat plane. In other words, $R_F = 1$ (θ^W is equal to θ^0) for perfectly smooth surfaces and $R_F > 1$ for a rough surface. The model predicts that a hydrophobic surface becomes even more hydrophobic with an increase in roughness, and that hydrophilic surfaces become even more hydrophilic with increasing roughness. For hydrophilic surfaces with a certain roughness, the liquid completely wets the surface and the roughness grooves completely absorbs the wetting liquid. However, for non-wetting surfaces composed out of small protrusions, the liquid cannot completely penetrate the texture, resulting in the formation of air pockets. The so-called Cassie-Baxter Model (Eq. 3) describes this wetting phenomenon.

$$\cos \theta^{CB} = \emptyset_S (1 + \cos \theta^0) - 1 \qquad \text{(Eq. 3)}$$

In Equation 3, θ^{CB} corresponds to the apparent contact angle, θ^0 refers contact angle of the ideal flat surface, and the surface fraction $\emptyset_s$ corresponds to the ratio of the surface on top of the roughness grooves (in contact with the liquid) and the apparent surface of the substrate. In the Cassie-Baxter model, basic guidelines emerge for the fabrication of superhydrophobic surfaces with extremely high contact angles. First, the fraction of the solid ($\emptyset_s$) should be as small as possible. Second, the material should show the highest possible contact angle for an ideally flat surface (θ^0). It should be mentioned that both models, the Wenzel state and Cassie-Baxter state, represent two extremes. In reality, the air can only be entrapped to a certain degree, indicating various transition states between Wenzel and Cassie-Baxter states.[13]
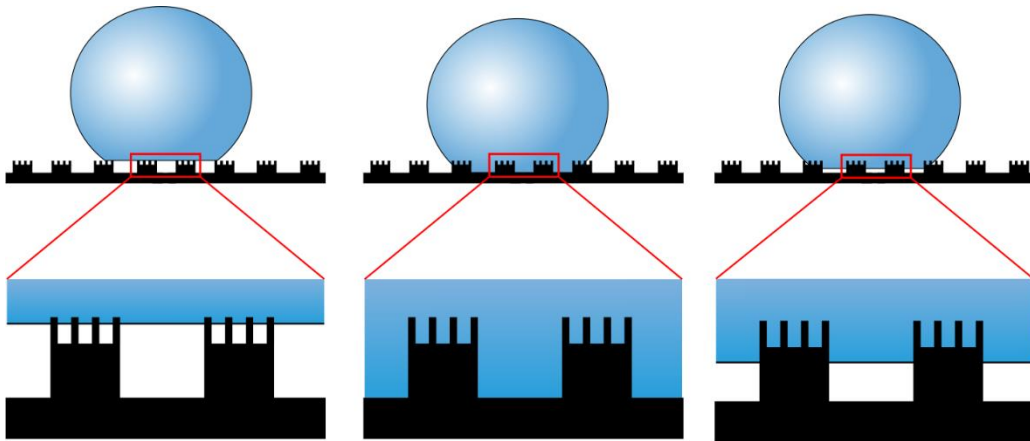
Figure 3. Schematic illustration of droplet a droplet in (a) the Wenzel state, (b) the Cassie Baxter state, and (c) Cassie-Baxter to Wenzel transition state.

2.1.3 Contact Angle Hysteresis and Dynamic Contact Angle

The dynamic contact angles and the contact angle hysteresis (CAH) are other important characteristics of a solid-liquid interface.[14-15] Dynamic contact angles are non-equilibrium CAs and can be observed in a moving droplet. The contact angle hysteresis (CAH) is given by the difference of the contact angle (CA) at the front of the moving droplet (advancing CA) and the CA at the back of the moving droplet (receding CA, Figure 4). The CAH is a result of roughness and heterogeneity of a surface. The CAH can be measured by increasing or decreasing the volume of a droplet and monitoring the CA and the change in the solid-liquid interface. When the volumes of the droplet are increased, the CA of the largest possible drop that can stay without increasing the interfacial area between the liquid and solid corresponds to the advancing angle. Similarly, when the volume is removed from the droplet, the CA of the smallest possible droplet without a change in the liquid-solid contact line is referred to as the receding CA. The CAH of the droplet on the surface is crucial for the design of non-wetting surfaces such as superhydrophobic or superamphiphobic surfaces.
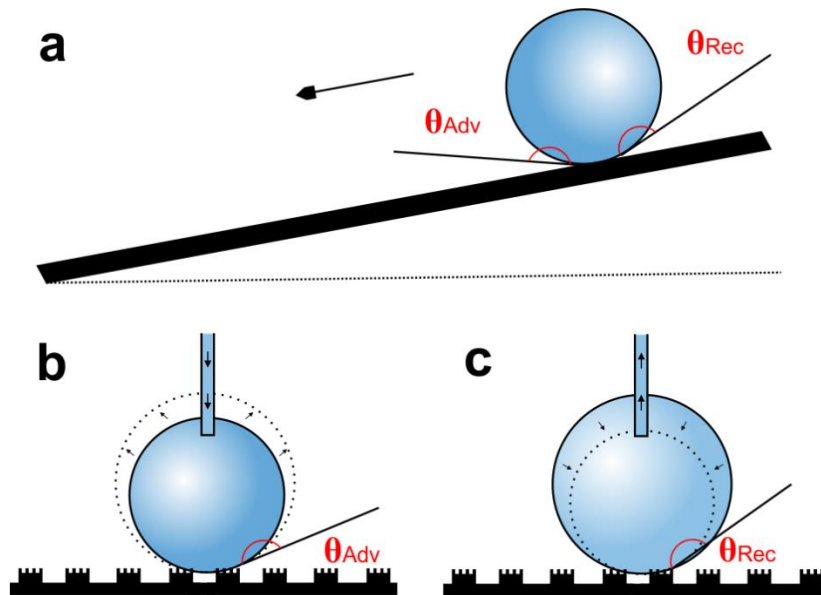
Figure 4. (a) Tilted surface profile with a droplet rolling down showing an advancing (θ_{Adv}) and a receding contact angle (θ_{Rec}). (b) and (c) Schematic illustration of the techniques for determination the θ_{Adv}, θ_{Rec}, and the correlated hysteresis.

The CAH is a parameter for describing the energy dissipation during the flow of a droplet along the surface. Consequently, surfaces with low CAH show nearly no adhesion of the droplet and low rolling-off or tilting angles. The tilting angle or rolling-off angle refers to the critical angle between the substrates and the horizontal, at which the water droplet begins to roll off the surface. Surfaces with a high water CA (over 150°) and low CAH (below 10°) are described by

the Cassie-Baxter model. The air is entrapped inside the roughness grooves supports the water droplet on top and pins the three-phase contact line on the topside of the surface structure. In contrast, surfaces in the Wenzel mode show significantly higher CAH than in the Cassie-Baxter mode. As a result, the surface typically shows a relatively high adhesion and the droplet strongly pins to the surface.

2.1.4   Cassie-Baxter to Wenzel State Transition

The Cassie-Baxter and the Wenzel State are considered separate energy minima with an energy barrier in between. Based on the textured solid-air-liquid interface, a water droplet on a superhydrophobic surface remains in the Cassie-Baxter state, which prevents the transition in the completely wetted Wenzel state. However, the balance of solid-air-liquid interface can only be maintained until a certain impalement pressure, which is proportional to the surface tension of a liquid (Equation 4).[16]

$$P \approx \frac{2 \times \gamma \times R}{a^2} \, sin^2 \frac{\Theta_M}{2} \qquad \text{(Eq. 4)}$$

In Equation 4, γ is the surface tension of the liquid, R is the radius of the spherical aggregates, r is the minimal distance between protrusions, and Θ_M is the advancing contact angle of the liquid on a flat fluorinated surface (see Figure 5). The transition from the Cassie-Baxter state to the Wenzel state is an irreversible process, because the droplet in Wenzel state is energetically more favored. The transition can occur mainly because of drop impact from a certain height, applying external pressure, evaporation of droplet, or vibration of the surface.
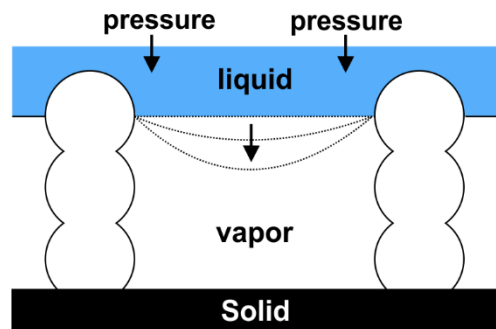
Figure 5. Schematic of the superamphiphobic layer consisting of pillars of spheres from side and top view. The liquid is suspended on top in the Cassie state. If no pressure is applied, the liquid surface is planar. With pressure the contact line moves downwards and the interface starts to curve.

2.2   Special Wettability / Superwettability

2.2.1   Superhydrophobicity and the Lotus Effect

Superhydrophobic surfaces are the most analyzed systems with special wettability and the research on it dates back more than one century. In 1907, Ollivier firstly described a CA of close to 180° on a surface coated with soot, arsenic trioxide, and lycopodium powder.[17] A few years later, Coghill and Anderson found in 1923 that a rough surface of galena modified with stearic acid showed a CA of more than 160°. However, despite these and other examples, research on superhydrophobic surfaces received limited attention and slowly developed until the mid-1990s, because of the lack of a general principle for superhydrophobicity. In 1997, Barthlott et al. first described the lotus effect and laid the foundation for a complete area of research.[1] With the help of scanning electron microscopy (SEM), they first described the lotus leaves' surface structure in detail. They found that the surface consists of many micrometer-scaled bumps, which are further covered with many small hydrophobic, nanometer-scaled wax crystalloids. They pointed out that superhydrophobicity is the result of a combination of a micro-/nanostructured surface and a hydrophobic material with a low surface free energy. With this basic understanding of concept of superhydrophobicity, a scientific boom was triggered and there still is an accelerating increase in publications in this area. Many studies have pointed out the importance of hierarchical structures with two-tier roughness on both the micro- and the nano-levels with low CAH and the associated self-cleaning effect.[18-21] The lotus leaves are one of the most famous examples among all natural occurring superhydrophobic surfaces (Figure 6).[22-24] A water droplet placed on the leaf has almost a spherical shape, shows a CA of 164° with a CAH of 3°, and can easily roll off. The Lotus effect is a well-known slogan and has its origin in the self-cleaning properties of the plant leaves. For a surface contaminated with dust particles, the contact area and the interfacial interactions between the dust particles and the surface are minimized. Consequently, the adhesion of the dust particle to the surface is very low. When water droplets from rainfall rolls over the dust particles, they can collect the contamination particles and carry them away by rolling off the surface. Besides the lotus leaves, many plants or insects, such as water striders, butterflies, and the cicada also show superhydrophobic properties.[25-26] The water striders are remarkable, because their superhydrophobic legs enable them to stand effortlessly on water.[27] Inspired by these remarkable properties in nature, to date, more than a thousand different strategies have been reported for the fabrication of artificial superhydrophobic surfaces for many potential

applications in various areas, such as self-cleaning, anti-corrosive, non-sticky, anti-bacterial or anti-fouling surfaces.[2-3, 28]
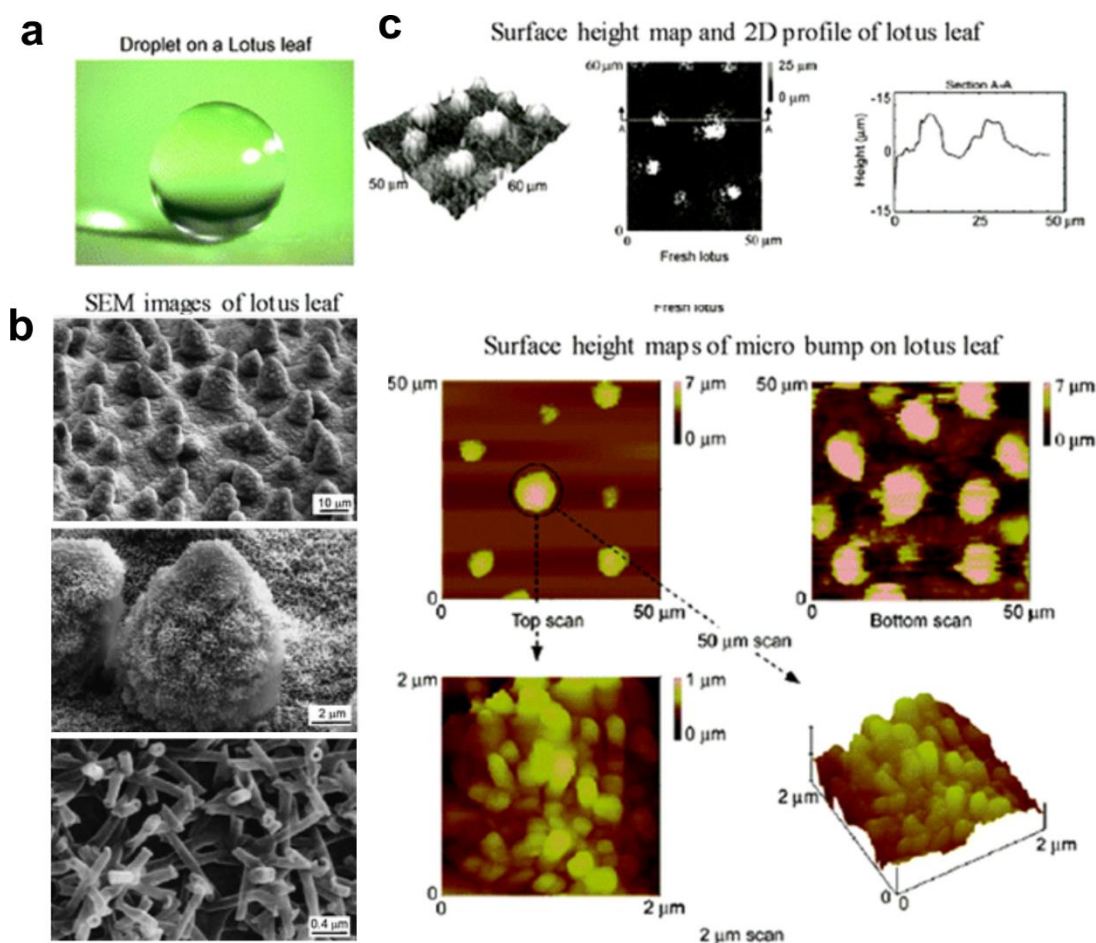
Figure 6. (a) Lotus leaves, which exhibit impressive water repellency on their upper side. (b) Atomic force microscopy (AFM) image and surface height map of the upper leaf side the hierarchical surface structure consisting of papillae, wax clusters and wax tubules, (c) Scanning electron microscopy (SEM) image of the upper leaf side. Wax tubules on the upper leaf side. Modified reprint with permission from ref. [18, 22]. Copyright 2009 and 2013 Royal Chemical Society.

2.2.2 Superamphiphobicity

Superhydrophobic surfaces usually are wetted by liquids with surface tensions lower than water (~ 72 mN/m). Therefore, it remains a challenge to fabricate superolephilic surfaces that repel even liquids with a much lower surface tension than water (< 30 mN/m). In general, a surface is considered superoleophobic when the organic solvents such as hexadecane (27.5 mN/m) contacting the surface show a CA over 150° and the rolling-off angle is less than 10°.[29] Most superoleophobic surfaces are also superhydrophobic, because water can be repelled more easily

9

due to its high surface tension. However, surfaces have recently been reported that are superoleophobic and yet superhydrophilic.[30-31] Therefore, surfaces that display both superhydrophobicitiy and superoleophobicity are considered as superamphiphobic surfaces (see Figure 7). Unfortunately, the nomenclature in the literature is not always clear and the terms superamphiphobic, superoleophobic, and superomniophobic are often used as synonyms. Here it is worth mentioning that, unlike superhydrophobic surfaces, superamphiphobic surfaces cannot be found in nature and are completely artificial. However, their outstanding repellent properties result in a much broader range of applications, which opens the door for a solvent-free synthesis of polymeric microspheres on a surface or handling of biologically sensitive liquids.[32-33] However, the established ways to fabricate superhydrophobic surfaces are no longer sufficient to produce superamphiphobic surfaces and an even more precise design of micro- to nano-scaled hybrid structures is required.[16] In the last decade, there have been several reports about the importance of re-entrant structures and hierarchical surface roughness, which led to several examples for superamphiphobic surfaces with precisely designed surface topographies.[34-39] However, all superamphiphobic surfaces display some limitations and repel liquids only down to a certain surface tension. In some examples in the literature, it was possible to repel liquids with surface tensions down to 20 mN/m (e.g., octane or heptane) by electrospinning microbeads of fluoropolymers on stainless steel meshes.[40-41]
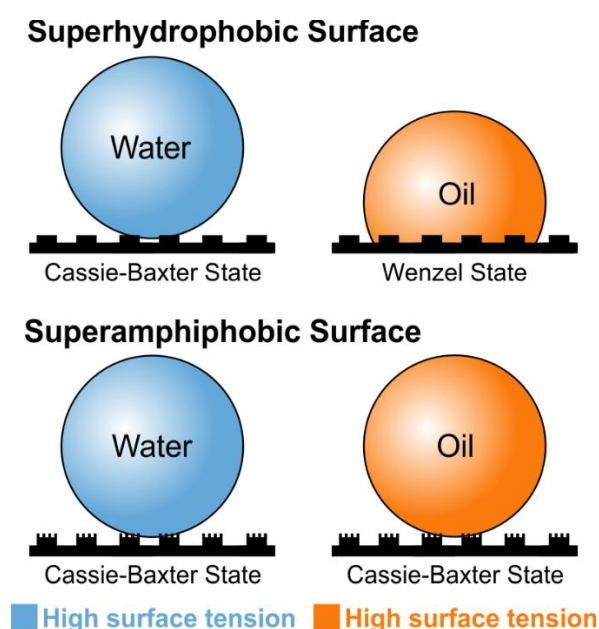
Figure 7. The liquids with low surface tension cause the transition from the Cassie-Baxter state to the Wenzel state on a superhydrophobic surfaces but not on superamphiphobic surfaces.

In a recent example, it was possible to repel liquids with the lowest known value of 10 mN/m (i.e., FC-72) by a special designed double-reentrant structure.[42] This example is of particular interest, because it shows that even an inherent oleophilic material can be tuned superoleophobic, which is contradictory to our basic understanding of wetting as discussed in Chapter 2.1. This phenomenon was further analyzed by Whyman and Bormashenko.[43] They studied the stability of the Cassie–Baxter state for different shapes of roughness patterns calculating the potential barrier separating the Cassie-Baxter and Wenzel states. These shapes can include spheres and spherical cavities and pillars with changing cross section and with side facets (Figure 8). For hydrophobic surfaces, the multiscale roughness increases the energy barrier for the wetting transition. More interestingly, even for inherently hydrophilic materials, the energy gain due to the wetting of a hydrophilic pore is overcompensated by the energy loss due to the growth of a water–air interface. Consequently, apparent hydrophobicity on an inherently hydrophilic material is possible when the appropriate pattern is introduced.
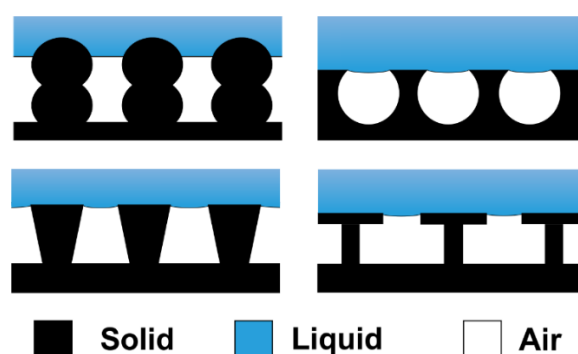
Figure 8. Surface profiles with potential barriers for the Casse-Baxter to Wenzel transition: spheres and spherical cavities, overtuned truncated cones, and pillars with side facets.

2.2.3 Superhydrophilic and Slippery Surfaces

Superhydrophilic surfaces that represent the opposite extreme of wettability have received less attention compared to superhydrophobic surfaces.[44-46] However, superhydrophilic surfaces have their own advantages and are extremely promising candidates regarding oil/water separation, anti-fogging, or water harvesting.[22, 47-48] In general, a superhydrophilic surface shows a CA of less than 10° and the droplet completely spreads over the surface. A general guideline to construct superhydrophilic surfaces is to create rough structures with a hydrophilic component according to Wenzel's theory.[23, 49] An alternative approach is to irradiate titanium dioxide (TiO_2) with UV, which leads to a photo-induced hydrophilic (PIH) effect that generates a superhydrophilic surface even without a microstructure.[50] Zink oxide (ZnO) also possesses

the same PIH mechanism. Furthermore, TiO_2 and ZnO have a photocatalytic effect on decomposing organic waste, thus are very useful in the area of self-cleaning surfaces.[51-52] Although the photogeneration is a reliable method to prepare superhydrophilic surfaces, the materials with the PIH effect are limited to TiO_2, ZnO, tin dioxide (SnO_2), tungsten trioxide (WO_3), and vanadium oxide (V_2O_5) until now.[53] The Nepenthes pitcher plant is an example of a natural SHL surface that is always lubricated, which is due to the extreme hydrophilicity. As a result, the liquid-infused surface becomes highly slippery and insects can easily fall into the pitcher-shaped leaves. Inspired by the Nepenthes pitcher plant, Aizenberg and coworkers reported slippery liquid-infused porous surfaces (SLIPS) as a good alternative to classical air-supported super-repellent systems.[54] The concept of SLIPS is based on the infiltration of a low-surface-energy porous surface with a fluorinated lubricating liquid (Figure 9). The reported SLIPS surface easily repelled various liquids and showed extremely low sliding angles, even for extremely complex liquids with a low surface tension such as human blood. The infused lubricant has to fulfill three requirements. First, the lubricant should be captured safely inside the porous texture. Second, the substrate should be preferentially wetted by the lubricant rather than by the liquid to be repelled. Last, the lubricant and the liquid to be repelled should be immiscible. To date, various SLIPS made out of various materials and lubricants have been reported. All these examples confirmed that the concept of SLIPS represents a straightforward solution for liquid repellency, resistance to fouling, pressure stability, and anti-icing properties combined with an extremely simple fabrication process.[55-59]
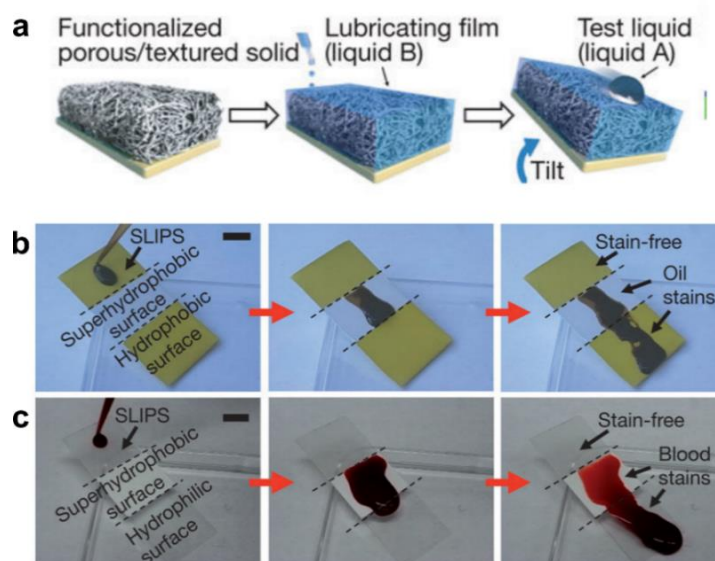
Figure 9. (a) Schematics showing the fabrication of a slippery surface. Repellency of the SLIPS fluids such as (b) crude oil and (c) human blood. Modfied reprint from ref. [54] with permission. Copyright 2011 Nature Publishing Group.

2.2.4 The Concept of Superwettability

In the last decade, there was a significantly accelerated development of nature-inspired artificial surfaces with extreme wetting states. Besides classical wetting conditions for surfaces in air, various extreme wetting states under different media (e.g., under oil/water) have been discovered.[60] The recently introduced concept of superwettability combines all these different wetting states. In total, there are 24 different wetting states, which are summarized in Figure 10. The inner circle shows the extreme wetting states under, for example, superhydrophobicity, superhydrophilicity, superoleophilicity, and superoleophobicity, superamphiphobicity, and superamphiphilicity. The outer circle shows extreme wetting states under different media including, in particular, superoleophilicity, superoleophobicity, superaerophilicity, and superaerophobicity under water; and superhydrophilicity, superhydrophobicity, superaerophilicity, and superaerophobicity under oil.[61-62]
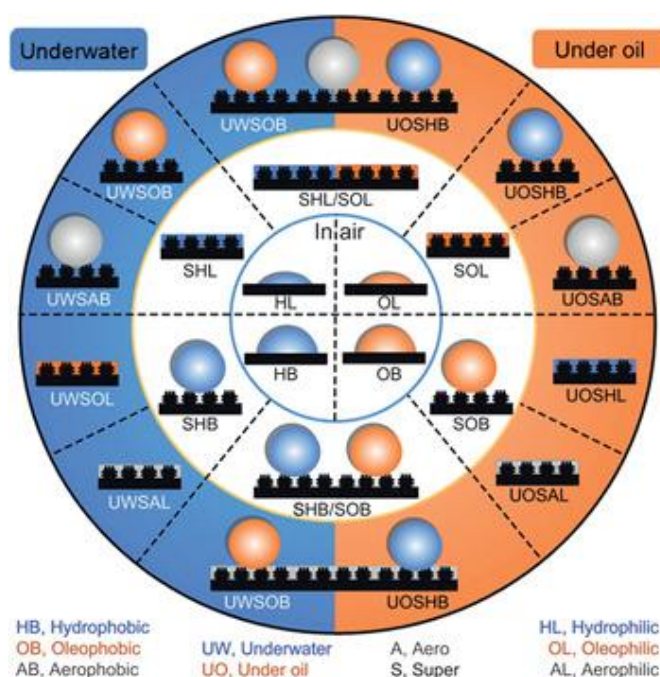
Figure 10. The concept of superwettability. The middle part: different wetting states in air before and after introducing micro/nanoscale two-tier roughness. Left blue semicircle: wetting states under water upon rough substrates. Right orange semicircle: wetting states under oil upon rough substrates. Reprint with permission from reference [61]. Copyright 2016 American Chemical Society.

2.2.5 Design Principles for Surfaces with Superwettability

Both Wenzel and Cassie-Baxter theories have pointed out that a certain surface roughness is essential for enhancing hydrophobicity or hydrophilicity. In addition to the fundamental theories of wetting of surfaces, the study of biological surfaces with superwettability plays a key role to reveal the mechanism behind it. Figure 11 shows some selected examples of natural surfaces with special wetting properties, including superhydrophobic, superhydrophilic, anisotropic, and superadhesive surfaces.
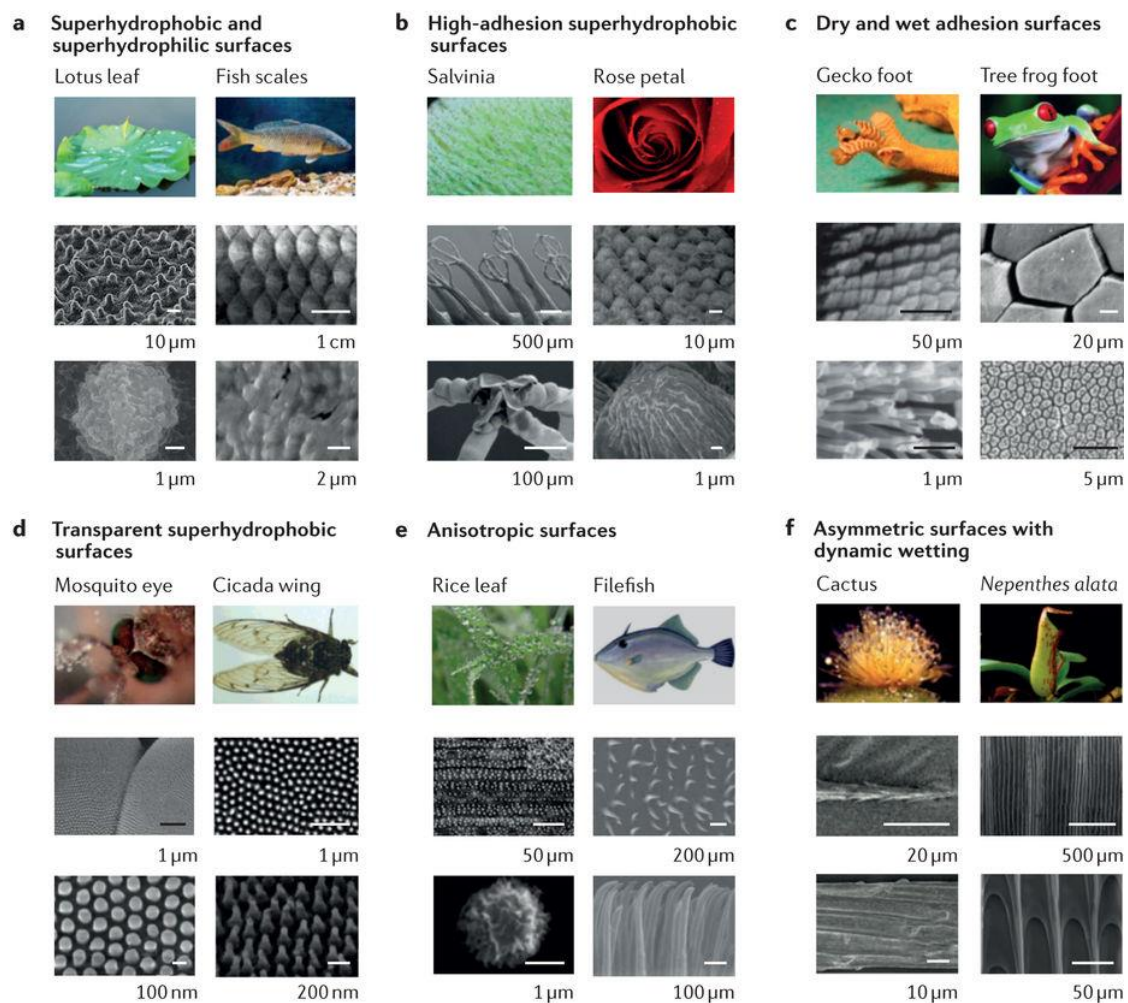
Figure 11. Examples of biological surfaces with superwettability and their multiscale structures. (a) Superhydrophobic lotus leaf and superhydrophilic fish scales; high adhesion surfaces of (b) salvinia and rose petals and (c) the foot of a gecko and a tree frog; (d)| transparent superhydrophobic surfaces of the mosquito eye and cicada wing; (e) anisotropic surfaces of the rice leaf and filefish skin; (f) asymmetric surfaces with dynamic wettability. Reprint with permission from ref. [10] and all included references. Copyright 2017 Nature Publishing Group.

Interestingly, every single example displays multiscale structures and a certain surface roughness. These and many other examples from biomimetic research revealed that the combination of multiscale roughness and the intrinsic wetting properties of the material are responsible for the extreme wetting properties and the resulting multifunctionality. From these findings, three major principles can be deduced. First, two-tier roughness on both micro and nano levels have a key role in determining superwetting or anti-wetting properties of a solid material. Second, the arrangement and orientation of the multiscale structures can control the dynamics of the wetting state and motion of the droplet. Lastly, the intrinsic wetting threshold (IWT) determines whether a roughness-enhanced surface will result in either a superwetting or anti-wetting surface. In other words, when multiscale roughness is introduced into an intrinsic hydrophobic/oleophobic material, a superhydrophobic/superolephobic surface is obtained. When multiscale roughness is introduced to an intrinsic hydrophilic/oleophilic material, a superhydrophilic/superoleophilic surface is obtained. This correlation is highlighted in Figure 12.
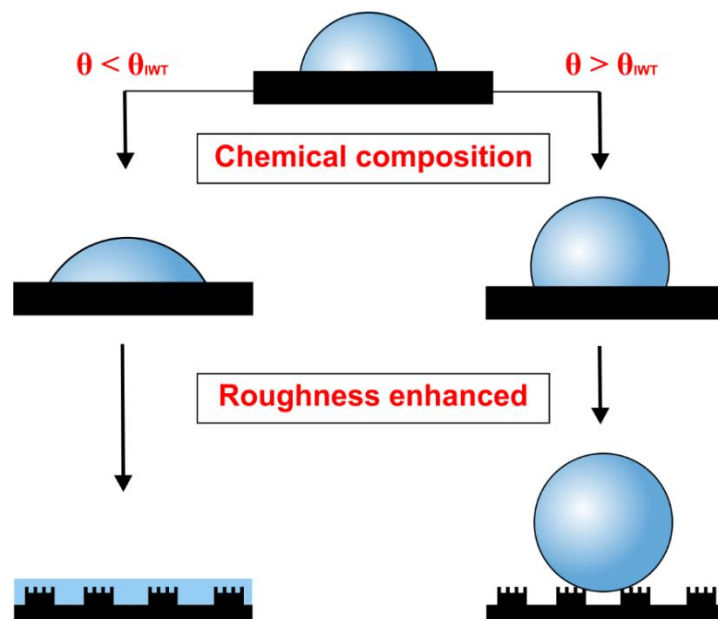
Figure 12. Design principle of surfaces with superwettability. Roughness enhanced the intrinsic wetting properties of a material. The intrinsic wetting threshold (IWT) determines whether a roughness-enhanced surface will result in a superwetting or an anti-wetting surface.

2.2.6 Fabrication of Surfaces with Superwettability

According to the discussed design principles, artificial surfaces with superwettability are fabricated by combining rough surface morphologies and right chemical compositions or functionalization. The introduction of roughness into a solid material can be obtained by physical and chemical methods.

Physical Methods

The physical methods usually describe the direct introduction of roughness into a material by using nanofabrication processes, such as template[63-65] and lithographic methods,[66-68] micromachining,[69] etching, and plasma treatments.[70-71] These physical methods are also referred to as top-down approaches in the literature. Among them, photolithography has turned out to be the most common technology, especially in the academic area for fundamental studies about wettability. In photolithographic approaches, light is irradiated through a photomask (with the desired patterns) onto a substrate with a photoactive polymer layer (photoresist). The desired pattern is obtained after removal of the exposed or unexposed polymer in the developed area and subsequent etching. The importance of photolithography for academic research become obvious in taking an example from Butt.[72] They analyzed the influence of pattern consisting out of pillars generated by photolithography using SU-8 as photoresist on different wetting phenomena (see Figure 13). The wetting properties of the pattern surface were precisely controlled by changing the height, diameter, and the distance between the pillars. This and other examples clearly demonstrate that the importance of precise design of patterned surfaces tremendously contribute to our general understanding of material wetting.
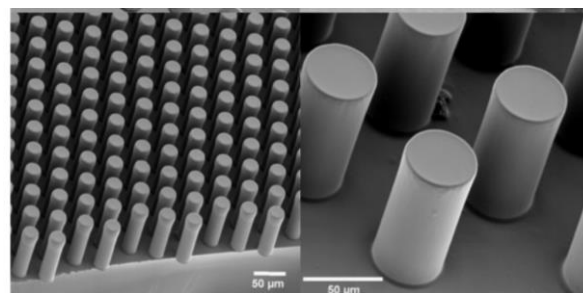
Figure 13. Scanning Electron Microscopy (SEM) image of patterned SU-8 surfaces at different magnification. Reprint with permission from ref. [73]. Copyright 2004 Institute of Physics Publishing.

Chemical Methods

On the other hand, smaller building blocks are used in the bottom-up approaches to construct a more complex nanoscale assembly resulting in a low-energy surface. Contrary to the physical approaches, the chemical fabrication methods (also called bottom-up approaches) usually utilize smaller precursors to build up a more complex structure on a substrate. These smaller components can be molecules, nanoparticles, or single atoms, which have the ability to self-assemble and to self-organize into nanostructures like sheets, rods, fibers, spheres, pillars, or wires to give a material a certain roughness. Bottom-up approaches have been used for the preparation of surfaces with superwettability by many different methods, such as chemical vapor/bath deposition (CVD/CBD),[74-76] layer-by-layer assembly,[77-78] colloidal assembly,[79-80] sol–gel methods,[24, 81] or chemical synthesis.[82-83] In general, these bottom-up methods have several advantages: they are usually very cheap, easy to perform, do not require any large and expensive manufacturing machines, and various functional units can be integrated into the structure, which leads to a variety of functional surfaces.

Chemical Post-Functionalization

In general, two main approaches have been developed to generate surfaces with superwettability. One approach is to directly increase the above-described surface roughness of hydrophobic/hydrophilic materials to obtain superhydrophobic/superhydrophilic surfaces, respectively. In the second approach, first a certain surface roughness is created, which is then further chemically modified to decrease or increase the surface free energy. The most common way to post-modify a surface is to deposit a monolayer coating by using self-assembled monolayers (SAMs) or chemical functionalization that can anchor or react with the surface.[84-85] Typical anchor groups are thiols for gold, silanes for silicon oxide, phosphates for metals, and activated carboxylic acids for amine rich surfaces. Depending on the monolayer's tail, coating the wetting properties can be tuned. For a superhydrophobic surface, long hydrophobic alkyl or fluorinated side chains are necessary to lower the surface energy. To achieve superamphiphobicity fluorination of the surface is necessary. In the case of superhydrophilic surfaces, more hydrophilic side chains such as zwitterionic polymers or other charged polymers should be used.

2.2.7   Application of Surfaces with Superwettability

In addition to the continuous development of novel fabrication protocols, the applications of surfaces with special wettability have come into the focus of academic and industrial research. There are a great many applications now available ranging from the classic areas, e.g., anti-corrosion, self-cleaning or anti-icing surfaces, to emerging applications, such as printing, oil-water separation, and control of bioadhesion. These and more examples of applications for surfaces are exemplified in Figure 14.[15, 86] In the following, some applications of particular interest are discussed in more detail.
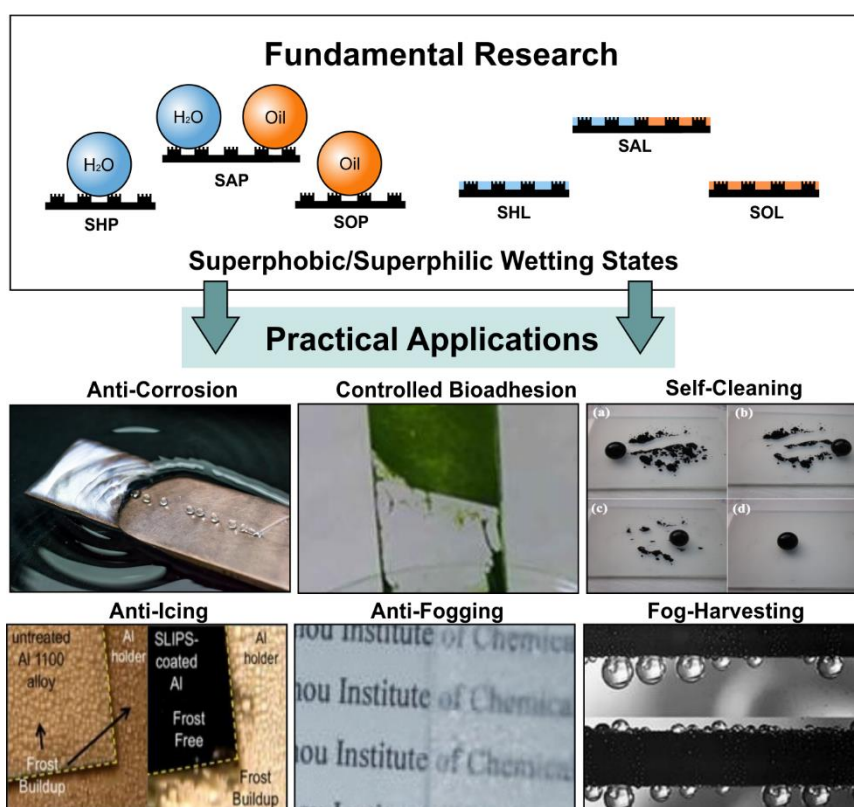
Figure 14. Examples for different extreme wetting states resulting in various applications such as fog-harvesting, self-cleaning, anti-corrosion, controlled bioadhesion, anti-icing, and anti-fogging. Modified reprint with permission from ref. [87-92]. Copyright 2016 American Association for the Advancement of Science, 2016 Nature Publishing Group, 2013 Elsevier, 2017 Applied Physics Letters Publishing, 2012 American Chemical Society, and 2007 Institute of Physics Publishing

Self-Cleaning

The probably most famous applications of superwettability application are self-cleaning surfaces. Their advantage is obvious: if active cleaning becomes unnecessary, large amounts of energy, water and detergents can be saved. Therefore, self-cleaning surfaces not only increase our standard of living but can also contribute towards sustainability and environmental protection. The self-cleaning technology has already emerged in diverse areas ranging from window glass and anti-soiling architectural coatings to solar cell panels.[93] Most of the technically produced self-cleaning materials are based on lotus effect-inspired superhydrophobic surfaces or TiO_2-based superhydrophilic self-cleaning surfaces.[15, 53, 86] Except for several commercial products, however, there has not much widespread distribution of these products because of the inherent drawbacks of superhydrophobic surfaces, such as pressure dependency, susceptibility to mechanical wear, or failure towards oils and surfactant-containing solution. For this reason, novel technologies (e.g., superamphiphobic surfaces or slippery surfaces) have recently become the focus.

Anti-Icing

Passive anti-icing surfaces are areas of great interest because of their significant economic, energy, and safety implications in the prevention of icing. Textured surfaces with superwettability have emerged as a powerful tool to influence water-phase-transition phenomena, such as icing or condensation. For example, a multiscale hierarchical superhydrophobic surface can stay ice-free down to a temperature of -30 °C because of the entrapped air that acts as a lubricating, thermal protection barrier between the solid and the liquid.[94] Recently, slippery surfaces have received a great deal of attention, because they are considered an alternative anti-icing strategy that overcomes the inherent drawbacks of superhydrophobic systems.[55, 88] However, which superwettability approach works best is still under debate.[95-97] Therefore, it is important to understand the nature of ice repellency in all environments to identify the limitations of current solutions and to design new materials with robust anti-icing properties.

Fog-Harvesting

Another interesting example is the water collection mechanism of the Namib Desert beetle.[98] Based on a special structure on their back, which consists of an array of hydrophilic bumps distributed on a superhydrophobic background, they are capable of harvesting fog. Tiny water

droplets can accumulate at the hydrophilic area of the structure and coalesce. When the droplet reaches a certain size, gravity of the droplet will overcome the binding forces of the hydrophilic region. Consequently, the droplet detaches and rolls down the superhydrophobic surface to the beetle's mouth. In addition to this amazing water collection method, surfaces with superhydrophobic and superhydrophilic patterns have further applications in microfluidic channels and biological assays.[99]

Oil-Water Separation

To address the environmental problem of oil pollution by industrial discharge or accidents during offshore oil production, the oil-water separation has received a great deal of interest in the last decade. Interfacial materials with superwettability have proven to be highly efficient for oil-water separation purposes.[100-105] Porous materials in combination with superhydrophobicity and superoleophilicity can selectively filter or absorb oil from oil–water. On the other hand, material that combines superhydrophilicity and underwater superoleophobicity can selectively separate water from oil–water mixtures.[106]

Controlled Bioadhesion

Selective cell or protein adhesion has become one of the most important aspects in the design of biomaterials for in vivo applications. In the last decade, various systems with superwettability have been used in the control of bioadhesion. In the area of antifouling coatings, a common strategy is to use superhydrophilic, polymer coatings to prevent non-specific protein adsorption or cell adhesion. These extreme hydrophilic coatings highly interact with water, which then acts as a lubricating protection layer that prevents the protein adsorption.[107-111] As an alternative, superamphiphobic surfaces were recently reported to show nearly no protein adsorption for complex biological liquids (e.g., human serum or blood) by taking advantage of the nearly contact-free solid-liquid interface.[32] The geometry of the texture of the superamphiphobic surfaces creates an energy barrier to prevent the liquid from penetrating into the pores. In this case, the entrapped air acts as a lubricating protection layer. Recently, Aizenberg and coworkers also reported fluorinated lubricant-infused slippery surfaces (SLIPS) alternative antifouling coating.[57] In comparison to superamphiphobic coatings, slippery surfaces can withstand high pressures, and can bear strong shear forces and mechanical damage. However, the role of a fluorinated lubricant in contact with human blood or in general inside the human body is still under debate.

2.3 Substrate-Independent Universal Coatings

2.3.1 Universal Polymer Coatings

Modification of common materials properties plays an increasingly important in many aspects of physical, chemical, biomedical and material science. In order to cope with the high demand for functional materials, the area of universal polymer coatings has grown enormously in recent years. Unlike conventional coating strategies, universal coatings are suitable to modify the properties of a broad range of different materials. Ideally, universal coatings are substrate-independent regardless of the chemical and physical properties of the underlying substrate.[112] To develop such universal coatings, the design of the anchoring interaction of the polymer and the substrates is crucial. Specific covalent binding between the polymer and the substrate (as for example in self-assembled monolayers) must be avoided in order to achieve substrate-independency. In the past various approaches based on chemical, physical and bio-inspired processes have been developed. Irradiative chemisorption by irradiation with high energy in combination in combination with subsequent polymerization, is one example for a universal coating technology for organic materials.[113-114] Various radiation methods, including plasma, UV light, lasers, and electronic beams, have been used to activate the corresponding materials surface.[115-117] The chemical functionality of the resulting surface can be tuned by the choice of the monomer during the polymerization. On the other hand, physisorption by multiple noncovalent interactions, such as electrostatic attraction, hydrophobic interaction, van der Waals forces, and hydrogen bonding, is another well-established strategy for universal coatings. These noncovalent interactions are relatively weak in comparison to covalently attached polymers. Therefore additional intra-layer interactions, such as physical or chemical crosslinking can be used to enhance the stability of the coating. Based on these universal interactions, some technologies, including layer-by-layer (LbL) assembly, spin coating, and CVD, have been developed to obtain universal coatings.[118-121] Within the last decade, bio-inspired coatings have emerged as an extremely efficient fabrication method for completely substrate-independent, universal coatings. Such bio-inspired coatings various processes in nature, such as the adhesion of blood proteins,[122-123] mussel foot proteins,[124] or polyphenols in plants.[125] Among them, the mussel-inspired coatings are the most widely used universal coating approach and will be discussed and discussed in detail.

2.3.2 Mussel-Inspired Chemistry for Surface Modification

Marine mussels adhere rapidly under extremely harsh environmental conditions onto solid surfaces in the sea.[126-127] The reason for these unique, outstanding adhesion properties is a complex protein mixture containing 25-30 different mussel foot proteins (mfp). These complex protein cocktail is expressed and excreted by the mussel to form the so-called adhesive byssus.[4] White and coworkers were the first ones to systemically analyze the mussel byssus and describe the underlying biochemistry.[4] They described 3,4-dihydroxyphenyl-l-alanine (DOPA) and its key role in the bonding mechanism, because 3,4-DOPA contributes to cohesion, builds crosslinks between adhesive proteins, and is responsible for the adhesion to the substrate.[128] The byssus is a bundle of mussel threads that are tipped with mussel plaque. Although both parts are necessary for the mussel rapid adhesion, the plaque shows the most adhesive proteins and plays the key role in the bonding mechanism. Inside the plaque, the mfp 3 and mfp 5 are considered the most adhesive proteins located in the byssal-substrate interface (see Figure 15).[129] Exactly these two proteins show a conspicuously high amount of catechol (in the form of DOPA) and amine groups that further proves the importance of these functionalities for the adhesion process.
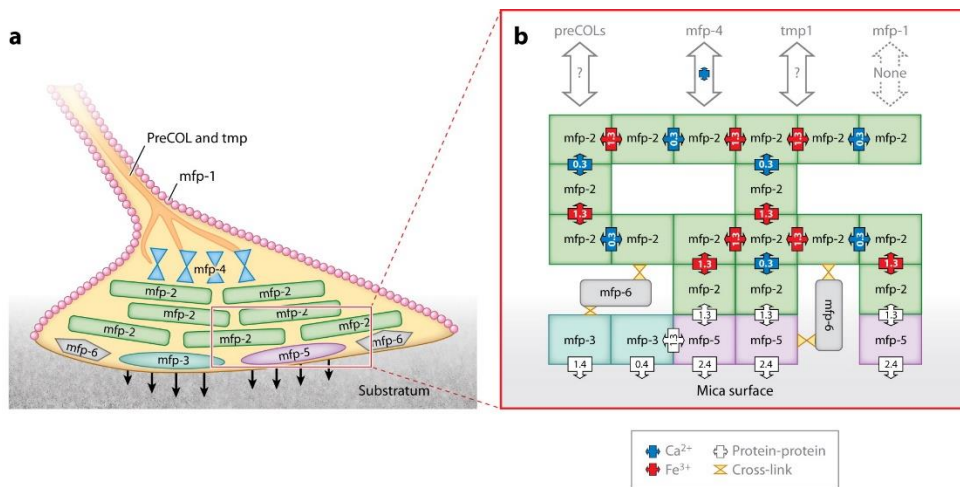
Figure 15. (a) Schematic illustration of mussel foot proteins (mfps) in a byssal plaque showing the approximate location of the major proteins. (b) Schematic view of all known mfp interactions as determined by atomic force microscopy (AFM). Reprint from with permission ref. [4]. Copyright 2011 Copyright Clearance Center.

2.3.3 Polydopamine

Inspired by these two functional groups, Messersmith et al. reported PDA as the ideal strategy for substrate-independent coatings.[124] In general, PDA is formed by pH-induced, oxidative polymerization of dopamine in alkaline solutions. The simple immersion of a substrate into an aqueous solution of dopamine buffered to alkaline pH results in a spontaneous deposition of a thin PDA film. Although the preparation is relatively simple, the molecular mechanism of the coating formation has not been completely understood yet. It is widely agreed that the first steps include the oxidation of dopamine to the dopamine-quinone (Figure 16), the intramolecular cyclization to the dopamine chrome, and formation of 5,6-dihydroxyindole (DHI) and 5,6-indolequinone (IDQ).[130-132] The IDQ molecules then undergo further crosslinking reactions with each other to oligomers, which then aggregate via a combination of hydrogen bonds and π-stacking interactions to form a stable coating (see Figure 16).
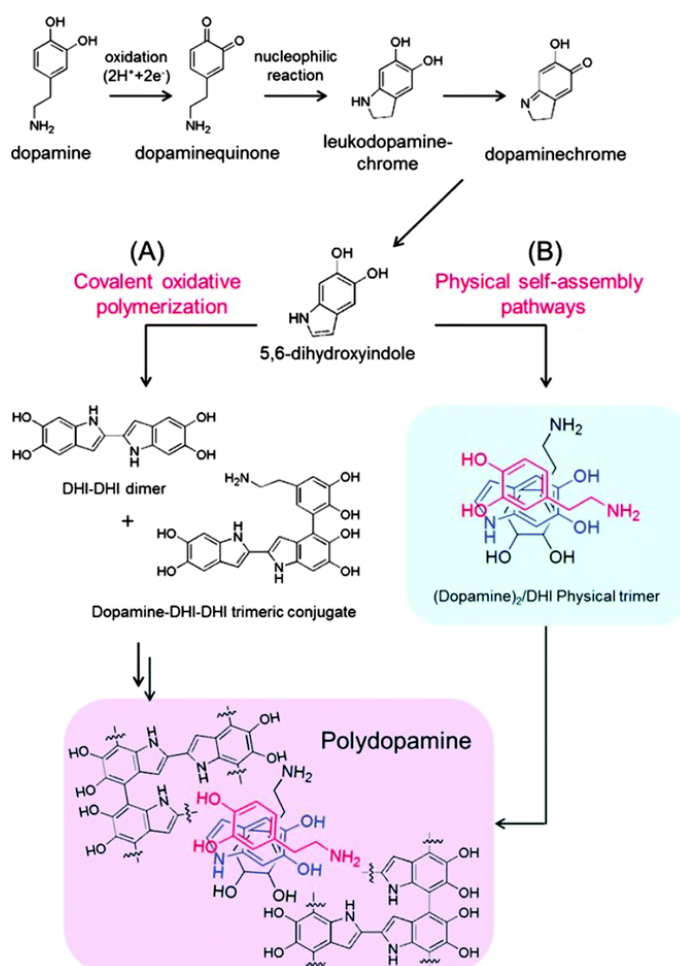
Figure 16. Polydopamine synthesis occurring via two pathways. Reprinted with permission from Ref. [133]. Copyright 2017 Royal Chemical Society.

Various interactions of the catechol moiety, including hydrogen bonding, metal–catechol coordination, electrostatic interaction, cation–π interaction, and π–π aromatic interactions, are responsible for the strong adhesion to different substrates (Figure 17).[129, 134] Strong non-covalent interactions (hydrogen bonds or π–π stacking interactions) can be found between catechol groups and inorganic substrates such as glass or mica.[135-136] In the case of metal oxides (e.g., TiO$_2$), catechol groups have been assumed to form strong metal–catechol coordination bonds.[137] In the case of more hydrophobic substrates or even inert polymer materials, hydrophobic interaction, π-stacking, and van der Waals' forces between catechol and the substrate are believed to contribute to the strong interaction.[138-139] Moreover, the covalent and noncovalent cross-linking of the PDA oligomers extend the monovalent interaction with substrates to polyvalent anchoring, which results in a stable coating.[112]
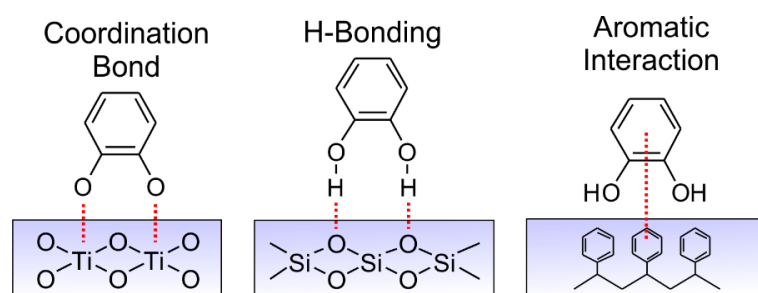
Figure 17. Catechol-mediated adhesion to different substrates such as mica, polystyrene (PS), TiO$_2$ via hydrogen bonding, aromatic interactions, and metal coordination. Modified reprint with permission from Ref. [140]. Copyright 2017 American Chemical Society.

One interesting property of PDA is the possibility for various secondary modifications that can be applied by immobilizing different functional molecules onto polydopamine coatings *via* residual free amine and catechol groups. For this reason, PDA became one of the most popular universal surface coatings and its versatility has been demonstrated in many examples in literature (Figure 18).[141-142] In several reports, PDA coatings were functionalized with hydrophilic, bioinert top layers to form antifouling coatings in a substrate-independent approach.[143-144] Biospecific molecules, such as vascular endothelial growth factor, adhesion peptides, and glycosaminoglycan, have been immobilized onto PDA coatings to obtain coatings with specific cell adhesion.[145-146] By using the reducing effect of the catechol groups, in-situ deposition of nanoparticle (e.g. silver) coatings with excellent antibacterial properties were obtained.[147-148] In other examples, PDA was combined with nano particles, templates or meshes to construct rough surfaces with superhydrophobic properties.[149-150] Since the first report of polydopamine in 2007, researchers have developed various PDA coating strategies

using UV light, microwave or oxidant accelerated coatings, spray-coating approaches, or organic solvent based coatings.[151-155] Among the various strategies, the most widely used approach is called one-pot PDA functionalization. In this method, the target molecule (with a certain function) is immobilized on the substrate by co-dissolving it in the coating mixture.[156]
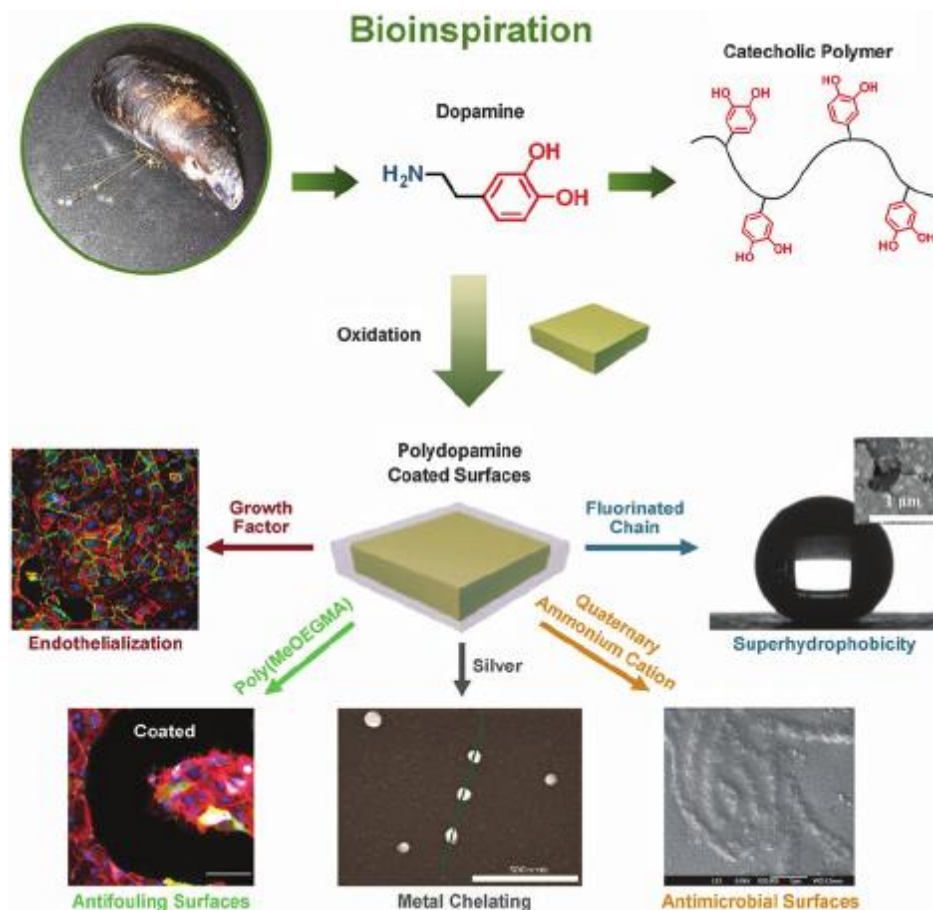
Figure 18. Mussel-inspired polydopamine (PDA) as universal multifunctional coatings for various applications by simple post-functionalization. Reprint with permission from Ref. [112] and all included references. Copyright 2015 Royal Chemical Society.

2.3.4 Polymeric Mussel-Inspired Adhesives

While in nature the adhesion and solidification of a mussel byssus only requires 3-10 min, the approximate coating time for a 50 nm thick PDA film requires more than 20 hours.[124, 157] Several researchers addressed this problem and reported various methods to accelerate the speed of PDA-based coatings. However, the most obvious reason lies in the difference of the precursor for the coating. The responsible protein for the adhesion, the mfp-5, is a high molecular weight biopolymer with multiple catechol and amine groups. Dopamine effectively mimics the chemical functionality, but neither the molecular weight nor the molecular structure is taken into account. For this reason, the direct attachment of catechol derivatives to polymer architectures has turned out to be a good strategy to overcome these inherent drawbacks of PDA (Figure 19).[109, 158-161] Catechol functionalities can be incorporated into macromolecules as main, side, and end-chain groups by employing various synthetic pathways. In these macromolecular architectures, the catechol normally serves as an anchor and crosslinking group at the same time. The amount of catechol inside such a polymer is crucial for the adhesion to the substrate and has to be adjusted depending on the substrate.[162] Because the adhesion to metal oxide surfaces (e.g., TiO_2) of the catechol is the strongest, only one catechol unit per molecule might be enough for the adhesion to the substrate. However, due to oxidative detachment, multiple catechol units are required to anchor the surface. In the case of inert substrates, such as Teflon, an even higher amount of catechol groups is necessary or hydrophobic moieties are required to form a stable coating.
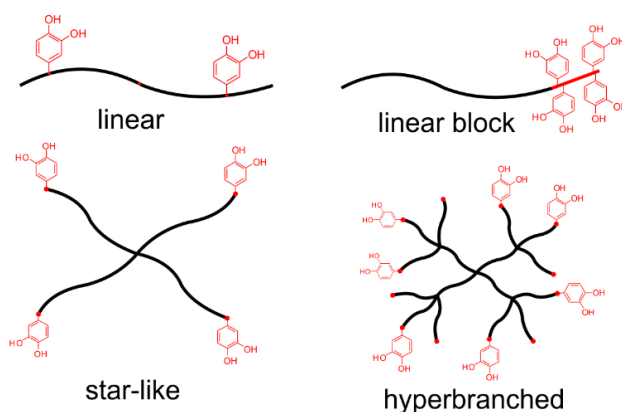
Figure 19. Schematic illustration of different mussel-inspired polymer architectures, such as linear, linear block, star-like or hyperbranched polymers. Modified reprint with permission from Ref. [140]. Copyright 2017 American Chemical Society.

2.3.5 Mussel-Inspired Polyglycerol

Haag and Wei recently introduced mussel-inspired dendritic polyglycerol (MI-dPG) that not only mimics the functional groups of mfp-5 but also their molecular weight and molecular structure (Figure 20).[163] MI-dPG is a dendritic polyglycerol scaffold functionalized with 60% amine and 40% catechol moieties. Similar to the natural protein, the combination of both the catechol and amine functionalities is responsible for the strong adhesion to the substrate. Buffered to alkaline pH, the MI-dPG can undergo covalent crosslinking and form a stable coating on the various substrates. Amines can couple with catechols under oxidizing conditions via Michael addition or Schiff base reactions to enhance the crosslinking of the coatings.[164] As a result, the MI-dPG can form stable multilayer coatings on nearly every kind of material.
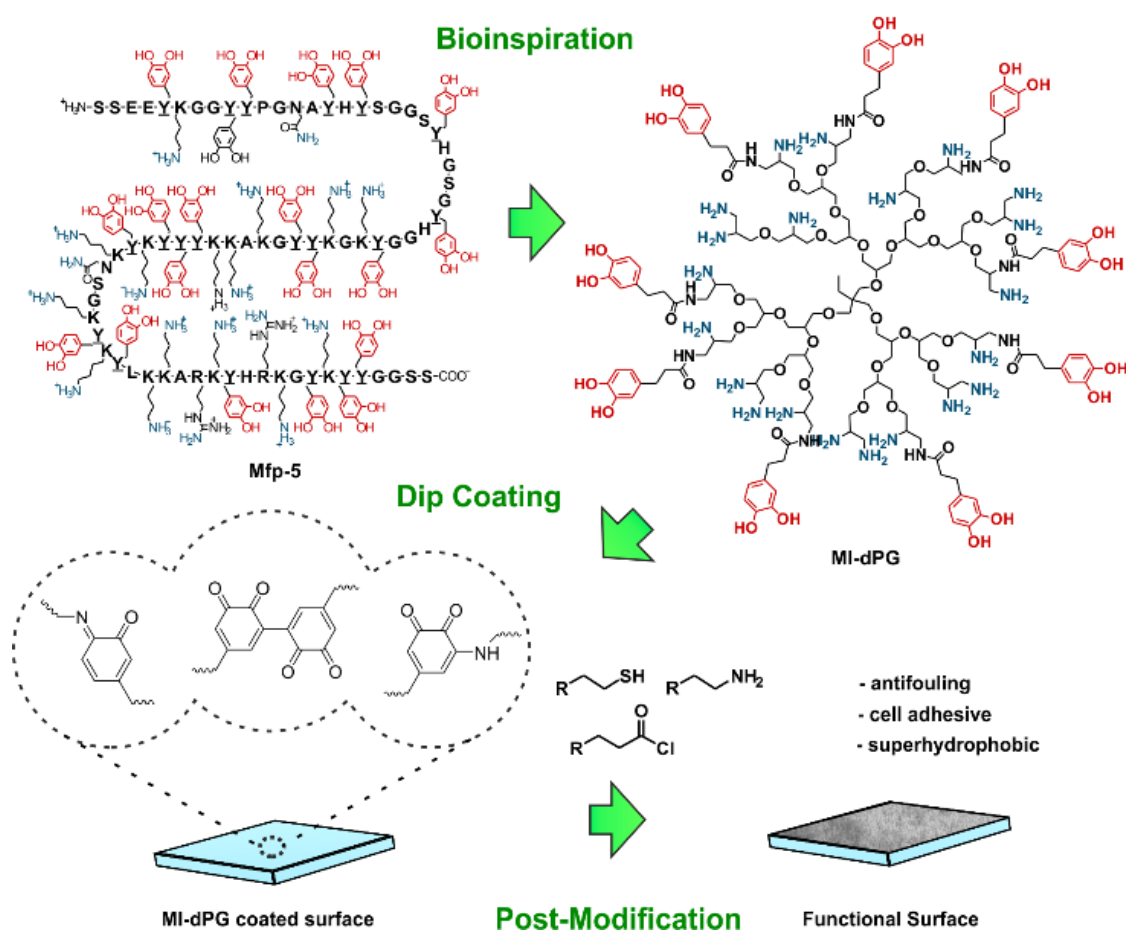
Figure 20. Top left: structural formula of the mussel-foot proteins mfp-5 shows the peptide sequence that contains amine (blue) and catechol (red) units in their side chains. Top right: the chemical structure of mussel-inspired dendritic polyglycerol (MI-dPG). Bottom: the covalent crosslinks of the universal surface coatings. Reprint with permission from Ref. [140]. Copyright 2017 American Chemical Society.

The MI-dPG coatings are still chemically active surfaces due to numerous catechol and amine groups on top. Different amines, thiols, or carboxylic acids can be immobilized on the surface to generate a variety of functional surfaces. By post-functionalization of the MI-dPG adhesive layer with hydrophilic polymers (e.g., dendritic polyglycerol with a small amount of catechol groups), a perfect antifouling surface can be achieved. This coating can totally prevent protein and cell adhesion. Another important property of the MId-PG is the influence on the physical properties (e.g., surface roughness and morphology) of the coating. It was shown that the MI-dPG could form a coating with micrometer-scaled roughness within several hours. The change in surface roughness highly affected the wetting properties of the coating and a superhydrophilic surface was obtained. Subsequent perfluorination of the coating resulted in a superhydrophobic surface with a water contact angle higher than 150° (Figure 21).
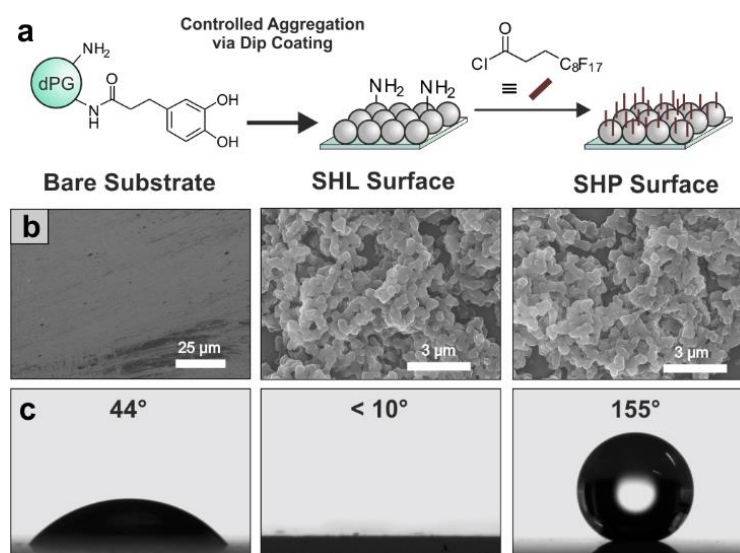
Figure 21. (a) Synthetic coating concept of the superhydrophilic (SHL) and superhydrophobic (SHP) MIdPG. (b) The surface morphology of the bare glass and the superhydrophilic and superhydrophobic coatings on glass. (c) The related static water contact angle of the bare substrate, SHL, and SHP MI-dPG. Modified reprint with permission from Ref. [140]. Copyright 2017 American Chemical Society.

2.3.6 Substrate-Independent Superwettability

As discussed in Chapter 1.2, there are several ways to fabricate surfaces with special wetting properties. To address the problem of substrate specificity of most coatings with superwettability, several groups focused on the development of novel substrate-independent methods to construct superwetting surfaces on any kind of substrate by PDA-based approaches during. In recent years, several attempts were utilized with PDA to prepare superhydrophobic surfaces. For example, Hong reported a perfluorinated dopamine derivative that formed a structurally rough film of various materials upon oxidative polymerization.[165] The resulting superhydrophobic coatings showed water contact angles higher than 150° and low sliding off angles. In other examples PDA was combined with various particles, templates, or meshes to obtain superhydrophobic surface coatings.[149-150] Furthermore, several groups reported mussel-inspired chemistry as a versatile strategy to tailor the wettability of membranes and/or sponges to obtain effective oil-water separation materials.[102, 166-167] In a recent example from Li and coworkers, it was even possible to construct a microscale porous superamphiphobic coating by combining PDA silica NPs with ice templation and chemical vapor deposition.[168] However, all these examples show that PDA-based coatings cannot directly be used to produce sufficient roughness that is necessary for superwettability systems. Reasons for this are the narrow aggregate size and limited coating thickness of PDA-based coatings. In all these reported examples, the lack of roughness control was overcome by the combination of PDA with various particles and meshes.

3 Scientific Goals

3.1 Mussel-Inspired Polyglycerol as Platform for Superwettability

From the theoretical part of this work, two main points appeared. First, fabrication of a surface with special wetting properties has been the subject of extensive study over last the few decades. Nevertheless, the preparation processes mainly involve a complex fabrication protocol, specialized equipment, and/or are limited to certain substrates. Facile approaches for fabricating substrate-independent coatings with special wettability are limited. Second, mussel-inspired polyglycerol (MI-dPG) has emerged as a highly efficient way to produce a variety of functional surfaces on nearly every kind of substrate. Furthermore, physical properties such as surface roughness and morphology could be influenced during the coating.

Therefore, the main objective of this work is to combine the unique mussel-inspired adhesion properties of catechol-functionalized polyglycerols with highly hierarchical lotus-like structures to develop a universal fabrication method for various systems with special wettability on any kind of material (Figure 22). In order to achieve this, the MI-dPG coating process will be analysed in detail to gain a complete understanding of its coating mechanism. The effect of the various coating parameters, such as pH-value, concentration, and coating time or coating depth will be studied. By accurately adjusting the coating parameter, control is achievable over the surface roughness. The final goal is to build up a highly hierarchical structure on every kind of material that can serve as a universal platform for various superwettability systems. Subsequent post-modification of these highly hierarchical structures with hydrophobic molecules yields a surface with super-repellent properties. Through the specific choice of the side chain of the hydrophobic molecule, various super-repellent wetting states will be obtainable. By fluorination of the hierarchical structures superamphiphobic surfaces that repel both water and oil shall be obtained. These superamphiphobic surfaces will be also analyzed regarding their repellency towards biofluids and their antifouling properties. As an alternative to fluorinated surfaces, the post-modification with fatty acids shall yield a superhydrophobic/superoleophilic coating. Based on the superhydrophobic/superoleophilic properties the potential for the oil/water separation will be studied. Furthermore, such a highly hierarchical alkylated surface can be infiltrated by a non-fluorinated lubricant (e.g., oils) that will yield a completely fluorine-free slippery surface.
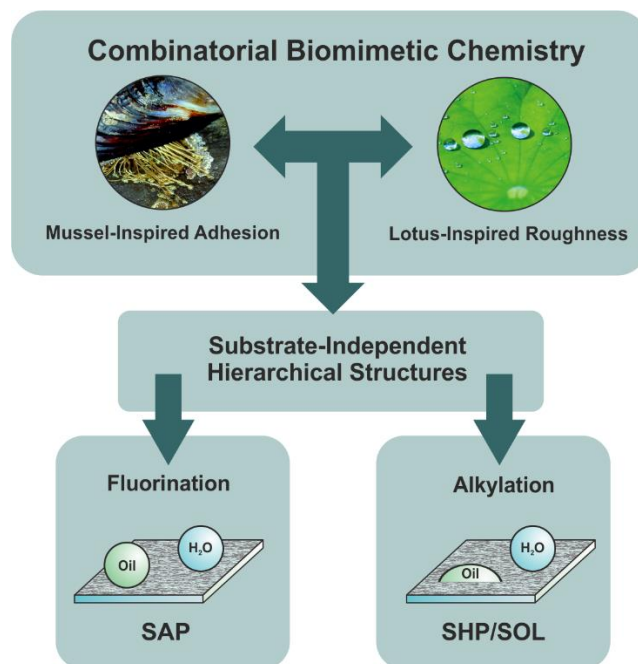
Figure 22. Combinatorial Biomimetic approach for the design of highly hierarchical surfaces on any kind of material by combining mussel-inspired adhesion with lotus-inspired roughness.

Another project of this work focuses on the simplifying the MI-dPG coating process in order to get one step closer to an industrial application. The major drawback of a mussel-inspired adhesive, is the requirement for dip-coating. To address this problem, the MI-dPG will be applied as a universal spray coating using a simple gas driven spray coater. The spray coating shall be analyzed regarding stability, roughness, wetting properties, and post-modification possibilities.

3.2   Hydrogel Bead Preparation on Super-Repellent Surfaces

In another part of this work, new fabrication methods of micro gels based on the super-repellent properties of superamphiphobic and slippery surfaces will be established. It is expected that a droplet of a hydrogel precursor solution will be repelled by the superamphiphobic surface. The droplet will be forced in a spherical shape on the superamphiphobic and a hemispherical shape on the slippery surface that is probably remained during the gelation. By depositing small micro droplets of various gel precursor solutions, micro gel beads will be easily accessible. Furthermore, the cell encapsulation with this newly proposed method will be tested.

3.3 Supramolecular Polymers as Surface Coatings

In the last part of this work aims to utilize the properties of low-molecular-weight gelators (LMWGs) to self-assemble into fibrous network of supramolecular polymers with superhydrophobic properties (Figure 23). Fluorinated LMWGs meet all the requirements for application as a superhydrophobic surface coating. In particularly, their versatility to form complex and nanostructures will be utilized to form hierarchical structures with low surface energy. Because LMWGs have never been applied in such a supramolecular polymerization process on a surface, the first step shall be the quantitation of the process and a systematic study about the coating parameters. Furthermore, the fibrous network made by gelators will be used as a skeleton to entrap a fluorinated lubricant to enhance the liquid repellency. Since supramolecular polymers are dynamic systems and well known for their self-healing ability, both super-repellent surfaces shall be studied regarding their self-healing properties.
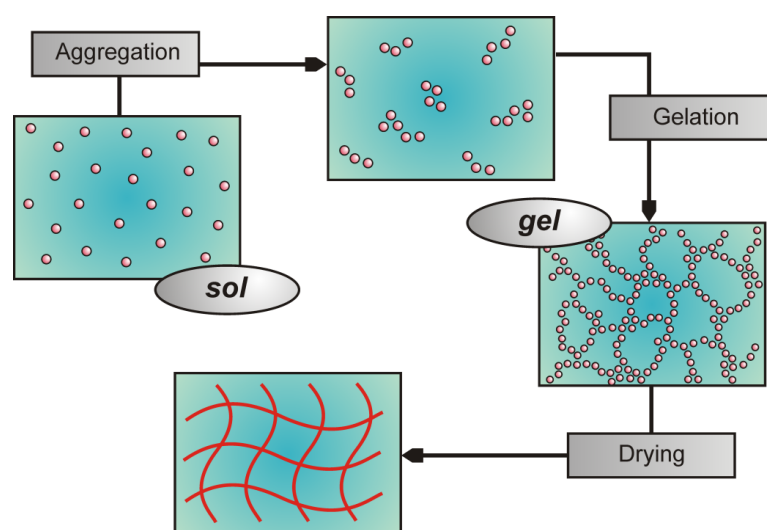
Figure 23. Schematic illustrations of the supramolecular polymerization process leading to gelation and network formation.

4 Publications

4.1 Surface-Independent Hierarchical Coatings with Superamphiphobic Properties
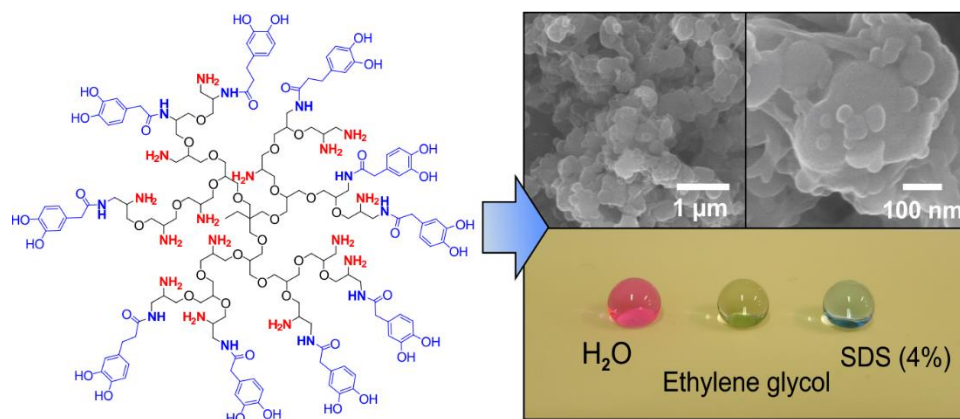
Figure 24. Graphical abstract. Modified reprint with permission from ref. [169]. Copyright 2016 American Chemical Society.

Christoph Schlaich, Luis Cuellar Camacho, Leixiao Yu, Katharina Achazi, Qiang Wei*, and Rainer Haag*

Author Contribution

Christoph Schlaich designed the project, performed the main experiment, and wrote the paper. Luis Cuellar Camacho performed AFM measurements. Leixiao Yu supported the synthesis. Katharina Achazi supported the biological experiments. Qiang Wei and Rainer Haag supervised the project, provided scientific guidelines and suggestions, and corrected the manuscript.

4.2 Fluorine-Free Super-Wetting Systems: Construction of Environmentally Friendly Superhydrophilic, Superhydrophobic, and Slippery Surfaces on Various Substrates

Figure 25. Graphical abstract. Reprint with permission from ref. [170]. Copyright 2016 Royal Chemical Society.

Christoph Schlaich, Leixiao Yu, Luis Cuellar Camacho, Qiang Wei*, and Rainer Haag*

Author Contribution

Christoph Schlaich designed the project, performed the main experiment, and wrote the paper. Leixiao Yu supported the synthesis. Luis Cuellar Camacho performed AFM measurements. Qiang Wei and Rainer Haag supervised the project, provided scientific guidelines and suggestions, and corrected the manuscript.

4.3 Mussel-Inspired Polymer-based Universal Spray Coating for Fast Surface Modification
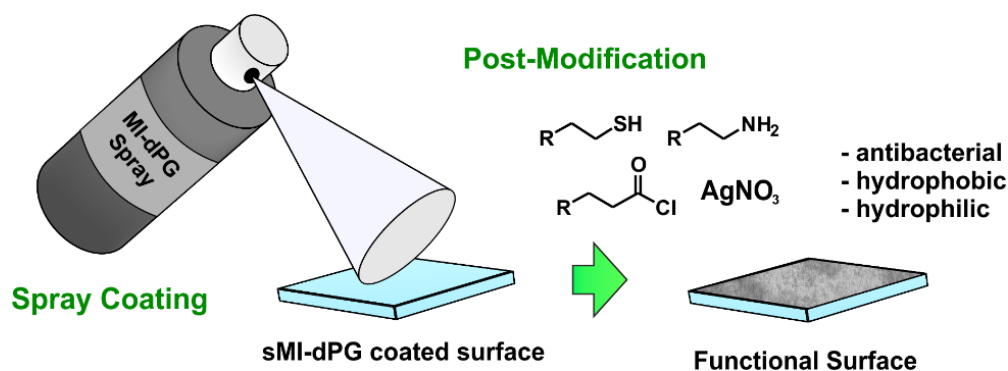
Figure 26. Graphical abstract. Universal MI-dPG spray coating (sMI-dPG) and post-modification strategies.

Christoph Schlaich, Mingjun Li, Chong Cheng, Ievgen S. Donskyi, Leixiao Yu, Geonho Song, Ernesto Osorio, Qiang Wei,[*] and Rainer Haag[*]

Author Contribution

Christoph Schlaich designed the project, performed the main experiment, and wrote the paper. Mingjun Li performed the antibacterial tests. Chong Cheng performed AFM measurements. Ievgen S. Donskyi performed the XPS measurements. Leixiao Yu, Ernesto Osorio, and Geonho Song supported the synthesis. Qiang Wei and Rainer Haag supervised the project, provided scientific guidelines and suggestions, and corrected the manuscript.

4.4 Surfactant-Free Preparation of Hydrogel Beads on Superamphiphobic and Slippery Surfaces
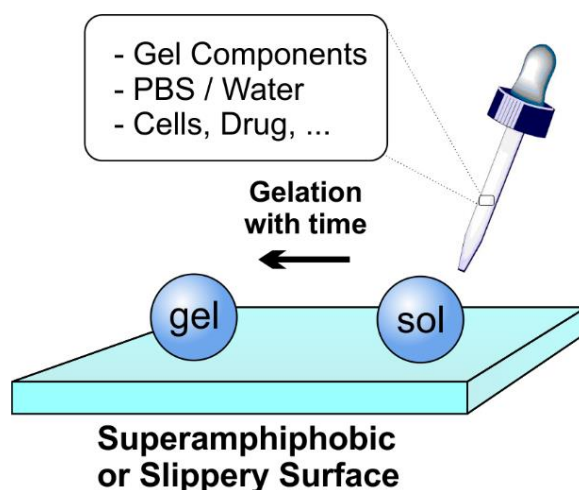
Figure 27. Graphical abstract. Gel bead preparation on top of superamphiphobic and slippery surfaces.

Christoph Schlaich, Yue Fan, Pradip Dey, Qiang Wei,* Rainer Haag,* and Xu Deng*

Author Contribution

Christoph Schlaich designed the project, performed the main experiments, and wrote the manuscript. Yue Fan supported the preparation of the coatings. Pradip Dey synthesized the dPG-based hydrogels. Qiang Wei, Rainer Haag, and Xu Deng supervised the project, provided scientific guidelines and suggestions, and corrected the manuscript.

4.5 Supramolecular Polymers as Surface Coatings: Rapid Fabrication of Healable Superhydrophobic and Slippery Surfaces

Figure 28. Graphical abstract. Modified reprint with permission from ref. [171]. Copyright 2016 Royal Chemical Society.

Qiang Wei[#], **Christoph Schlaich[#]**, Sylvain Prévost, Andrea Schulz, Christoph Böttcher, Michael Gradzielski, Zhenhui Qi*, Rainer Haag*, Christoph A. Schalley*

[#]These authors contributed equally to this work.

Author Contribution

Christoph Schlaich contributed to the design of the project, performed all the synthesis, and prepared and characterized the superhydrophobic surface. Qiang Wei contributed to the design of the projects, prepared and characterized the slippery surface. Sylvain Prévost and Michael Gradzielski performed the SANS measurements. Andrea Schulz and Christoph Böttcher performed the SEM measurements. Zhenhui Qi provided scientific guidelines and wrote the manuscript. Rainer Haag, Christoph A. Schalley supervised the project, provided scientific guidelines and suggestions, and corrected the manuscript.

5   Summary and Conclusion

This work deals with the developments of novel bio-inspired surface coatings with extreme wetting properties such as superhydrophobicity, superamphiphobicity, or superhydrophilicity. Surfaces with such extreme wetting properties exhibit a variety of interesting properties that makes them promising candidates for functional coatings, such as self-cleaning, antireflective, non-sticking or icing-resistant coatings. A technical implementation of surfaces with such properties into our daily life, would not only mean an increase in our standard of living, but also contribute to the sustainability and environmental protection. In the last decade, there was a tremendous amount of interest for coatings with extreme wetting properties. Although, numerous examples for different preparation methods, a wide distribution of such coatings in our society has not yet been found. Reason for this is that most coatings are limited to a certain substrates, show relatively poor durability, and involve a complex multistep fabrication protocol. In contrast, mussels in nature developed an outstanding adhesion mechanism that could solve all the above-mentioned problems. Thanks to extremely adhesive proteins mussel can adhere to nearly every kind of surface under extremely harsh conditions. The aim of this work was to mimic mussel adhesion with the purpose to use it for surface coatings with extreme wetting properties. By combining two separate biomimetic concepts, the mussel-inspired adhesion and that of the lotus-like hierarchical structures, a substrate-independent method for the preparation of stable coatings with extreme wetting properties on any kind of surface was developed. To achieve this goal, a catechol- and amine-functionalized dendritic polyglycerol (MI-dPG) was used that effectively mimics the most adhesive proteins of the mussel with regard to its chemical functionality, structure and molecular weight. By dipping any object into an alkaline-buffered solution of MI-dPG, a polymeric film can be coated on any substrate, regardless of the material.

In the first part of this thesis, mussel-inspired dendritic polyglycerol (MI-dPG) was successfully applied as a universal hierarchical coating for various surfaces with superwettability. To achieve this goal, the first project (see Section 4.1) focused on the quantification of the MI-dPG process in order to gain control over the aggregate size and the resulting surface roughness and morphology. Based on this control over surface roughness, a two-layer approach for the fabrication of highly hierarchical structures was introduced. Additionally, the MI-dPG coating was combined with in-situ generated silver or gold nanoparticles to construct hierarchical structures by using the reducing effect of the remaining catechol groups inside the coating. The generated hMI-dPG coatings showed universal

applicability with moderate mechanical robustness on various rigid and flexible solid substrates including plastic, ceramic, metal, and metal oxide materials. Perfluoralkylation of these hMI-dPG coatings resulted in a superamphiphobic coatings with impressive repellency to water, surfactant-containing solutions, and biological liquids, such as human serum. In the second project (see Section 4.2), the problem of non-degradability and bioaccumulation of fluorinated buildings was addressed. Based on alkylation of the hMI-dPG coatings, an entirely fluorine-free approach was investigated for constructing more environmentally friendly coatings with superhydrophobic/superoleophilic properties. The fluorine-free superhydrophobic/superoleophilic coating was applied to commercially available sponges to transfer them into an adsorbent material for the oil-water separation. Furthermore, the alkylated hMI-dPG structures could be infused with sunflower oil, and fluorine-free slippery surfaces were obtained. Both the fluorine-free superhydrophobic/superoleophilic and the slippery surfaces showed similar anti-wetting properties as their fluorinated analog regarding water. In conclusion, the biomimetic concepts of mussel-inspired adhesion and lotus-like hierarchical structures were successfully combined. Therefore, hMI-dPG represents a universal superwettability platform that can be used as a highly efficient strategy to construct coatings with extreme wetting properties on any material.

In the third project area (see Section 4.3) of this thesis, MI-dPG was successfully applied as a universal spray-coating strategy for substrate-independent surface modification using a gas driven spray coater. The MI-dPG spray-coated substrates (sMI-dPG) were further functionalized with various functional nanoparticles via spray coating. Post-modification with an aqueous $AgNO_3$ solution via spray coating resulted in an AgNP-embedded sMI-dPG surface with excellent, long-term antimicrobial properties. Additionally, a universal superhydrophobic spray was developed by combining sMI-dPG with hydrophobic SiO_2 nanoparticles. Finally, the sMI-dPG spray coating approach provided an easy-to-use strategy for multifunctional surface modification for large surfaces, which opens the door for industrial applications of mussel-inspired coatings.

The fourth project (4.4) was focused on developing a novel, simple, surfactant-free method for preparing macrogel beads. This method utilized the super-repellent properties of superamphiphobic and slippery surfaces to force a droplet of a gel precursor solution into a specific shape. A droplet on a superamphiphobic surface and slipper surface showed a spherical and hemispherical shape, respectively. Both shapes were maintained during the gelation process. The final gel particles could be removed easily from the super-repellent layer without

any surfactant. This makes this method simple to use for gel bead preparation and compatible for cell encapsulation. Because of the perfect antifouling properties of superamphiphobic surfaces, living cells and proteins hardly interacted with the coated substrate. Therefore, the cell encapsulation of MC3T3 cells was possible in situ. In conclusion, the results from this project proved the applicability of super-repellent surfaces for microgel preparation and cell encapsulation.

The fifth project focused on application of supramolecular polymers as an easy and efficient method to fabricate superhydrophobic and slippery surfaces. Based on the cooperative and hierarchical polymerization of fluorinated bis-amide LMWGs and their ability to self-assemble and self-organize into a highly entangled fibrous network, the construction of a lotus-like hierarchical structure was possible. The synergistic effect of hydrogen-bonding-mediated polymerization into long fibers and the fluorinated side chains resulted in the construction of a self-cleaning, superhydrophobic surface. Furthermore, it was shown that the fibrous network could be infused by a fluorinated lubricant yielding a slippery surface with enhanced liquid repellency. Both surfaces, the superhydrophobic and the slippery surface, showed self-healing properties, because of the dynamic properties on supramolecular scaffold. In conclusion, it was demonstrated that supramolecular polymers and LMWGs have an excellent potential for a simple and rapid fabrication of functional surfaces.

6 Outlook

This work demonstrated the universal applicability of the MI-dPG to build up highly hierarchical structures on any kind of material and to influence the wetting properties. Therefore, MI-dPGs possess a great potential for various industrial and technological applications. The transfer from a dip to a spray coating of the MI-dPG-coating process was already a large step towards large-scale industrial application of mussel-inspired adhesives. However, unlike in academic research, it is necessary to reduce production costs and use easily or even commercially available starting materials. Therefore, the development of simpler mussel-inspired polymers with similar properties as the MI-dPG is highly desired. Here, commercially available, hyperbranched polyethylene imine (PEI) could be of great interest. PEI could be functionalized with catechol moieties in a one-step synthesis yielding a hyperbranched mussel-inspired polymer with a nearly similar structure as the MI-dPG (Figure 24). Alternatively, PEI could be directly copolymerized with pyrocatechol (1,2-dihydroxybenzene) to achieve a universal coating only by using exclusively commercially available starting materials. Both PEI-based systems would mean a significant decrease in the reduction of the synthetic effort and production costs in comparison to the MI-dPG.
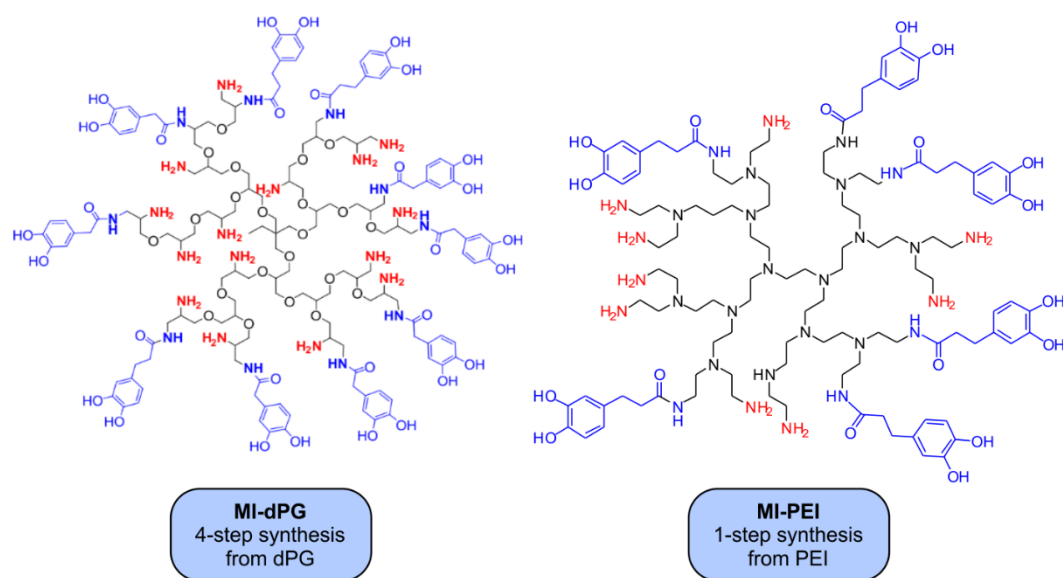
Figure 29. A structure comparison of a four-step MI-dPG synthesis (left) to the one-step, mussel-inspired hyperbranched polyethylene imine synthesis (right). Both are expected to show similar coating properties.

7 Kurzzusammenfassung

In der vorliegenden Arbeit geht es um die Entwicklung von neuen biologisch inspirierten Oberflächenbeschichtungen mit superhydrophoben (wasserabweisend) und superamphiphoben (wasser- und ölabweisend) Eigenschaften. Solche Oberflächen mit extremen Benetzungszustände zeigen äußerst interessante Eigenschaften für verschiedene Anwendungen, wie zum Beispiel selbstreinigende, antireflektierende, nichthaftende, oder vereisungsgeschützte Beschichtungen. Eine technische Implementierung von Oberflächen mit solchen Eigenschaften würde nicht nur eine Steigerung unseres Lebensstandards bedeuten, sondern auch einen Beitrag zur Nachhaltigkeit von Materialien und Umweltschutz leisten. Obwohl in der Literatur zahlreiche Beispiele für die Herstellung solche Oberflächenbeschichtungen zu finden sind, ist eine weite Verbreitung in unserer Gesellschaft noch ausgeblieben. Das liegt vor allem an drei Gründen: Erstens, viele dieser Beschichtungsmethoden sind äußerst komplex und verlangen eine Vielzahl von Synthese- und Arbeitsschritten oder spezielle Ausrüstung. Zweitens, die meisten der bekannten Beschichtungen sind abhängig von zu beschichtenden Substrat und können nicht universell eingesetzt werden. Und der letzte Punkt sind die hohe Anfällig gegenüber Kratzen oder anderen mechanischen Einflüssen, was sich in einer kurzen Haltbarkeit bemerkbar macht. Die Muschel und ihre starke Adhäsion ist ein Beispiel, das sehr elegant die genannten Probleme lösen könnte. Dank extrem adhäsiver Proteine, haften Muscheln nicht nur an alles möglichen Materialien, sondern das auch noch extrem stark und schnell. Das Ziel dieser Arbeit war es das Muscheladhäsion nachzuahmen und es für die Herstellung für Oberflächenbeschichtungen mit extremen Benetzungseigenschaften zu verwenden. Durch die Kombination zweier biomimetischer Konzepte, das der Muscheladhäsion und das der Lotus-artigen hierarchischen Strukturen, wurde ein substratunabhängiges Verfahren entwickelt, das es erlaubt superbenetzbare oder superabstoßende Eigenschaften auf allen möglichen Materialien hervorzurufen. Hierzu wurde Brenzcatechin- und Amin-funktionalisierte dendritisches Polyglycerol (MI-dPG) verwendet, welches das adhäsivste Muschelprotein bezüglich der chemischen Funktionalität, der Struktur und auch des Molekulargewichts nachahmt. Durch Eintauchen in eine basisch gepufferte Lösung aus MI-dPG kann ein Substrat, unabhängig vom Material, mit einem Polymerfilm überzogen werden. Im ersten Projekt der vorliegenden Arbeit konnte durch gezielte Einstellung der Beschichtungsparameter Kontrolle über die entstehende Rauigkeit der Beschichtung gewonnen werden. Mit Hilfe der Rauigkeitskontrolle konnten durch schrittweiser Ablagerung verschieden großer Aggregate oder Nanopartikel (NP) hoch Lotus-ähnlichen hierarchische Strukturen (hMI-dPG) mit superhydrophilen Eigenschaften

hergestellt werden. Dadurch konnten die Benetzungseigenschaften von extrem hydrophoben Materialen (z.B. Teflon) komplett verändert werden. Durch Perfluorierung der hMI-dPG Oberflächen konnten superamphiphobischen Oberflächen mit beeindruckenden Abstoßungseigenschaften gegenüber biologische Flüssigkeiten (z.B. Blut oder Serum) und/oder Ölen gewonnen werden. In dem zweiten Projekt dieser Arbeit, konnten dank der hoch hierarchischen Struktur, durch Alkylierung der hMI-dPG Oberflächen mittels verschiedener Fettsäurechloriden, komplett fluorfreie superhydrophobe Beschichtungen erlangt werden. Im Vergleich zu den fluorierten superhydrophoben Beschichtungen zeigten diese fluorfreie Beschichtungen keinerlei Einschränkungen bezüglich ihrer wasserabstoßenden Eigenschaften. Allerding zeigten die fluorfreien Beschichtung neben den superhydrophoben Eigenschaften eine extreme Oleophilie (Superolephilität). Durch Beschichtung kommerziell erhältlicher Schwämme mit dieser fluorfreien superhydrophoben/superoleophilen Beschichtung konnten Ölabsorber hergestellt werden, die selektiv Öl aufsagen und gleichzeitig Wasser abstoßen. In dem dritten Projekt dieser Arbeit wurde das MI-dPG auf ein Sprühbeschichtungsverfahren übertragen um den Beschichtungsprozess zu vereinfachen (sMI-dPG). Dabei wurde gezeigt das die Eigenschaften der sprühbeschichtenden Oberflächen mit denen aus dem Tauchbeschichtungsverfahren sehr ähnlich sind. Weiterhin wurde durch Zugabe von hydrophoben SiO_2 extrem wasserabweisende Sprühbeschichtungen erlangt. Durch Funktionalisierung (mittels Sprühbeschichtung) der sMI-dPG Beschichtungen mit einer Silbernitratlösung, wurden Silbernanopartikel in-situ auf der Oberfläche reduziert und stabil eingelagert. Diese mit Silbernanopartikeln funktionalisierte sMI-dPG Schicht zeigte perfekte antibakterielle Eigenschaften.

In vierten Projekt dieser Arbeit wurde ein neues, tensidfreies Verfahren zur Herstellung von Makrogelen etabliert. Diese neue Methode basiert auf die extrem hydrophoben Eigenschaften von superamphiphobischen und von mit einem Schmiermittel-imprägnierten rutschigen Oberflächen (Englisch: slippery Liquid-infused surface, SLIPS). Wenn ein Tropfen einer Lösung mit einem geeigneten Gelierungsmittel (z.B. Gelatinelösung) auf eine solche superabweisende Oberfläche platziert wird, wird der Tropfen in eine spezifische Form gezwungen, welche während der Gelierung erhalten bleibt. So kann nach der Gelierung auf der superamphiphobischen Oberfläche eine rundes Makrogel und auf der rutschigen Oberfläche eine halbkugelförmiges Makrogel erhalten werden. Die darauf resultierenden Gelpartikel konnten hafteten nicht auf den abweisenden Oberflächen und konnten leicht von der Oberfläche

durch Neigung abgerollt und gesammelt werden. Basierend auf den bioinerten Eigenschaften (Englisch: antifouling) von superamphiphobischen oder rutschigen Oberflächen, war es möglich die Methode für die Verkapselung von Zellen in die Gelpartikel durchzuführen. Der Nachweis der Machbarkeit wurde über die Einkapselung von MC3T3-Zellen in ein 4-arm PEG-Gel gezeigt auf der superamphiphobischen Oberfläche gezeigt.

Das fünfte Projekt konzentrierte sich auf die Anwendung von supramolekularen Polymeren als eine einfache und effiziente Methode zur Herstellung von superhydrophoben und mit Schmiermittel-imprägnierten rutschigen Oberflächen. Basierend auf der kooperativen supramolekularen Polymerisation von fluorierten niedermolekularen Gelatoren (Englisch: low-molecular weight gelators, LMWGs), und ihrer Fähigkeit zur Selbstorganisation zu einem stark verstrickten Fasernetzwerk, war der Aufbau einer Lotus-ähnlichen hierarchischen Struktur möglich. Der synergistische Effekt der des faterartigen Netzwerk mit hoher Rauigkeit und der fluorierten Seitenketten resultierende in einer selbstreinigenden, superhydrophoben Oberfläche. Weiterhin, wurde gezeigt, dass das faserige Netzwerk mit einem fluorierten Schmiermittel (FC-70) imprägniert werden kann, und eine rutschige Oberfläche mit erhalten wird. Beide Oberflächen zeigten selbstheilende Eigenschaften aufgrund der dynamischen Eigenschaften des supramolekularen Polymergerüsts. Diese supramolekularen Polymere haben ein großes Potential für die Herstellung von dynamischen, funktionellen Oberflächen.

8 References

[1]   W. Barthlott, C. Neinhuis, *Planta* **1997,** *202*, 1-8. Purity of the Sacred Lotus, or Escape from Contamination in Biological Surfaces.

[2]   C. Hao, Y. Liu, X. Chen, J. Li, M. Zhang, Y. Zhao, Z. Wang, *Small* **2016,** *12*, 1825-1839. Bioinspired Interfacial Materials with Enhanced Drop Mobility: From Fundamentals to Multifunctional Applications.

[3]   L. Wen, Y. Tian, L. Jiang, *Angew. Chem., Int. Ed.* **2015,** *54*, 3387-3399. Bioinspired Super-Wettability from Fundamental Research to Practical Applications.

[4]   B. P. Lee, P. B. Messersmith, J. N. Israelachvili, J. H. Waite, *Annu. Rev. Mater. Res.* **2011,** *41*, 99-132. Mussel-Inspired Adhesives and Coatings.

[5]   T. Young, *Philosophical Transactions of the Royal Society of London* **1805,** *95*, 65-87. An Essay on the Cohesion of Fluids.

[6]   E. A. Vogler, *Adv. Colloid Interface Sci.* **1998,** *74*, 69-117. Structure and Reactivity of Water at Biomaterial Surfaces.

[7]   C. Guo, S. Wang, H. Liu, L. Feng, Y. Song, L. Jiang, *J. Adhes. Sci. Technol.* **2008,** *22*, 395-402. Wettability Alteration of Polymer Surfaces Produced by Scraping.

[8]   J. M. Berg, L. G. T. Eriksson, P. M. Claesson, K. G. N. Borve, *Langmuir* **1994,** *10*, 1225-1234. Three-Component Langmuir-Blodgett Films with a Controllable Degree of Polarity.

[9]   L. Wang, Y. Zhao, Y. Tian, L. Jiang, *Angew. Chem., Int. Ed.* **2015,** *54*, 14732-14737. A General Strategy for the Separation of Immiscible Organic Liquids by Manipulating the Surface Tensions of Nanofibrous Membranes.

[10]   M. Liu, S. Wang, L. Jiang, *Nat. Mater. Rev.* **2017,** *2*, 17036. Nature-Inspired Superwettability Systems.

[11]   A. B. D. Cassie, S. Baxter, *Trans. Faraday Soc.* **1944,** *40*, 546-551. Wettability of Porous Surfaces.

[12]   R. N. Wenzel, *Ind. Eng. Chem.* **1936,** *28*, 988-994. Resisctance of Solid Surfaces to Wetting by Water.

[13]   S. Wang, L. Jiang, *Adv. Mater.* **2007,** *19*, 3423-3424. Definition of Superhydrophobic States.

[14]   B. Bharat, J. Yong Chae, *J. Phys.: Condens. Matter* **2008,** *20*, 225010. Wetting, Adhesion and Friction of Superhydrophobic and Hydrophilic Leaves and Fabricated Micro/Nanopatterned Surfaces.

[15]   B. Bhushan, Y. C. Jung, K. Koch, *Philosophical Transactions of The Royal Society A Mathematical Physical and Engineering Sciences* **2009,** *367*, 1631-1672. Micro-, Nano- and Hierarchical Structures for Superhydrophobicity, Self-Cleaning and Low Adhesion.

[16]   H.-J. Butt, C. Semprebon, P. Papadopoulos, D. Vollmer, M. Brinkmann, M. Ciccotti, *Soft Matter* **2013,** *9*, 418-428. Design Principles for Superamphiphobic Surfaces.

[17]   H. R. Ollivier, *J. Phys. Theor. Appl.* **1907,** *6*, 757–782. Sur La Capillarité

[18]   K. Koch, B. Bhushan, Y. C. Jung, W. Barthlott, *Soft Matter* **2009,** *5*, 1386-1393. Fabrication of Artificial Lotus Leaves and Significance of Hierarchical Structure for Superhydrophobicity and Low Adhesion.

[19]   B. Bharat, J. Yong Chae, *Nanotechnology* **2006,** *17*, 2758. Micro- and Nanoscale Characterization of Hydrophobic and Hydrophilic Leaf Surfaces.

[20]   L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, *Adv. Mater.* **2002,** *14*, 1857-1860. Super-Hydrophobic Surfaces: From Natural to Artificial.

[21]   N. Michael, B. Bhushan, *Microelectron. Eng.* **2007,** *84*, 382-386. Hierarchical Roughness Makes Superhydrophobic States Stable.

[22] S. Nishimoto, B. Bhushan, *RSC Advances* **2013,** *3*, 671-690. Bioinspired Self-Cleaning Surfaces with Superhydrophobicity, Superoleophobicity, and Superhydrophilicity.

[23] B. Bhushan, Y. C. Jung, *Prog. Mat. Sc.* **2011,** *56*, 1-108. Natural and Biomimetic Artificial Surfaces for Superhydrophobicity, Self-Cleaning, Low Adhesion, and Drag Reduction.

[24] R. Blossey, *Nat. Mater.* **2003,** *2*, 301-306. Self-Cleaning Surfaces [Mdash] Virtual Realities.

[25] G. D. Bixler, B. Bhushan, *Soft Matter* **2012,** *8*, 11271-11284. Bioinspired Rice Leaf and Butterfly Wing Surface Structures Combining Shark Skin and Lotus Effects.

[26] X. Gao, X. Yan, X. Yao, L. Xu, K. Zhang, J. Zhang, B. Yang, L. Jiang, *Adv. Mater.* **2007,** *19*, 2213-2217. The Dry-Style Antifogging Properties of Mosquito Compound Eyes and Artificial Analogues Prepared by Soft Lithography.

[27] X. Gao, L. Jiang, *Nature* **2004,** *432*, 36-36. Biophysics: Water-Repellent Legs of Water Striders.

[28] Z. Wang, M. Elimelech, S. Lin, *Environ. Sci. Technol.* **2016,** *50*, 2132-2150. Environmental Applications of Interfacial Materials with Special Wettability.

[29] Y. Tian, L. Jiang, *MRS Bull.* **2015,** *40*, 155-165. Design of Bioinspired, Smart, Multiscale Interfacial Materials with Superwettability.

[30] A. K. Kota, G. Kwon, W. Choi, J. M. Mabry, A. Tuteja, *Nat. Commun.* **2012,** *3*, 1025. Hygro-Responsive Membranes for Effective Oil-Water Separation.

[31] J. Yang, Z. Zhang, X. Xu, X. Zhu, X. Men, X. Zhou, *J. Mater. Chem.* **2012,** *22*, 2834-2837. Superhydrophilic-Superoleophobic Coatings.

[32] M. Paven, P. Papadopoulos, S. Schöttler, X. Deng, V. Mailänder, D. Vollmer, H.-J. Butt, *Nat. Commun.* **2013,** *4*, 2512. Super Liquid-Repellent Gas Membranes for Carbon Dioxide Capture and Heart–Lung Machines.

[33] X. Deng, M. Paven, P. Papadopoulos, M. Ye, S. Wu, T. Schuster, M. Klapper, D. Vollmer, H. J. Butt, *Angew. Chem., Int. Ed.* **2013,** *52*, 11286-11289. Solvent-Free Synthesis of Microparticles on Superamphiphobic Surfaces.

[34] Y. Wang, B. Bhushan, *ACS Appl. Mater. Interfaces* **2015,** *7*, 743-755. Wear-Resistant and Antismudge Superoleophobic Coating on Polyethylene Terephthalate Substrate Using Sio2 Nanoparticles.

[35] Y. Lu, S. Sathasivam, J. Song, C. R. Crick, C. J. Carmalt, I. P. Parkin, *Science* **2015,** *347*, 1132-1135. Robust Self-Cleaning Surfaces That Function When Exposed to Either Air or Oil.

[36] F. Chen, J. Song, Y. Lu, S. Huang, X. Liu, J. Sun, C. J. Carmalt, I. P. Parkin, W. Xu, *J. Mater. Chem. A* **2015,** *3*, 20999-21008. Creating Robust Superamphiphobic Coatings for Both Hard and Soft Materials.

[37] X. Deng, L. Mammen, H.-J. Butt, D. Vollmer, *Science* **2012,** *335*, 67-70. Candle Soot as a Template for a Transparent Robust Superamphiphobic Coating.

[38] A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, R. E. Cohen, *Proc. Natl. Acad. Sci.* **2008,** *105*, 18200-18205. Robust Omniphobic Surfaces.

[39] M. Nosonovsky, B. Bhushan, *Phil. Trans. R. Soc. A* **2016,** *374*, 20160185. Why Re-Entrant Surface Topography Is Needed for Robust Oleophobicity.

[40] A. K. Kota, Y. Li, J. M. Mabry, A. Tuteja, *Adv. Mater.* **2012,** *24*, 5838-5843. Hierarchically Structured Superoleophobic Surfaces with Ultralow Contact Angle Hysteresis.

[41] S. Pan, A. K. Kota, J. M. Mabry, A. Tuteja, *J. Am. Chem. Soc.* **2013,** *135*, 578-581. Superomniphobic Surfaces for Effective Chemical Shielding.

[42] T. L. Liu, C.-J. C. Kim, *Science* **2014,** *346*, 1096-1100. Turning a Surface Superrepellent Even to Completely Wetting Liquids.

[43] G. Whyman, E. Bormashenko, *Langmuir* **2011,** *27,* 8171-8176. How to Make the Cassie Wetting State Stable?

[44] L. Zhang, N. Zhao, J. Xu, *J. Adhes. Sci. Technol.* **2014,** *28,* 769-790. Fabrication and Application of Superhydrophilic Surfaces: A Review.

[45] J. Drelich, E. Chibowski, D. D. Meng, K. Terpilowski, *Soft Matter* **2011,** *7,* 9804-9828. Hydrophilic and Superhydrophilic Surfaces and Materials.

[46] J. Drelich, E. Chibowski, *Langmuir* **2010,** *26,* 18621-18623. Superhydrophilic and Superwetting Surfaces: Definition and Mechanisms of Control.

[47] T. Guo, L. Heng, M. Wang, J. Wang, L. Jiang, *Adv. Mater.* **2016,** *28,* 8505-8510. Robust Underwater Oil-Repellent Material Inspired by Columnar Nacre.

[48] Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, L. Jiang, *Adv. Mater.* **2011,** *23,* 4270-4273. A Novel Superhydrophilic and Underwater Superoleophobic Hydrogel-Coated Mesh for Oil/Water Separation.

[49] M. Liu, L. Jiang, *Adv. Funct. Mater.* **2010,** *20,* 3753-3764. Switchable Adhesion on Liquid/Solid Interfaces.

[50] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, *Nature* **1997,** *388,* 431-432. Light-Induced Amphiphilic Surfaces.

[51] S. Banerjee, D. D. Dionysiou, S. C. Pillai, *Applied Catalysis B: Environmental* **2015,** *176–177,* 396-428. Self-Cleaning Applications of Tio2 by Photo-Induced Hydrophilicity and Photocatalysis.

[52] S. Amini, S. Kolle, L. Petrone, O. Ahanotu, S. Sunny, C. N. Sutanto, S. Hoon, L. Cohen, J. C. Weaver, J. Aizenberg, N. Vogel, A. Miserez, *Science* **2017,** *357,* 668-673. Preventing Mussel Adhesion Using Lubricant-Infused Materials.

[53] A. Fujishima, X. Zhang, D. A. Tryk, *Surf. Sci. Rep.* **2008,** *63,* 515-582. Tio2 Photocatalysis and Related Surface Phenomena.

[54] T.-S. Wong, S. H. Kang, S. K. Y. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, J. Aizenberg, *Nature* **2011,** *477,* 443-447. Bioinspired Self-Repairing Slippery Surfaces with Pressure-Stable Omniphobicity.

[55] P. Kim, T.-S. Wong, J. Alvarenga, M. J. Kreder, W. E. Adorno-Martinez, J. Aizenberg, *ACS Nano* **2012,** *6,* 6569-6577. Liquid-Infused Nanostructured Surfaces with Extreme Anti-Ice and Anti-Frost Performance.

[56] L. Xiao, J. Li, S. Mieszkin, A. Di Fino, A. S. Clare, M. E. Callow, J. A. Callow, M. Grunze, A. Rosenhahn, P. A. Levkin, *ACS Appl. Mater. Interfaces* **2013,** *5,* 10074-10080. Slippery Liquid-Infused Porous Surfaces Showing Marine Antibiofouling Properties.

[57] D. C. Leslie, A. Waterhouse, J. B. Berthet, T. M. Valentin, A. L. Watters, A. Jain, P. Kim, B. D. Hatton, A. Nedder, K. Donovan, E. H. Super, C. Howell, C. P. Johnson, T. L. Vu, D. E. Bolgen, S. Rifai, A. R. Hansen, M. Aizenberg, M. Super, J. Aizenberg, D. E. Ingber, *Nat. Biotechnol.* **2014,** *32,* 1134-1140. A Bioinspired Omniphobic Surface Coating on Medical Devices Prevents Thrombosis and Biofouling.

[58] X. Hou, Y. Hu, A. Grinthal, M. Khan, J. Aizenberg, *Nature* **2015,** *519,* 70-73. Liquid-Based Gating Mechanism with Tunable Multiphase Selectivity and Antifouling Behaviour.

[59] J. Wang, K. Kato, A. P. Blois, T.-S. Wong, *ACS Appl. Mater. Interfaces* **2016,** *8,* 8265-8271. Bioinspired Omniphobic Coatings with a Thermal Self-Repair Function on Industrial Materials.

[60] P. Zhang, S. Wang, S. Wang, L. Jiang, *Small* **2015,** *11,* 1939-1946. Superwetting Surfaces under Different Media: Effects of Surface Topography on Wettability.

[61] B. Su, Y. Tian, L. Jiang, *J. Am. Chem. Soc.* **2015**. Bioinspired Interfaces with Superwettability: From Materials to Chemistry.

[62] Y. Tian, B. Su, L. Jiang, *Adv. Mater.* **2014,** *26*, 6872-6897. Interfacial Material System Exhibiting Superwettability.

[63] K. Y. Suh, S. Jon, *Langmuir* **2005,** *21*, 6836-6841. Control over Wettability of Polyethylene Glycol Surfaces Using Capillary Lithography.

[64] B. He, N. A. Patankar, J. Lee, *Langmuir* **2003,** *19*, 4999-5003. Multiple Equilibrium Droplet Shapes and Design Criterion for Rough Hydrophobic Surfaces.

[65] D. O. H. Teare, C. G. Spanos, P. Ridley, E. J. Kinmond, V. Roucoules, J. P. S. Badyal, S. A. Brewer, S. Coulson, C. Willis, *Chem. Mater.* **2002,** *14*, 4566-4571. Pulsed Plasma Deposition of Super-Hydrophobic Nanospheres.

[66] E. Martines, K. Seunarine, H. Morgan, N. Gadegaard, C. D. W. Wilkinson, M. O. Riehle, *Nano Lett.* **2005,** *5*, 2097-2103. Superhydrophobicity and Superhydrophilicity of Regular Nanopatterns.

[67] N. A. Patankar, *Langmuir* **2004,** *20*, 8209-8213. Mimicking the Lotus Effect: Influence of Double Roughness Structures and Slender Pillars.

[68] N. A. Patankar, *Langmuir* **2003,** *19*, 1249-1253. On the Modeling of Hydrophobic Contact Angles on Rough Surfaces.

[69] Z. Yoshimitsu, A. Nakajima, T. Watanabe, K. Hashimoto, *Langmuir* **2002,** *18*, 5818-5822. Effects of Surface Structure on the Hydrophobicity and Sliding Behavior of Water Droplets.

[70] J. Fresnais, L. Benyahia, F. Poncin-Epaillard, *Surf. Interface Anal.* **2006,** *38*, 144-149. Dynamic (De)Wetting Properties of Superhydrophobic Plasma-Treated Polyethylene Surfaces.

[71] S. Minko, M. Müller, M. Motornov, M. Nitschke, K. Grundke, M. Stamm, *J. Am. Chem. Soc.* **2003,** *125*, 3896-3900. Two-Level Structured Self-Adaptive Surfaces with Reversibly Tunable Properties.

[72] P. Papadopoulos, L. Mammen, X. Deng, D. Vollmer, H.-J. Butt, *Proc. Natl. Acad. Sci.* **2013,** *110*, 3254-3258. How Superhydrophobicity Breaks Down.

[73] N. J. Shirtcliffe, S. Aqil, C. Evans, G. McHale, M. I. Newton, C. C. Perry, P. Roach, *Journal of Micromechanics and Microengineering* **2004,** *14*, 1384-1389. The Use of High Aspect Ratio Photoresist (Su-8) for Super-Hydrophobic Pattern Prototyping.

[74] M. Ma, Y. Mao, M. Gupta, K. K. Gleason, G. C. Rutledge, *Macromolecules* **2005,** *38*, 9742-9748. Superhydrophobic Fabrics Produced by Electrospinning and Chemical Vapor Deposition.

[75] H. Liu, L. Feng, J. Zhai, L. Jiang, D. Zhu, *Langmuir* **2004,** *20*, 5659-5661. Reversible Wettability of a Chemical Vapor Deposition Prepared Zno Film between Superhydrophobicity and Superhydrophilicity.

[76] F. Shi, Z. Wang, X. Zhang, *Adv. Mater.* **2005,** *17*, 1005-1009. Combining a Layer-by-Layer Assembling Technique with Electrochemical Deposition of Gold Aggregates to Mimic the Legs of Water Striders.

[77] J. T. Han, Y. Zheng, J. H. Cho, X. Xu, K. Cho, *J. Phys. Chem.* **2005,** *109*, 20773-20778. Stable Superhydrophobic Organic−Inorganic Hybrid Films by Electrostatic Self-Assembly.

[78] J. Ji, J. Fu, J. Shen, *Adv. Mater.* **2006,** *18*, 1441-1444. Fabrication of a Superhydrophobic Surface from the Amplified Exponential Growth of a Multilayer.

[79] G. Zhang, D. Wang, Z.-Z. Gu, H. Möhwald, *Langmuir* **2005,** *21*, 9143-9148. Fabrication of Superhydrophobic Surfaces from Binary Colloidal Assembly.

[80] A. Nakajima, C. Saiki, K. Hashimoto, T. Watanabe, *J. Mater. Sci. Lett.* **2001,** *20*, 1975-1977. Processing of Roughened Silica Film by Coagulated Colloidal Silica for Super-Hydrophobic Coating.

[81] X.-X. Zhang, S. Cai, D. You, L.-H. Yan, H.-B. Lv, X.-D. Yuan, B. Jiang, *Adv. Funct. Mater.* **2013,** *23*, 4361-4365. Template-Free Sol-Gel Preparation of Superhydrophobic Ormosil Films for Double-Wavelength Broadband Antireflective Coatings.

[82] X. Zhang, F. Shi, J. Niu, Y. Jiang, Z. Wang, *J. Mater. Chem.* **2008,** *18*, 621-633. Superhydrophobic Surfaces: From Structural Control to Functional Application.

[83] X.-M. Li, D. Reinhoudt, M. Crego-Calama, *Chem. Soc. Rev.* **2007,** *36*, 1350-1368. What Do We Need for a Superhydrophobic Surface? A Review on the Recent Progress in the Preparation of Superhydrophobic Surfaces.

[84] S. Casalini, C. A. Bortolotti, F. Leonardi, F. Biscarini, *Chem. Soc. Rev.* **2017,** *46*, 40-71. Self-Assembled Monolayers in Organic Electronics.

[85] C. Vericat, M. E. Vela, G. Corthey, E. Pensa, E. Cortes, M. H. Fonticelli, F. Ibanez, G. E. Benitez, P. Carro, R. C. Salvarezza, *RSC Advances* **2014,** *4*, 27730-27754. Self-Assembled Monolayers of Thiolates on Metals: A Review Article on Sulfur-Metal Chemistry and Surface Structures.

[86] R. Fürstner, W. Barthlott, C. Neinhuis, P. Walzel, *Langmuir* **2005** *21*, 956-961. Wetting and Self-Cleaning Properties of Artificial Superhydrophobic Surfaces.

[87] C. Howell, T. L. Vu, J. J. Lin, S. Kolle, N. Juthani, E. Watson, J. C. Weaver, J. Alvarenga, J. Aizenberg, *ACS Appl. Mater. Interfaces* **2014,** *6*, 13299-13307. Self-Replenishing Vascularized Fouling-Release Surfaces.

[88] H. A. Stone, *ACS Nano* **2012,** *6*, 6536-6540. Ice-Phobic Surfaces That Are Wet.

[89] X. Tian, T. Verho, R. H. A. Ras, *Science* **2016,** *352*, 142-143. Moving Superhydrophobic Surfaces toward Real-World Applications.

[90] Y. Chen, Y. Zhang, L. Shi, J. Li, Y. Xin, T. Yang, Z. Guo, *Appl. Phys. Lett.* **2012,** *101*, 033701. Transparent Superhydrophobic/Superhydrophilic Coatings for Self-Cleaning and Anti-Fogging.

[91] X. Zhang, Y. Guo, Z. Zhang, P. Zhang, *Appl. Surf. Sci.* **2013,** *284*, 319-323. Self-Cleaning Superhydrophobic Surface Based on Titanium Dioxide Nanowires Combined with Polydimethylsiloxane.

[92] S. Andreas, C. Zdenek, F. S. Boris, S. Manuel, B. Wilhelm, *Bioinspiration & Biomimetics* **2007,** *2*, S126. The Dream of Staying Clean: Lotus and Biomimetic Surfaces.

[93] S. Andreas, C. Zdenek, F. S. Boris, S. Manuel, B. Wilhelm, *Bioinspir. Biomim.* **2007,** *2*, 126-134. The Dream of Staying Clean: Lotus and Biomimetic Surfaces.

[94] L. Mishchenko, B. Hatton, V. Bahadur, J. A. Taylor, T. Krupenkin, J. Aizenberg, *ACS Nano* **2010,** *4*, 7699-7707. Design of Ice-Free Nanostructured Surfaces Based on Repulsion of Impacting Water Droplets.

[95] M. J. Kreder, J. Alvarenga, P. Kim, J. Aizenberg, *Nat. Mater. Rev.* **2016,** *1*, 15003. Design of Anti-Icing Surfaces: Smooth, Textured or Slippery?

[96] S. Bengaluru Subramanyam, V. Kondrashov, J. Rühe, K. K. Varanasi, *ACS Appl. Mater. Interfaces* **2016,** *8*, 12583-12587. Low Ice Adhesion on Nano-Textured Superhydrophobic Surfaces under Supersaturated Conditions.

[97] S. B. Subramanyam, K. Rykaczewski, K. K. Varanasi, *Langmuir* **2013,** *29*, 13414-13418. Ice Adhesion on Lubricant-Impregnated Textured Surfaces.

[98] T. Nørgaard, M. Dacke, *Front. Zool.* **2010,** *7*, 23. Fog-Basking Behaviour and Water Collection Efficiency in Namib Desert Darkling Beetles.

[99] D. Seo, J. Lee, C. Lee, Y. Nam, *Sci. Rep.* **2016,** *6*, 24276. The Effects of Surface Wettability on the Fog and Dew Moisture Harvesting Performance on Tubular Surfaces.

[100] Z. Wang, Y. Xu, Y. Liu, L. Shao, *J. Mater. Chem. A* **2015,** *3*, 12171-12178. A Novel Mussel-Inspired Strategy toward Superhydrophobic Surfaces for Self-Driven Crude Oil Spill Cleanup.

[101] G. Wang, Y. He, H. Wang, L. Zhang, Q. Yu, S. Peng, X. Wu, T. Ren, Z. Zeng, Q. Xue, *Green Chem.* **2015,** *17*, 3093-3099. A Cellulose Sponge with Robust Superhydrophilicity and under-Water Superoleophobicity for Highly Effective Oil/Water Separation.

[102] Z. Chu, Y. Feng, S. Seeger, *Angew. Chem., Int. Ed.* **2015,** *54*, 2328-2338. Oil/Water Separation with Selective Superantiwetting/Superwetting Surface Materials.

[103] Z. Xue, Y. Cao, N. Liu, L. Feng, L. Jiang, *J. Mater. Chem. A* **2014,** *2*, 2445-2460. Special Wettable Materials for Oil/Water Separation.

[104] C. Ruan, K. Ai, X. Li, L. Lu, *Angew. Chem., Int. Ed.* **2014,** *53*, 5556-5560. A Superhydrophobic Sponge with Excellent Absorbency and Flame Retardancy.

[105] X. Zhang, Z. Li, K. Liu, L. Jiang, *Adv. Funct. Mater.* **2013,** *23*, 2881-2886. Bioinspired Multifunctional Foam with Self-Cleaning and Oil/Water Separation.

[106] K. Li, J. Ju, Z. Xue, J. Ma, L. Feng, S. Gao, L. Jiang, *Nat. Commun.* **2013,** *4*, 2276. Structured Cone Arrays for Continuous and Effective Collection of Micron-Sized Oil Droplets from Water.

[107] A. Pranzetti, S. Salaün, S. Mieszkin, M. E. Callow, J. A. Callow, J. A. Preece, P. M. Mendes, *Adv. Funct. Mater.* **2012,** *22*, 3672-3681. Model Organic Surfaces to Probe Marine Bacterial Adhesion Kinetics by Surface Plasmon Resonance.

[108] I. Banerjee, R. C. Pangule, R. S. Kane, *Adv. Mater.* **2011,** *23*, 690-718. Antifouling Coatings: Recent Developments in the Design of Surfaces That Prevent Fouling by Proteins, Bacteria, and Marine Organisms.

[109] Q. Wei, T. Becherer, P.-L. M. Noeske, I. Grunwald, R. Haag, *Adv. Mater.* **2014,** *26*, 2688-2693. A Universal Approach to Crosslinked Hierarchical Polymer Multilayers as Stable and Highly Effective Antifouling Coatings.

[110] Q. Wei, T. Becherer, S. Angioletti-Uberti, J. Dzubiella, C. Wischke, A. T. Neffe, A. Lendlein, M. Ballauff, R. Haag, *Angew. Chem., Int. Ed.* **2014,** *53*, 8004-8031. Protein Interactions with Polymer Coatings and Biomaterials.

[111] D. M. Yebra, S. Kiil, K. Dam-Johansen, *Prog. Org. Coat.* **2004,** *50*, 75-104. Antifouling Technology—Past, Present and Future Steps Towards Efficient and Environmentally Friendly Antifouling Coatings.

[112] Q. Wei, R. Haag, *Mater. Horiz.* **2015,** *2*, 567-577. Universal Polymer Coatings and Their Representative Biomedical Applications.

[113] D. O. H. Teare, W. C. E. Schofield, V. Roucoules, J. P. S. Badyal, *Langmuir* **2003,** *19*, 2398-2403. Substrate-Independent Growth of Micropatterned Polymer Brushes.

[114] C. Rodriguez-Emmenegger, O. Kylián, M. Houska, E. Brynda, A. Artemenko, J. Kousal, A. B. Alles, H. Biederman, *Biomacromolecules* **2011,** *12*, 1058-1066. Substrate-Independent Approach for the Generation of Functional Protein Resistant Surfaces.

[115] A. M. Hynes, M. J. Shenton, J. P. S. Badyal, *Macromolecules* **1996,** *29*, 4220-4225. Pulsed Plasma Polymerization of Perfluorocyclohexane.

[116] C. Tarducci, E. J. Kinmond, J. P. S. Badyal, S. A. Brewer, C. Willis, *Chemistry of Materials* **2000,** *12*, 1884-1889. Epoxide-Functionalized Solid Surfaces.

[117] B. Yameen, H. U. Khan, W. Knoll, R. Förch, U. Jonas, *Macromolecular Rapid Communications* **2011,** *32*, 1735-1740. Surface Initiated Polymerization on Pulsed Plasma Deposited Polyallylamine: A Polymer Substrate-Independent Strategy to Soft Surfaces with Polymer Brushes.

[118] D. Y. Ryu, K. Shin, E. Drockenmuller, C. J. Hawker, T. P. Russell, *Science* **2005,** *308*, 236-239. A Generalized Approach to the Modification of Solid Surfaces.

[119] P. Mansky, Y. Liu, E. Huang, T. P. Russell, C. Hawker, *Science* **1997,** *275*, 1458-1460. Controlling Polymer-Surface Interactions with Random Copolymer Brushes.

[120] K. L. Choy, *Progress in Materials Science* **2003,** *48*, 57-170. Chemical Vapour Deposition of Coatings.

[121] B. S. Shim, P. Podsiadlo, D. G. Lilly, A. Agarwal, J. Lee, Z. Tang, S. Ho, P. Ingle, D. Paterson, W. Lu, N. A. Kotov, *Nano Letters* **2007,** *7*, 3266-3273. Nanostructured Thin Films Made by Dewetting Method of Layer-by-Layer Assembly.

[122] M. Wahlgren, T. Arnebrant, *Trends in Biotechnology* **1991,** *9*, 201-208. Protein Adsorption to Solid Surfaces.

[123] K. K. Goli, O. J. Rojas, J. Genzer, *Biomacromolecules* **2012,** *13*, 3769-3779. Formation and Antifouling Properties of Amphiphilic Coatings on Polypropylene Fibers.

[124] H. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* **2007,** *318*, 426-430. Mussel-Inspired Surface Chemistry for Multifunctional Coatings.

[125] T. S. Sileika, D. G. Barrett, R. Zhang, K. H. A. Lau, P. B. Messersmith, *Angewandte Chemie International Edition* **2013,** *52*, 10766-10770. Colorless Multifunctional Coatings Inspired by Polyphenols Found in Tea, Chocolate, and Wine.

[126] Y. H. Ding, M. Floren, W. Tan, *Biosurf. Biotribol.* **2016,** *2*, 121-136. Mussel-Inspired Polydopamine for Bio-Surface Functionalization.

[127] H. Lee, N. F. Scherer, P. B. Messersmith, *Proc. Natl. Acad. Sci.* **2006,** *103*, 12999-13003. Single-Molecule Mechanics of Mussel Adhesion.

[128] J. H. Waite, M. L. Tanzer, *Science* **1981,** *212*, 1038-1040. Polyphenolic Substance of Mytilus Edulis: Novel Adhesive Containing L-Dopa and Hydroxyproline.

[129] P. Kord Forooshani, B. P. Lee, *J. Polym. Sci. A Polym. Chem.* **2017,** *55*, 9-33. Recent Approaches in Designing Bioadhesive Materials Inspired by Mussel Adhesive Protein.

[130] J. Yang, M. A. Cohen Stuart, M. Kamperman, *Chem. Soc. Rev.* **2014,** *43*, 8271-8298. Jack of All Trades: Versatile Catechol Crosslinking Mechanisms.

[131] M. d'Ischia, A. Napolitano, V. Ball, C.-T. Chen, M. J. Buehler, *Acc. Chem. Res.* **2014,** *47*, 3541-3550. Polydopamine and Eumelanin: From Structure–Property Relationships to a Unified Tailoring Strategy.

[132] S. Hong, Y. S. Na, S. Choi, I. T. Song, W. Y. Kim, H. Lee, *Adv. Funct. Mater.* **2012,** *22*, 4711-4717. Non-Covalent Self-Assembly and Covalent Polymerization Co-Contribute to Polydopamine Formation.

[133] R. Batul, T. Tamanna, A. Khaliq, A. Yu, *Biomat. Sci.* **2017,** *5*, 1204-1229. Recent Progress in the Biomedical Applications of Polydopamine Nanostructures.

[134] M. A. Gebbie, W. Wei, A. M. Schrader, T. R. Cristiani, H. A. Dobbs, M. Idso, B. F. Chmelka, J. H. Waite, J. N. Israelachvili, *Nat. Chem.* **2017**. Tuning Underwater Adhesion with Cation–Π Interactions.

[135] S. A. Mian, L.-M. Yang, L. C. Saha, E. Ahmed, M. Ajmal, E. Ganz, *Langmuir* **2014,** *30*, 6906-6914. A Fundamental Understanding of Catechol and Water Adsorption on a Hydrophilic Silica Surface: Exploring the Underwater Adhesion Mechanism of Mussels on an Atomic Scale.

[136] T. H. Anderson, J. Yu, A. Estrada, M. U. Hammer, J. H. Waite, J. N. Israelachvili, *Adv. Funct. Mater.* **2010,** *20*, 4196-4205. The Contribution of Dopa to Substrate–Peptide Adhesion and Internal Cohesion of Mussel-Inspired Synthetic Peptide Films.

[137] R. Rodríguez, M. A. Blesa, A. E. Regazzoni, *J. Colloid Interface Sci.* **1996,** *177*, 122-131. Surface Complexation at the Tio2(Anatase)/Aqueous Solution Interface: Chemisorption of Catechol.

[138] Y. Li, M. Qin, Y. Li, Y. Cao, W. Wang, *Langmuir* **2014,** *30*, 4358-4366. Single Molecule Evidence for the Adaptive Binding of Dopa to Different Wet Surfaces.

[139] J. Yu, Y. Kan, M. Rapp, E. Danner, W. Wei, S. Das, D. R. Miller, Y. Chen, J. H. Waite, J. N. Israelachvili, *Proc. Natl. Acad. Sci.* **2013,** *110*, 15680-15685. Adaptive Hydrophobic and Hydrophilic Interactions of Mussel Foot Proteins with Organic Thin Films.

[140] C. Schlaich, Q. Wei, R. Haag, *Langmuir* **2017**. Mussel-Inspired Polyglycerol Coatings with Controlled Wettability: From Superhydrophilic to Superhydrophobic Surface Coatings.

[141] Y. Liu, K. Ai, L. Lu, *Chem. Rev.* **2014**, *114*, 5057-5115. Polydopamine and Its Derivative Materials: Synthesis and Promising Applications in Energy, Environmental, and Biomedical Fields.

[142] B. K. Ahn, *J. Am. Chem. Soc.* **2017**, *139*, 10166-10171. Perspectives on Mussel-Inspired Wet Adhesion.

[143] C. Rodriguez-Emmenegger, C. M. Preuss, B. Yameen, O. Pop-Georgievski, M. Bachmann, J. O. Mueller, M. Bruns, A. S. Goldmann, M. Bastmeyer, C. Barner-Kowollik, *Adv. Mater.* **2013**, *25*, 6123-6127. Controlled Cell Adhesion on Poly(Dopamine) Interfaces Photopatterned with Non-Fouling Brushes.

[144] J. H. Jiang, L. P. Zhu, L. J. Zhu, H. T. Zhang, B. K. Zhu, Y. Y. Xu, *ACS Appl. Mater. Interfaces* **2013**, *5*, 12895-12904. Antifouling and Antimicrobial Polymer Membranes Based on Bioinspired Polydopamine and Strong Hydrogen-Bonded Poly(N-Vinyl Pyrrolidone).

[145] K. Yang, J. S. Lee, J. Kim, Y. B. Lee, H. Shin, S. H. Um, J. B. Kim, K. I. Park, H. Lee, S.-W. Cho, *Biomaterials* **2012**, *33*, 6952-6964. Polydopamine-Mediated Surface Modification of Scaffold Materials for Human Neural Stem Cell Engineering.

[146] K. Wang, Y. Luo, *Biomacromolecules* **2013**, *14*, 2373-2382. Defined Surface Immobilization of Glycosaminoglycan Molecules for Probing and Modulation of Cell–Material Interactions.

[147] T. S. Sileika, H.-D. Kim, P. Maniak, P. B. Messersmith, *ACS Appl. Mater. Interfaces* **2011**, *3*, 4602-4610. Antibacterial Performance of Polydopamine-Modified Polymer Surfaces Containing Passive and Active Components.

[148] C. Nie, C. Cheng, Z. Peng, L. Ma, C. He, Y. Xia, C. Zhao, *J. Mater. Chem. B* **2016**, *4*, 2749-2756. Mussel-Inspired Coatings on Ag Nanoparticle-Conjugated Carbon Nanotubes: Bactericidal Activity and Mammal Cell Toxicity.

[149] I. You, Y. Chang Seo, H. Lee, *RSC Advances* **2014**, *4*, 10330-10333. Material-Independent Fabrication of Superhydrophobic Surfaces by Mussel-Inspired Polydopamine.

[150] L. Zhang, J. Wu, Y. Wang, Y. Long, N. Zhao, J. Xu, *J. Am. Chem. Soc.* **2012**, *134*, 9879-9881. Combination of Bioinspiration: A General Route to Superhydrophobic Particles.

[151] Q. Wei, F. Zhang, J. Li, B. Li, C. Zhao, *Polym. Chem.* **2010**, *1*, 1430-1433. Oxidant-Induced Dopamine Polymerization for Multifunctional Coatings.

[152] I. You, H. Jeon, K. Lee, M. Do, Y. C. Seo, H. A. Lee, H. Lee, *J. Ind. Eng. Chem.* **2017**, *46*, 379-385. Polydopamine Coating in Organic Solvent for Material-Independent Immobilization of Water-Insoluble Molecules and Avoidance of Substrate Hydrolysis.

[153] C. Zhang, Y. Ou, W. X. Lei, L. S. Wan, J. Ji, Z. K. Xu, *Angew. Chem., Int. Ed.* **2016**, *55*, 3054-3057. Cuso4/H2o2-Induced Rapid Deposition of Polydopamine Coatings with High Uniformity and Enhanced Stability.

[154] S. H. Hong, S. Hong, M. H. Ryou, J. W. Choi, S. M. Kang, H. Lee, *Adv. Mater. Interf.* **2016**, *3*, 1500857. Sprayable Ultrafast Polydopamine Surface Modifications.

[155] X. Du, L. Li, J. Li, C. Yang, N. Frenkel, A. Welle, S. Heissler, A. Nefedov, M. Grunze, P. A. Levkin, *Adv. Mater.* **2014**, *26*, 8029-8033. Uv-Triggered Dopamine Polymerization: Control of Polymerization, Surface Coating, and Photopatterning.

[156] S. M. Kang, N. S. Hwang, J. Yeom, S. Y. Park, P. B. Messersmith, I. S. Choi, R. Langer, D. G. Anderson, H. Lee, *Adv. Funct. Mater.* **2012**, *22*, 2949-2955. One-Step Multipurpose Surface Functionalization by Adhesive Catecholamine.

[157] J. H. Waite, in *Structure, Cellular Synthesis and Assembly of Biopolymers* (Ed.: S. T. Case), Springer Berlin Heidelberg, Berlin, Heidelberg, **1992**, pp. 27-54.

[158]   S. Moulay, *Polym. Rev.* **2014,** *54,* 436-513. Dopa/Catechol-Tethered Polymers: Bioadhesives and Biomimetic Adhesive Materials.

[159]   H. Lee, K. D. Lee, K. B. Pyo, S. Y. Park, H. Lee, *Langmuir* **2010,** *26,* 3790-3793. Catechol-Grafted Poly(Ethylene Glycol) for Pegylation on Versatile Substrates.

[160]   F. Zhang, S. Liu, Y. Zhang, Z. Chi, J. Xu, Y. Wei, *J. Mater. Chem.* **2012,** *22,* 17159-17166. A Facile Approach to Surface Modification on Versatile Substrates for Biological Applications.

[161]   L. Yu, C. Cheng, Q. Ran, C. Schlaich, P.-L. M. Noeske, W. Li, Q. Wei, R. Haag, *ACS Appl. Mater. Interfaces* **2017**. Bioinspired Universal Monolayer Coatings by Combining Concepts from Blood Protein Adsorption and Mussel Adhesion.

[162]   Y.-K. Gong, L.-P. Liu, P. B. Messersmith, *Macromol. Biosci.* **2012,** *12,* 979-985. Doubly Biomimetic Catecholic Phosphorylcholine Copolymer: A Platform Strategy for Fabricating Antifouling Surfaces.

[163]   Q. Wei, K. Achazi, H. Liebe, A. Schulz, P. L. Noeske, I. Grunwald, R. Haag, *Angew. Chem., Int. Ed.* **2014,** *53,* 11650-11655. Mussel-Inspired Dendritic Polymers as Universal Multifunctional Coatings.

[164]   N. F. Della Vecchia, R. Avolio, M. Alfè, M. E. Errico, A. Napolitano, M. d'Ischia, *Adv. Funct. Mater.* **2013,** *23,* 1331-1340. Building-Block Diversity in Polydopamine Underpins a Multifunctional Eumelanin-Type Platform Tunable through a Quinone Control Point.

[165]   D. Hong, K. Bae, S.-P. Hong, J. H. Park, I. S. Choi, W. K. Cho, *Chem. Commun.* **2014,** *50,* 11649-11652. Mussel-Inspired, Perfluorinated Polydopamine for Self-Cleaning Coating on Various Substrates.

[166]   H.-C. Yang, K.-J. Liao, H. Huang, Q.-Y. Wu, L.-S. Wan, Z.-K. Xu, *J. Mater. Chem. A* **2014,** *2,* 10225-10230. Mussel-Inspired Modification of a Polymer Membrane for Ultra-High Water Permeability and Oil-in-Water Emulsion Separation.

[167]   L. Shao, Z. X. Wang, Y. L. Zhang, Z. X. Jiang, Y. Y. Liu, *J. Membr. Sci.* **2014,** *461,* 10-21. A Facile Strategy to Enhance Pvdf Ultrafiltration Membrane Performance Via Self-Polymerized Polydopamine Followed by Hydrolysis of Ammonium Fluotitanate.

[168]   F. Li, M. Du, Q. Zheng, *ACS Nano* **2016,** *10,* 2910-2921. Dopamine/Silica Nanoparticle Assembled, Microscale Porous Structure for Versatile Superamphiphobic Coating.

[169]   C. Schlaich, L. Cuellar Camacho, L. Yu, K. Achazi, Q. Wei, R. Haag, *ACS Appl. Mater. Interfaces* **2016,** *8,* 29117-29127. Surface-Independent Hierarchical Coatings with Superamphiphobic Properties.

[170]   C. Schlaich, L. X. Yu, L. C. Camacho, Q. Wei, R. Haag, *Polym. Chem.* **2016,** *7,* 7446-7454. Fluorine-Free Superwetting Systems: Construction of Environmentally Friendly Superhydrophilic, Superhydrophobic, and Slippery Surfaces on Various Substrates.

[171]   Q. Wei, C. Schlaich, S. Prevost, A. Schulz, C. Bottcher, M. Gradzielski, Z. Qi, R. Haag, C. A. Schalley, *Adv. Mater.* **2014,** *26,* 7358-7364. Supramolecular Polymers as Surface Coatings: Rapid Fabrication of Healable Superhydrophobic and Slippery Surfaces.

9 Publication and Conference Contribution

[12] **C. Schlaich**, Y. Fan, P. Dey, Q. Wei, R. Haag, X. Deng, *Adv. Mater. Interfaces* **2018**. Universal, Surfactant-Free Preparation of Hydrogel Beads on Superamphiphobic and Slippery Surfaces.

[11] **C. Schlaich**, C. Cheng, I. Donskyi, M. Li, G. Song, E. Osorio, Q. Wei, R. Haag, *Adv. Mater. Interfaces* **2018**. Mussel-Inspired Polymer-Based Universal Spray Coating for Surface Modification: Fast Fabrication of Antibacterial and Superhydrophobic Surface Coatings.

[10] Leixiao Yu, Yong Hou, Chong Cheng, **C. Schlaich**, Paul-Ludwig Michael Noeske, Qiang Wei, Rainer Haag *ACS Appl. Mater. Interfaces* **2017**. High-antifouling Polymer Brush Coatings on Nonpolar Surfaces via Adsorption-Crosslinking Strategy.

[9] J. Zhang, Z. Meng, J. Liu, **C. Schlaich**, Z. Yu and X. Deng, *J. Mat. Chem. A* **2017**. Breathe Figure Lithography for the Construction of a Hierarchical Structure in Sponges and Their Applications to Oil/Water Separation.

[8] M. Li, L. Gao, **C. Schlaich**, J. Zhang, I. S. Donskyi, G. Yu, W. Li, Z. Tu, J. Rolff, T. Schwerdtle, R. Haag, N. Ma, *ACS Appl. Mater. Interfaces* **2017**.

[7] **C. Schlaich**, Q. Wei, R. Haag, *Langmuir* **2017**. Mussel-Inspired Polyglycerol Coatings with Controlled Wettability: From Superhydrophilic towards Superhydrophobic Surface Coatings.

[6] L. Yu, C. Cheng, Q. Ran, **C. Schlaich**, P.-L. M. Noeske, W. Li, Q. Wei, R. Haag, *ACS Appl. Mater. Interfaces* **2017**, *9*, 6624–6633. Bioinspired Universal Monolayer Coatings by Combining Concepts from Blood Protein Adsorption and Mussel Adhesion.

[5] **C. Schlaich**, L. Yu, L. C. Camacho, Q. Wei, R. Haag, *Polym. Chem.* **2016**, *7*, 7446-7454. Fluorine-free Superwetting Systems: Construction of Environmentally Friendly Superhydrophilic, Superhydrophobic, and Slippery Surfaces on Various Substrates.

[4] **C. Schlaich**, L. Cuellar Camacho, L. Yu, K. Achazi, Q. Wei, R. Haag, *ACS Appl. Mater. Interfaces* **2016**, 8, 29117-29127. Surface-Independent Hierarchical Coatings with Superamphiphobic Properties.

[3] **C. Schlaich**, Q. Wei, S. Prévost, A. Schulz, C. Böttcher, M. Gradzielski, Z. Qi, R. Haag and C. A. Schalley, *Adv. Mater.* **2014**, 26, 7358–7364. Supramolecular Polymers as Surface Coatings: Rapid Fabrication of Healable Superhydrophobic and Slippery Surfaces.

[2] Z. Qi, N. L. Traulsen, P. Malo de Molina, **C. Schlaich**, M. Gradzielski, C. A. Schalley, *Org. Biomol. Chem.* **2014**, *12*, 503-510. Self-recovering Stimuli-responsive Macrocycle-equipped Supramolecular Ionogels with Unusual Mechanical Properties.

[1] Z. Qi, **C. Schlaich**, C. A. Schalley, *Chem. Eur. J.* **2013**, *19*, 14867-14875. Multivalency in the Gas Phase: H/D Exchange Reactions Unravel the Dynamic "Rock'n'Roll" Motion in Dendrimer-Dendrimer Complexes.

Oral Presentations

[1] **C. Schlaich**, R. Haag, C.A. Schalley
Supramolecular Polymers as Surface Coatings: Rapid Fabrication of Healable
Superhydrophobic and Slippery Surfaces.
GRK "Fluorine as a Key Element" Meeting 2014

[2] **C. Schlaich**, R. Haag
Surface-Independent Hierarchical Coatings with Superamphiphobic Properties
GRK "Fluorine as a Key Element" Workshop 2015

[3] **C. Schlaich**, R. Haag
Mussel-Inspired Polyglycerols as Surface Coatings with Controlled Wettability
GRK "Fluorine as a Key Element" Meeting 2016

Poster Presentations

[1] **C. Schlaich**, Qiang Wei, R. Haag
Mussel-Inspired Polyglycerol as Universal Multifunctional Coatings
79th Prague Meeting on Macromolecules: Functional Polymers at Bio-Material
Interfaces 2015

[2] **C. Schlaich**, R. Haag,
Surface-Independent Hierarchical Coatings with Superamphiphobic Properties
Gordon Research Conference "Bioinspired Materials" 2016

[3] **C. Schlaich**, R. Haag, C.A. Schalley
Mussel-Inspired Polyglycerols as Surface Coatings with Controlled Wettability
GDCh-Wissenschaftsforums Chemie 2017

10 Curriculum Vitae

Der Lebenslauf ist aus Gründen des Datenschutzes nicht enthalten.